Olefin Metathesis for the Synthesis of Supramolecular Structures

Thesis by

Marcus Weck

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than she ever wanted to know after proofreading each chapter of this thesis at least five times, and correcting my "German" English.

Abstract

The research presented in this thesis combines the versatility of olefin metathesis with the concept of supramolecular chemistry. Several supramolecular architectures, such as liquid crystalline polymers, catenanes, and self-assembled monolayers were designed with olefin metathesis.

Chapter 1 introduces several ABA triblock copolymers synthesized by well-defined, bimetallic catalysts and norbornene-based monomers. Sequential addition of these monomers yielded the triblock copolymers with low polydispersities and controlled molecular weight.

One objective of this thesis is the synthesis of side-chain liquid crystalline material *via* ROMP. Therefore the synthesis and polymerization of a number of norbornene and cyclobutene-based monomers bearing nitrostilbene side-chains is presented. The liquid crystalline behavior was determined by differential scanning calorimetry (DSC) and optical polarized microscopy. The poly(norbornene)s show nematic mesophase behavior whereas the poly(cyclobutene)s display enantiotropic smectic A mesomorphism. A 1:1 diblock copolymer also shows enantiotropic smectic A mesomorphism. This difference in mesophase behavior was attributed to varying degrees of backbone rigidity.

As an extension of the work described above, Chapter 3 describes the synthesis and characterization of discotic liquid crystalline material for their use as hole transport materials. Norbornene- and cyclobutene monomers containing triphenylenes were synthesized introducing a newly developed strategy for the synthesis of the triphenylene-based side-chain. The mesomorphic behavior of the polymers was investigated by DSC and powder diffraction X-ray scattering and was identified as discotic liquid crystalline.

In an effort to synthesize a variety of supramolecular structures *via* RCM, Chapter 4 illustrates a new strategy for obtaining self-assembled interlocked and intertwined architectures. Three different self-assembly approaches based on metal templating,

hydrogen bonding, and π-π interactions followed by RCM to yield catenane or rotaxane structures are introduced.

The final chapter presents a new strategy to polymerize directly from surfaces through ROMP. Using a two-step self-assembly approach, a 'molecular wire' molecule containing norbornene and thiol was anchored to gold surfaces pretreated with dodecanethiol. Addition of a ruthenium catalyst to the functionalized surface followed by addition of monomer resulted in the synthesis of polymer brushes on the surface. The polymer brushes were characterized by scanning tunneling microscopy, atomic force microscopy, and scanning electron microscopy.

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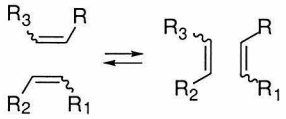
List of Abbreviations

ADMET	Acyclic Diene Metathesis
AFM	Atomic Force Microscopy
Cp	Cyclopentyl
Cy	Cyclohexyl
DSC	Differential Scanning Calorimetry
ETL	Electron Transport Layer
FAB	Fast Atom Bombardment Mass Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
HTL	Hole Transport Layer
ITO	Indium-Tin-Oxide
LC	Liquid Crystals
LED	Light Emitting Diodes
MCLCP	Main-Chain Liquid Crystalline Polymers
NLO	Non-Linear Optic
PDI	Polydispersity
RCM	Ring-Closing Metathesis
ROMP	Ring-Opening Metathesis Polymerization
SAM	Self-Assembled Monolayer
SCLCP	Side-Chain Liquid Crystalline Polymers
SEM	Scanning Electron Microscopy
STM	Scanning Tunneling Microscopy
TMAFM	Tunneling Mode Atomic Force Microscopy
WAXS	Wide-Angle X-Ray Scattering
XPS	X-Ray Photoelectron Spectroscopy

Introduction to Olefin Metathesis and Supramolecular Chemistry

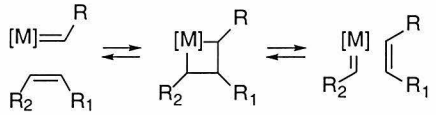
Olefin Metathesis

General Aspects. Olefin metathesis is a transition-metal catalyzed reaction which transposes the alkylidine groups of two substituted alkenes (Scheme 1).[1]



Scheme 1. General principle of olefin metathesis.

The mechanism for this reaction, originally proposed in 1971 by Chauvin,[2] involves the formation and subsequent cleavage of a metallocyclobutane as outlined in Scheme 2. Cleavage of the metallocyclobutane can either occur in a non-productive fashion to yield starting material and the initial metal carbene, or in a productive fashion generating the new olefin and a new metal carbene.



Scheme 2. Mechanism of olefin metathesis according to the Chauvin model.

First generation catalysts employed for olefin metathesis were ill-defined, multicomponent mixtures which only polymerized strained cyclic olefins in a non-living fashion.[1] However, over the last 10 years, a series of new, well-defined complexes has been developed which are converted *in situ* to exceedingly tolerant catalysts for olefin metathesis (Figure 1).[1,3-8]

The titanocyclobutane complex in Figure 1 was the first example of an isolated well-defined catalyst system.[3,4] It demonstrated the ability to polymerize norbornenes in a living fashion.[3,4] However, the general use of this catalyst was limited due to its reactivity with esters, aldehydes, and ketones. This result was followed by a series of single-component, well-defined Schrock type metal carbene catalysts based on Ta, and Re, as outlined in Figure 1.

In the late 1980's and early 1990's, Schrock and coworkers revealed new molybdenum and tungsten catalysts which were able to rapidly polymerize a variety of monomers, including norbornenes and barrelenes, in a living fashion.[3] Although these molybdenum and tungsten catalysts demonstrated a limited stability at room temperature and decompose in the presence of several functional groups, such as alcohols and amines.

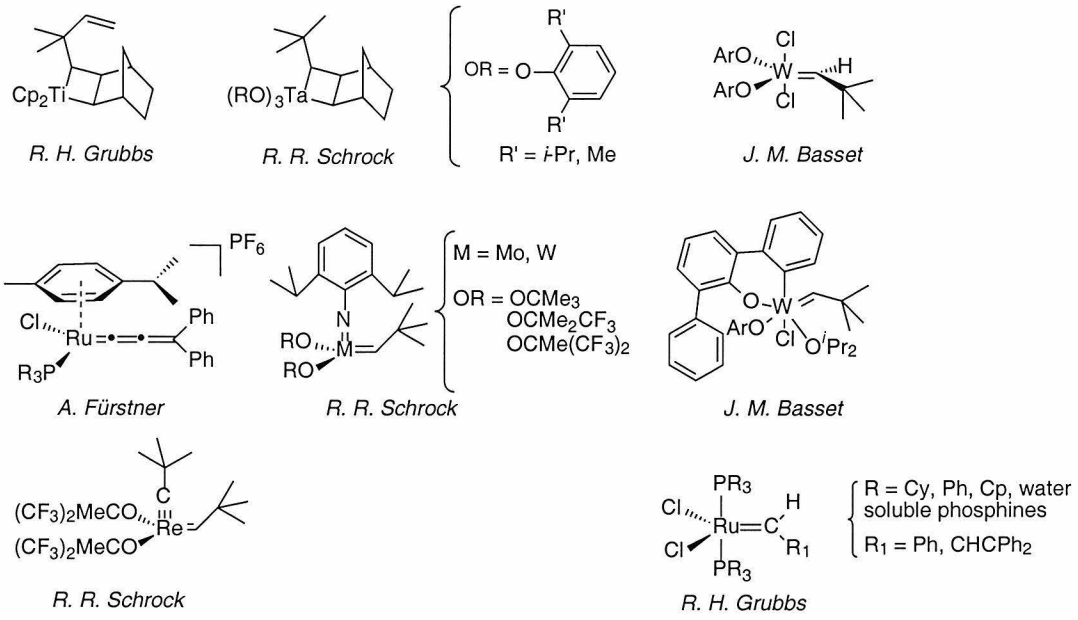
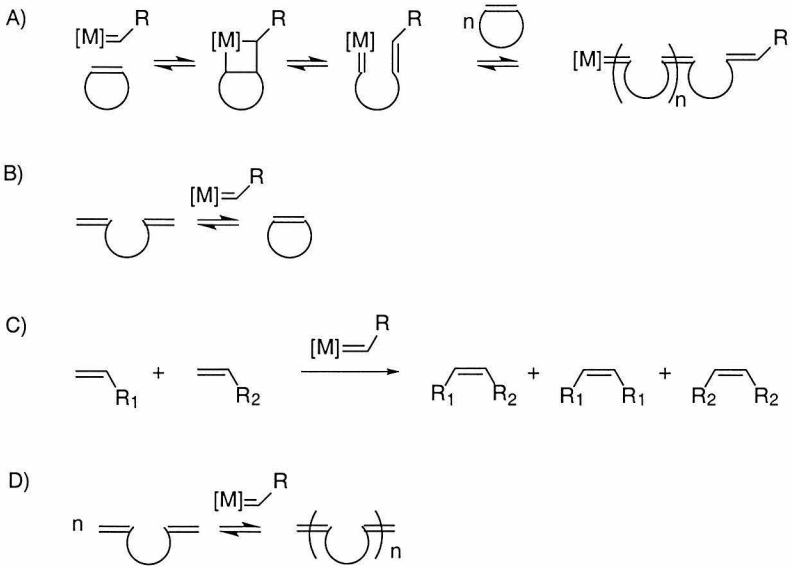


Figure 1. Single-component transition metal catalysts for olefin metathesis.

In 1992, Grubbs reported the synthesis of a new class of well-defined metathesis catalysts based on ruthenium.[5-7] In contrast to all other reported catalyst systems, these ruthenium catalysts were found to be stable to a large variety of functional groups (alcohols, aldehydes, etc.) and conditions, including air, protic solvents and water.[7] Their increased activity and tolerance towards polar functional groups, protic media, and air enabled the following investigations.

Current catalyst research focuses on the development of more active and stable catalysts,[6a] chiral catalysts,[8] more stable catalysts for the use in protic solvents such as water or methanol,[7] easier routes to synthesize catalysts,[6] and photoinduced catalytic systems.[9]

In general, olefin metathesis can be utilized in three closely related reactions: (a) ring opening metathesis polymerization (ROMP) (Scheme 3a); (b) ring-closing metathesis (RCM) (Scheme 3b); and (c) acyclic cross metathesis (Scheme 3c) which results in acyclic diene metathesis (ADMET; Scheme 3d) when carried out on diolefins as polymerization.



Scheme 3. General mechanism of (A) ring-opening metathesis polymerization (ROMP), (B) ring-closing metathesis (RCM), (C) cross-metathesis of two terminal alkenes, and (D) acyclic diene metathesis polymerization (ADMET).

Ring-Opening Metathesis Polymerization. ROMP is the 'oldest' of the reactions described above.[1,10-16] A strained cycloalkene can be polymerized to yield a polymer with olefins in the backbone. The ultimate driving force of the reaction is the release of ring-strain in the monomer. Therefore, monomers with less ring-strain, such as cyclopentenes, are more difficult to polymerize. However, highly strained olefins such as norbornenes,[10-11] cyclobutenes,[12] barrelenes,[13] and cyclooctadienes[14] are easily polymerized (Figure 2).

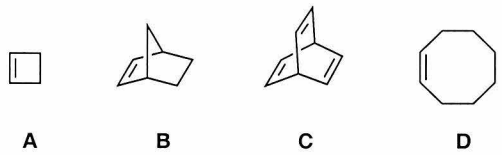
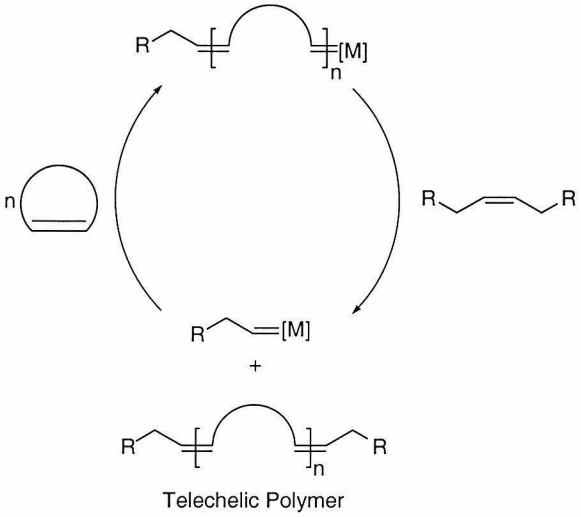


Figure 2. Monomers used in ROMP: (a) cyclobutene, (b) norbornene, (c) barrelene, and (d) cyclooctadiene.

A variety of homopolymers with low polydispersities[10-17] as well as block copolymers *via* sequential addition of different monomers with low polydispersities[16] have been synthesized using ROMP.

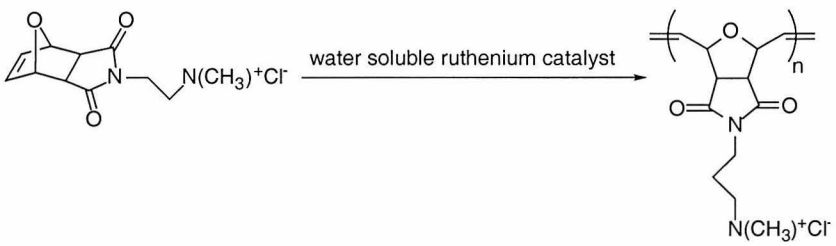
Recently, ROMP has been successfully used to synthesize a variety of functionalized polymers for electronic purposes including side-chain liquid-crystalline polymers,[11] electroluminescent polymers,[10j,13] and poly(norbornene)-based light emitting diodes (LEDs) as well as well-defined polymer architectures. Moreover, ROMP has been used for the synthesis of a variety of end-functionalized polymers (telechelic) which are otherwise not readily accessible (Scheme 4).[15]



Scheme 4. General scheme for the synthesis of telechelic polymers using ROMP.

The most intriguing result in the last few years has been the successful realization of a polymerization in water by Grubbs.[7] By using two water soluble ruthenium catalysts,

they demonstrated the living character of the ROMP in water using a variety of water soluble monomers.



Scheme 5. Synthesis of water soluble polymers using ROMP.

The main advantage of ROMP over most other polymerization methods, such as radical polymerization, is that it proceeds in a living manner in most cases. Living polymerizations provide maximum control over polydispersity, composition, and molecular weight for the synthesis of polymers with well-defined structures and are therefore an active area of research. Furthermore, living polymerizations allow the synthesis of block copolymers which are otherwise impossible to obtain.

Ring-Closing Metathesis. Ring-closing metathesis (Scheme 3B) of α,ω-dienes to yield cycloolefins is a relatively new reaction with an increasing importance in organic chemistry.[18-24] In contrast to ROMP, RCM is enthalpically disfavored. However, the release of ethylene provides an entropic driving force for most reactions.

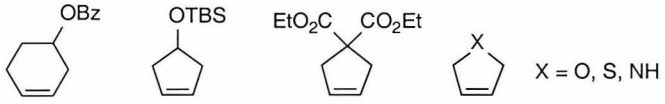


Figure 3. Early examples of organic compounds cyclized using RCM.

Since the first reports in 1993, the cyclization of a large variety of medium sized rings (six, seven, and eight-membered)[18] and more recently of larger ring systems containing different functionalities have been reported.[18,19] More elaborate examples include the use of RCM to mimic and stabilize tertiary peptide structures like ß-turns

(Figure 3) and α-helices[19b] or to synthesize peptide based nanotubes as reported by Ghadiri.[19k]

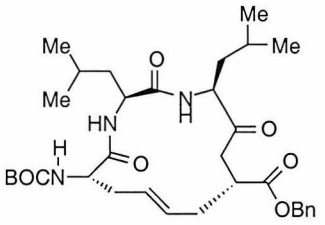
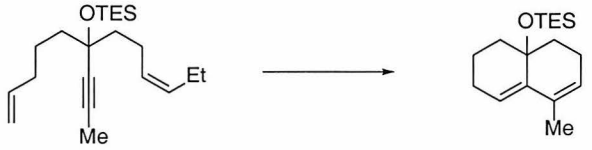


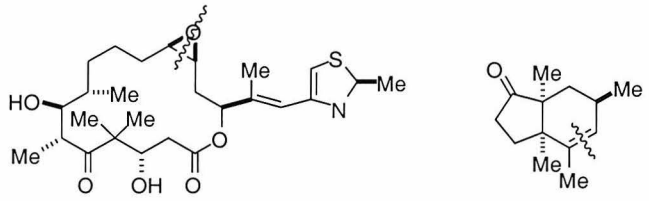
Figure 4. Peptide analogous ß-turn synthesized by RCM.

A useful variation of RCM is the 'tandem RCM' reported by Grubbs.[20] Sequential RCM results in the formation of multicyclic ring systems as shown in Scheme 6.



Scheme 6. Example of a tandem RCM reaction.

Perhaps one of the most impressive indicators for the synthetic versatility of RCM is the number of natural products that have been reported using RCM as a key step in their synthetic strategy.[18] Natural products based on large ring systems such as epothilone A reported by Nicolaou,[21] as well as bicyclic compounds such as coronafacic acid have been synthesized *via* RCM (Figure 4).[18]

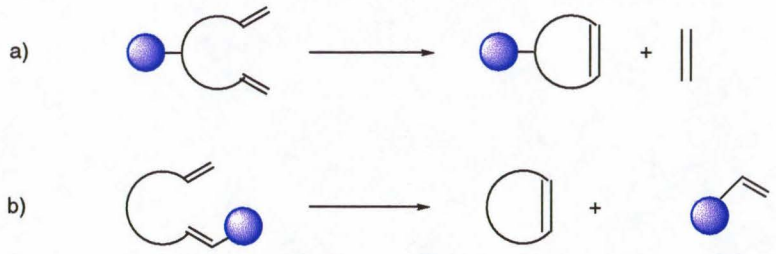


epothilone A coronafacic acid

Figure 5. Natural products synthesized by RCM.

Other recent advances using RCM include the cyclization of diolefins in carbon dioxide[22] and the RCM of dialkynes as reported by Fürstner.[23] Furthermore, RCM has

been used as the key reaction in combinatorial chemistry[24] and the RCM of solid supported substrates using two different strategies (Scheme 7).[18]



Scheme 7. RCM of solid support substrates: (a) resultant solid bound substrates; (b) RCM with simultaneous cleavage.

Cross-Metathesis. Cross-metathesis (Scheme 3 C and D) between acyclic olefins offers interesting possibilities for the synthesis of higher-substituted alkenes.[25,26] In analogy to RCM, the formation of small volatile molecules, such as ethylene, provides the driving force for cross-metathesis. Traditionally, the use of highly substituted or asymmetric olefins is not practical because statistic mixtur8es of products were obtained.

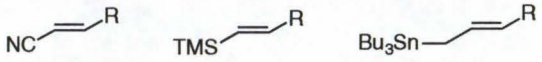
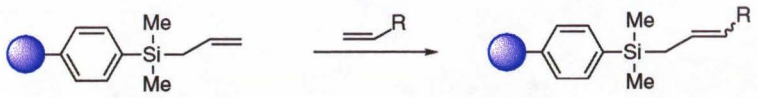


Figure 6. Compounds synthesized by cross-metathesis.

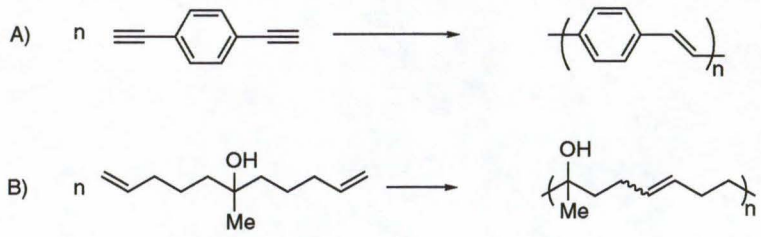
It was not until 1993 that cross-metathesis using a well-defined catalyst system was reported.[26] Since then relatively few reports on this subject have been published, mainly from the groups of Blechert and Crowe.[25] While early reports on cross-metathesis are based mostly on the synthesis of simple substituted olefins bearing a variety of functionalities (Figure 5), recent reports are more concerned with the use of this technique for the synthesis of molecules for special applications. For example, Schreiber used cross-metathesis for the dimerization of highly biological active proteins such as FK 506.[25d]

In analogy to RCM, olefins on solid support have been used in cross-metathesis to yield polymer bound di-substituted olefins for a large variety of applications in biology and chemistry (Scheme 8).[25b]



Scheme 8. Synthesis of di-substituted polymer-bound olefins *via* cross-metathesis.

Besides ROMP, the second polymerization method based on olefin metathesis is acyclic-diene metathesis (ADMET) which has attracted some attention in the past 8 years. It has proven to be applicable for a variety of monomers containing olefinic groups and alkynes.[26] Recent advances in ADMET include the synthesis of side-chain functionalized polymers, such as ferroelectric liquid crystalline polymer,[26e] of perfectly branched poly(ethylene),[26h] and highly conjugated polymers such as poly(phenylvinylenes)s (Scheme 9A).[26g] Furthermore, a simple route to alcohol functionalized polymers *via* ADMET has been introduced by Wagner (Scheme 9B).[26a]



Scheme 9. Synthesis of (A) PPV and (B) alcohol functionalized polymers *via* ADMET.

However, ADMET must be done without solvents and produces a variety of cyclic and macrocyclic olefins in addition to the desired polymer, resulting in an inseparable mixture of products. Therefore, ROMP is generally favored over ADMET as an olefin metathesis polymerization method.

Supramolecular Chemistry

Supramolecular chemistry, the chemistry of non-covalent intermolecular interactions such as hydrogen bonds, ionic interactions, metal-ion interactions or the hydrophobic effect, is essential for processes in biological and synthetic systems, including molecular recognition, catalysis, transport, and self-assembly.[27-28] It has become a highly

interdisciplinary field of science covering the chemical, physical, and biological features of chemical species held together and organized by means of intermolecular weak binding interactions. Its roots are found in organic chemistry, with synthetic procedures for receptor construction, in coordination chemistry and metal ion-ligand complexes, in physical chemistry and the experimental and theoretical studies of interactions, and in biochemistry.[27]

During the last twenty years, this relatively new area has been conceptualized, defined, and structured into a coherent system incorporating earlier data with the extensive results obtained through rapidly growing activity in numerous research groups.[27-32] Based on the chemical, physical, and biological features of supramolecular systems, novel lines of investigation have been developed concerned with the design of molecular devices and systems displaying higher forms of molecular and supramolecular behavior such as self-organization,[27-35] regulation,[27-28] cooperativity,[27-34] communication,[27-29,31-33] and replication.[34] To achieve this supramolecular behavior, molecular information crucial for the process to take place must be stored in the structural features of the molecules.

The selective binding of a substrate by a molecular receptor to form a supermolecule involves molecular recognition resting on the information stored in the interacting partners. It requires the design of receptors possessing steric and electronic features complementary to those of the substrate to be bound, and a balance between rigidity and flexibility suitable for the function to be performed. Molecular recognition events represent the basis of information processing at the molecular level. They may give rise to changes in electronic, ionic, optical, and conformational properties.

Research Goals

The research presented in this thesis combines the versatility of olefin metathesis with the concept of supramolecular chemistry. Several supramolecular architectures, such

as liquid crystalline polymers, catenanes, and self-assembled monolayers were designed with olefin metathesis.

Chapter 1 describes the synthesis of several ABA triblock copolymers using living ROMP.[36] Well-defined, bimetallic catalysts which are able to initiate polymerization on two ends were prepared. These catalysts were found to initiate a living polymerization with norbornene-based monomers. Sequential addition of different monomers yielded ABA triblock copolymers with low polydispersities and controlled molecular weight.

Chapter 2 describes the synthesis and polymerization of a number of norbornene and cyclobutene based monomers bearing nitrostilbene side-chains.[37] The polymers displayed low polydispersities and controlled molecular weight. The liquid crystalline behavior was determined by differential scanning calorimetry (DSC) and polarized microscopy. The poly(norbornene)s show nematic mesophase behavior whereas the poly(cyclobutene)s display enantiotropic smectic A mesomorphism. A 1:1 diblock copolymer also shows enantiotropic smectic A mesomorphism. This difference in mesophase behavior can be attributed to varying degrees of backbone rigidity.

In Chapter 3, ROMP was used to synthesize a variety of discotic liquid crystals which can be used as LEDs.[38] Norbornene- and cyclobutene monomers containing triphenylenes were synthesized introducing a new strategy for the synthesis of the triphenylene-based side-chain. The mesomorphic behavior of the polymers was investigated by DSC and powder diffraction X-ray scattering and was identified as discotic liquid crystalline.

Chapter 4 describes a new approach for the synthesis of self-assembled interlocked and intertwined architectures using RCM.[39] Three different self-assembly approaches based on metal templating, hydrogen bonding, and π-π interactions followed by ring-closing metathesis to yield catenane or rotaxane structures are introduced.

The last chapter presents a new strategy to polymerize directly from surfaces using ROMP. Using a two-step self-assembly strategy a norbornene and thiol containing

'molecular wire' molecule was anchored on gold surfaces pretreated with dodecanethiol. Followed treatment of the functionalized surface with a ruthenium catalyst yielded initiated norbornene molecules on the surface. Addition of monomer resulted in ROMP from the surface. The polymerization was followed by scanning tunneling microscopy (STM), atomic force microscopy (AFM), and scanning electron microscopy (SEM).

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(1) For a general introduction to olefin metathesis, see: (a) Leconte, M.; Basset, J.M.; Quignard, F.; Larroche, C. *Reactions of Coordinated Ligands*. Braterman P.S. ed.; Plenum: New York **1986**, *Vol 1*, pp. 371. and references therein. (b) Ivin, K.J. *Olefin Metathesis*, Academic Press: London, **1996**. (c) Pariya, C.; Jayaprakash K.N.; Sarkar, A. *Coord. Chem. Rev.* **1998**, *168*, 1. (d) Schuster, M.; Blechert, S. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2036.

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Chapter 1

Synthesis of Block Copolymers of Norbornenes and 7-Oxanorbornenes *via* Living Ring-Opening Metathesis Polymerization

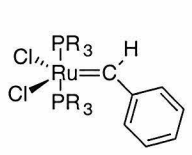
Abstract

Norbornene and 7-oxanorbornene derivatives were polymerized by ring-opening metathesis polymerization (ROMP) in a living manner by employing three monometallic well-defined ruthenium catalysts $(PR_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4\text{-}C(H)$ [R=Ph, **1**; R=Cy (cyclohexyl), **2**; R=Cyp (cyclopentyl), **3**] and three bimetallic well-defined ruthenium catalysts $(PR_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4\text{-}C(H)=)RuCl_2(PR_3)_2$ [R=Ph, **4**; R=Cy, **5**; R=Cyp, **6**] as initiators to obtain block copolymers with low polydispersities. Reactions of 7-oxanorbornenes **8** and **9** or norbornene **10** containing silicon with **2**, **3**, or **6** resulted in polymers with low polydispersities ranging from 1.10 to 1.19, while polymerizations initiated by **2** displayed higher polydispersities ranging from 1.20 to 1.35. Polymerizations of **8**-**10** catalyzed by **2**,**3**,**5** and **6** fulfill all requirements for a living polymerization. However, catalysts **1** and **4** were found not suffciently reactive to polymerize functionalized norbornenes or 7-oxanorbornenes. The living polymerizations were successfully used to prepare several diblock copolymers as well as three ABA triblock copolymers of monomers **8**-**10**. In all cases, the block copolymers had higher molecular weights than the homopolymers and all polydispersities remained low.

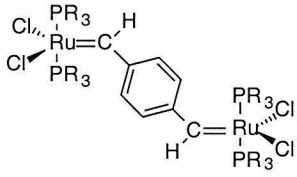
Introduction

Block copolymers have unique physical properties. Many phase-separated block copolymers behave as thermoplastic elastomers or can be used as semipermeable membranes.[1] They also provide excellent model systems to understand the complex morphological and dynamical response of microstructured materials.[2] In particular, the detailed analysis of morphologies,[3] phase behavior[4] and rheological properties[5] as well as their mixtures with homopolymer blends,[6] have been investigated. Living ring-opening metathesis polymerization (ROMP) has been the subject of numerous studies for the preparation of novel block copolymers with special properties and applications.[7-8] Recently, several ABA triblock copolymers synthesized by ROMP have been reported,[8b,g-i,9] which, in most cases, were obtained *via* a three-step polymerization. So far, difunctional norbornene initiators were successfully used for the preparation of ABA triblock copolymers in a two step polymerization.[9] In this study, the first objective was to study the living ROMP of functionalized norbornenes and 7-oxanorbornene derivatives using new monometallic ruthenium catalysts. Using three bimetallic, well-defined ruthenium catalysts, the second goal was the examination of a two-step ring-opening metathesis polymerization which is living at both chain ends and thus results in the formation of ABA triblock copolymers.

Recently, there has been considerable effort to explore the metathesis activity of well-defined ruthenium complexes which are generally more tolerant of polar or functionalized groups than their early transition metal counterparts.[10,11] These investigations resulted in the development of a new class of ruthenium catalysts $RuCl_2(=CHR')(PR_3)_2$ (R=Ph, **1**; Cy, **2**; Cyp, **3**; R'= Ph)[11c,d] which are highly active for ROMP[11] and ring-closing metathesis (RCM)[12] as well as their bimetallic ruthenium (bis)-alkylidenes counterparts $(PR_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4\text{-}C(H)=)RuCl_2(PR_3)_2$ (R=Ph, **4**; R=Cy, **5**; R=Cyp, **6**) which were expected to initiate at both carbene moieties to yield a polymer that is living at both chain ends.

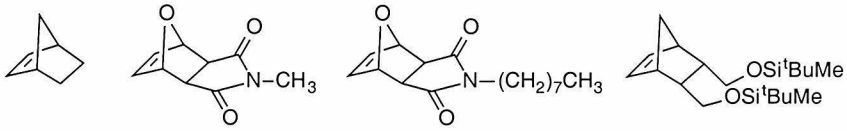


1: R=Ph
2: R=Cy
3: R=Cyp



4: R=Ph
5: R=Cy
6: R=Cyp

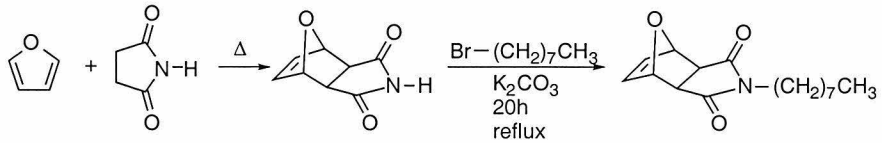
The preparation of a series of homopolymers of norbornene **7**, 7-oxanorbornenes **8** and **9** and a norbornene derivative containing silicon **10**, employing catalysts **1**-**6**, is presented. Monomer **10** was selected for the potential utility of silicon-containing polymers as semiconductors, photoconductors, photoresists and non-linear optical materials,[13,8f] while monomers **8** and **9** were chosen for their hydrophilicity. The present work demonstrates that the above mentioned alkylidenes are useful catalysts for the polymerization of norbornene, functionalized norbornenes and functionalized 7-oxanorbornenes to obtain AB diblock and ABA triblock copolymers.



7 **8** (exo) **9** (exo) **10**

Results

Monomer Syntheses. Monomers **8** and **10** were prepared as previously reported.[8f,14] Monomer **9** was synthesized in analogy to monomer **8** from the Diels-Alder reaction of furan and maleimide in ether (Scheme 1).[14] Compound **11** (exo product) crystallized from the reaction upon cooling and was isolated in 93% yield. Alkylation of **11** using 1-bromooctane produced compound **9** in 68% yield.



11 **9**

Scheme 1. Preparation of monomer **9**.

Homopolymer Synthesis. Homopolymerizations were examined with each monomer (**7-10**) in dichloromethane at room temperature. All reactions were accompanied by a characteristic color-change from brown or purple to orange or red which indicates complete initiation. The degree of initiation can also be judged by the appearance of a new propagating species in the NMR concurrent with the disappearance of the initiating species. For example, in the polymerization of **8** catalyzed by **6**, the propagating species (18.82 ppm (t)) can be clearly distinguished from the initiating species (20.64 ppm (s)). The polymerizations were terminated by adding ethyl-vinyl-ether. It was found that catalysts **1** and **4** can quantitatively polymerize norbornene at room temperature in dichloromethane (PDI = 1.15, M_n (number average molecular weight) = 65,000).[15] However, they were not sufficiently reactive to polymerize 7-oxanorbornenes and functionalized norbornenes.[11c,d]

In contrast to **1**, ruthenium alkylidenes **2** and **3** were found to polymerize 7-oxanorbornenes and functionalized norbornenes in a living fashion. Due to chain transfer and back-biting, the formation of monodisperse polymers with norbornene was not possible.[8f,11c,d] Table 1 summarizes the GPC results for the polymerizations catalyzed by **2** and **3**.

Table 1. ROMP of 7-oxanorbornenes (**8** and **9**) and functionalized norbornene (**10**) with $(PR_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4)$ (R=Cy, **2**; R=Cyp, **3**) in CH_2Cl_2 at room temperature.

Catalyst	Monomer	Time(min.)	Yield %	[M]/[C]	M_w	M_n	PDI
3	**8**	15	>98	106	28000	24000	1.13
3	**10**	30	>98	44	19000	17000	1.17
2	**8**	15	>98	249	94000	84000	1.11
2	**9**	15	>98	11.5	7000	6000	1.10
2	**10**	30	>98	143	37000	35000	1.09

Encouraged by these results, the ROMP of 7-oxanorbornenes and functionalized norbornenes using catalysts **5** and **6** was examined. As expected, both catalysts polymerized monomers **8**-**10** in a living manner. As observed with the ROMP of norbornene with **2**, no monodisperse polymers were obtained by the polymerization of norbornene. Catalyst **5** polymerized monomers **8** and **10** in quantitative yields with polydispersities between 1.20 and 1.35 (Table 2). This is relatively high for a living polymerization of 7-oxanorbornenes, as in the case of monomer **8**, and can be explained by a change in the rates of initiation and propagation. Polydispersity is affected by the relative rates of initiation (k_i) and propagation (k_p); narrow PDIs are obtained if the initiation rate is within the range of the propagation rate or faster. We believe that the relatively high PDI of the polymer obtained by the polymerization of monomer **8** with catalyst **5** stemmed from a larger value for k_p/k_i than for the other systems. In the case of the polymerization of **8** catalyzed by **6**, full initiation was observed by NMR after 1 minute, while for the polymerization of **8** with **5** the initiation was slow and took almost 10 minutes. This resulted in a complex that started to propagate on one chain end while the other carbene unit of the catalyst had not yet completed initiation, leading to a polymer with a higher PDI.

In contrast to complex **5**, catalyst **6** quantitatively polymerized monomers **8**-**10** to produce polymers with lower PDIs (for example 1.10 for the polymerization of **8** or **9**, or 1.19 for the polymerization of **10**). Table 2 summarizes the GPC results for the homopolymers obtained from the reactions with initiators **5** and **6**.

Table 2. ROMP of 7-oxanorbornenes (**8** and **9**) and functionalized norbornene (**10**) with $(PR_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4\text{-}C(H)=)RuCl_2(PR_3)_2$ (R=Cy, **5**; R=Cyp, **6**) in CH_2Cl_2 at room temperature.

Catalyst	Monomer	Time(min.)	Yield %	[M]/[C]	10^{-4} M_w	10^{-4} M_n	PDI
5	**8**	25	>98	89	2.47	1.83	1.35
5	**10**	30	>98	130	4.86	4.05	1.20
6	**8**	25	>98	98	1.86	1.69	1.10
6	**10**	30	>98	96	5.55	4.65	1.19
6	**9**	30	>98	62	1.70	1.55	1.10

Controlled molecular weights, high efficiency of the catalyst, and absence of chain transfer and termination are characteristics of a living ring-opening metathesis polymerization system. Quirk and Lee proposed several experimental criteria for the characterization of living polymerizations.[16] One of the main criteria for living polymerizations is that the molecular weight should be controlled by the stoichiometry of the reaction, which can be shown by the linear relationship between M_n and the corresponding monomer/catalyst ([M]/[C]) feed ratios. All polymerizations catalyzed by **2**, **3**, **5** or **6** fulfill this criterion. For example, Figure 1 shows these linear relationships for various homopolymers prepared with complexes **5** and **6**.

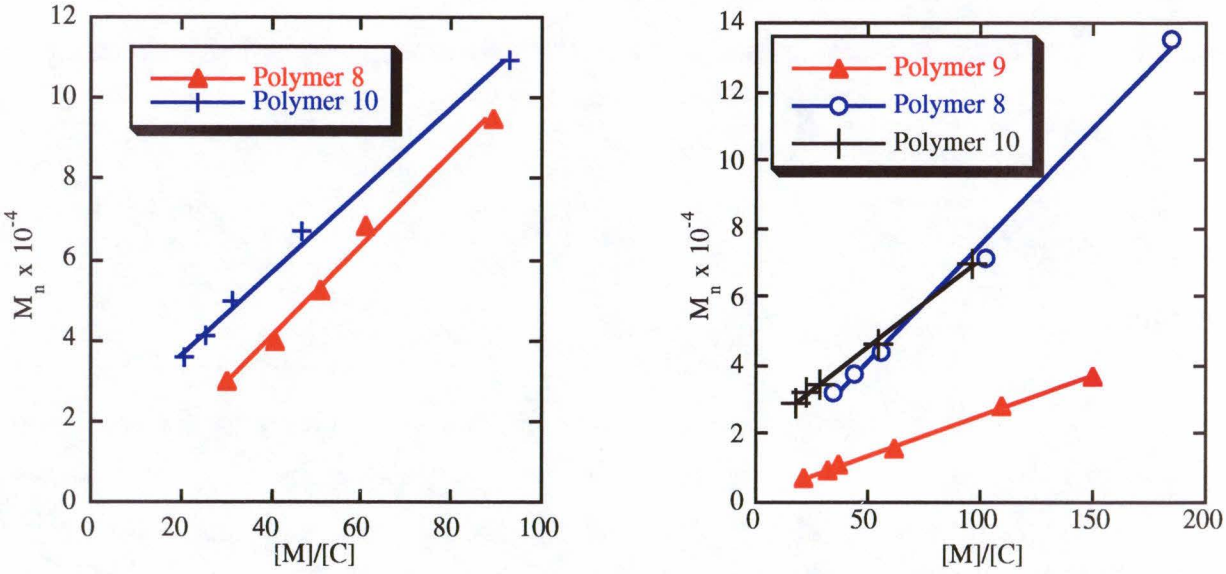


Figure 1. Plot of number average molecular weight (M_n) versus monomer/catalyst ratio ([M]/[C]). (A) For polymers obtained from catalyst **5** at room temperature in CH_2Cl_2. (B) For polymers obtained from catalyst **6** at room temperature in CH_2Cl_2.

Another fundamental criterion for living polymerization is that the polymerization has to proceed until all monomer is consumed.[16] Further addition of monomer must result in continued polymerization to produce a homopolymer with a higher molecular weight, or a block copolymer when a different monomer is used, i.e. the polymerization proceeds in the absence of chain termination and chain transfer. To demonstrate this criterion, a two-step polymerization using monomer **8** and catalyst **6** was carried out. Monomer **8** was polymerized until polymer growth stopped, the polymerization was allowed to sit for 4 hours, and a second aliquot of **8** was added to the reaction. After 30 minutes, the polymerization was terminated with ethyl-vinyl-ether. The molecular weight increased dramatically for the final polymer relative to the first peak, and no residual base polymer was observed. Both chain termination and chain transfer would produce dead polymer chains which will not increase in molecular weight upon addition of more monomer. The PDI increased moderately from 1.10 to 1.20 while the PDI for the first block remained at

1.10 after sitting for 4 hours. This clearly demonstrates the absence of chain transfer and chain termination supporting the living character of the system. Figure 2 shows the GPC traces of the first and the second polymer.

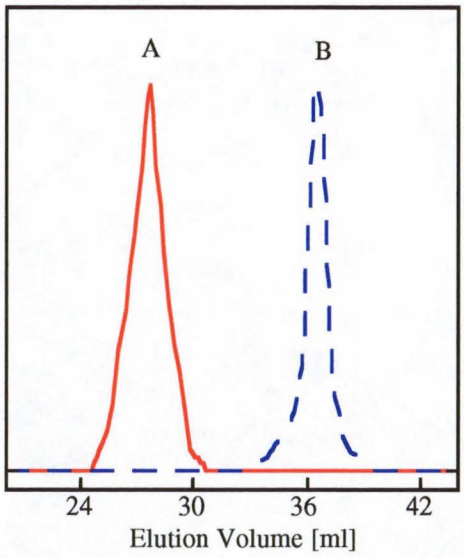
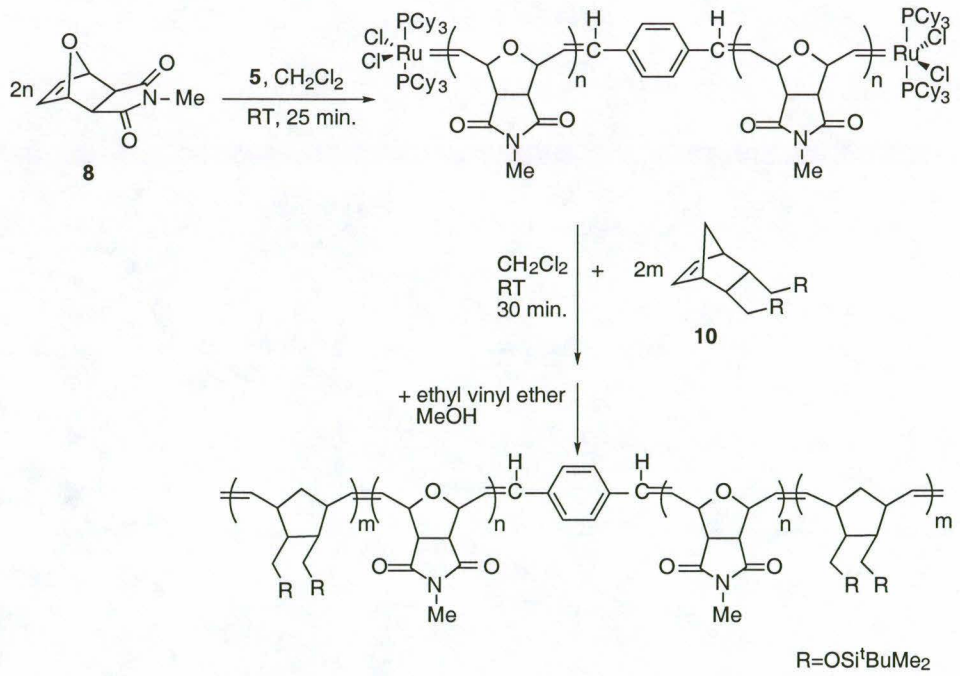


Figure 2. Gel permeation chromatograph traces for polymers obtained from **8** initiated by **6**. The peaks represent (B) polymer after complete incorporation of the monomer (PDI = 1.10), (A) polymer after standing for 4 hours followed by polymerization of additional monomer (PDI = 1.20).

Block Copolymerization. Catalysts **2**, **3**, **5** or **6** were used to form AB or ABA block copolymerizations of **8** with **9** or **10**. In all cases, **8** was polymerized to completion, followed by addition of either **9** or **10**. The polymerization was terminated by adding ethyl-vinyl-ether. Several block copolymerizations were monitored by GPC analysis of samples taken from the reaction mixture after the first monomer had been consumed. The ^{1}H NMR spectra of the block copolymers show the peaks corresponding to the homopolymers of the monomers.[17] Scheme 2 illustrates the polymerization the ABA triblock copolymerization of monomers **8** and **10** with catalyst **5**.



Scheme 2. Synthesis of the ABA triblock copolymer of monomers **8** and **10** initiated by **5**.

The formation of diblock copolymers employing the living systems catalyzed by **2** and **3** was investigated. All diblock copolymers had a higher molecular weight than the homopolymers. In all four cases, polydispersities ranged from 1.15 to 1.18 (Table 3).

Table 3. AB Diblock copolymers of 7-oxanorbornenes (**8** and **9**) and functionalized norbornene (**10**) with $(PR_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4)$ (R=Cy, **2**; R=Cyp, **3**).

Catalyst	First Monomer	Second Monomer	10^{-4} M_w	10^{-4} M_n	PDI
2	**8**	**9**	1.31	1.13	1.16
2	**8**	**10**	0.76	0.65	1.16
3	**8**	**9**	0.31	0.26	1.15
3	**8**	**10**	1.22	1.03	1.18

Diblock copolymers using monomers **8** and **10** have been reported before, using a different ruthenium catalyst $RuCl_2(=CHR')(PR_3)_2$ (R=Ph; Cy; R'= $CH=CPh_2$).[8f] However, in all these cases the PDI's were higher and ranged from 1.21 to 1.26.

The polydispersities of the triblock copolymers ranged from 1.38 to 1.50, depending on the molecular weight. The polydispersities decreased as the molecular weight of the polymers increased over the range from 100,000 to 250,000.[15] The lowest polydispersity was achieved for the block copolymerization of monomers **8** and **9** using catalyst **6**. For example, the molecular weight increased from 27,000 for the homopolymer of **8** to 43,000 for the copolymer,[15] while the polydispersity increased slightly from 1.10 to 1.11 (Figure 3).

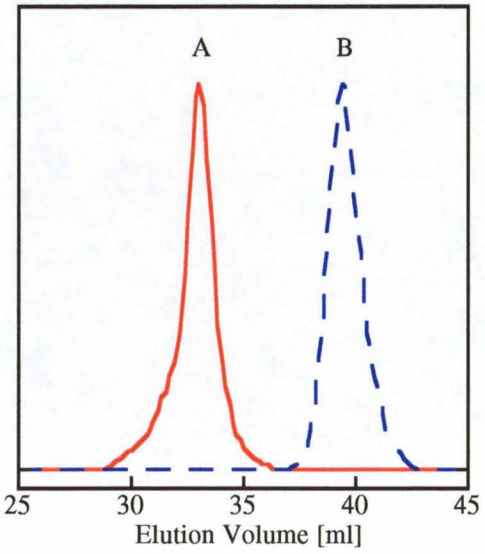


Figure 3. Molecular weight distribution curves of (A) the ABA triblock copolymer resulting from the successive polymerization of **8** and **9** with **6**, and (B) precursor poly-7-oxanorbornene obtained by the polymerization of **8** with **6**.

The synthesis of a triblock copolymer based on monomers **8** and **10** with initiator **6** was also examined. The resulting triblock copolymer had a higher molecular weight (M_n = 133,000) compared to the homopolymer of **8** (M_n = 100,000) and the polydispersities ranged from 1.26 to 1.28.[15] In all cases the polymerizations were terminated prior to

quantitative incorporation of the second monomer. Table 4 summarizes the GPC results of some of the triblock copolymers obtained.

Table 4. ABA Triblock copolymer of 7-oxanorbornenes (**8** and **9**) and functionalized norbornene (**10**) with $(PR_3)_2Cl_2Ru(=CH\text{-}p\text{-}C_6H_4\text{-}C(H)=)RuCl_2(PR_3)_2$ (R=Cy, **5**; R=Cyp, **6**).

Catalyst	First Monomer	Second Monomer	[M1]/[M2]/[C]	10^{-4} M_w	10^{-4} M_n	PDI
5	**8**	**10**	189/137/1	18.25	13.27	1.38
6	**8**	**10**	200/112/1	13.35	10.62	1.26
6	**8**	**9**	216/116/1	10.27	9.35	1.11

Conclusion

This chapter presents the living ring-opening metathesis polymerization of 7-oxanorbornenes (**8**, **9**) and functionalized norbornenes (**10**) with two mono- and two bimetallic well-defined ruthenium catalysts. These living polymerizations can be used for the preparation of new block copolymers. ABA Triblock copolymers were synthesized for the first time in a two-step process using two well-defined bimetallic catalysts.

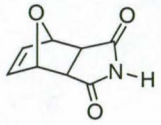
Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4Å molecular sieves (Linde). NMR spectra were recorded on a GE QE-300 Plus (300.10 MHz ^1H; 75.49 MHz ^{13}C) spectrometer. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane and referenced with respect to residual protio solvent. Coupling constants are reported in Hertz (Hz). IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. GPC analyses in dichloromethane were obtained on a HPLC system utilizing an Altex Model 110A pump, a Rheodyne model 7125 injector with a 100μl injection loop, through two American

Polymer Standards 10 micron mixed bed columns, and a Knauer differential-refractometer. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. Elemental analyses were performed by Fenton Harvey at the California Institute of Technology Elemental Analysis Facility.

Materials. Dichloromethane was distilled from calcium hydride and degassed by repeated freeze-pump-thaw cycles. All other solvents were used without further purification unless otherwise noted. Furan, N-methylmaleimide, maleimide, sodium hydride, 1-bromooctane, piperidine, trifluorormethanesulfonic-acid-tert-butyldimethyl-silyl-ester, and potassium carbonate were purchased from the Aldrich Chemical Company and used without further purification. Monomers **8** and **10** were prepared as previously reported.[8f,14] All ruthenium complexes were graciously provided by Dr. Peter Schwab. Purified norborn-2-ene-4,5-dimethanol was graciously provided by David Lynn.

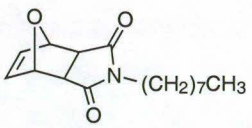
Synthesis of *exo*-N-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (11):



A mixture of furan (11.8 ml, 0.16 mol), and maleimide (8 g, 0.083 mol) in ether (25 ml) was degassed in a heavy-walled flask equipped with a Teflon seal. The flask was sealed under vacuum and then heated to 90°C in an oil bath for 12 hours. White crystals formed in the reaction flask upon cooling. The crystals were collected and recrystallized from water to yield white crystals in 93% yield.

^{1}H-NMR ($CDCl_3$) δ 8.17 (s, 1H), 6.54 (s, 2H), 5.33 (s, 2H), 2.91 (s, 2H).

Synthesis of *exo*-N-octyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (9):



To a solution of **11** (2 g, 0.012 mol) in dimethylformamide (50 ml), potassium carbonate (5 g, 0.036 mol) was added and the mixture was stirred at 90°C for 30 minutes. 1-Bromooctane (2.4 g, 0.012 mol) in dimethylformamide (30 ml) was added dropwise, the mixture was then stirred at 90°C for 1 hour followed by 3 hours at room temperature. The reaction mixture was filtered, the solution poured into water (200 ml), and extracted three times with ether (200 ml). The organic phase was dried over magnesium sulfate and evaporated to yield a dark red solution. Final purfication was achieved by column chromatography (silica gel/dichloromethane) to obtain a light red oil (68%).
^{1}H NMR (CD_2Cl_2) δ 6.47 (s, 2H), 5.21 (s, 2H), 3.45 (t, 2H, J = 7.2 Hz), 2.79 (s, 2H), 1.53 (m, 2H), 1,21 (m, 10H), 0.86 (t, 3H, J = 6.4 Hz); Anal. calcd. for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05, found: C, 68.71; H, 8.16; N, 4.96.

General Procedure for the Homopolymerizations. In a drybox, the catalyst and the monomer were weighed into vials and dissolved in 1 ml and 2 ml of dichloromethane, respectively. The reaction was initiated by adding the catalyst solution to the vigorously stirred monomer solution. The solution was stirred at room temperature for 20 min (monomer **8** and **9**) or for 30 min (monomer **10**). The polymerization was then quenched by addition of a small amount of ethyl-vinyl-ether. The reaction mixture was poured into 30-50 ml of methanol to precipitate the polymer. The resulting white polymer was purified by dissolving in dichloromethane and reprecipitation from methanol several times, and dried *in vacuo*. The ^{1}H NMR spectra of the homopolymers of monomers **8** and **10** were identical to those previously reported.[8f, 14]

^{1}H NMR polymer resulting from **9** (CD_2Cl_2) δ 6.06 (bs, trans), 5.77 (bs, cis), 5.00 (bs, cis), 4.43 (bs, trans), 3.43 (bs), 3.28 (bs), 1.53 (bs) , 1.24 (bs), 0.85 (bt); ^{13}C NMR ($CDCl_3$) δ 175.48, 131.88, 130.92, 81.02, 77.92, 53.45, 52.34, 38.94, 31.69, 29.03, 27.59, 26.71, 22.52, 13.95; IR (thin film on a NaCl plate): 3612, 3462, 2926, 2856, 1775, 1702, 1465, 1438, 1398, 1368, 1268, 1212, 1168, 1138, 1034, 969, 914, 815, 735, 649, 590 cm^{-1}; Anal. calcd. for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05, found: C, 68.95; H, 8.11; N, 5.11.

General Procedure for Diblock Copolymerization. In a typical polymerization, a small vial was charged with monomer **8**, catalyst **2** and a small magnetic stir bar. Degassed dichloromethane was added *via* syringe. The solution was allowed to stir under nitrogen for 25 min. The second monomer was inserted *via* syringe and the solution was stirred for an additional 30 minutes (monomer **9**) or 35 minutes (monomer **10**). The polymerization was terminated with ethyl-vinyl-ether and precipitated from methanol to yield a white solid. The resulting white polymer was purified by dissolving in dichloromethane, reprecipitation from methanol several times, and dried *in vacuo*. The ^{1}H NMR spectra of the block copolymer of monomer **8** and **10** were identical with those previously reported.[8f]

^{1}H NMR polymer resulting from **8** and **9** (CD_2Cl_2) δ 6.04 (bs, trans), 5.78 (bs, cis), 5.01 (bs, cis), 4.44 (bs, trans), 3.43 (bs), 3.28 (bs), 1.53 (bs), 1.24 (bs), 0.85 (bt); ^{13}C NMR ($CDCl_3$) δ 175.49, 131.88, 130.92, 81.04, 77.92, 53.45, 52.37, 38.94, 31.69, 29.03, 27.59, 26.72, 22.52, 13.95; IR (thin film on a NaCl plate): 3442, 2928, 2857, 1775, 1700, 1438, 1384, 1358, 1284, 1168, 1131, 1030, 967, 914 cm^{-1}; Anal. calcd. for $C_{42.4}H_{66.7}N_2O_{8.3}Si_{2.3}$ (entry 2 on Table 2): C, 63.45; H, 8.33; N, 3.50; found: C, 62.68; H, 8.15; N, 3.67.

General Procedure for Triblock Copolymerization. Monomer **8** was polymerized according to the procedure outlined above. After 25 minutes, a monomer solution of **9** or **10** was added *via* a gas-tight syringe, and the solution was stirred vigorously. After 20 minutes (monomer **9**) or 30 minutes (monomer **10**) the polymerization was terminated by addition of a small amount of ethyl vinyl ether and the resulting polymers were purified as described above. All ABA triblock copolymers are white, floculent solids, soluble in dichloromethane and chloroform, and stable under air at room temperature.

^{1}H NMR polymer resulting from **8** and **9** (CD_2Cl_2) δ 6.04 (bs, trans), 5.78 (bs, cis), 5.00 (bs, cis), 4.44 (bs, trans), 3.43 (bs), 3.28 (bs), 1.53 (bs), 1.24 (bs), 0.85 (bt); ^{13}C NMR ($CDCl_3$) δ 175.48, 131.88, 130.92, 81.02, 77.92, 53.45, 52.34, 38.94, 31.69, 29.03, 27.59, 26.71, 22.52, 13.95; IR (thin film on a NaCl plate): 3444, 2928, 2856, 1775, 1700, 1438, 1384, 1358, 1284, 1168, 1130, 1030, 967, 913 cm^{-1}; Anal. calcd. for $C_{42.4}H_{66.7}N_2O_{8.3}Si_{2.3}$ (entry 2 on Table 2): C, 63.45; H, 8.33; N, 3.50, found: C, 62.61; H, 8.05; N, 3.78.

^{1}H NMR polymer resulting from **8** and **10** (CD_2Cl_2) δ 6.06 (bs, trans), 5.81 (bs, cis), 5.48 (bs, trans), 4.95 (bs, cis), 4.49 (bs, trans), 3.68 (bs), 3.63 (bs), 2.96 (bs), 1.55 (bs), 0.90 (bs), 0.11 (bs); ^{13}C NMR ($CDCl_3$) δ 175.42, 131.67, 130.80, 77.23, 80.61, 53.25, 52.14, 38.72, 31.46, 28.77, 28.81, 27.38, 26.56, 24.79, 22.30, 13.74; IR (thin film on a NaCl plate): 3584, 2953, 2928, 2856, 1777, 1700, 1438, 1384, 1284, 1255, 1131, 1076, 1026, 971, 913, 836, 774, 743 cm^{-1}; Anal. calcd. for $C_{19}H_{23}N_{1.6}O_5$ (entry 3 on Table 2): C, 64.49; H, 6.52; N, 6.45, found: C, 63.95; H, 6.49; N, 6.53.

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(17) The ^{1}H NMR spectra of the homopolymers of monomer **5** and **7** have been previously reported (Ref. 8f,14).

Chapter 2

Influence of Backbone Rigidity on the Thermotropic Behavior of Side-Chain Liquid Crystalline Polymers Synthesized by Ring-Opening Metathesis Polymerization

Abstract

The effect of backbone flexibility on the mesomorphic behavior of side-chain liquid crystalline polymers synthesized by ring-opening metathesis polymerization was investigated. The synthesis of norbornene and cyclobutene monomers containing a *p*-nitrostilbene moiety as the mesogenic group and polymerization of these monomers to produce side-chain liquid crystalline polymers with low polydispersities and defined molecular weights was accomplished. The relatively rigid poly(norbornene)s displayed enantiotropic nematic mesomorphism with glass transitions from 44-64°C and isotropization temperatures between 108-121°C, whereas the more flexible poly(butadiene)s showed enantiotropic smectic A mesomorphism with glass transition temperatures from 14-31°C and isotropization temperatures between 74-111°C. A diblock copolymer containing a 1:1 mixture of the poly(norbornene) and poly(butadiene) exhibited a smectic A mesophase as well. The dependence of the degree of polymerization and flexible spacer length on the phase transitions of these systems was determined demonstrating stabilization of the mesophase by both increasing molecular weight and flexible spacer length.

Introduction

Since their discovery in 1888 by Reinitzer,[1] liquid crystalline (LC) polymers with the mesogen in the main chain or in the side group have been investigated intensely for their scientific and technological potentials.[2] The reasons are the fascinating ability of anisotropic molecules to form supramolecular structures through self-organization and the resulting properties of such systems.[2] As information about these material was accumulated, it was observed that increasing liquid crystalline order was found in many systems on passing from low molecular weight monomeric compounds to the corresponding polymeric material.[2] The type and extent of molecular order is controlled by the synthesis of molecules with appropriate molecular geometries. Liquid crystalline polymers can be divided into two major classes: (1) polymers containing the mesogenic group in the backbone (main-chain liquid crystalline polymers; MCLCPs) and (2) polymers bearing the mesogenic group on a side-chain (side-chain liquid crystalline polymer; SCLCPs), the latter constitute the focus of this chapter.[2] All LC polymers contain rod-like moieties[3] or disc like mesogens[4] (Figure 1).

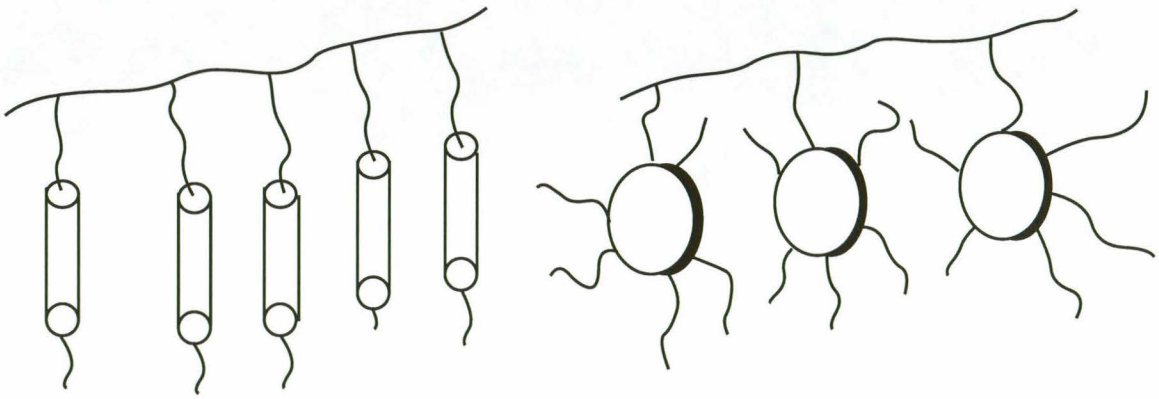


Figure 1. Schematic representation of polymers with rod-like and disc-like mesogens as side groups.

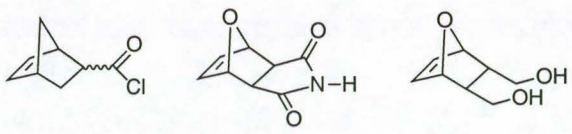
In both mesophase systems the characteristic molecular axes are approximately parallel: the long axes of the rods and the short axes of the disc-like mesogens.[5] If this is the only principle of organization, there exists only a nematic phase (n). An additional

positional order of the molecule gives rise to the different layer structures of the smectic phases[3] (for the rod like moieties) or stack structures of the columnar phases[5] (for discotic systems).

Rod-like side-chain liquid crystalline polymer synthesized by ROMP. Ringsdorf *et al.* discovered that the addition of a flexible spacer between the mesogenic unit and the backbone enhances the liquid crystallinity in SCLCPs.[6] The flexible spacer allows a partial decoupling of the mesogenic unit from the backbone providing the mesogens with the ability to stack in organized domains. These initial studies prompted the synthesis of a large variety of SCLCPs utilizing various polymer backbones including poly(acrylate)s,[7] poly(methacrylate)s,[8] poly(siloxane)s,[9] and poly(phosphazane)s.[10] However, most of these side-chain liquid crystalline polymers have been prepared by radical polymerizations, hydrosilations, and ring-opening polymerizations. Due to the nature of these polymerizations most were carried out in a non-living manner. These methods do not allow control of the molecular weight or the polydispersities of the polymers and there is limited data about the influence of the molecular weight and the polydispersities. Recently, group transfer polymerization and living cationic polymerization methods have been used to prepare SCLC polymers in a living manner.[11]

ROMP is another powerful tool for the preparation of polymers synthesized in a living fashion with a variety of functional groups and narrow polydispersities.[12] Recently, this technique has been successfully applied to the synthesis of norbornene-based SCLC polymers which display nematic mesomorphism.[13-16] Efforts have been devoted to investigate the effects of the flexible spacer length, the degree of polymerization, and the mesogen employed on the phase behavior for these systems,[13-16] while the influence of the polymer backbone has not yet been elucidated. This chapter forms part of the research addressing the influence of the polymer backbone on phase behavior by comparing the rigid poly-norbornene based SCLC polymers with the more flexible poly-cyclobutene,

which is formally a 1,4-poly(butadiene) structure. Three different norbornene precursors were selected for their rigidity and number of possible liquid crystalline side chains.



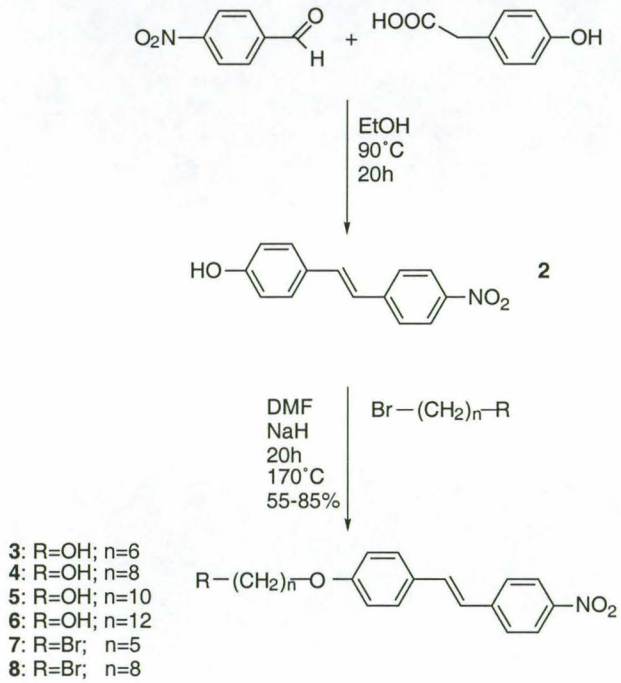
10 9

Figure 2. Norbornene precursors used in this study.

This chapter reports the living ROMP of mesogenic norbornene derivatives using $(PCy_3)_2Cl_2Ru(=CH\text{-}C_6H_5)$ **1** as the initiator[17] and describes the influence of spacer length and molecular weight on the phase behavior of the resulting polymers.

Results

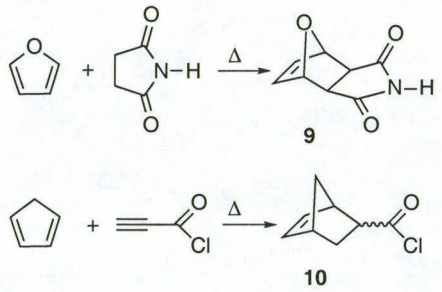
Monomer syntheses. *p*-Nitrostilbene **2** was chosen as mesogen for its known liquid crystalline and non-linear optic (NLO) activity, and was synthesized as shown in Scheme 1 following the description of Mc Culloch et al.[18]



3: R=OH; n=6
4: R=OH; n=8
5: R=OH; n=10
6: R=OH; n=12
7: R=Br; n=5
8: R=Br; n=8

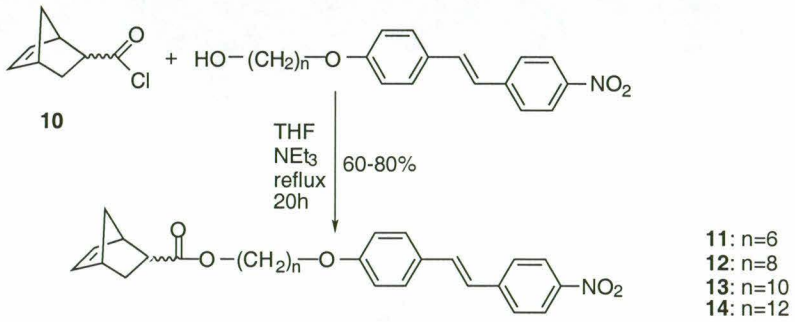
Scheme 1. Synthesis of side-chain precursors **3** - **8**.

Subsequent alkylation of the mesogen with dibromoalkanes or bromoalcohols yielded the side-chain precursor in high yields (Scheme 1). The norbornene precursors **9** and **10** were synthesized by Diels-Alder reactions as described in the literature (Scheme 2).[19]



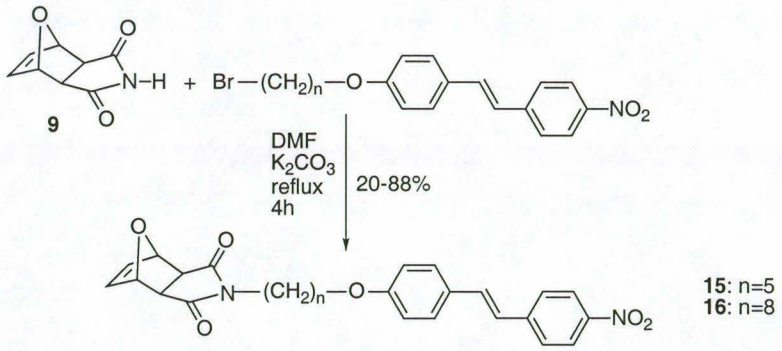
Scheme 2. Synthesis of the norbornene precursor **9** and **10**.

Monomers **11** to **14** (exo:endo ≈ 1:4) were synthesized in good yields from the reaction of the corresponding acid chloride **10** with the *p*-nitrostilbene mesogen **2** containing different alkyl spacer lengths (precursor **3**-**6**) (Scheme 3). All monomers were yellow, crystalline solids which formed no mesophases. They exhibited only a single melting endotherm on heating and a single crystallization exotherm on cooling, as observed by differential scanning calorimetry (DSC).



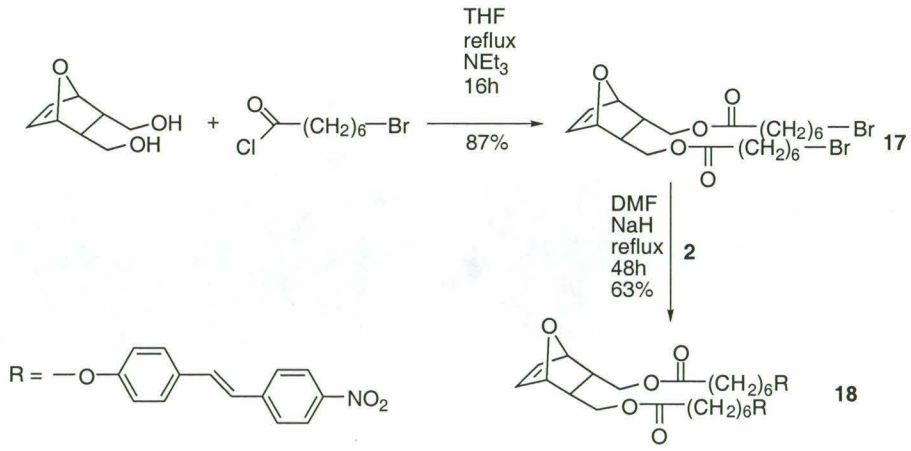
Scheme 3. Synthesis of monomers **11** to **14**.

Monomers **15** and **16** were selected because of their relatively high backbone rigidity compared to monomers **11** to **14**. The synthesis of the substituted 7-oxanorbornenes monomers **15** and **16** is outlined in Scheme 4. Both monomers were obtained by alkylation of **9** with **7** or **8** as light yellow solids in high yields.



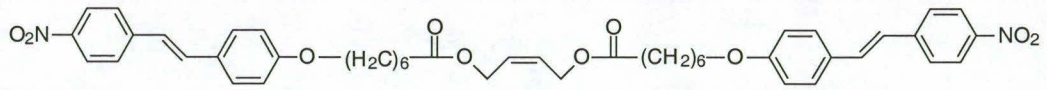
Scheme 4. Preparation of monomers **15** and **16**.

Monomer **18** was designed because it can be alkylated in two positions, thus yielding a monomer with two LC side-chains. These two chains were expected to have different order behavior and to show a dramatic change in stereochemistry[16] compared to monomers **11** to **16** therefore resulting in interesting new polymers with several mesophases. Recently, Stelzer and coworkers were able to show that liquid-crystalline 2,3-disubstituted norbornene derivatives resulted in polymers which show metastable nematic and smectic A phases with respect to the crystalline phases.[16] These polymers exhibit a stabilization of the liquid crystalline phase compared to their monosubstituted counterparts.[13] **18** was synthesized as shown in Scheme 4. The first step consisted of nucleophilic displacement of the halide of 1-bromo-6-hexanoyl-chloride with norborn-2-ene-4,5-dimethanol under basic conditions. The resulting norbornene derivative was treated with **2** to yield **18** as a yellow solid.



Scheme 5. Preparation of monomer **18**.

Employing the same procedure outlined above, monomer **20** was synthesized using 1,4-butendiol. Acyclic olefins acted as chain transfer agents in the ROMP of cyclic olefins.

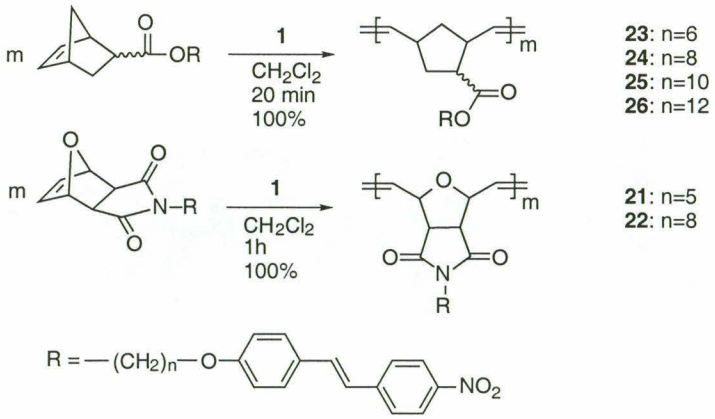


20

Scheme 5a. Chain transfer agent **20**.

Incorporation of these functional groups at the end of every polymer resulted in telechelic polymers.[20] If the chain transfer agent bore a mesogenic unit, polymerization would result in a polymer with only two LC functionalities at the ends of the polymer. Recently, Feast and coworkers were able to synthesize LC polymers with only one mesogenic unit at the end of polyacetylene *via* the Durham route.[21] Unfortunately, they were not able to prove the existence of an ordered phase as a result of the relatively high molecular mass of their polymers.

Polymerizations. Polymerizations of **11** to **16** with the well-defined ruthenium catalyst **1** were carried out in dichloromethane at room temperature. The monomers were polymerized for 1 hour (monomers **11** to **14**) or for 20 minutes (monomers **15** and **16**) followed by treatment with an excess of ethyl vinyl ether to cleave the catalyst from the polymer chain. Precipitation from methanol resulted in polymers **21** to **26** as fluffy, yellow solids in 90-99% isolated yields (Scheme 6).



Scheme 6. Preparation of the SCLC poly(norbornenes) **21** to **26**.

Monomers **11** to **14** were polymerized at a monomer/catalyst ratio ([M]/[C]) of each 25/1 to determine the effect of the spacer length on the phase behavior. In addition, **12** was polymerized at [M]/[C] ratios of 5, 10, 25, 50 and 100 to examine the effect of molecular weight on the phase behavior. In all cases polydispersities ranged from 1.08 to 1.11, depending on the chain length. Monomers **15** and **16** were polymerized in quantitative yields employing catalyst **1** with narrow polydispersities. Table 1 summarizes the GPC results of these polymerizations.

Table 1. ROMP of norbornenes **11-16** with $(PCy_3)_2Cl_2Ru(=CH\text{-}C_6H_5)$ **1** at room temperature.

Monomer	Time (min)	Yield %	[M]/[C]	10^{-3} M_W	10^{-3} M_n	PDI
11	60	>98	25	14.5	13.4	1.08
12	60	>98	25	13.7	13	1.08
13	60	>98	25	24.4	22	1.11
14	60	>98	25	22.9	20.8	1.10
15	20	>98	21	16.7	15.1	1.10
16	20	>98	50	30.7	26.2	1.17
12	60	>98	5	8.1	7.3	1.11
12	60	>98	10	10.7	9.8	1.09
12	60	>98	25	13.7	13	1.08
12	60	>98	50	19.2	18	1.07
12	60	>98	100	25	23.2	1.08

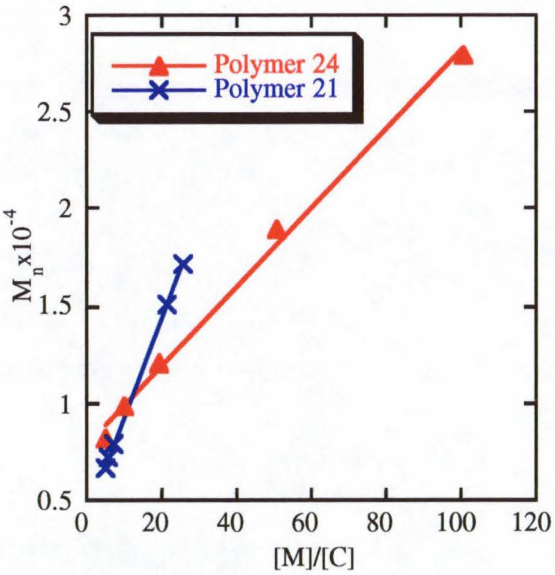


Figure 3. Plot of number average weight (M_n) versus monomer/catalyst ratio ([M]/[C]) for polymer **21** and polymer **24**.

The polymerizations catalyzed by **1** fulfill all criteria of a living ring-opening metathesis polymerization as described by Quirk and Lee.[22] In all cases a linear relationship between M_n and the corresponding monomer/catalyst feed ratio was observed. Figure 3 shows two examples (polymer **21** and polymer **24**) of this linear relationship.

In living systems, the polymerization proceeds until all monomer is consumed, and further addition of monomer results in a continued polymerization as outlined in chapter 2.[22] Figure 4 shows the two-step polymerization of **12** as experimental verification of this criterion. Monomer **12** was polymerized, using catalyst **1** until all monomer was consumed. The polymerization was allowed to sit for 3 hours and a second aliquot of **12** was added to the solution. The molecular weight of the final polymer shifted dramatically relative to polymer after the first polymerization, while the PDI increased only moderately from 1.08 to 1.10. The fact that no low molecular weight peaks were observed after the second polymerization clearly demonstrated the living character of the polymerization.

Both chain transfer and chain termination would produce dead polymer which would not increase in molecular weight upon addition of more monomer.

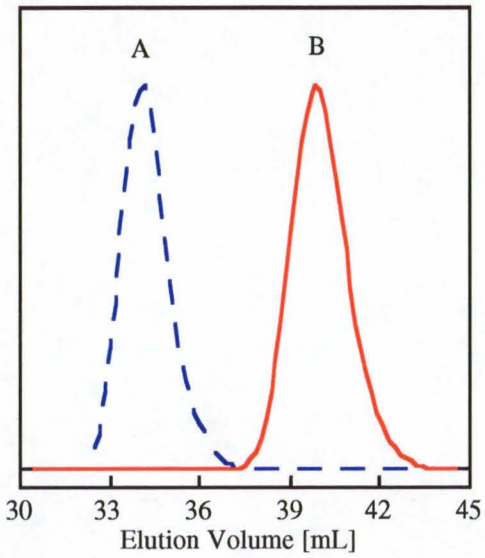
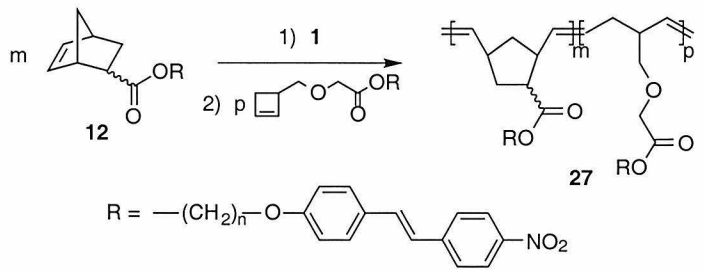


Figure 4. Gel permeation chromatograph traces for polymers obtained from **12** initiated by **1**. The peaks represent B) polymer after complete incorporation of the monomer (PDI = 1.08), A) polymer after standing for 3 hours followed by continued polymerization of additional monomer (PDI = 1.10).

Also a block-copolymerization of monomer **12** and a cyclobutene containing a liquid-crystalline side chain was accomplished with a $[M_1]/[M_2]/[C]$ ratio of 25/25/1 through sequential addition of both monomers. Polymerization of **12** for 1 hour at room temperature was followed by addition of the cyclobutene at 45°C for 24 hours. Precipitation from acidic methanol resulted in polymer **27** as a fluffy, yellow solid in 95% yield (Scheme 7).



Scheme 7. Preparation of block copolymer **27**.

It was not possible to polymerize monomer **18** with either catalyst **1** or molybdenum catalysts of the Schrock type.[12b] This could be a result of the relatively high steric hindrance. The oxygen atom in the 7-oxanorbornenes constitutes another potential problem: coordination of the metal center to oxygen can slow down or even shut down the catalytic activity of the catalyst. Also, the chain transfer polymerization of **20** with cyclooctadiene (COD) was unsuccessful. The polymerization only resulted in poly-COD and no end-functionality was obtained. In this case as well, either the steric hindrance or the concentration of the chain transfer agent seems to be the main reason for the failure to incorporate the chain transfer reagent.

Polymer thermal characterizations. Phase behavior of the polymers was analyzed by differential scanning calorimetry (DSC) and polarized optical microscopy. The first and subsequent DSC heating scans were essentially identical and all heating and cooling scans were completely reversible for each of the polymers. All poly(norbornenes) displayed enantiotropic mesophases over the entire range of spacer length and molecular weights. An increase of the molecular weight and the spacer length resulted in a stabilization of the mesophases. As expected, the glass transition drops with longer spacer length while the nematic/isotropic transition decreased slightly with increasing spacer length. Figure 5 shows the second heating and the first cooling scans of polymers **23** to **26**.

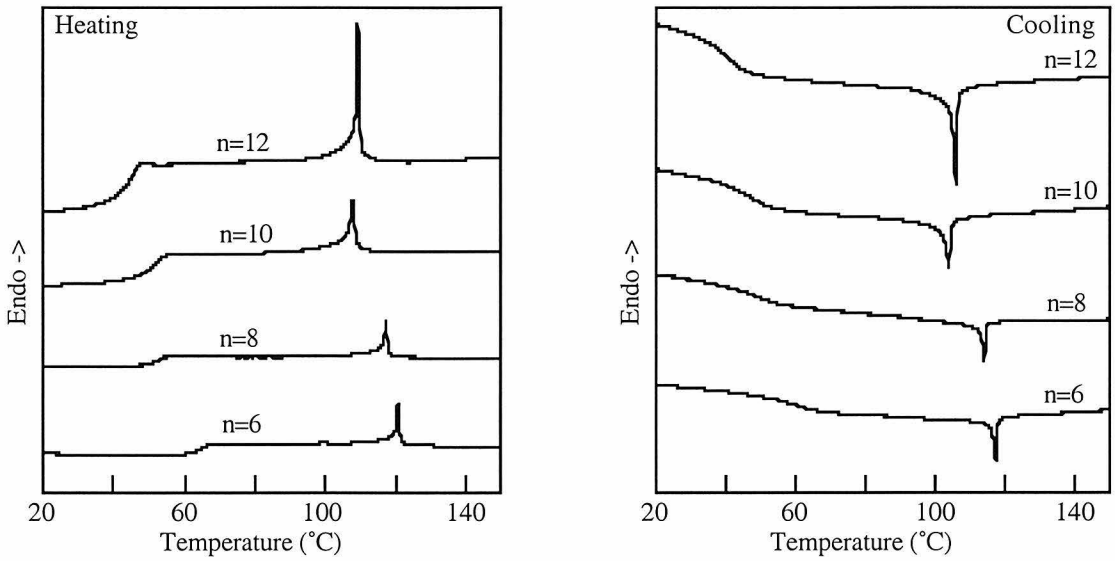


Figure 5. Normalized DSC thermograms of polymers **23** to **26**: A) second heating scans; B) first cooling scans.

The spacer length did affect the temperature of the transition. In general, the isotropization temperatures decreased slightly as the spacer length increased while glass transitions decreased rapidly with increasing spacer length. This lead to a broader temperature window of the mesophases as the spacer length increased. Additionally, due to increasing viscosity, transitions of higher molecular weight polymers were higher than those of lower molecular weight polymers, with the result that the transition occured over a broader temperature range. The transition started to become independent of molecular weight when the chains contained between 25 and 50 repeat units. Figure 6 shows the DSC traces of polymer **24** with a theoretical degree of polymerization of approximately 5 to 100.

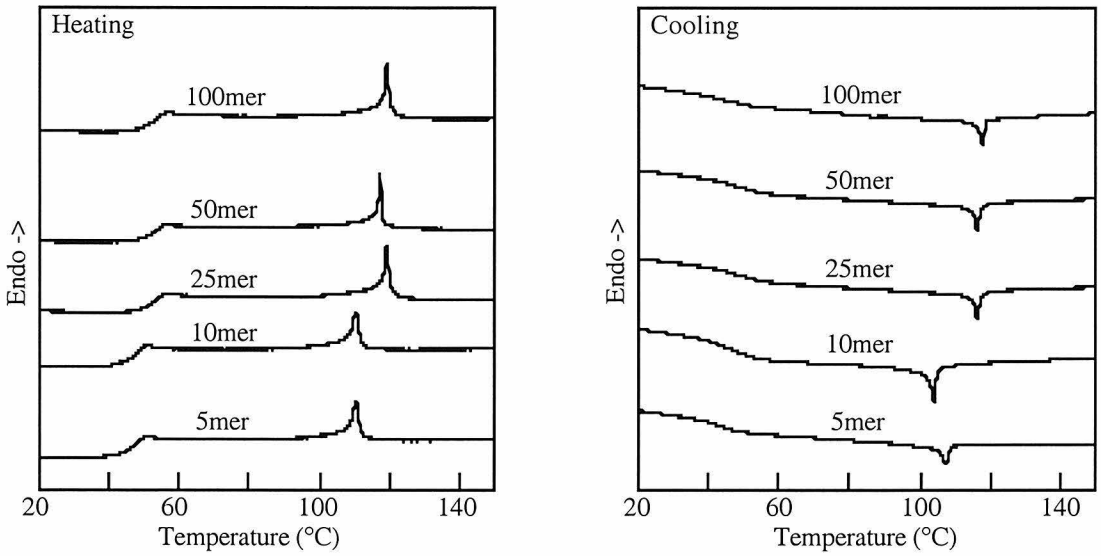


Figure 6. Normalized DSC thermograms of polymer **24** dependent on the monomer/catalyst ratio: A) second heating scans; B) first cooling scans.

For the poly(7-oxanorbornene)s **21** and **22** the glass transitions were substantially higher than for polymers **23** to **26** (70°C and 105°C) while the nematic/isotropic transitions were at 90°C and 127°C, respectively. This lead to a much smaller temperature window of the mesophases. The higher T_g for this 7-oxanorbornene backbone is well known and stems from the more rigid backbone.[19a] The decrease of the nematic/isotropic transition and a large decrease of the enthalpy peaks in the DSCs clearly indicate weaker mesophases. The more rigid backbone does not have the flexibility for a good alignment, and the mesophase is less stable.

All polymers are stable under air at room temperature for months. At the onset of substantial mass loss (T_d) under argon atmosphere the temperatures were between 340 and 346°C, while the T_d dropped to 327 to 362 under an air atmosphere. All thermal characterizations and thermal stability of polymers **21** to **26** are summarized in Table 2.

Table 2. Thermal and thermogravimetric analysis of polymers **21** to **26**.

Polymer	[M]/[C]	M_n	PDI	Phase Transition (°C) heating	Phase Transition (°C) cooling	Thermogravimetric Analysis Atmosphere	Thermogravimetric Analysis Temp. of 10% weight loss (°C)
21	21	17000	1.10	g105n127i			
22	30	26000	1.17	g70n92i		air/argon	339/362
23	25	13400	1.08	g64n121i	i117n60g	air/argon	327/330
24	25	13000	1.08	g57n117i	i114n48g	air/argon	362/341
25	25	22000	1.11	g50n108i	i104n46g	air/argon	347/340
26	25	20800	1.10	g44n108i	i106n40g	air/argon	336/346
24	5	7300	1.11	g46n108i	i107n43g		
24	10	9800	1.09	g50n114i	i111n46g		
24	25	13000	1.08	g57n117i	i114n48g		
24	50	18000	1.07	g51n118i	i116n50g		
24	100	23200	1.08	g49n121i	i118n44g		

Thermal polarized optical microscopy demonstrated that polymers **23** to **26** exhibit textures characteristic of nematic mesophases.[3] The polymers with high molecular weight ([M]/[C] > 25) exhibited Schlieren textures with rather small domains due to the restricted mobility and flexibility of the polymers. Annealing of these polymers at the liquid crystalline phases had no effect on the size of the domains. The low molecular weight polymers showed Schlieren textures with significantly larger domains because of enhanced polymer mobility. Annealing of these polymers at the liquid crystalline phase resulted in even larger domains. As a result of the weak mesophase of polymers **21** and **22**, it was not possible to observe a LC mesophase by polarized optical microscopy. Figure 7 is a representative polarized optical micrograph showing the Schlieren textures of polymer **24**.

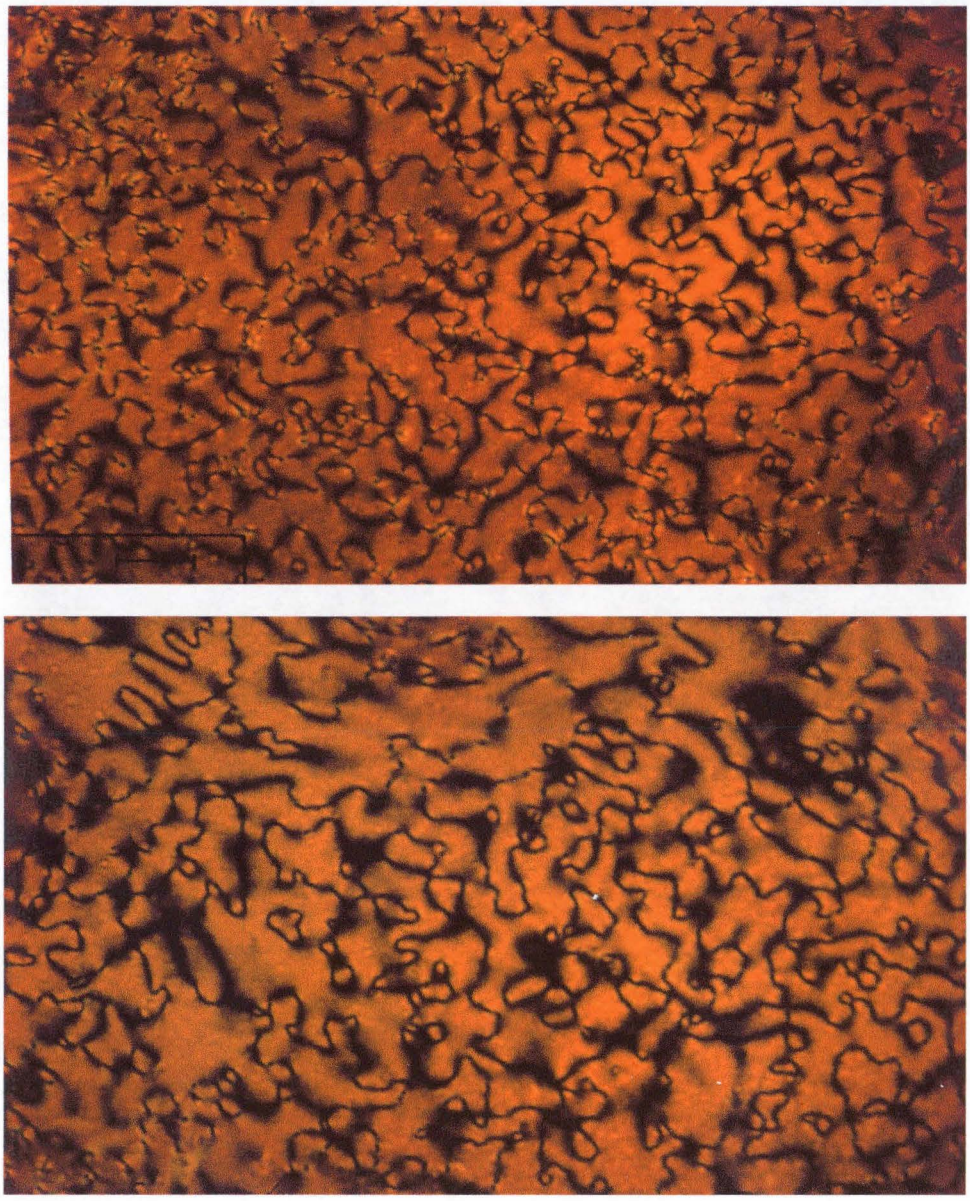


Figure 7. Polarized optical micrograph (magnification 50x) of the nematic Schlieren texture observed on cooling **24** from the isotropic state at 100.0°C (A) before and (B) after annealing at 115.0°C for 15 minutes.

As mentioned before, this research was part of a joint project with Dr. Bob R. Maughon addressing the influence of the backbone rigidity. Dr. Maughon used the above synthesized mesogen precursors **3** to **6** for the synthesis of SCLC polymers with the more flexible poly(butadiene) backbone. These polymers have lower DSC transition peaks and

display bâtonnet textures in the polarized optical micrograph typical for smectic A mesophases.[3]

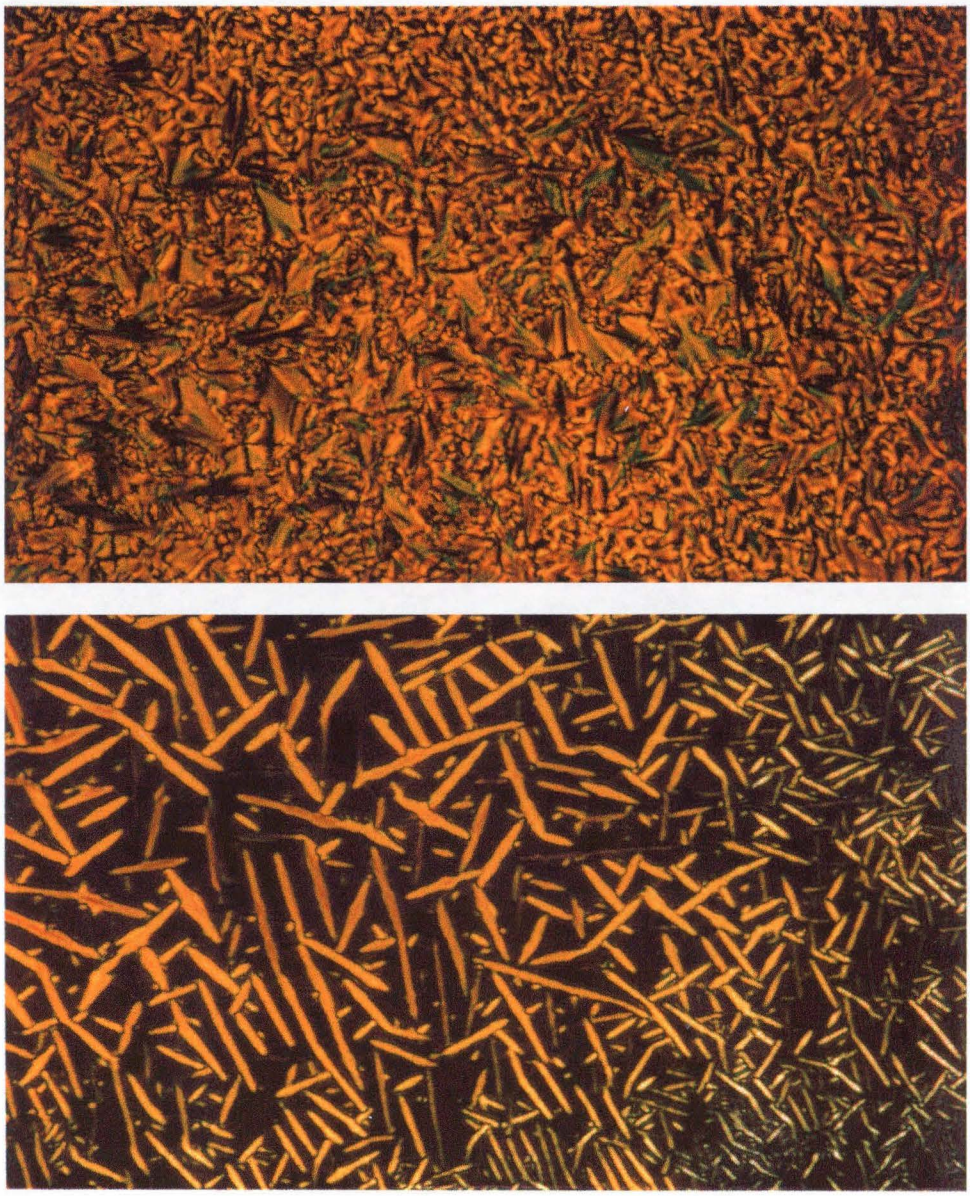


Figure 8. Polarized optical micrograph (magnification 50x) of the smectic A texture observed on cooling a cyclobutene polymer from the isotropic state at 100.0°C (A) regular smectic A texture, (B) bâtonnet texture at 118.8°C.

These results suggest that the difference in the mesogenic behavior of these poly-cyclobutenes compared to the polynorbornenes can be attributed to the enhanced flexibility of the polybutadiene backbone, allowing for a higher degree of alignment among the

mesogenic moieties. In order to ascertain which mesophase will be dominant in determining the phase behavior, block copolymer **27** was synthesized. Table 3 summarizes the DSC results of **27**.

Table 3. DSC results of polymer **27**.

			Phase Transition (°C)	
[M]/[M]/[C]	M_n	PDI	heating	cooling
25/25/1	128000	1.12	g27s104i	i103s26g

The glass temperature and the smectic/isotropic transitions of **27** lie between the T_g and the transition of the poly(norbornene)s and the poly(butadiene)s. Polarized optical micrograph clearly exhibits a smectic A mesophase demonstrating the dominance of the flexible poly(butadiene) backbone in determining the phase behavior. Figure 9 shows the bâtonnet texture of **27**.

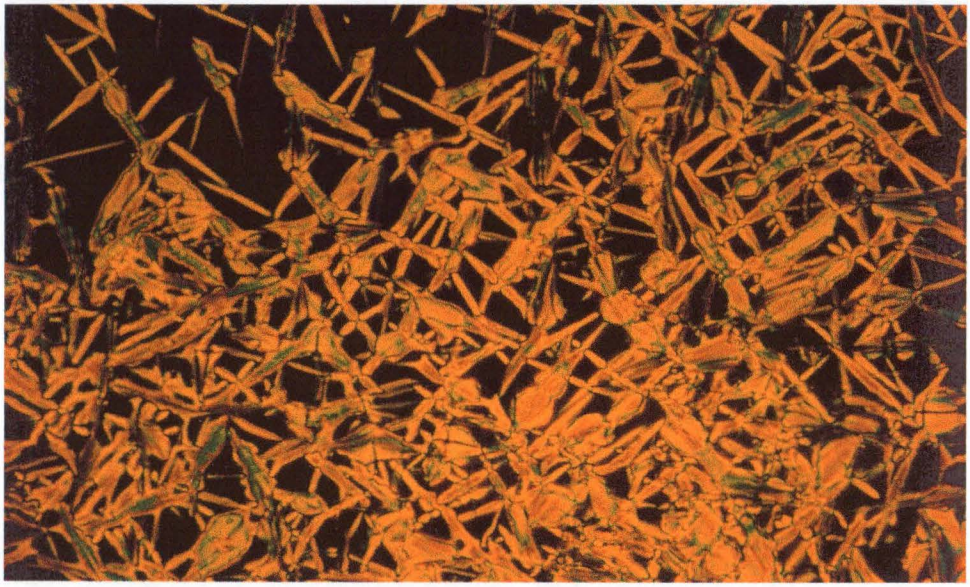


Figure 9a. Polarized optical micrograph (magnification 50x) of the smectic A texture (bâtonnet texture) observed on cooling **27** from the isotropic state at 111.0°C.

Figure 9b. Polarized optical micrograph (magnification 50x) of the regular smectic A texture observed on cooling **27** from the isotropic state at 110.3°C.

Conclusion

Living ring-opening metathesis polymerization has been employed to polymerize norbornenes and 7-oxanorbornenes containing a *p*-nitrostilbene mesogen to yield side-chain liquid crystalline polymers. All poly(norbornene)s exhibited enantiotropic nematic mesophases, whereas the norbornene/cyclobutene block copolymer exhibited a smectic A mesophase as observed before with poly(butadiene) SCLC. This demonstrates the prevailing influence of the poly(butadiene) backbone in determining the phase behavior. In the case of the poly(norbornene)s, the transitions became independent of molecular weight when the chains contained around 25 repeat units. In all cases an increase in molecular weight and spacer length resulted in a stabilization of the mesophases. In comparison to the SCLC poly(butadiene)s synthesized by Dr. Maughon, the poly(norbornene)s displayed a lower order of alignment clearly demonstrating the large influence of the backbone on the thermotropic behavior.

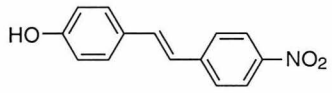
Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4Å molecular sieves (Linde). NMR spectra were recorded on a GE QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane and referenced to residual protio solvent. Coupling constants are reported in Hertz (Hz). IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. GPC analyses in dichloromethane were obtained on a HPLC system utilizing an Altex Model 110A pump, a Rheodyne model 7125 injector with a 100µl injection loop, through two American Polymer Standards 10 micron mixed bed columns, and a Knauer differential-refractometer. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-7or a Mettler DSC 30 with a 10K/min scan rate, and the thermogravimetric analysis was accomplished on a Perkin-Elmer TGA-2. Microscopic observations of the textures were made using a Zeiss Axiophot polarizing microscope equipped with a Linkam THM 600 hot stage and a TMS 90 thermal control unit. All polarizing micrographs were taken with a 50-fold magnification unless noted otherwise. At this magnification the scale corresponds to 20µm. Elemental analyses were performed by Fenton Harvey at the California Institute of Technology Elemental Analysis Facility.

Materials. Dichloromethane and dichloroethane were distilled from calcium hydride and degassed by repeated freeze-pump-thaw cycles. All other solvents were used without further purification unless otherwise noted. Furan, p-nitrophenylacetic acid, p-hydroxybenzaldehyde, maleimide, acryloylchloride, dicyclopentadiene, catechol, 1-bromohexane, 1-bromopentane, borontrifluoro-etherate, boron trifluoride-diethylether, vanaduim oxytrifluoride, bromine, iron powder, 1,5-dibromopentane, 1,8-dibromooctane, 1-bromo-6-hexanol, 1-bromo-8-octanol, 1-bromo-10-decanol, 1-bromo-12-dodecanol, 1-

bromo-6-hexanoyl-chloride, piperidine, n-buthyllithium, trimethyl-borate, palladium-tetra(triphenyl)phosphine, sodium hydride, triethylamine and potassium carbonate were purchased from the Aldrich Chemical Company and used without further purification. The ruthenium complex was graciously provided by Dr. Peter Schwab. Purified cyclooctadiene and norborn-2-ene-4,5-diol were graciously provided by David Lynn and 2-cyclobutene-5-[2-carbonyl-8-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-octane-ester]-ethane by Dr. Maughon.

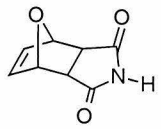
Synthesis of 4-hydroxy-4'-nitrostilbene (2):



Following the procedure by Mc Culloch,[18] piperidine (44 ml) was added dropwise to a hot solution of p-nitrophenylacetic acid (100 g, 0.55 mol) and p-hydroxybenzaldehyde (68.8 g, 0.55 mol) in ethanol. The reaction mixture was stirred under reflux for 20 hours. After 30 min the color changed from yellow to dark red. The reaction was neutralized with 1N hydrochloride acid. The resulting precipitate was collected and recrystallized from 1.5 l of ethanol/water (18:1) to yield 61.9 g (46.7%) of orange colored powder.

^{1}H-NMR (aceton d^6) δ 8.72 (s, 1H), 8,20 (d, 2H, *J* = 8.9 Hz), 7.78 (d, 2H, *J* = 8.9 Hz), 7.53 (d, 2H, *J* = 8.4 Hz), 7.44 (d, 1H, *J* = 16.4 Hz), 7.19 (d, 1H, *J* = 16.4 Hz), 6.88 (d, 2H, *J* = 8.4 Hz); ^{13}C-NMR (aceton d^6) δ 158, 146, 144.6, 133.1, 128.4, 128.0, 126.4, 123.6, 123, 115.5; IR (thin film on a NaCl plate) 3422, 1631, 1587, 1500, 1438, 1339, 1318, 1266, 1213, 1193, 1109, 974, 955, 872, 844, 818, 750, 688, 535 cm^{-1}.

Synthesis of *exo*-N-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (9):



A mixture of furan (11.8 ml, 0.16 mol) and maleimide (8 g, 0.083 mol) in diethyl ether (25 ml) was degassed in a heavy-walled flask equipped with a Teflon seal. The flask was sealed under vacuum and then heated to 90°C in an oil bath for twelve hours. White crystals formed in the reaction flask upon cooling. The crystals were collected and recrystallized from water to yield white crystals in 93% yield.

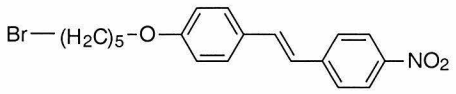
^{1}H-NMR ($CDCl_3$) δ 8.17 (s, 1H), 6.54 (s, 2H), 5.33 (s, 2H), 2.91 (s, 2H).

Synthesis of norborn-2-ene-5-carbonyl-chloride (10):

Following the procedure by Jacobine et al,[13] freshly cracked cyclopentadiene (76 g, 1.15 mol) was added dropwise under argon to a solution of acryloyl chloride (100 g, 1.1 mol) in toluene (250 ml) at such a rate that the temperature of the reaction slowly climbed to 55-60°C. Upon completion of the addition, the reaction mixture was slowly warmed to 90°C and stirred for one hour. The cooled reaction mixture was then concentrated under reduced pressure and distilled *in vacuo* to yield 140 g (82%) as a clear liquid (endo/exo = 4/1).

^{1}H-NMR ($CDCl_3$) δ 6.24 (d of d, 1H, J = 3 Hz, endo), 6.18 (d of d, 1H, exo), 6.09 (d of d, 1H, exo), 6.00 (d of d, 1H, J = 3 Hz, endo), 3.45-3.40 (m, 2H, endo), 3.26-3.23 (m, 2H, exo), 2.95 (m, 1H, endo), 2.74-2.68 (m, 1H, exo), 2.15-1.88 (m, 2H, endo+exo), 1.50-1.29 (m, 6H, endo + exo).

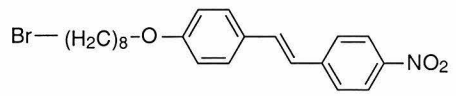
Synthesis of 1-bromo-5-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-pentane (7):



Potassium carbonate (14g, 0.1 mol) was added to a solution of **2** (7g, 0.029 mol) in dimethylformamide (250 ml), and the mixture was stirred at room temperature for 15 min. 1,5-Dibromopentane (100g, 0.43 mol) was added dropwise and the mixture was stirred at 100°C for an additional 24 hours. The reaction was filtered, the solution poured into water (500 ml) and then extracted three times with diethyl ether (200 ml). The organic phase was dried over magnesium sulfate and evaporated to yield a yellow precipitate. Final purification was achieved by column chromatography (silica gel/dichloromethane) to obtain a yellow precipitate in 67% (7.5 g) yield.

^{1}H-NMR ($CDCl_3$) δ 8.19 (d, 2H, *J* = 8.4 Hz), 7.58 (d, 2H, *J* = 8.4 Hz), 7.47 (d, 2H, *J* = 8.4 Hz), 7.21 (d, 1H, *J* = 16.5 Hz), 6.99 (d, 1H, *J* = 16.5 Hz), 6.90 (d, 2H, *J* = 8.4 Hz), 3.99 (t, 2H, *J* = 6.4 Hz), 3.43 (t, 2H, *J* = 6.9 Hz), 1.94 (q, 2H, *J* = 7 Hz), 1.82 (q, 2H, *J* = 7 Hz), 1.63 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 159.4, 146.1, 144.1, 132.7, 128.4, 128.2, 126.3, 123.9, 123.8, 114.6, 67.5, 33.4, 32.2, 28.2, 24.6; IR (thin film on a NaCl plate) 2950, 2868, 1592, 1572, 1508, 1474, 1341, 1320, 1250, 1177, 1111, 1038, 999, 959, 844, 748, 686, 538 cm^{-1}; Anal. calcd. for $C_{19}H_{20}BrNO_3$: C, 58.47; H, 5.17; N, 3.59, found: C, 57.67; H, 5.24; N, 3.61.

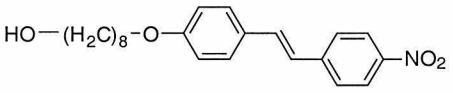
Synthesis of 1-bromo-8-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-octane (8):



8 was obtained in analogy to **7** as a yellow solid using **2** (6.27 g, 0.026 mol) and 1,8-dibromooctane (100 g, 0.37 mol). Yield 8.2 g (73%).

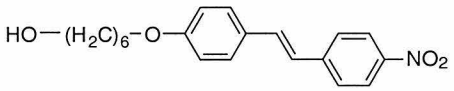
^{1}H-NMR ($CDCl_3$): δ/ppm 8.18 (d, 2H, *J* = 8.7 Hz), 7.57 (d, 2H, *J* = 8.7 Hz), 7.46 (d, 2H, *J* = 8.4 Hz), 7.20 (d, 1H, *J* = 16.3 Hz), 6.98 (d, 1H, *J* = 16.3 Hz), 6.90 (d, 2H, *J* = 8.4 Hz), 3.97 (t, 2H, *J* = 6.4 Hz), 3.40 (t, 2H, *J* = 7.2 Hz), 1.90-1.74 (m, 4H), 1.47-1.35 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 159.6, 146.1, 144.1, 132.7, 128.5, 128.2, 126.2, 123.9, 123.7, 114.6, 67.8, 33.7, 32.5, 28.9, 28.4, 28.3, 27.8, 25.7; IR (thin film on a NaCl plate) 2926, 2850, 1654, 1586, 1508, 1466, 1334, 1245, 1173, 1107, 1019, 968, 842, 534 cm^{-1}; Anal. calcd. for $C_{22}H_{26}BrNO_3$: C, 61.10; H, 6.06; N, 3.24, found: C, 61.25; H, 6.20; N, 3.34.

Synthesis of 8-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-1-octanol (4):



A solution of **2** (14 g, 0.058 mol) and sodiumhydride (1.6 g, 0.065 mol) in dry dimethylformamide (200 ml) was treated with a solution of 8-bromo-1-octanol (13 g, 0.062 mol) in dry dimethylformamide (20 ml) and stirred at 90°C for three hours, during which a color change from deep purple to yellow was observed. The product precipitated as a yellow solid after three days in the refrigerator. The solid was purified by column chromatography (silica gel/dichloromethane) to yield a yellow solid in 60% (13 g) yield. ^{1}H-NMR ($CDCl_3$) δ 8.18 (d, 2H, *J* = 8.7 Hz), 7.57 (d, 2H, *J* = 8.7 Hz), 7.46 (d, 2H, *J* = 8.4 Hz), 7.20 (d, 1H, *J* = 16.2 Hz), 6.98 (d, 1H, *J* = 16.2 Hz), 6.90 (d, 2H, *J* = 8.4 Hz), 3.70 (t, 2H, *J* = 6.4 Hz), 3.63 (t, 2H, *J* = 6.4 Hz), 1.82 (m, 2H), 1.60 (q, 2H, *J* = 6.7 Hz), 1.39 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 159.6, 146.1, 144.1, 132.7, 128.5, 128.2, 126.2, 123.9, 123.7, 114.6, 67.9, 62.7, 32.5, 29.1, 29.0, 25.7, 25.4; IR (thin film on a NaCl plate) 3542, 2931, 2855, 1606, 1587, 1572, 1511, 1474, 1424, 1344, 1306, 1272, 1254, 1175, 1111, 1037, 970, 962, 874, 842, 809, 750, 717, 688, 583, 533 cm^{-1}; Anal. calcd. for $C_{22}H_{27}NO_4$: C, 71.52; H, 7.37; N, 3.79, found: C, 70.98; H, 7.39;N, 3.66.

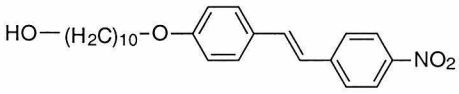
Synthesis of 6-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-1-hexanol (3):



3 was synthesized in analogy to **4** using **2** (11.5 g, 0.048 mol) and 1-bromo-6-hexanol (10 g, 0.055 mol) in 65% (10.7 g) yield.

^{1}H-NMR ($CDCl_3$) δ 8.18 (d, 2H, *J* = 8.7 Hz), 7.57 (d, 2H, *J* = 8.7 Hz), 7.46 (d, 2H, *J* = 8.7 Hz), 7.20 (d, 1H, *J* = 16.3 Hz), 6.98 (d, 1H, *J* = 16.3 Hz), 6.90 (d, 2H, *J* = 8.7 Hz), 4.00 (t, 2H, *J* = 7.6 Hz), 3.50 (t, 2H, *J* = 5.9 Hz), 1.76 (q, 2H, *J* = 7.0 Hz), 1.53-1.40 (m, 6H); ^{13}C-NMR ($CDCl_3$) δ 159.6, 146.2, 144.1, 135.5, 132.7, 128.5, 128.2, 126.2, 123.9, 123.7, 114.7, 67.7, 62.3, 32.4, 29.5, 28.9, 28.8, 25.6, 25.3; IR (thin film on a NaCl plate) 3424, 2932, 2859, 1639, 1508, 1344, 1254, 1178, 1110, 1021, 959, 842, 745, 533 cm^{-1}; Anal. calcd. for $C_{20}H_{23}NO_4$: C, 70.17; H, 7.07; N, 4.09, found: C, 69.59; H, 7.17; N, 3.98.

Synthesis of 10-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-1-decanol (5):

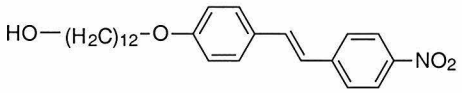


5 was synthesized according to the procedure described above using **2** (9.66 g, 0.04 mol) and 1-bromo-10-decanol (10 g, 0.042 mol) in 89% yield (14.1 g).

^{1}H-NMR ($CDCl_3$) δ 8.19 (d, 2H, *J* = 8.7 Hz), 7.58 (d, 2H, *J* = 8.7 Hz), 7.47 (d, 2H, *J* = 8.4 Hz), 7.21 (d, 1H, *J* = 16.1 Hz), 6.98 (d, 1H, *J* = 16.1 Hz), 6.90 (d, 2H, *J* = 8.4 Hz), 3.98 (t, 2H, *J* = 6.4 Hz), 3.64 (t, 2H, *J* = 6.7 Hz), 1.79 (q, 2H, *J* = 7.0 Hz), 1.56-1.31 (m, 14H); ^{13}C-NMR ($CDCl_3$) δ 159.6, 146.1, 144.1, 132.8, 128.4, 128.2, 126.2, 123.9, 123.7, 114.7, 67.9, 62.8, 32.5, 29.2, 29.2, 29.1, 29.0, 25.8, 25.5; IR (thin film on a NaCl plate) 3544, 2924, 2850, 1586, 1572, 1509, 1473, 1341, 1256, 1180, 1110,

1053, 1021, 960, 841, 688, 533 cm^{-1}; Anal. calcd. for $C_{24}H_{31}NO_4$: C, 72.61; H, 7.86; N, 3.52, found: C, 71.98; H, 8.01; N, 3.59.

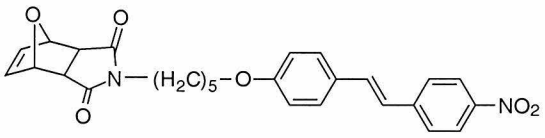
Synthesis of 12-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-1-dodecanol (6):



6 was synthesized according to the procedure described above using **2** (4.5 g, 0.019 mol) and 1-bromo-12-dodecanol (5 g, 0.02 mol) in 69% yield (5.5 g).

^{1}H-NMR ($CDCl_3$) δ 8.19 (d, 2H, *J* = 8.7 Hz), 7.58 (d, 2H, *J* = 8.7 Hz), 7.47 (d, 2H, *J* = 8.4 Hz), 7.21 (d, 1H, *J* = 16.3 Hz), 6.98 (d, 1H, *J* = 16.3 Hz), 6.90 (d, 2H, *J* = 8.4 Hz), 3.98 (t, 2H, *J* = 6.6 Hz), 3.63 (t, 2H, *J* = 6.7 Hz), 1.79 (q, 2H, *J* = 7.8 Hz), 1.56-1.28 (m, 18H); ^{13}C-NMR ($CDCl_3$) δ 159.6, 146.1, 144.1, 132.8, 128.5, 128.2, 126.2, 123.9, 123.7, 114.6, 67.9, 62.8, 32.6, 29.3, 29.2, 29.1, 29.0, 25.8, 25.5; IR (thin film on a NaCl plate) 3542, 2921, 2850, 1606, 1586, 1572, 1509, 1474, 1424, 1341, 1321, 1270, 1255, 1195, 1181, 1111, 1056, 1039, 960, 871, 748, 718, 687, 584, 533 cm^{-1}; Anal. calcd. for $C_{26}H_{35}NO_4$: C, 73.54; H, 8.24; N, 3.27, found: C, 73.72; H, 8.31; N, 3.24.

Synthesis of *exo*-N{-5-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-pentane}-7-oxa-bicyclo-[2.2.1]-hept-5-ene-2,3-dicarboximide (15):

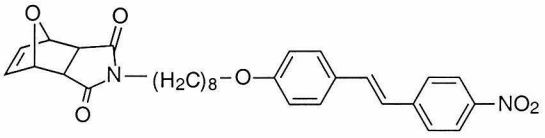


A mixture of **9** (0.32 g, 1.9 mmol), dissolved in dry dimethylformamide (30 ml) and potassium carbonate (0.74 g, 5.5 mmol) was stirred at 90°C for 30 min. **7** (0.7 g/ 1.4 mmol) in dry dimethylformamide (10 ml) was added dropwise and the mixture was stirred

at 90°C for 30 min, followed by three hours at room temperature. The reaction mixture was filtered, the solution poured into water (200 ml) and extracted three times with diethyl ether (100 ml). The organic phase was dried over magnesium sulfate and evaporated to yield a yellow solid. Final purification was achieved by column chromatography (silica gel /dichloromethane) to obtain a yellow solid in 87.5% (0.7 g) yield.

^{1}H-NMR ($CDCl_3$) δ 8.23 (d, 2H, *J* = 8.9 Hz), 7.62 (d, 2H, *J* = 8.9 Hz), 7.50 (d, 2H, *J* = 8.4 Hz), 7.25 (d, 1H, *J* = 16.1 Hz), 7.02 (d, 1H, *J* = 16.1 Hz), 6.92 (d, 2H, *J* = 8.4 Hz), 6.54 (s, 2H), 5.29 (s, 2H), 3.99 (t, 2H, *J* = 6.3 Hz), 3.54 (t, 2H, *J* = 7.2 Hz), 2.86 (s, 2H), 1.81 (q, 2H, *J* = 7.1 Hz), 1.64 (q, 2H, *J* = 7.1 Hz), 1.46 (q, 2H, *J* = 7.1 Hz); ^{13}C-NMR ($CDCl_3$) δ 176.0, 159.5, 146.1, 144.1, 136.3, 132.8, 128.6, 128.2, 126.2, 123.9, 123.7, 114.6, 80.7, 67.5, 47.2, 38.5, 28.4, 27.1, 23.0; IR (thin film on a NaCl plate) 2943, 2867, 1771, 1698, 1630, 1588, 1511, 1473, 1437, 1402, 1340, 1252, 1174, 1109, 1015, 958, 918, 879, 842, 750, 718, 651, 535 cm^{-1}; Anal. calcd. for $C_{27}H_{26}N_2O_6$: C, 68.34; H, 5.52; N, 5.90, found: C, 68.19; H, 5.56; N, 5.95; HRMS (FAB) calcd. for $C_{27}H_{26}N_2O_6$ $(MH)^+$ 474.1790, found: 474.1800.

Synthesis of *exo*-N{-8-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-octane}-7-oxa-bicyclo-[2.2.1]hept-5-ene-2,3-dicarboximide (16):

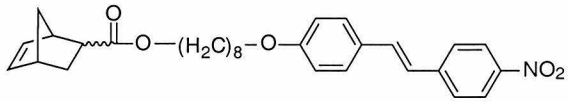


A mixture of **9** (0.25 g, 1.5 mmol), dissolved in dry dimethylformamide (30 ml) and potassium carbonate (0.5 g, 3.6 mmol) was stirred at 90°C for one hour. **8** (0.45 g/ 1 mmol) in dry dimethylformamide (30 ml) was added dropwise and the mixture was stirred at 90°C for 14 hours. The reaction mixture was hot filtered and poured into water (300 ml). The solvent was removed under dynamic vacuum to obtain a brown solid. Final

purification was achieved by column chromatography (silica gel /dichloromethane) to obtain a yellow solid in 20% (120 mg) yield.

^{1}H-NMR ($CDCl_3$) δ 8.23 (d, 2H, *J* = 8.9 Hz), 7.62 (d, 2H, *J* = 8.9 Hz), 7.50 (d, 2H, *J* = 8.4 Hz), 7.25 (d, 1H, *J* = 16.1 Hz), 7.02 (d, 1H, *J* = 16.1 Hz), 6.92 (d, 2H, *J* = 8.4 Hz), 6.54 (s, 2H), 5.25 (s, 2H), 3.96 (t, 2H, *J* = 6.3 Hz), 3.45 (t, 2H, *J* = 7.2 Hz), 2.87 (s, 2H), 1.74 (q, 2H, *J* = 7.2 Hz), 1.54 (q, 2H, *J* = 7.2 Hz), 1.43-1.23 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 159.6, 146.2, 144.1, 132.8, 128.5, 128.2, 126.2, 123.9, 123.7, 114.6, 67.9, 62.8, 32.5, 29.1, 28.9, 25.7, 25.4; IR (thin film on a NaCl plate) 3417, 2931, 2855, 1633, 1589, 1514, 1470, 1343, 1255, 1175, 1110, 1022, 970, 873, 841, 718, 687, 530 cm^{-1}.

Synthesis of 5-{n-[8-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-octyl]-carbonyl}-bicyclo-[2.2.1]-hept-2-ene (12):

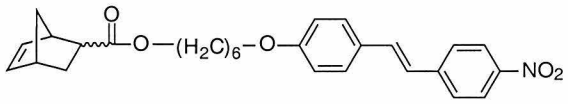


A solution of **4** (6 g, 0.016 mol) and triethylamine (1.6 g) in tetrahydrofuran (300 ml) was treated with a solution of **10** (2.52 g, 0.016 mol) in tetrahydrofuran (10 ml) and stirred under reflux for 18 hours, during which a white solid precipitated. The solution was filtered and the solvent was evaporated under dynamic vacuum to obtain a yellow solid. The solid was purified by column chromatography (silica gel/ dichloromethane) to obtain a yellow solid in 68% (5.3 g) yield.

^{1}H-NMR ($CDCl_3$) δ 8.19 (d, 2H, *J* = 8.4 Hz), 7.58 (d, 2H, *J* = 8.4 Hz), 7.47 (d, 2H, *J* = 8.4 Hz), 7.21 (d, 1H, *J* = 16.2 Hz), 6.98 (d, 1H, *J* = 16.2 Hz), 6.90 (d, 2H, *J* = 8.4 Hz), 6.17 (d of d, 1H, *J* = 3 Hz), 5.90 (d of d, 1H, *J* = 3 Hz), 4.03-3.95 (m, 4H), 3.19 (m, 1H), 2.96-2.89 (m, 2H), 1.89-1.24 (m, 14H); ^{13}C-NMR ($CDCl_3$) δ 195.5, 174.5, 159.8, 146.3, 144.3, 137.7, 132.9, 132.3, 128.7, 128.4, 126.4, 124.1, 123.9, 114.8,

68.0, 64.2, 49.59, 45.7, 43.3, 42.5, 29.2, 29.1, 28.6, 25.9; IR (thin film on a NaCl plate) 2932, 2854, 1715, 1633, 1590, 1574, 1514, 1474, 1392, 1338, 1308, 1271, 1255, 1176, 1108, 1030, 980, 952, 913, 876, 843, 824, 798, 749, 715, 686, 583, 531 cm^{-1}; Anal. calcd. for $C_{30}H_{35}NO_5$: C, 73.58; H, 7.21; N, 2.86, found: C, 73.03; H, 6.82; N, 2.91; HRMS (FAB) calcd. for $C_{30}H_{35}NO_5$ $(MH)^+$ 489.2515, found: 489.2531.

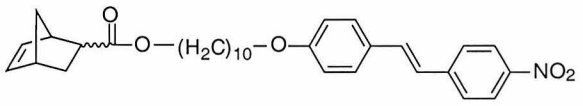
Synthesis of 5-{n-[-6-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-hexyl]-carbonyl}-bicyclo-[2.2.1]-hept-2-ene (11):



11 was prepared from **3** (3.75, 0.011 mol), triethylamine (0.41 g) and **10** (1.56 g, 0.01 mol) in 50 ml tetrahydrofuran according to the procedure described above. Yield (2.7 g/ 59%).

^{1}H-NMR ($CDCl_3$) δ 8.15 (d, 2H, *J* = 8.4 Hz), 7.55 (d, 2H, *J* = 8.4 Hz), 7.45 (d, 2H, *J* = 8.4 Hz), 7.19 (d, 1H, *J* = 16.3 Hz), 6.95 (d, 1H, *J* = 16.3 Hz), 6.88 (d, 2H, *J* = 8.4 Hz), 6.16 (d of d, 1H, *J* = 2.9 Hz), 5.90 (d of d, 1H, *J* = 2.9 Hz), 4.04-3.95 (m, 4H), 3.18 (m, 1H), 2.93-2.89 (m, 2H), 1.89-1.23 (m, 10H); ^{13}C-NMR ($CDCl_3$) δ 195.5, 174.5, 159.6, 146.1, 144.1, 137.5, 132.7, 132.1, 128.5, 128.2, 126.2, 123.9, 123.7, 114.6, 67.7, 63.9, 49.4, 45.5, 43.1, 42.3, 29.0, 28.9, 28.4, 25.5, 25.4; IR (thin film on a NaCl plate) 2943, 2807, 1727, 1630, 1590, 1571, 1514, 1467, 1391, 1340, 1271, 1254, 1175, 1108, 1065, 1022, 973, 957, 873, 842, 749, 714, 687, 536 cm^{-1}; Anal. calcd. from $C_{28}H_{31}NO_5$: C, 72.86; H, 6.77; N, 3.03, found: C, 72.42; H, 6.48; N, 2.95; HRMS (FAB) calcd. for $C_{28}H_{31}NO_5$ $(MH)^+$ 461.2202, found: 461.2210.

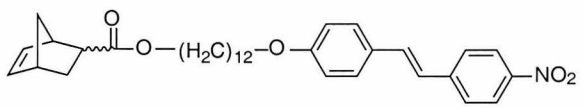
Synthesis of 5-{n-[-10-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-decyl]-carbonyl}-bicyclo-[2.2.1]hept-2-ene (13):



13 was synthesized in analogy to the procedure described above using **5** (5 g, 0.013 mol) and **10** (2 g, 0.013 mol) in tetrahydrofuran in 68% yield (4.5 g).

^{1}H-NMR ($CDCl_3$) δ 8.19 (d, 2H, *J* = 8.4 Hz), 7.58 (d, 2H, *J* = 8.4 Hz), 7.48 (d, 2H, *J* = 8.4 Hz), 7.21 (d, 1H, *J* = 16.2 Hz), 6.99 (d, 1H, *J* = 16.2 Hz), 6.91 (d, 2H, *J* = 8.4 Hz), 6.19 (d of d, 1H, *J* = 3 Hz), 5.94 (d of d, 1H, *J* = 3 Hz), 4.09-3.96 (m, 4H), 3.22 (m, 1H), 2.98-2.91 (m, 2H), 1.95-1.27 (m, 18H); ^{13}C-NMR ($CDCl_3$) δ 195.5, 174.6, 159.6, 146.1, 144.1, 137.5, 132.8, 132.1, 128.5, 128.2, 126.2, 123.9, 123.6, 114.6, 67.9, 64.1, 49.4, 45.5, 43.1, 42.3, 29.2, 29.1, 29.0, 28.4, 25.8, 25.7; IR (thin film on a NaCl plate) 2935, 2851, 1810, 1718, 1630, 1591, 1574, 1519, 1474, 1423, 1389, 1339, 1299, 1271, 1250, 1176, 1108, 1066, 1042, 1025, 980, 952, 913, 876, 843, 824, 797, 748, 716, 686, 671, 583, 530 cm^{-1}; Anal. calcd. from $C_{32}H_{39}NO_5$: C, 74.36; H, 7.61; N, 2.71, found: C, 73.97; H, 7.55; N, 2.65; HRMS (FAB) calcd. for $C_{32}H_{39}NO_5$ $(MH)^+$ 517.2749, found: 517.2791.

Synthesis of 5-{n-[-12-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-dodecyl]-carbonyl}-bicyclo-[2.2.1]hept-2-ene (14):

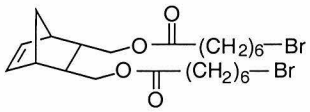


14 was synthesized according to the procedure described above using **6** (3 g, 0.007 mol) and **10** (1.2 g, 0.0075 mol) in tetrahydrofuran in 81% yield (3.1 g).

^{1}H-NMR ($CDCl_3$) δ 8.19 (d, 2H, *J* = 8.7 Hz), 7.58 (d, 2H, *J* = 8.7 Hz), 7.47 (d, 2H, *J* = 8.7 Hz), 7.22 (d, 1H, *J* = 16.2 Hz), 6.99 (d, 1H, *J* = 16.2 Hz), 6.90 (d, 2H, *J* = 8.7

Hz), 6.18 (d of d, 1H, J = 3 Hz), 5.91 (d of d, 1H, J = 3 Hz), 4.07-3.96 (m, 4H), 3.19 (m, 1H), 2.96-2.88 (m, 2H), 1.88-1.27 (m, 22H); ^{13}C-NMR ($CDCl_3$) δ 195.5, 174.6, 159.7, 146.1, 144.1, 137.5, 132.8, 132.1, 128.5, 128.2, 126.2, 123.9, 123.6, 114.6, 67.9, 64.1, 49.4, 45.5, 43.1, 42.3, 29.3, 29.2, 29.0, 28.5, 25.8, 25.7; IR (thin film on a NaCl plate) 2916, 2851, 1717, 1590, 1574, 1518, 1474, 1389, 1339, 1270, 1246, 1176, 1109, 1040, 980, 953, 913, 875, 843, 824, 795, 748, 716, 686, 671, 530 cm^{-1}; Anal. calcd. from $C_{34}H_{43}NO_5$: C, 74.97; H, 7.94; N, 2.57, found: C, 74.32; H, 8.00; N, 2.53; HRMS (FAB) calcd. for $C_{34}H_{43}NO_5$ $(MH)^+$ 545.3141, found: 545.3152.

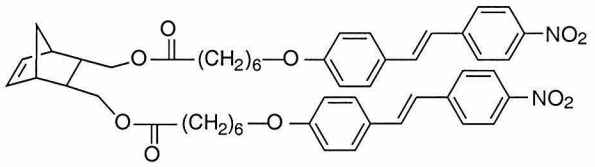
Synthesis of 4,5-([6-bromo-hexane]-bicyclo-[2.2.1]-hept-2-ene)-ether (17):



To a solution of norborn-2-ene-5,6-diol (3 g, 0.018 mol) and triethylamine (4.5 g) in dry tetrahydrofuran (200 ml) 1-bromo-6-hexanoyl-chloride (10 g, 0.047 mol) was added dropwise during which a white precipitate was formed. The suspension was stirred under reflux for 16 hours. The reaction mixture was filtered and the tetrahydrofuran removed under reduced pressure. Final purification was achieved by column chromatography (silica gel/ dichloromethane) to obtain a light yellow liquid in 87% (8 g) yield.

^{1}H-NMR (CD_2Cl_2) δ 6.39 (s, 1H), 4.80 (s, 1H), 4.25 (d of d, 2H, J = 5.1 Hz), 3.98 (q, 2H, J = 9.9 Hz), 3.42 (t, 4H, J = 6.3 Hz), 2.36 (t, 4H, J = 6.5 Hz), 1.95 (q, 2H, J = 4.2), 1.84 (q, 4H, J = 7.2 Hz), 1.63 (q, 4H, J = 7.8 Hz), 1.44 (q, 4H, J = 6.9 Hz); ^{13}C-NMR ($CDCl_3$) δ 172.7, 135.3, 80.1, 63.5, 39.1, 33.8, 33.0, 32.1, 27.4, 23.8; IR (thin film on a NaCl plate) 3444, 2939, 2864, 1732, 1633, 1460, 1418, 1389, 1360, 1310, 1253, 1170, 1124, 1081, 1046, 1024, 1009, 973, 900, 840, 871, 778, 732, 693, 643, 561 cm^{-1}; Anal. calcd. from $C_{20}H_{30}O_5$: C, 47.08; H, 5.93, found: C, 47.17; H, 5.90.

Synthesis of 4,5-([6-{6-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)}-hexane]-bicyclo-[2.2.1]-hept-2-ene)-ether (18):



A suspension of **2** (2 g, 8.3 mmol) and sodiumhydride (0.22 g) in dry dimethylformamide (150 ml) was stirred for 15 min under reflux. Then **17** (2 g, 3.9 mmol) in dry dimethylformamide (20 ml) was added dropwise and the mixture was stirred an additional 48 hours during which the dark purple solution turned yellow/brown. The product precipitated after three days in the refrigerator as a yellow solid. The precipitate was filtered, washed with methanol and purified by column chromatography (silica gel/ dichloromethane) to yield a yellow solid in 63% (1.45 g) yield.

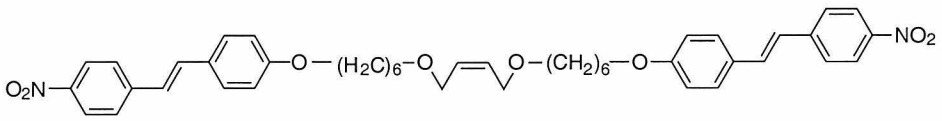
^{1}H-NMR (CD_2Cl_2) δ 8.17 (d, 4H, *J* = 8.4 Hz), 7.57 (d, 4H, *J* = 8.4 Hz), 7.45 (d, 4H, *J* = 8.4 Hz), 7.20 (d, 2H, *J* = 16.2 Hz), 6.97 (d, 2H, *J* = 16.2 Hz), 6.88 (d, 4H, *J* = 8.4 Hz), 5.73 (q, 2H, *J* = 4.2 Hz), 4.68 (d, 4H, *J* = 4.5 Hz), 3.97 (m, 6H), 2.35 (t, 4H, *J* = 6.5 Hz), 1.80 (q, 4H, *J* = 7.2 Hz), 1.70 (q, 4H, *J* = 7.8 Hz), 1.52 (q, 4H, *J* = 6.9 Hz); ^{13}C-NMR ($CDCl_3$) δ 172.9, 159.5, 146.2, 144.1, 132.7, 128.6, 128.2, 127.9, 126.2, 123.9, 123.8, 114.6, 67.5, 59.7, 33.8, 28.6, 25.4, 24.4; IR (thin film on a NaCl plate) 3433, 2941, 2868, 1725, 1626, 1608, 1586, 1573, 1472, 1460, 1439, 1420, 1380, 1338, 1322, 1299, 1274, 1256, 1196, 1175, 1108, 1049, 1025, 958, 900, 875, 840, 806, 750, 730, 688, 528 cm^{-1}; Anal. calcd. from $C_{48}H_{50}N_2O_{11}$: C, 70.24; H, 4.91; N, 3.41, found: C, 69.95; H, 5.05; N, 3.38; HRMS (FAB) calcd. for $C_{48}H_{50}N_2O_{11}$ $(MH)^+$ 820.2632, found: 821.2747.

Synthesis of 1,4-[6-bromohexane]-butene-ether (19):

1-Bromo-6-hexanoyl-chloride (10 g, 0.047 mol) was added dropwise to a stirring solution of 1,4-butendiol (1.76 g, 0.02 mol) in tetrahydrofuran (150 ml) and triethylamine (4.2 g) at room temperature for one hour during which a white solid precipitated. The solution was heated up and stirred under reflux for 16 hours. The suspension was filtered and concentrated on a rotavap. The resulting light yellow oil was purified by a silica gel column chromatography (dichloromethane). Isolated yield was 6.8 g (77%).

^{1}H-NMR ($CDCl_3$) δ 5.70 (t, 2H, *J* = 3.9 Hz), 4.64 (d, 4H, *J* = 3.9 Hz), 3.37 (t, 4H, *J* = 6.9 Hz), 2.30 (t, 4H, *J* = 7.2 Hz), 1.83 (q, 4H, *J* = 7.2 Hz), 1.62 (q, 4H, *J* = 7.5 Hz), 1.43 (q, 4H, *J* = 6.9 Hz); ^{13}C-NMR ($CDCl_3$) δ 172.6, 127.8, 59.6, 33.6, 33.1, 32.1, 27.3, 23.7; Anal. calcd. from $C_{16}H_{26}BrO_4$: C, 43.46; H, 5.93, found: C, 43.54; 5.83.

Synthesis of 1,4-[6-{6-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)}-hexane]-butene-ether (20):



A solution of **2** (3 g, 0.012 mol) and sodiumhydride (0.34 g) in dry dimethylformamide (200 ml) was treated with a solution of **19** (2.5 g, 5.7 mmol) in dimethylformamide (20 ml) and stirred under reflux for 10 hours during which a color change from dark purple to yellow/brown was observed and a white solid precipitated. The reaction was filtered and the product precipitated as a yellow solid after three days in the refrigerator. The precipitate was filtered and washed several times with methanol to obtain a yellow solid in 68% (2.95 g) yield.

^{1}H-NMR ($CDCl_3$) δ 8.19 (d, 4H, *J* = 8.4 Hz),7.57 (d, 4H, *J* = 8.4 Hz), 7.47 (d, 4H, *J* = 8.7 Hz), 7.22 (d, 2H, *J* = 16.5 Hz), 6.99 (d, 2H, *J* = 16.5 Hz), 6.90 (d, 4H, *J* = 8.7 Hz), 5.76 (t, 2H, *J* = 4.2 Hz), 4.70 (d, 4H, *J* = 4.2 Hz), 3.99 (t, 4H, *J* = 6.3 Hz), 2.37 (t, 4H, *J* = 7.2 Hz), 1.82 (q, 4H, *J* = 7.2 Hz), 1.72 (q, 4H, *J* = 7.8 Hz), 1.52 (q, 4H, *J* = 6.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 172.9, 159.5, 146.2, 144.1, 132.7, 128.6, 128.2, 127.9, 126.2, 123.9, 123.8, 114.6, 67.5, 59.7, 33.8, 28.6, 25.4, 24.4; IR (thin film on a NaCl plate) 2942, 2863, 1725, 1626, 1608, 1586, 1573, 1511, 1472, 1426, 1380, 1337, 1322, 1270, 1256, 1175, 1108, 1025, 957, 876, 840, 750, 730, 688, 583, 527 cm^{-1}; Anal. calcd. from $C_{44}H_{46}N_2O_{10}$: C, 69.28; H, 6.08; N, 3.67, found: C, 69.16; H, 6.18; N, 3.75; HRMS (FAB) calcd. for $C_{44}H_{46}N_2O_{10}$ $(MH)^+$ 762.3152, found: 762.3168.

General Polymerization Procedure containing an *exo*-N-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide or a norborn-2-ene-5-carbonyl backbone: Under an inert atmosphere, the catalyst and the monomer were weighed into vials and dissolved in dichloromethane (~1 ml CH_2Cl_2 for every 100 mg of monomer). The reaction was initiated by adding the catalyst solution to the vigorously stirred monomer solution. The rection mixture was allowed to stir under argon for 25 min (the *exo*-N-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide backbone) or for one hour (the norborn-2-ene-5-carbonyl backbone). The reaction mixture was terminated by adding a small amount of ethyl-vinyl-ether and poured into ~50 ml methanol to precipitate the polymer. The resulting yellow polymer was purified by dissolving it in dichloromethane and precipitation into methanol several times and dried *in vacuo*. Yields ranged from 85 to 99% (100% by ^{1}H-NMR).

Polymer (21): ^{1}H-NMR ($CDCl_3$) δ 8,17 (bs, 2H), 7.54 (bs, 2H), 7.45 (bs, 2H), 7.16 (bs, 1H), 6.98 (bs, 1H), 6.88 (bs, 2H), 6.08 (bs, trans), 5,80 (bs, cis), 5.02 (bs, cis), 4.45 (bs, trans), 3.95 (bs, 2H), 3.49 (bs, 2H), 3.30 (bs, 2H), 1.80 (bs, 2H),

1.65 (bs, 2H), 1.46 (bs, 2H); ^{13}C-NMR ($CDCl_3$) δ 175.3, 159.4, 158.6, 146.3, 144.4, 144.0, 133.2, 132.6, 131.7, 130.8, 129.9, 129.3, (133.2 - 129.3 double bond C's, backbone) 128.8, 82.1, 80.8, 67.4, 53.3, 52.1, 39.1, 38.5, 28.4, 27.0, 26.9, 23.0, 22.7; IR (thin film on NaCl plate) 3440, 2939, 2864, 1701, 1588, 1510, 1398, 1337, 1252, 1173, 1109, 965, 842, 750, 530 cm^{-1}.

Polymer (22): ^{1}H-NMR ($CDCl_3$) δ 8.18 (bd, 2H), 7.56 (bd, 2H), 7.45 (bd, 2H), 7.19 (bd, 1H), 6.96 (bd, 1H), 6.88 (bd, 2H), 6.06 (bs, trans), 5.77 (bs, cis), 4.99 (bs, cis), 4.42 (bs, trans), 3.93 (bs, 2H), 3.45 (bs, 2H), 3.31 (bs, 2H), 1.75 (bs, 2H), 1.41 (bs, 2H), 1.31 (bs, 8H); ^{13}C-NMR ($CDCl_3$) δ 175.4, 173.7, 159.6, 146.3, 144.1, 133.3, 132.7, 131.6, 130.6, 129.9, 129.3, (133.3 - 129.3 double bond C's, backbone) 128.6, 128.1, 126.5, 123.8, 123.3, 82.1, 80.8, 67.9, 53.4, 53.2, 53.0, 52.1, (53.4-52.1 single bond C's, backbone) 50.9, 50.7, 47.5, 39.1, 38.7, 28.9, 28.7, 27.3, 27.2, 26.4, 25.6; IR (thin film on NaCl plate) 3440, 2934, 2856, 1774, 1699, 1589, 1511, 1400, 1339, 1253, 1175, 1109, 1022, 967, 841, 750, 534 cm^{-1}.

Polymer (23): ^{1}H-NMR ($CDCl_3$) δ 8.15 (bd, 2H), 7.54 (bd, 2H), 7.43 (bd, 2H), 7.17 (bd, 1H), 6.95 (bd, 1H), 6.87 (bd, 2H), 5.38 (bs, 1H), 5.28 (bs, 1H), 3.94 (bs, 2H), 2.85-2.74 (bm, 2H), 2.40 (bs, 1H), 1.75 (bs, 2H), 1.40 (bs, 2H), 1.25 (bs 4H); ^{13}C-NMR ($CDCl_3$) δ 195.4, 174.2, 159.6, 146.3, 144.0, 134.3, 132.7, 130.2-131.0 (4s) 129.4, (134.3 - 129.4 [except 132.7] double bond C's, backbone)128.7, 128.1, 126.2, 123.8, 114.7, 67.7, 63.8, 49.4, 48.1, 45.4, 42.4, 40.5, 40.2, 39.7, 39.5, 37.5, 36.0, 35.6, (49.4-35.6 single bond C's, backbone) 28.8, 28.4, 25.6, 25.5; IR (thin film on NaCl plate) 3422, 2941, 2860, 1723, 1632, 1588, 1511, 1339, 1252, 1174, 1109, 968, 842, 749, 688, 533 cm^{-1}.

Polymer (24): ^{1}H-NMR ($CDCl_3$) δ 8.14 (bd, 2H), 7.53 (bd, 2H), 7.42 (bd, 2H), 7.16 (bd, 1H), 6.94 (bd, 1H), 6.86 (bd, 2H), 5.37 (bs, 1H), 5.28 (bs, 1H), 3.92 (bs, 2H), 2.84-2.72 (bm, 2H), 2.39 (bs, 1H), 1.74 (bs, 2H), 1.41 (bs, 2H), 1.31 (bs 8H); ^{13}C-NMR ($CDCl_3$) δ 195.4, 174.2, 159.6, 146.3, 144.0, 134.3, 132.7, 130.3-131.0 (4s) 129.4, (134.3 - 129.4 [except 132.7] double bond C's, backbone)128.7, 128.1, 126.2, 124.1, 114.7, 67.9, 63.9, 48.1, 45.4, 42.5, 40.5, 40.2, 39.5, 37.5, 35.9, 35.6, (48.1-35.6 single bond C's, backbone) 29.0, 28.5, 25.7; IR (thin film on NaCl plate) 2934, 2855, 1723, 1631, 1606, 1588, 1511, 1472, 1393, 1338, 1303, 1253, 1174, 1109, 1025, 967, 873, 841, 750, 688, 668, 533 cm^{-1}.

Polymer (25): ^{1}H-NMR ($CDCl_3$) δ 8.15 (bd, 2H), 7.53 (bd, 2H), 7.43 (bd, 2H), 7.17 (bd, 1H), 6.94 (bd, 1H), 6.87 (bd, 2H), 5.37 (bs, 1H), 5.28 (bs, 1H), 3.93 (bs, 2H), 2.87-2.74 (bm, 2H), 2.40 (bs, 1H), 1.75 (bs, 2H), 1.40 (bs, 2H), 1.27 (bs 12H); ^{13}C-NMR ($CDCl_3$) δ 195.4, 174.3, 159.7, 146.3, 144.0, 134.3, 132.7, 130.2-131.0 (4s) 129.4, 129.3, (134.3 - 129.3 [except 132.7] double bond C's, backbone)128.6, 128.1, 126.2, 123.8, 114.7, 67.9, 64.0, 48.1, 45.4, 42.5, 40.8, 40.4, 39.7, 39.5, 37.5, 36.1, 35.6, (48.1-35.6 single bond C's, backbone) 29.3, 29.1, 29.0, 28.5, 25.8; IR (thin film on NaCl plate) 2927, 2854, 1725, 1633, 1588, 1512, 1470, 1393, 1338, 1253, 1174, 1109, 1022, 967, 841, 750, 688, 666, 534 cm^{-1}.

Polymer (26): ^{1}H-NMR ($CDCl_3$) δ 8.15 (bd, 2H), 7.54 (bd, 2H), 7.43 (bd, 2H), 7.17 (bd, 1H), 6.95 (bd, 1H), 6.87 (bd, 2H), 5.36 (bs, 1H), 5.28 (bs, 1H), 3.94 (bs, 2H), 2.85-2.75 (bm, 2H), 2.41 (bs, 1H), 1.75 (bs, 2H), 1.42 (bs, 2H), 1.25 (bs 16H); ^{13}C-NMR ($CDCl_3$) δ 195.4, 174.2, 159.7, 146.3, 144.1, 134.3, 132.7, 130.2-131.0 (4s), 129.3, (134.3 - 129.3 [except 132.7] double bond C',s backbone)128.6, 128.1, 126.2, 123.8, 114.7, 68.0, 64.0, 49.5, 48.1, 45.4, 42.5, 41.5, 40.4, 40.3, 39.5, 37.5, 36.0, 35.6, (49.5-35.6 single bond C's, backbone) 29.3, 29.1, 29.0, 28.5, 25.8;

IR (thin film on NaCl plate) 3023, 2925, 2853, 1725, 1630, 1606, 1589, 1512, 1467, 1393, 1339, 1303, 1254, 1175, 1109, 1023, 967, 871, 841, 750, 688, 668, 581, 534 cm^{-1}.

Synthesis of the Block-copolymer (27): 12 was polymerized in analogy to the procedure outlined above. After 30 min, 2-cyclobutene-5-[2-carbonyl-8-(4-[2-(4-nitrophenyl)-vinyl]-phenoxy)-octane-ester]-ethane (150 mg) in dichloromethane (1 ml) was added via a gas tight syringe. The vial was sealed and the mixture stirred for 24 hours at 45°C. The solution was then poured into methanol (100 ml) containing 10% 0.1M hydrochloric acid. The yellow precipitate was filtered and reprecipitated several times from the system dichloromethane/ methanol to yield **27** in 96% (288 mg) yield.

^{1}H-NMR ($CDCl_3$) δ 8.13 (bs), 7.52 (bs), 7.42 (bs), 7.15 (bd), 6.93 (bd), 6.85 (bs), 5.36 (bs), 4.08 (bs), 4.01 (bs), 3.92 (bs), 3.38 (bs), 3.16 (bs), 2.84 (bs), 2.71 (bs), 2.34 (bs), 1.94 (bs), 1.73 (bs), 1.54 (bs), 1.40 (bs), 1.30 (bs); ^{13}C-NMR ($CDCl_3$) δ 195.4, 174.2, 174.2, 159.6, 146.2, 144.0, 134.3, 132.7, 130.6, 129.4, (134.3 - 129.4 [except 132.7] double bond C',s backbone)128.6, 128.1, 126.2, 123.8, 114.7, 74.5, 68.3, 67.9, 64.4, 63.9, 48.1, 45.5, 42.5, 41.5, 40.4, 40.3, 39.7, 39.5, 38.0, 37.7, 35.6, 34.9, (49.5-34.9 single bond C's, backbone) 29.0, 28.9, 28.5, 28.4, 25.7, 25.5.

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Chapter 3

Synthesis of Discotic Columnar Side-Chain Liquid Crystalline Polymers by Ring-Opening Metathesis Polymerization

Abstract

Discotic liquid crystalline polymers bearing alkoxy-substituted triphenylene moieties in the side-chain were synthesized by ring-opening metathesis polymerization using a well-defined ruthenium initiator. To elucidate the effect of backbone flexibility on the mesomorphism, norbornene and cyclobutene monomers containing triphenylene moieties were synthesized yielding the relatively rigid poly(norbornene)s and the more flexible poly(butadiene)s after polymerization. To further increase the backbone flexibility, the poly(butadiene)s were hydrogenated using Crabtree's catalyst to yield triphenylene-substituted poly(butane)s. The mesomorphic behavior of the polymers was investigated by differential scanning calorimetry (DSC) and powder diffraction X-ray scattering (wide angle X-ray scattering, WAXS). All polymers bearing a 2,3,6,7,19-decyloxy-triphenylene-based mesogenic unit exhibited enantiotropic discotic hexagonal mesophases while the pentoxy analogous did not display liquid crystalline behavior. No effect of backbone rigidity on the mesomorphism could be detected. Furthermore, preliminary LED hole transport properties of these polymers are presented.

Introduction

Liquid crystals are promising materials for electronic applications, such as displays and photoconducting materials, because they can be oriented by applied electric and magnetic fields.[1-3] In particular, discotic liquid crystals which bear a flat, rigid core molecule as the mesogenic unit and are able to self-assemble into highly ordered columnar phases (Figure 1)[4,5] have been studied intensely over the last few years for potential applications in these fields.[2,3]

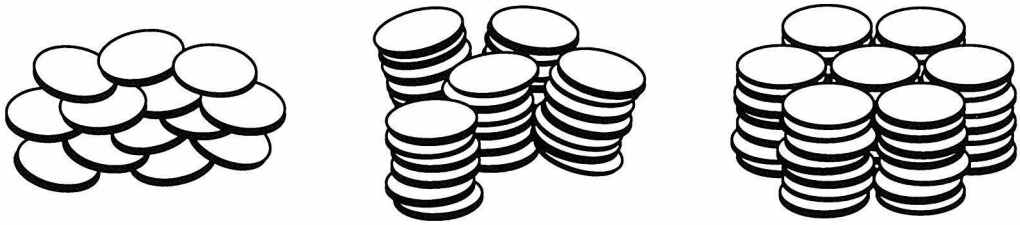


Figure 1. Possible alignment of the discotic core molecules in discotic liquid crystals: a) N_D: discotic nematic mesophase; b) N_C: discotic columnar mesophase; c) D_h: discotic hexagonal mesophase.

A variety of mesogens such as 2,3,6,7,10,11-alkoxytriphenylenes,[2,6-18] metallomesogens,[3,19-29] cyclotetraveratrylenes,[30] sugars,[31] hydrogen bonded oligoheterocycles,[32-33] solely carbon based structures,[34] and diaza-crowns[35] have been used to obtain discotic liquid crystalline materials. Some of these materials show high charge carrier mobilities. Triphenylenes in the highly ordered hexagonal columnar mesophases (D_h) for example display charge carrier mobilities of 0.1 $cm^2V^{-1}s^{-1}$ which are higher than any organic material except single crystal phases.[2,7g,h,t,8h,11,36] This enhanced photoconductivity has been attributed to long-range ordering along the columns of the discotic hexagonal and helical phases.

To move towards possible industrial applications polymeric materials are required because discotic liquid crystalline polymers provide a mechanically stable arrangement of the columnar assembly. Only a few examples of such oligomeric or polymeric discotic

liquid crystalline materials are known to date.[7a-e,8a,b,9b,d,10,14,19,22e,30,31a,37] Structural variations of these systems bear the mesogens either as a side group (Figure 2A),[7a-c,10] in the main chain (Figure 2B),[7d,8a,b,9b,d,14,19,22e,30,31a] or in a polymeric network (Figure 2C).[7e] Most materials in these examples were synthesized in step polymerizations or polymer-analogous reactions thus limiting control over molecular weight and polydispersity. This chapter presents ring-opening metathesis polymerization (ROMP), which is able to overcome these limitations, as an alternative method to obtain polymeric discotic liquid crystalline materials.

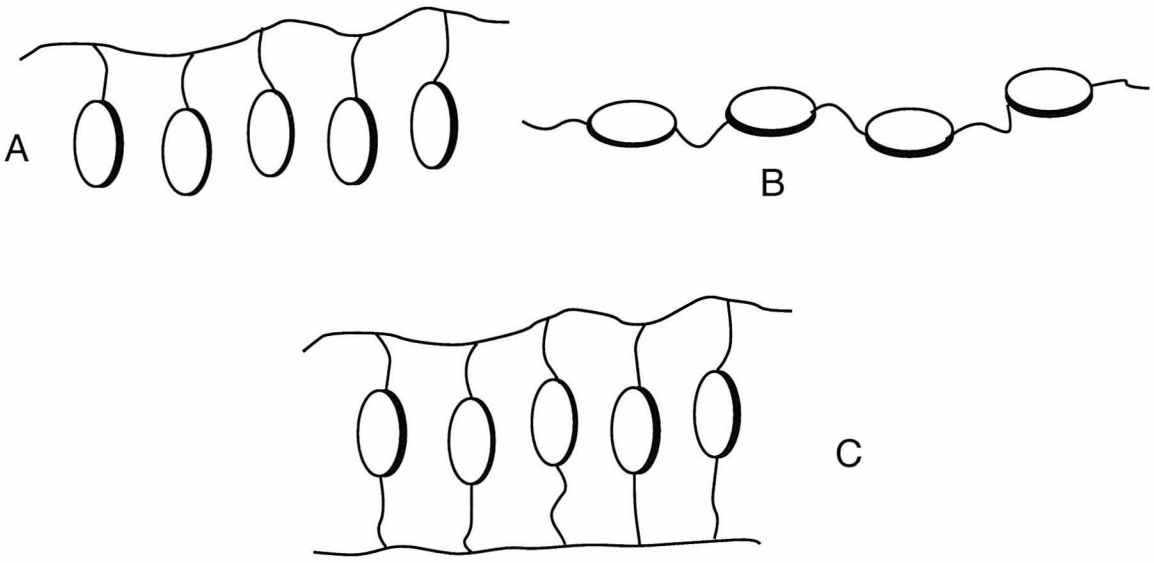
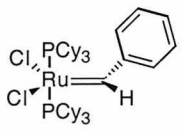


Figure 2. Possible molecular architectures for discotic liquid crystalline polymers: A) side-chain liquid crystalline polymer; B) main-chain liquid crystalline polymer; C) discotic network.

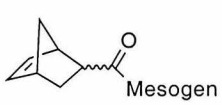
In the last decade, living ROMP has been established as an efficient method to control the polymer's molecular structure, size, and bulk properties by variations at the molecular level.[38] Recently, Grubbs and coworkers reported the synthesis of a new class of well-defined ruthenium complexes[39] which are highly active in ROMP[38] and ring-closing metathesis (RCM).[40] Initiator **1** $(PCy_3)_2Cl_2Ru(=CH\text{-}C_6H_5)$ in particular has been shown to polymerize a large variety of strained cyclic olefins in a living fashion as a result of its remarkable stability towards functional groups.[39] For example, it was shown that

cyclobutenes and norbornenes, bearing a large variety of side groups, can be polymerized in a living fashion using initiator **1**, yielding polymers and blockcopolymers with low polydispersities.[41,42]



1

This research presents a new strategy for the synthesis of discotic side-chain liquid crystalline materials using ring-opening metathesis polymerization. Utilizing cyclobutene or norbornene monomers **2** and **3**, the corresponding poly(norbornene)s and poly(butadiene)s bearing pentoxy- or decyloxy-substituted triphenylenes were obtained.



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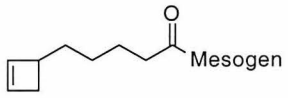


3

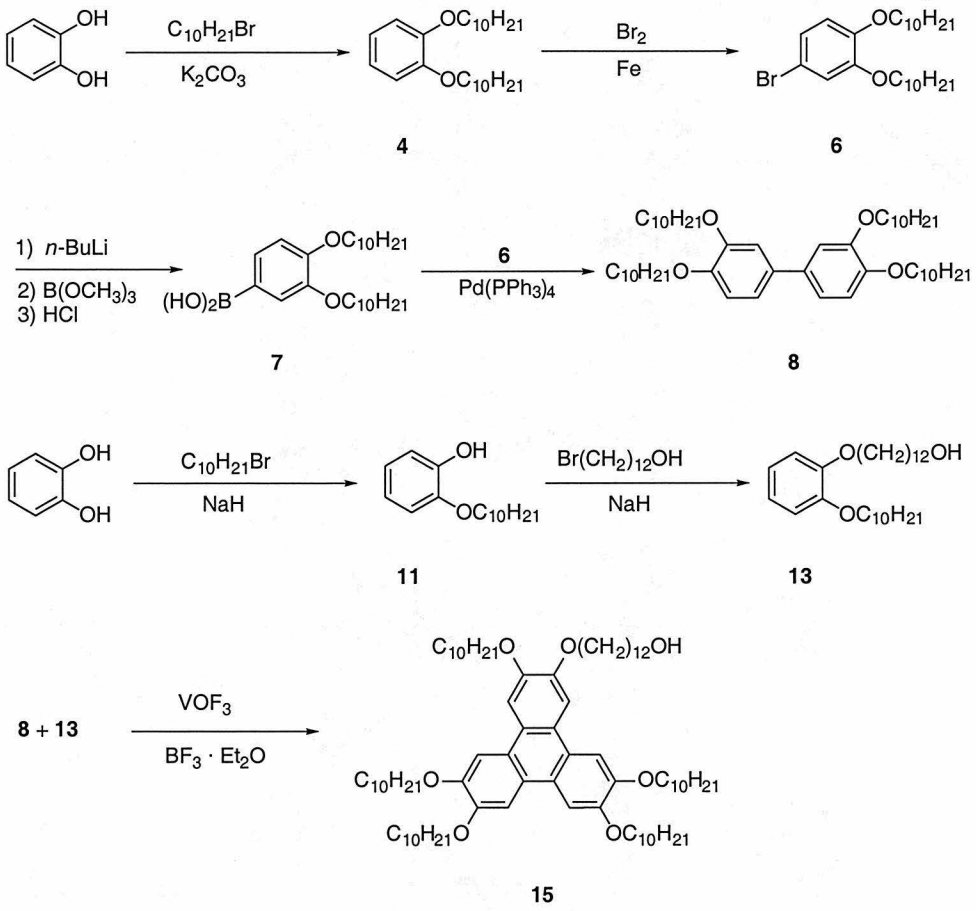
To investigate the role of backbone rigidity on the phase behavior, hydrogenation of the poly(butadiene)s was performed using Crabtree's catalyst $[Ir(COD)(Cy_3)(py)]PF_6$ to further increase the flexibility of this system. The phase behavior of the polymers was examined by differential scanning calorimetry (DSC) and powder diffraction X-ray scattering. Different routes for the synthesis of the monomers - depending on the length of the alkoxy chains and the polymerizable unit - are presented, and a new strategy for the aryl-aryl coupling to obtain alkoxy-substituted triphenylenes is introduced.

Results and Discussion

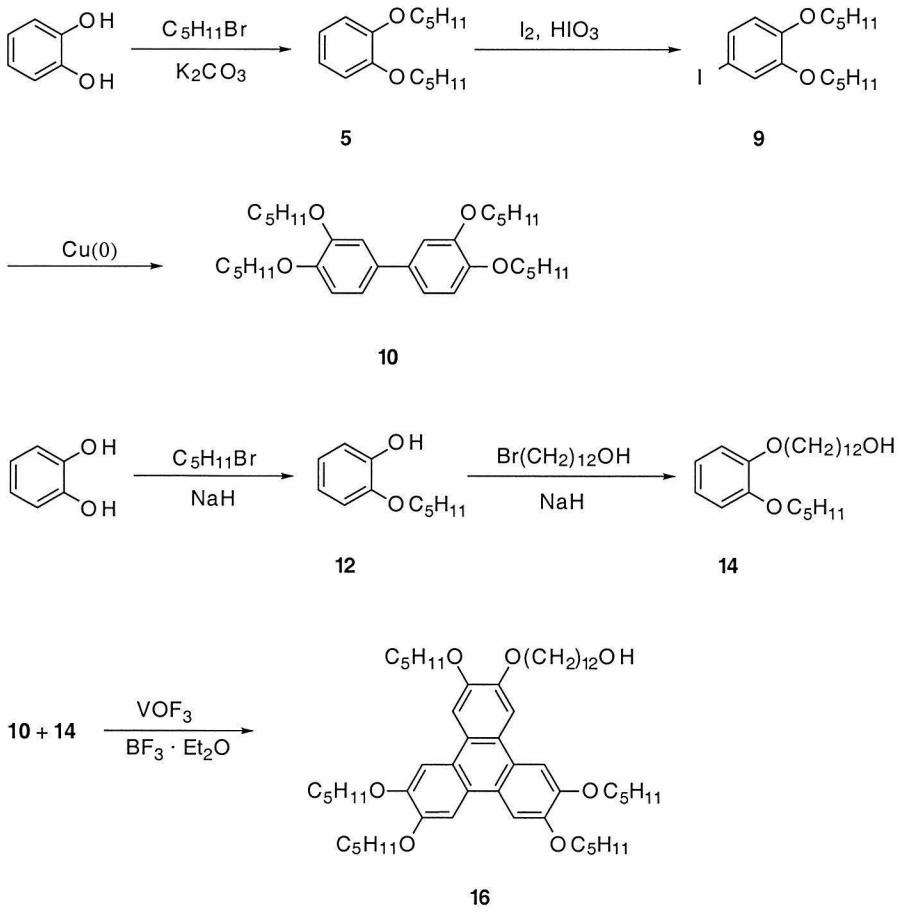
Monomer Syntheses. Alkoxy-substituted triphenylenes represent the most widely studied class of discotic mesogens.[2,6,7a-m,s,8a-e,9a,10-14] Synthetic strategies for these triphenylenes are based on the trimerization of o-dialkylbenzene derivatives,[8d] terphenyl intermediates,[43] or the biphenyl route.[7f,l,s,8e,] The o-dialkylbenzene approach

provides a statistical mixture of triphenylenes carrying two different alkoxy groups, while the reaction conditions (67% sulfuric acid) are incompatible with a large number of functionalities.[8d] The terphenyl strategy permits the preparation of highly functionalized triphenylenes especially for the synthesis of triphenylenes with fewer than six alkoxy groups.[43] The recently developed biphenyl route is based on the aryl-aryl coupling of a biphenyl with a catechol derivative using $FeCl_3$ as coupling agent which allows large scale preparations in good yields.[7f,l,s,8e] However, functionalities have to be introduced in a later step by a selective ether cleavage because of the incompatibility of most functional groups with $FeCl_3$.[7f,i-l,s] Another approach introduces the functionality by an electrophilic aromatic substitution after the coupling.[8c] Recently, Kumar and Manickam reported the use of $MoCl_5$ which allows the introduction of the functionality before the coupling.[15] This chapter presents a modified strategy for the synthesis of functionalized triphenylenes based on the biphenyl route, using VOF_3 as coupling agent. This route is compatible with most functional groups allowing their introduction prior to the coupling reaction.

Schemes 1 and 2 show the synthesis of the triphenylene precursors **15** and **16** by oxidative aryl-aryl coupling of the tetra alkoxy-substituted biphenyls **8** or **10** with the bis-alkylated catechols **13** or **14** using VOF_3 in the presence of boron trifluoride-diethyl ether.[44] **13** and **14** were obtained in high yields by mono-alkylation of catechol using the corresponding 1-bromoalkanes, followed by treatment with 1-bromo-12-dodecanol. Biphenyl **8** was synthesized by Suzuki-coupling of the aryl bromide **6** with the aryl boronic acid **7**.[45] **7** was derived from the conversion of **6** into the boronic acid. Alkylation of catechol followed by bromination yielded **6** in high yield. Biphenyl **10**, by contrast, was obtained in quantitative yield from the Ulman coupling of the aryl iodide **9** which was obtained by alkylation, and subsequent iodination of catechol.

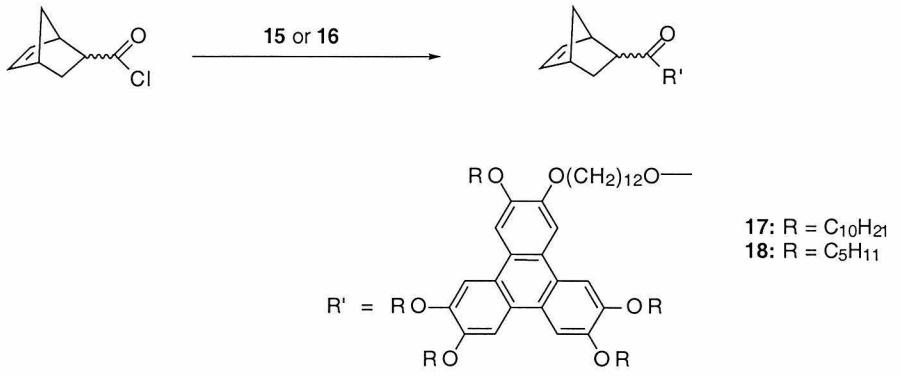


Scheme 1. Synthesis of triphenylene **15**.



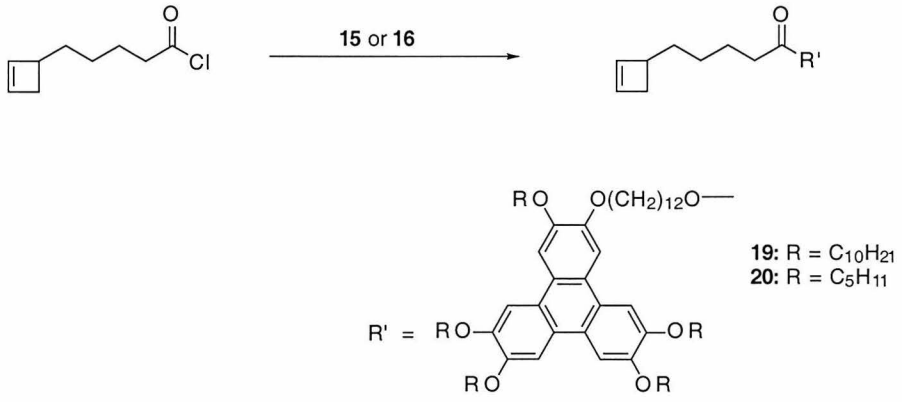
Scheme 2. Synthesis of triphenylene **16.**

Norbornene monomers **17** and **18** were synthesized by esterfication of norborn-2-ene-5-carbonyl chloride[46] with the hydroxy-functionalized triphenylenes **15** and **16**.[41] The reaction was carried out in tetrahydrofuran in the presence of triethylamine to yield **17** and **18** in nearly quantitative yields (Scheme 3).



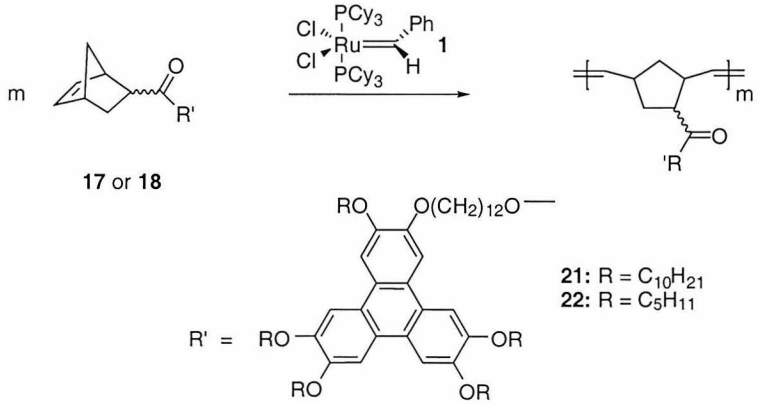
Scheme 3. Synthesis of norbornene monomers **17** and **18**.

It was anticipated that a more flexible backbone such as a poly(butadiene) might facilitate a better alignment of the mesogenic units. To obtain a poly(butadiene) backbone, the corresponding monomers **19** and **20** were synthesized in analogy to literature procedures[41,42] by the initial conversion of [3-oxa-4-(2-cyclobutene)]butyric acid[42] to the corresponding acid chloride and subsequent esterfication with the triphenylene precursors **15** and **16** in high yields (Scheme 4).



Scheme 4. Synthesis of cyclobutene monomers **19** and **20**.

Polymer Syntheses. Polymerization of norbornene monomers **17** and **18** was carried out using initiator **1**. The monomers were polymerized for six hours at room temperature in dichloromethane followed by treatment with an excess of ethyl-vinyl-ether to cleave the initiator from the polymer chain (Scheme 5). Repeated precipitation from methanol yielded polymers **21** and **22** as white solids in quantitative yield and low PDIs between 1.09-1.17 (Table 1).



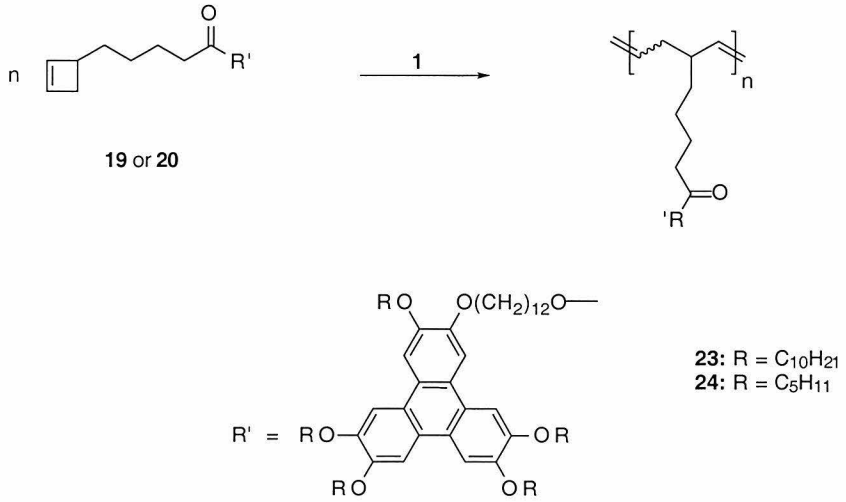
Scheme 5. Synthesis of the poly(norbornene)s **21** and **22**.

Table 1. Polymerization results

Polymer	$\overline{M}_n$[a]	PDI[a]	Phase Transition[b] (°C) heating	cooling
21	46500	1.09	g-3D_{hd1}36D_{hd2}42i	i20D_{hd}-4g
22	48500	1.17	g-4i	i-11g
23	33000	1.11	g-17D_{hd1}37D_{hd2}45i	i28D_{hd}-34g
24	157000	1.19	g-12i	i-12.5g
25	50000	1.11	g-18D_{hd1}34D_{hd2}43i	i26D_{hd}-34g
26	125000	1.32	g-17i	i-19g

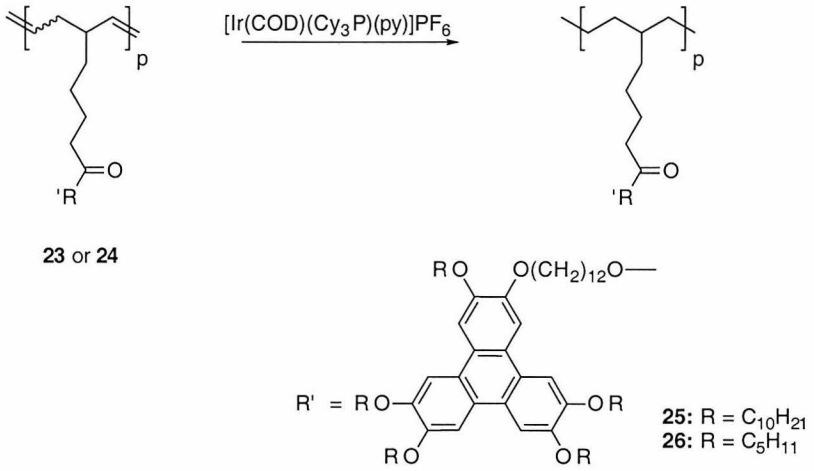
[a] Determined by gel permeation chromatography in dichloromethane relative to monodispersed polystyrene standards. [b] Analysis by differential scanning calorimetry with a scan rate of 10°K/min.

The polymerizations of the cyclobutene monomers **19** and **20** were performed with initiator **1** in dichloromethane at 45°C in a sealed vial for 1.5 hours (Scheme 6). As previously described for poly(butadiene)s, the initiator was cleaved from the polymer chain by precipitation into methanol containing 5% 1N hydrochloric acid [41,42] to yield the polymers **23** and **24** in quantitative yields. In analogy to the poly(norbornene)s, **21** and **22**, low polydispersities of 1.11-1.19 were observed as presented in Table 1.



Scheme 6. Synthesis of poly(cyclobutenes) **23** and **24**.

Chapter 3 discussed the influence of backbone rigidity on the thermotropic behavior of calamitic side-chain liquid crystalline polymers synthesized by ROMP.[41] In these studies the relatively rigid poly(norbornene) backbone was compared to the more flexible poly(butadiene) using a nitrostilbene as the mesogenic unit. These investigations showed that, as a consequence of an increase in backbone flexibility, a better alignment of the mesogens was possible resulting in a nematic mesophase behavior for the poly(norbornenes) and a smectic mesophase for the poly(butadiene)s. To further investigate the influence of backbone flexibility in the systems presented herein, a hydrogenation of the butadiene-backbone of polymers **23** and **24** was carried out using Crabtree's catalyst $[Ir(COD)(Cy_3)(py)]PF_6$ to obtain poly(ethylene)-based polymers **25** and **26** which have the most flexible backbone possible. The hydrogenation was performed in dichloromethane at 55°C at 120 psi for 16 hours with 5 to 10 mol percent catalyst to yield polymers **25** and **26** in quantitative yields as shown in Scheme 7. The molecular weights and the polydispersities for polymer **25** and **26** are summarized in Table 1.



Scheme 7. Synthesis of polymers **25** and **26**.

Thermal Characterization of the Polymers.

Analysis of the phase behavior of polymers **21-26** was accomplished using DSC and powder diffraction X-ray scattering (wide angle X-ray scattering; WAXS). For the

DSC measurements all heating and cooling scans were completely reversible for each of the polymers. The second heating and first cooling scans are reported in all cases. It was not possible to obtain optical polarized microscopical pictures of these compounds because of the formation of a homogeneous film, as previously described for discotic polymers.[7a,d]

DSC Measurements. All monomers exhibited only a single phase transition from the crystalline into the isotropic state. The DSC results of the polymers **21**-**26** are summarized in Table 1. Figure 3 shows the DSC traces of polymer **25** as a characteristic example of results obtained for polymers **21**, **23** and **25**, all bearing a decyloxy-substituted triphenylene.

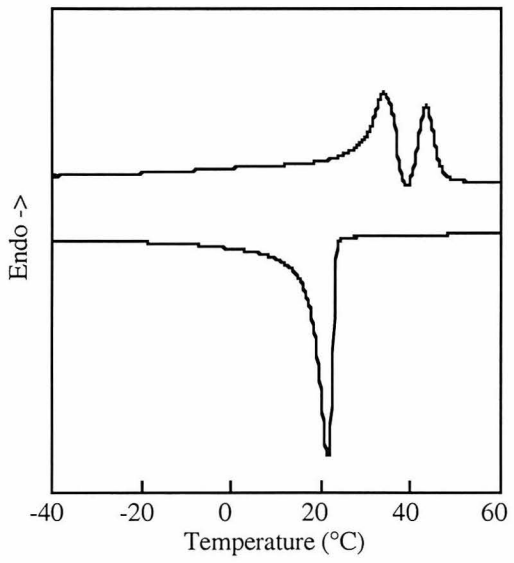


Figure 3. Normalized DSC thermograms for poly(butadiene) **25** with a scan rate of 10°C/min (the first cooling and the second heating scans are shown; all heating and cooling scans were completely reversible for each of the polymers). The phase transition enthalpies of the first disordered transitions (ΔH (D_h->i)) range from 7.5 J*g^{-1} (polymer **25**) to 10 J*g^{-1} (polymer **21**).

These polymers displayed a broad glass transition and two first order transitions during heating, while only one exothermic signal and a broad glass transition were observed during cooling. Similar behavior has been observed previously for discotic liquid crystalline polymers.[7a,8b,19,20,30,31a] The glass transition temperature (T_g) decreased from -3°C for the poly(norbornene)s to -17°C and -18°C for the more flexible poly(butadiene)s and poly(butane)s, respectively. For all polymers, the first disordering endotherms were observed between 34 and 37°C while the transition into the isotropic melt was found between 42 and 45°C. Due to a supercooling effect during the cooling scans, the transitions from the isotropic into the liquid crystalline phase and the broad glass transitions (over temperature ranges of 35°C) shifted to lower temperatures for polymers **21**, **23**, and **25**. As a result, exotherms could be observed at 20°C, 28°C and 26°C and the glass transitions at -4°C, -34°C and -34°C.

For polymers **22**, **24**, and **26**, which bore pentoxy-substituted triphenylenes, only a glass transition, but no disordering peaks, was observed, thus clearly showing that these polymers do not exhibit liquid crystalline behavior.

X-Ray Investigations. Diffraction data were collected on non-oriented samples of the polymers at temperatures ranging from -73 to 77°C. Figure 4 displays the diffraction patterns obtained for compound **25** at 0, 38 and 77°C. The *d*-spacings in Table 2 were calculated from 2θ values according to the Bragg equation ($n\lambda = 2d \sin\theta$).

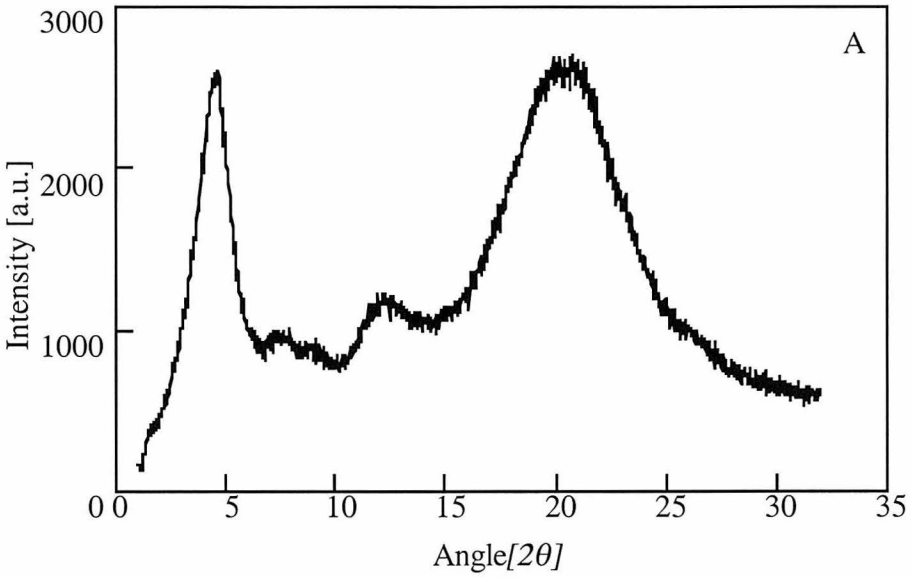


Figure 4a. Powder X-ray diffractogram of **25** at 0°C.

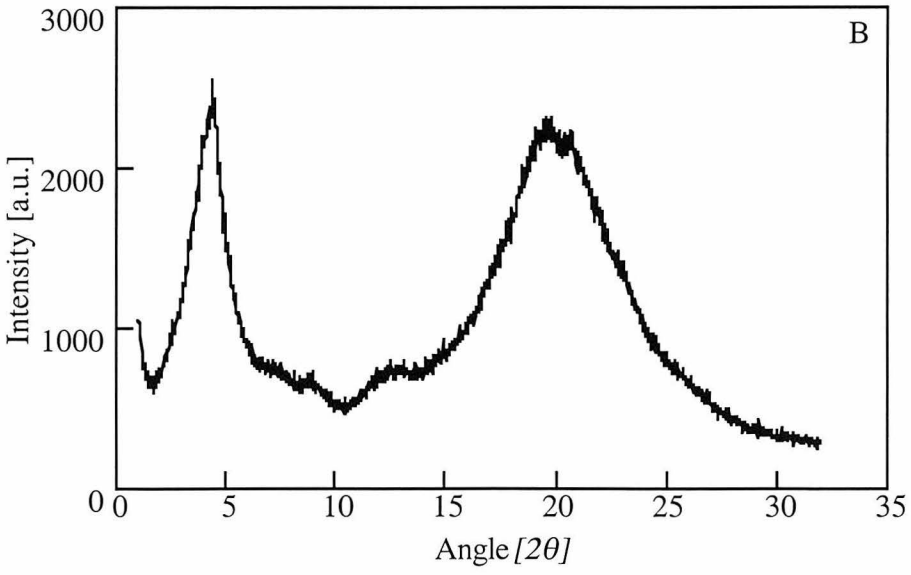


Figure 4b. Powder X-ray diffractogram of **25** at 38°C.

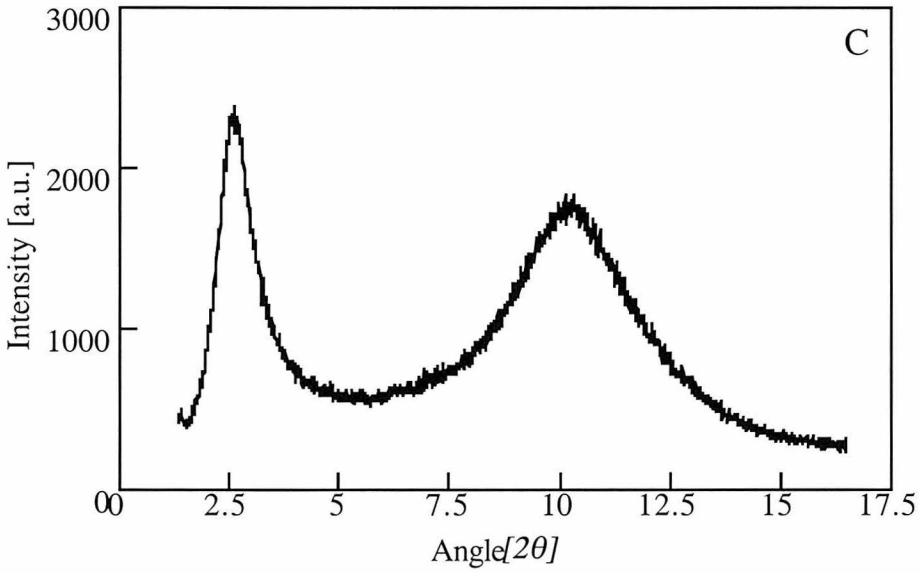


Figure 4c. Powder X-ray diffractogram of **25** at 77°C.

Table 2. Selected 2θ (deg) and derived *d*-spacing values (Å) and Miller Indices (*hkl*) of polymers **21**, **23** and **25** at 0°C and 77°C from powder X-ray diffraction measurements.

Polymer	T (°C)	2θ (deg)	d_{100} (Å)	2θ (deg)	d_{110} (Å)	2θ (deg)	d_{200} (Å)
21	0	4.50	19.64	7.64	11.57	8.92	9.91
21	77	4.20	21.04	-	-	-	-
23	0	4.46	19.81	7.08	12.49	8.80	10.05
23	77	4.18	21.14	-	-	-	-
25	0	4.62	19.13	7.26	12.18	8.84	10.00
25	77	4.18	21.14	-	-	-	-

The X-ray diagrams for polymers **21**, **23**, and **25** between -73 and 30°C display a high intensity reflection at low Bragg angles, a set of weak, secondary reflections in the small angle region, an amorphous halo and broad reflection at higher angles as reported

before for discotic columnar side-chain liquid crystalline polymers (Figure 4a).[7c] The intense reflection corresponding to a spacing of 19.64 Å for **21**, 19.81 Å for **23**, and 19.13 Å for **25** (at 0°C) can be attributed to the (100) reflection of a hexagonal columnar (D_h) mesophase. Small peaks observed around 12 Å and 10 Å for all three polymers result from the (110) and (200) reflections, respectively, while the broad peak around 7 Å could not be unequivocally assigned at the present state. These three peaks at small angles with values of Q in the ratio 1:√3:2 indicate that a hexagonal lattice exists from low temperatures to the isotropic phase, with intercolumnar distances of 22.68 Å for **21**, 22.78 Å for **23**, and 22.00 Å for **25** (at 0°C) in the mesophase. The diffuse halo at around 4.3 Å is characteristic for a liquid-like order of the alkyl chains. The lack of an ordered peak between 3-4 Å may indicate a disordered stacking of the core molecules. However, the possibility exists that this peak, which is normally weak, cannot be clearly observed over the background noise. In fact, the spectra of polymers **23** and **25** display an extremely weak peak on top of the diffuse halo which could correspond to the ordered peak. These data suggest that a discotic hexagonal mesophase for polymers **21**, **23**, and **25** exists, which is best identified as D_{hd} (discotic hexagonal disordered, labeled as D_{hd1} in Table 1), however a D_{ho} (discotic hexagonal ordered) mesophase cannot be entirely excluded, either.

No significant difference in the X-ray patterns of **21**, **23** and **25** could be observed on heating the polymers from 25°C to 37-42°C (Figure 4b), although a first order transition in the DSC could be observed between 34 and 37°C. Therefore, a discotic hexagonal mesophase, which is assigned as D_{hd2} in Table 1, was identified in this temperature range as well.

As shown in Table 2, a trend to longer distances between the columns with increasing temperatures could be observed in all polymers as a result of increased flexibility. When the temperature was increased beyond 43°C (the transition temperature from the liquid crystalline mesophase into the isotropic melt as observed by DSC), only the (100) peak and the diffuse halo were observed in all cases, while the higher ordered

reflections (110 and 200) were no longer present, indicating the existence of a lower order in the isotropic melt as previously observed.[7u] Figure 4c shows the diffraction pattern of polymer **25** at 77°C. In analogy to the DSC results, no difference in the X-ray patterns of polymers **21**, **23**, and **25** was observed, suggesting that the backbone rigidity does not play a role in the discotic liquid crystalline phase behavior of these polymers.

Unlike compounds **21**, **23**, and **25**, no diffraction pattern corresponding to a discotic mesophase was observed for polymers **22**, **24**, and **26**, indicating that these polymers exist only as amorphous material, which is consistent with the DSC results. Therefore, the DSC and X-ray measurements prove that the pentoxy substitution on triphenylenes is too short to stabilize a liquid crystalline mesophase.

Light Emitting Diodes Properties.

Low molecular weight[47] as well as polymeric[48] electroluminescent devices attracted considerable attention due to their possible application as large-area light emitting displays. In the context of semiconductor devices, polymers in particular allow fabrication of thin-film devices over large areas, which, with the exception of amorphous and polycrystalline silicon, has proved difficult to achieve with inorganic or low molecular weight organic materials. In most cases, these devices are thin film multilayers composed of a hole transport layer (HTL), an emission layer, and an electron transport layer (ETL) sandwiched between two electrodes.

In the last years a variety of molecules have been used as HTLs, including triphenyldiamine derivatives[49] and triphenylamines.[50] In 1994, Ringsdorf and coworkers showed that triphenylenes display the highest charge carrier mobilities of any known organic material except single crystal phases.[2] These high charge carrier mobilities stimulated several groups, including those of Haarer, Wendorff and Schmidt, to investigate the use of these materials as HTLs.[9b,d,11,51] A remarkable improvement of LED properties in a variety of systems was made possible which can be attributed to the high π-overlap of

the hexagonal discotic materials. Therefore, in collaboration with the groups of Haarer and Schmidt, the hole transport properties of polymers **21**, **22**, **23**, and **25** were investigated.

The LED devices using the polymers as HTL were prepared by evaporating 60 nm of the polymer onto an indium-tin-oxide (ITO) coated glass substrate. Subsequently, 80 nm of tris(8-quinolinolato)aluminum(III) complex (Alq_3) were vapor-deposited onto the polymer layer. In a last step, approximately 300 nm of aluminum were deposited onto the Alq_3 layer as the electron-injecting cathode. The emitting area was approximately 0.2 cm^2. Luminescence was measured either by a photomultiplier or by a Minolta luminescence meter at room temperature under ambient conditions.

In all cases the emitted light was yellow-green, which is typical for Alq_3. It was only possible to measure these devices up to a current of 20-25V. Above this voltage, the LEDs decomposed, which can be attributed to the low glass transition and the low isotropization temperatures of all polymers, since all devices are heating up while operating, therefore changing their liquid crystalline behavior.

Figure 5, 6, 7, and 8 show the current density electric field characteristic and the luminance of the LED device prepared of **21**, **23**, and **25**.

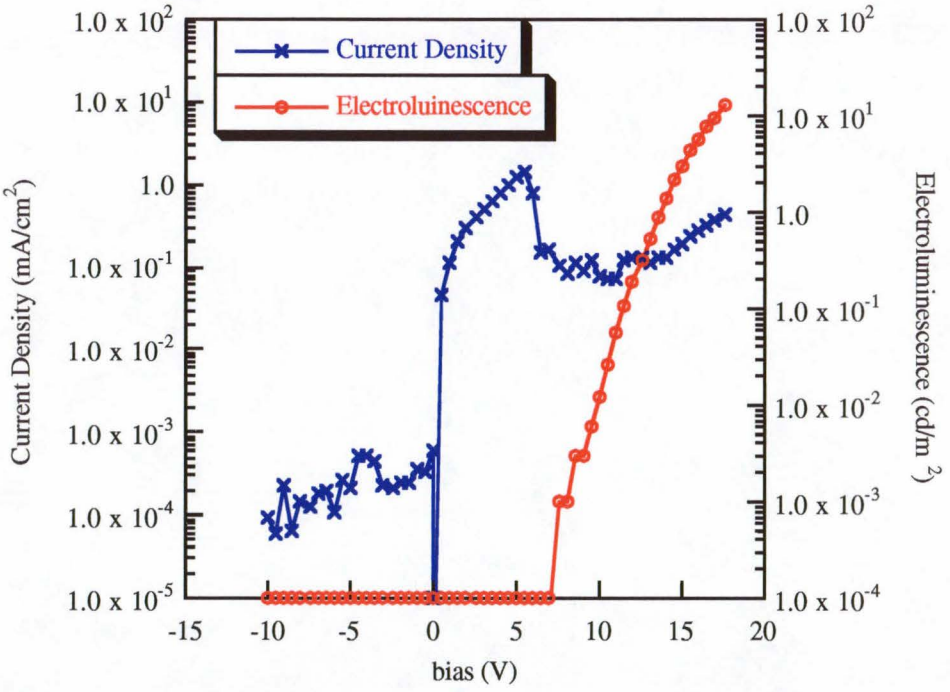


Figure 5. Current density and luminance as a function of the applied field for a two-layer LED device (ITO/**21**/Alq_3/Al).

Figure 5 presents the current density electric field characteristic and the luminance of the LED device containing **21**. Typically, this LED started to exhibit electroluminescence at a field of approximately 8 V, as detected by a photomultiplier operated at 600 V amplification, when operated in a continuous DC mode under forward bias with ITO as the positive electrode. A maximum luminance of 12.5 cd/m^2 at a current density of 0.44 mA/cm^2 was reached at a field of 17.5 V. As described above, it was not possible to measure the device at higher voltage because of decomposition.

Figure 6 displays another LED device based on polymer **21**. The polymer used for the LED device in this Figure had a lower polydispersity (1.09) than the one used in Figure 5 (PDI = 1.20). This difference resulted in a slightly higher maximum luminance of 21.6

cd/m^2 at a current density of 2.67 mA/cm^2 and a field of 22 V. Emission of the green light started at 7.5 V.

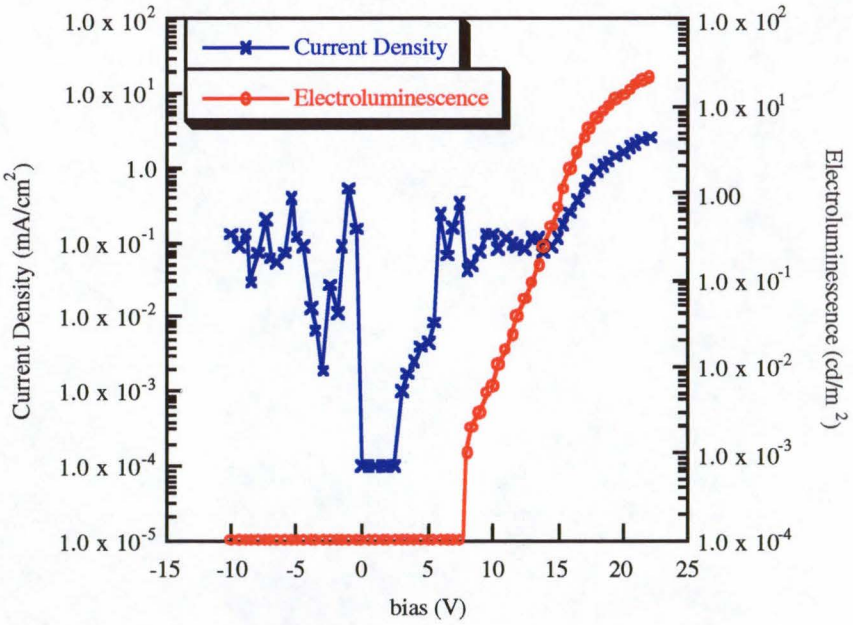


Figure 6. Current density and luminance as a function of the applied field for a two-layer LED device (ITO/**21**/Alq$_3$/Al).

In contrast to polymer **21**, polymers **23** and **25** did not show these high values for the luminance. As shown in Figure 7, **23** shows only a maximum luminance of 6.3 cd/m^2 at a current density of 0.77 mA/cm^2 and a field of 30 V. In this case yellow-green electroluminescence was first detected at a voltage of 14 V.

Polymer **25** displays even smaller maximum luminance values of 0.57 cd/m^2 at a current density of 0.22 mA/cm^2 and a field of 30 V (Figure 8). First yellow-green electroluminescence for polymer **25** was detected at approximately 9V.

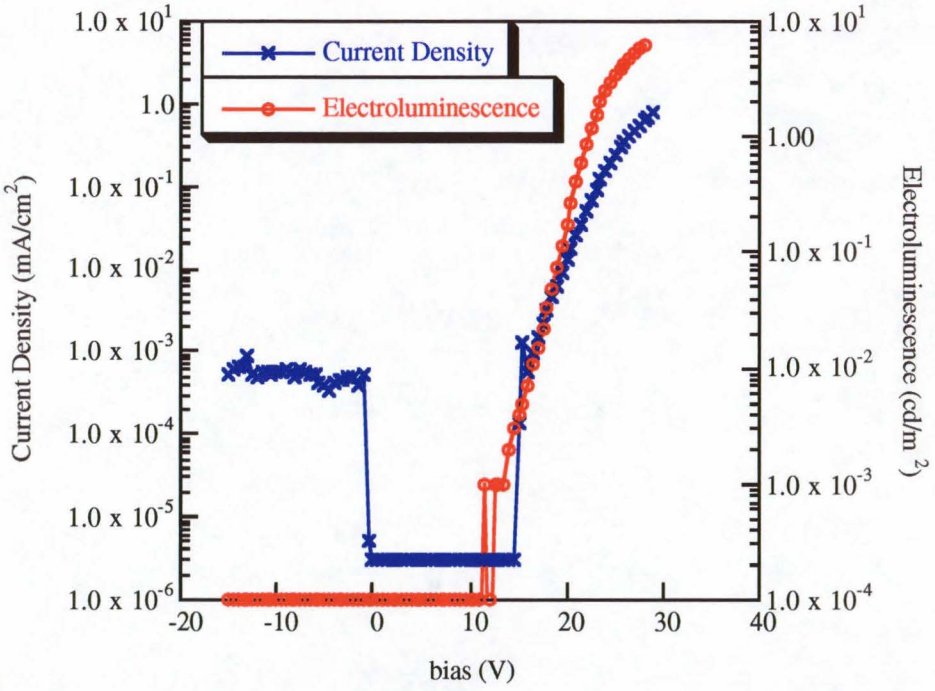


Figure 7. Current density and luminance as a function of the applied field for a two layer LED device (ITO/**23**/Alq_3/Al).

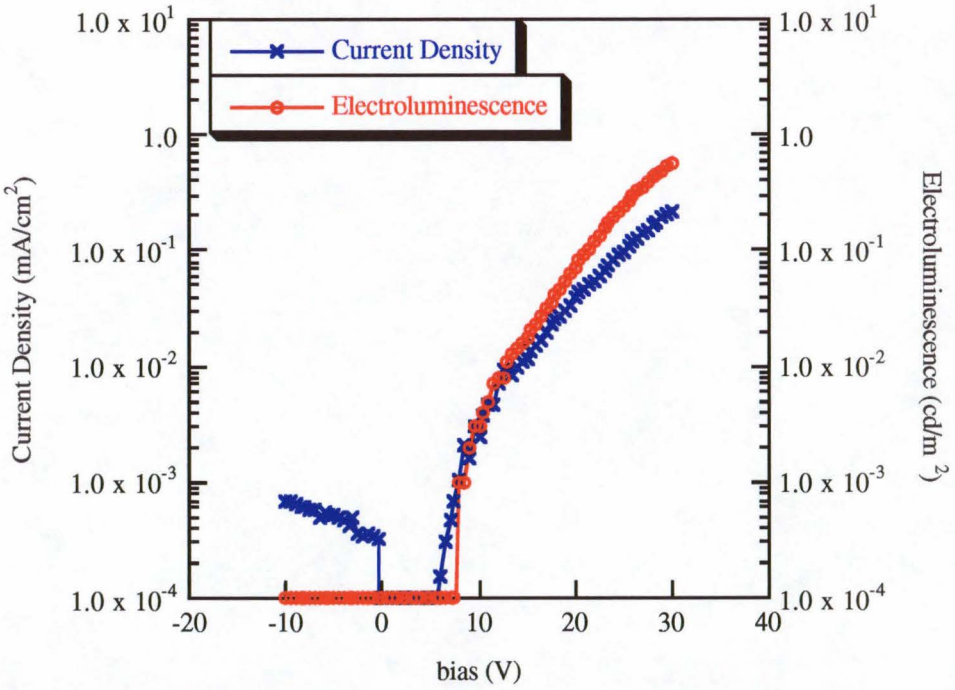


Figure 8. Current density and luminance as a function of the applied field for a two layer LED device (ITO/**25**/Alq_3/Al).

The data presented above show that polymers **21**, **23**, and **25** are hole transport and injection materials in two-layer LED devices. Of the investigated polymers, **21** is the most suitable hole transport material in LEDs, while poly(butadiene)s **23** and **25** only show weak hole transport properties. Several explanations for this trend are imaginable, ranging from small disorders in the discotic hexagonal arrangements of the poly(butadiene)s to lower temperature stabilities of the poly(butadiene)s.

However, all these data are preliminary. None of these LED devices are optimized as of yet in respect to polymer or Alq_3 thicknesses or temperatures.[11] Therefore, no final statement about the hole transport properties of these materials can be made at this point. Nevertheless, due to the high charge carrier mobilities as well as recent advances in LED properties of low molecular weight triphenylenes, optimized polymeric triphenylenes of

these polymers could have interesting and to low molecular weight triphenylenes comparable hole transports properties.

Conclusions

Ring-opening metathesis polymerization of norbornene and cyclobutene based monomers bearing alkoxy-substituted triphenylenes to obtain poly(norbornene)s and poly(butadiene)s with low polydispersities has been demonstrated. Poly(butane)-based polymers were synthesized by hydrogenation of the poly(butadiene)s using Crabtree's catalyst. Examination of the phase behavior of these polymers was carried out by DSC and X-ray diffraction. DSC measurements show that all polymers bearing decyloxy-substituted triphenylenes display mesogenic behavior up to 45°C, while those polymers containing pentoxy-substituted triphenylenes did not exhibit a mesophase behavior. The same trend could be substantiated by X-ray diffraction measurements which showed a discotic hexagonal mesophase for polymers containing decyloxy-substituted triphenylenes but not for the pentoxy-substituted polymers. In contrast to previous studies on similar systems, no dependency of the mesophase on backbone rigidity could be established. For the mesogen synthesis, a rational, universally applicable strategy using vanadiumoxofluoride as the aryl-aryl coupling reagent has been developed. Because this route is compatible with a large variety of functionalities, it should provide convenient access to functionalized triphenylenes. The synthesis introduced herein presents a facile and efficient route to discotic, columnar, side-chain liquid crystalline polymers. Preliminary results show that these polymers are promising materials as hole transporters in light emitting diodes (LED).

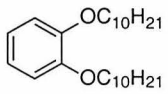
Experimental

General. Argon was purified by passage through columns of BASF R-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). NMR spectra were recorded on a GE QE-300 Plus (300.1 MHz; 75.49 MHz ^{13}C) spectrometer; IR spectra were recorded on a Perkin-Elmer

1600 series FT-IR spectrometer. Gel permeation chromatographs were obtained on a HPLC system using an Altex model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 micron mixed bed columns, and a Knauer differential-refractometer using CH_2Cl_2 as eluent at a 1.0 mL/min flow rate. Molecular weights and polydispersities were reported versus monodispersed polystyrene standards. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC-7 with a scan rate of 10°C/min. Wide angle X-ray scattering analysis was performed employing a goniometer from Siemens (D 500) with an Cu-K_α radiation of 1.5418 Å.

Materials. CH_2Cl_2 was distilled from calcium hydride and degassed by repeated freeze-pump-thaw cycles. All other solvents were used without further purification unless noted otherwise. Chemicals were purchased from the Aldrich Chemical Company unless noted otherwise and used without further purification. Crabtree's catalyst ($[Ir(COD)(Cy_3P)(py)]PF_6$) was purchased from Strem Chemical Company. Norbornene-2-ene-5-carbonyl-chloride and [5-(2-cyclobutenyl)]pentanoic acid were synthesized as previously reported.[41,42]

Synthesis of 1,2-didecyloxybenzene (4):

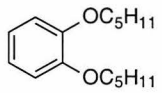


1-Bromodecane (100 g, 0.45 mol) was added dropwise under argon to a mixture of catechol (20 g, 0.182 mol) and potassium carbonate (82 g) in 200 mL dimethylformamide. After stirring under reflux for 24 hours, the mixture was filtered, and the product precipitated as a white solid at 0°C. The crystalline solid was dried *in vacuo* to yield 49.5 g (70%).

^{1}H-NMR ($CDCl_3$) δ 6.93 (s, 4H), 4.03 (t, 4H, J = 6.6 Hz), 1.87 (q, 4H, J = 6.9 Hz), 1.53 (m, 4H), 1.33 (m, 26H), 0.94 (t, 6H, J = 6.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 149.3, 121.1, 114.0, 69.3, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.9, 14.3; IR (thin film

on a NaCl plate) 3014, 2922, 2851, 1593, 1506, 1467, 1454, 1389, 1331, 1257, 1224, 1122, 1047, 1022, 988, 938, 896, 757, 737, 669, 599 cm^{-1}; Anal. calcd. for $C_{26}H_{46}O_2$: C, 79.94; H, 11.87, found: C, 80.40; H, 11.78; HRMS (FAB) calcd. for $C_{26}H_{46}O_2$ $(MH)^+$ 390.3498, found 390.3495.

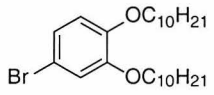
Synthesis of 1,2-dipentoxybenzene (5):



5 was synthesized according to the procedure described above using 1-bromopentane (55 g, 0.36 mol) and catechol (15 g, 0.14 mol) in 150 mL dimethylformamide to give 33.8 g (99%) of a colorless oil.

^{1}H-NMR ($CDCl_3$) δ 6.95 (s, 4H), 4.05 (t, 4H, J = 6.6 Hz), 1.89 (q, 4H, J = 1.2 Hz), 1.50 (m, 8H), 1.02 (t, 6H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$) δ 149.0, 120.8, 113.9, 69.0, 28.8, 28.0, 22.3, 13.8; IR (thin film on a NaCl plate) 3063, 2955, 2869, 1593, 1503, 1469, 1453, 1387, 1329, 1256, 1223, 1157, 1125, 1074, 1050, 1024, 1006, 991, 918, 832, 805, 738, 597 cm^{-1}; Anal. calcd. for $C_{16}H_{26}O_2$: C, 76.74; H, 10.47, found: C, 76.20; H, 10.04; HRMS (FAB) calcd. for $C_{16}H_{26}O_2$ $(MH)^+$ 250.3844, found 250.1931.

Synthesis of 1-bromo-3,4-didecyloxybenzene (6):

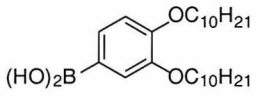


A solution of **4** (20 g, 0.051 mol) in 100 mL dichloromethane was cooled to -20°C and treated sequentially with a catalytic amount of iron powder and bromine (8.4 g, 0.053 mol) in 40 mL dichloromethane. The solution was stirred at -20°C for three hours and then at room temperature for 12 hours. The reaction was washed with saturated aqueous solutions of sodium dithionate and sodium carbonate. The organic phase was dried over magnesium

sulfate and the solvent was evaporated under reduced pressure to yield a light brown oil which was dissolved in methanol. The product precipitated as a white solid after two days in the refrigerator. Final purification was achieved by repeated recrystallization from methanol to yield 18.4 g (77%) of a white crystalline solid.

^{1}H-NMR ($CDCl_3$) δ 6.97 (d, 1H, *J* = 2.4 Hz), 6.95 (d, 1H, *J* = 1.8 Hz), 6.71 (d of d, 1H, *J* = 3.3 Hz), 3.94 (t, 2H, *J* = 6.6 Hz), 3.93 (t, 2H, *J* = 6.6 Hz), 1.77 (m, 4H), 1.41 (m, 4H), 1.25 (m, 26H), 0.86 (t, 6H, *J* = 6 Hz); ^{13}C-NMR ($CDCl_3$) δ 149.8, 148.1, 123.2, 116.7, 114.9, 112.5, 69.3, 69.1, 31.7, 29.4, 29.2, 29.0, 28.9, 25.7, 22.5, 13.9; IR (thin film on a NaCl plate) 3422, 2953, 2919, 2848, 1637, 1585, 1504, 1465, 1432,1400, 1392, 1324, 1295, 1252, 1220, 1134, 1070, 1046, 1023, 987, 938, 909, 890, 856, 832, 792, 722, 643, 577 cm^{-1}; Anal. calcd. for $C_{26}H_{45}O_2Br$: C, 66.51; H, 9.66, found: C, 66.82; H, 9.45; HRMS (FAB) calcd. for $C_{26}H_{45}O_2Br$ $(MH)^+$ 468.2603, found 468.2587.

Synthesis of 1-boronic acid-3,4-didecyloxybenzene (7):

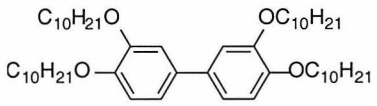


25 mL 1.6M n-butyllithium in hexane (40 mmol) was slowly added to a solution of **6** (14 g, 30 mmol) in ether (300 mL) at 0°C. The reaction mixture was stirred for 2 hours at room temperature, transferred to an addition funnel and carefully added to a solution of trimethyl borate (10.4 g, 100 mmol) in 100 mL dimethylether at -60°C. The reaction mixture was slowly warmed to room temperature after complete addition and stirring was continued for 20 hours under argon. The solution was hydrolized with 150 mL 2N hydrochlorid acid and extracted several times with ether. The combined organic phases were washed with water and dried over magnesium sulfate. The solvent was removed *in vacuo*. Final purification was achieved by a silica column chromatography. All starting materials and side products were removed using dichloromethane as eluent. The product

was obtained in high purity using ^{t}butyl-methyl-ether as eluent to yield 2.14 g (17%) of a white crystalline solid.

^{1}H-NMR ($CDCl_3$) δ 7.79 (d, 1H, J = 9 Hz), 7.67 (s, 1H), 6.98 (d, 1H, J = 8.1 Hz), 4.11 (t, 2H, J = 6.6 Hz), 4.06 (t, 2H, J = 6.6 Hz), 1.85 (m, 4H), 1.48 (m, 4H), 1.25 (m, 26H), 0.86 (t, 6H, J = 6 Hz); ^{13}C-NMR ($CDCl_3$) δ 153.0, 148.2, 129.7, 122.1, 120.3, 112.3, 69.3, 68.6, 31.7, 29.4, 29.3, 29.2, 29.0, 28.9, 25.9, 25.8, 22.5, 13.9; IR (thin film on NaCl plate) 2921, 2850, 1599, 1514, 1467, 1418, 1352, 1329, 1259, 1213, 1139, 1071, 1021, 987, 876, 813, 741, 712, 595 cm^{-1}.

Synthesis of 3,4,3',4'-tetradecyloxybiphenyl (8):

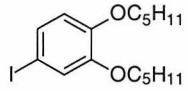


Solvents used in this reaction were dried and degassed. **6** (0.9 g, 1.9 mmol), **7** (0.9 g, 2.1 mmol) and palladium(0)-tetra-kis-(triphenyl)phosphine (24 mg) were added to the heterogeneous system 7.5 mL toluene, 5 mL tetrahydrofuran and 14 mL 2M potassium carbonate under vigorous stirring and heated to 100°C for 24 hours under argon. After 24 hours the same amount of catalyst was added and stirring was continued for 24 hours. Upon cooling to room temperature, the organic phase was seperated and the aqueous phase repeatedly extracted with ether. The combined organic phases were washed with water and dried over magnesium sulfate. After removal of the solvent *in vacuo*, the product was purified by column chromatography (silica gel/dichloromethane) to obtain a white crystalline solid in 96% (1.43 g) yield.

^{1}H-NMR ($CDCl_3$) δ 7.04-6.88 (m, 6H), 4.12 (m, 8H), 1.81 (q, 8H, J = 6.6 Hz), 1.46 (m, 8H), 1.25 (m, 55H), 0.86 (t, 12H, J = 6 Hz). ^{13}C-NMR ($CDCl_3$) δ 149.0, 148.3, 134.1, 119.1, 114.0, 113.0, 69.3, 69.2, 31.7, 29.4, 29.3, 29.2, 29.1, 25.8, 22.5, 13.9; IR (thin film on NaCl plate) 3076, 2916, 2850, 1640, 1465, 1368, 1352, 1264, 995, 911,

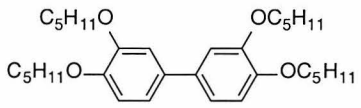
743, 707, 640, 555 cm^{-1}; Anal. calcd. for $C_{52}H_{90}O_4$: C, 80.21; H, 11.57, found: C, 79.98; H, 11.49; HRMS (FAB) calcd. for $C_{52}H_{90}O_4$ $(MH)^+$ 778.6839, found 778.6826.

Synthesis of 1-iodo-3,4-dipentoxybenzene (9):



5 (15 g, 0.06 mol), 30 mL acetic acid, 10 mL water, 10 mL chloroform, 0.5 mL sulfuric acid, iodine (5.1 g), and iodic acid (2.1 g, 0.01 mol) were mixed and vigorously stirred at 40°C. After 24 hours, 300 mL water was added and the organic phase was separated. The aqueous layer was extracted with dichloromethane several times. The combined organic phases were washed with $NaHSO_3$, $Na_2S_2O_3$ and water, dried over magnesium sulfate, and the solvent was removed *in vacuo*. Final purification was achieved by column chromatography (silica gel/dichloromethane) to obtain 19.8 g (88%) of a colorless liquid. ^{1}H-NMR ($CDCl_3$) δ 7.14 (m, 2H), 6.59 (d, 1H, J = 8.4 Hz), 3.92 (t, 4H, J = 6.6 Hz), 1.79 (m, 4H), 1.34 (m, 8H), 0.91 (t, 6H, J = 8.1 Hz). ^{13}C-NMR ($CDCl_3$) δ 149.9, 149.0, 129.6, 122.4, 115.4, 82.3, 69.2, 69.1, 28.7, 28.0, 22.2, 13.8; IR (thin film on NaCl plate) 3074, 2956, 2871, 1581, 1501, 1468, 1395, 1321, 1291, 1251, 1222, 1137, 1074, 1050, 1019, 989, 917, 854, 838, 796, 730, 631, 574 cm^{-1}; Anal. calcd. for $C_{16}H_{25}O_2J$: C, 51.07; H, 6.70, found: C, 50.61; H, 6.52; HRMS (FAB) calcd. for $C_{16}H_{25}O_2J$ $(MH)^+$ 376.0892, found 376,0722.

Synthesis of 3,3',4,4'-tetrapentoxybiphenyl (10):

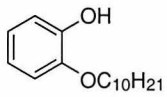


9 (10 g, 0.027 mol) was mixed with fine powdered copper (10 g) and heated to 250°C under argon and vigorous stirring. After 4 hours the temperature was lowered to 180°C,

and the hot solution was carefully poured into 200 mL of dichloromethane. The resulting mixture was filtered over celithe and the solvent was removed *in vacuo* to obtain a brown solid. Final purification was achieved by column chromatography (silica gel/hexane: dichloromethane 2:1 v/v) to obtain 5.7 g (86%) of a white crystalline solid.

^{1}H-NMR ($CDCl_3$) 7.05-6.89 (m, 6H), 4.02 (m, 8H), 1.83 (m, 8H), 1.41 (m, 16), 0.92 (t, 12H, J = 6.9 Hz). ^{13}C-NMR ($CDCl_3$) δ 149.0, 148.2, 134.1, 119.1, 113.9, 112.9, 69.3, 69.2, 28.8, 28.0, 22.3, 13.8; IR (thin film on NaCl plate) 2956, 2931, 2858, 1604, 1576, 1513, 1466, 1388, 1319, 1293, 1259, 1222, 1147, 1074, 1028, 1001, 988, 914, 833, 788, 734, 619 cm^{-1}; Anal. calcd. for $C_{32}H_{50}O_4$: C, 77.05; H, 10.11, found: C, 76.86; H, 10.41; HRMS (FAB) calcd. for $C_{32}H_{50}O_4$ $(MH)^+$ 498.3697, found 498.3533.

Synthesis of 1-decyloxy-2-hydroxybenzene (11):

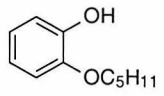


A solution of catechol (9 g, 0.082 mol) in 200 mL dimethylformamide was treated with sodiumhydride (3.36 g, 1.14 mol) under argon. After stirring under reflux for 1 hour the color changed to dark green. 1-Bromodecane (0.08 mol) was added dropwise and the reaction mixture was stirred under reflux for an additional 16 hours. The hot reaction mixture was filtered and the product precipitated after two days in the refrigerator. The obtained solid was filtered and recrystallized several times from ether to yield 11.5 g (56%) of a white crystalline solid.

^{1}H-NMR (acetone d^6) δ 6.62 (m, 4H), 3.92 (t, 2H, J = 7.2 Hz), 1.70 (q, 2H, J = 7.2 Hz), 1.27 (m, 14H), 0.87 (t, 3H, J = 5.7 Hz). ^{13}C-NMR ($CDCl_3$) δ 145.8, 121.1, 119.9, 114.4, 111.6, 68.5, 32.1, 29.8, 29.7, 29.6, 29.5, 28.8, 28.0, 22.8, 14.2; IR (thin film on a NaCl plate) 3549, 1051, 2926, 2854, 1614, 1598, 1501, 1468, 1393, 1367, 1302, 1258, 1223, 1198, 1108, 1035, 1019, 911, 786, 740 cm^{-1}; Anal. calcd. for

$C_{16}H_{26}O_2$: C, 76.74; H, 10.47, found: C, 76.40; H, 9.94; HRMS (FAB) calcd. for $C_{16}H_{26}O_2$ $(MH)^+$ 250.3844, found 250.1606.

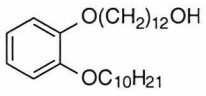
Synthesis of 1-pentoxy-2-hydroxybenzene (12):



12 was synthesized according to the procedure described above using 1-bromopentane (21 g, 0.14 mol) and catechol (20 g, 0.18 mol) in dimethylformamide to give 17.1 g (68%) of a colorless oil.

^{1}H-NMR ($CDCl_3$) δ 6.93 (m, 4H), 4.09 (t, 2H, *J* = 6.3 Hz), 1.89 (q, 2H, *J* = 6.9 Hz), 1.50 (m, 4H), 1.05 (t, 3H, *J* = 6.6 Hz). ^{13}C-NMR ($CDCl_3$) δ 145.7, 121.1, 119.8, 114.4, 111.5, 68.7, 28.8, 28.0, 22.3, 13.8; IR (thin film on NaCl plate) 3544, 3054, 2957, 2934, 2873, 1613, 1598, 1503, 1469, 1394, 1365, 1302, 1259, 1224, 1155, 1107, 1073, 1035, 1019, 989, 913, 840, 788, 742 cm^{-1}; Anal. calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95, found: C, 73.44; H, 9.09; HRMS (FAB) calcd. for $C_{11}H_{16}O_2$ $(MH)^+$ 180.2490, found 180.1153.

Synthesis of 2-(12'-hydroxydodecyloxy)-1-decyloxybenzene (13):

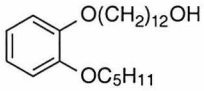


11 (4.8 g, 0.019 mol) was dissolved in 120 mL dimethylformamide. Sodiumhydride (0.49 g, 0.019 mol) was added and the mixture was allowed to stir under reflux for 30 min under argon. 12-Bromo-1-dodecanol (5g, 0.019 mol) was added dropwise and the mixture was allowed to stir for an additional 24 hours during which a white solid precipitated. The mixture was filtered and the product precipitated after one day in the refrigerator. The obtained solid was recrystallized from ether and dried *in vacuo*. Final purification was

achieved by column chromatography (silica gel/dichloromethane) to obtain 3.14 g of a yellow crystalline solid in 38% yield.

^{1}H-NMR ($CDCl_3$) δ 6.86 (s, 4H), 3.97 (t, 4H, *J* = 6.6 Hz), 3.60 (t, 2H, *J* = 6.6 Hz), 1.82 (q, 4H, *J* = 6.9 Hz), 1.51 (m, 4H), 1.48 (m, 4H), 1.26 (m, 24H), 0.87 (t, 3H, *J* = 6.6 Hz); ^{13}C-NMR ($CDCl_3$) δ 149.0, 120.8, 114.0, 69.1, 62.9, 32.6, 31.7, 29.4, 29.2, 29.1, 25.8, 25.5, 22.4, 13.9; IR (thin film on NaCl plate) 3422, 3058, 2932, 2857, 1641, 1593, 1501, 1468, 1457, 1390, 1327, 1255, 1222, 1155, 1124, 1051, 912, 788, 740, 599 cm^{-1}; Anal. calcd. for $C_{28}H_{50}O_3$: C, 77.36; H, 11.59, found: C, 77.07; H, 11.80; HRMS (FAB) calcd. for $C_{28}H_{50}O_3$ $(MH)^+$ 434.7089, found 434.7077.

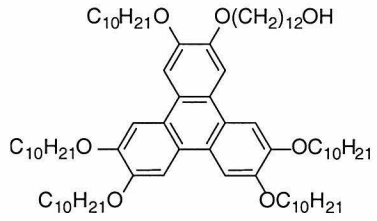
Synthesis of 2-(12'-hydroxydodecyloxy)-1-pentoxybenzene (14):



14 was synthesized in analogy to **13** using **12** (3.6 g, 0.019 mol) and 12-bromo-1-dodecanol (5 g, 0.019 mol) to yield 5.5 g of **14** as a colorless liquid (80%).

^{1}H-NMR ($CDCl_3$) δ 6.86 (s, 4H), 3.97 (t, 4H, *J* = 6.6 Hz), 3.60 (t, 2H, *J* = 6.6 Hz), 1.79 (m, 2H), 1.59-1.26 (m, 24H), 0.90 (t, 3H, *J* = 7.5 Hz). ^{13}C-NMR ($CDCl_3$) δ 149.0, 120.8, 113.9, 69.0, 62.8, 32.6, 29.4, 29.2, 29.1, 28.8, 25.8, 25.5, 22.3, 13.8; IR (thin film on NaCl plate) 3419, 3065, 2927, 2855, 1640, 1593, 1505, 1468, 1454, 1388, 1327, 1255, 1222, 1158, 1124, 1052, 912, 740, 597 cm^{-1}; Anal. calcd. for $C_{28}H_{50}O_3$: C, 75.78; H, 11.06, found: C, 74.60; H, 10.84; HRMS (FAB) calcd. for $C_{23}H_{40}O_3$ $(MH)^+$ 364.2967, found 364.2969.

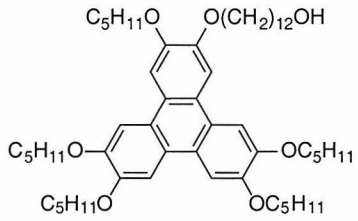
Synthesis of 11-(12'-hydroxydodecyloxy)-2,3,6,7,10-decyloxy-triphenylene (15):



A solution of **8** (0.7 g, 0.9 mmol) in 50 mL dichloromethane was treated sequentially with vanadiumoxytrifluoride (0.335 g, 2.7 mmol) and boron trifluoride-diethylether (0.27 g, 1.9 mmol) during which the solution turned dark purple. **13** (0.51 g, 1.2 mmol) was added dropwise over a period of 10 min and the solution was stirred at room temperature for an additional 20 min. Work-up was performed by adding 200 mL water, extracting the mixture several times with ether until the water phase was clear, drying the organic phase with magnesium sulfate, and evaporating the solvent followed by a short flash column chromatography (silica gel/dichloromethane). Yield 0.512 g (47%) of a white crystalline solid.

^{1}H-NMR ($CDCl_3$) δ 7.86 (s, 6H), 4.25 (t, 12H, J = 6.3 Hz), 3.64 (t, 2H, J = 6.6 Hz), 1.99 (q, 12H, J = 6.9 Hz), 1.58 (m, 12H), 1.31 (m, 76H), 0.91 (t, 15H, J = 4.2 Hz); ^{13}C-NMR ($CDCl_3$) δ 149.0, 123.6, 107.3, 69.7, 63.1, 32.9, 32.1, 29.8, 29.8, 29.7, 29.6, 29.5, 26.3, 25.9, 22.8, 14.3; IR (thin film on NaCl plate) 3103, 2928, 2859, 1617, 1518, 1468, 1389, 1340, 1264, 1171, 1054, 980, 894, 836, 757, 730, 666, 617, 602 cm^{-1}; Anal. calcd. for $C_{80}H_{136}O_7$: C, 79.41; H, 11.32, found: C, 78.93; H, 10.82; HRMS (FAB) calcd. for $C_{80}H_{136}O_7$ $(MH)^+$ 1209.9717, found 1209.9712.

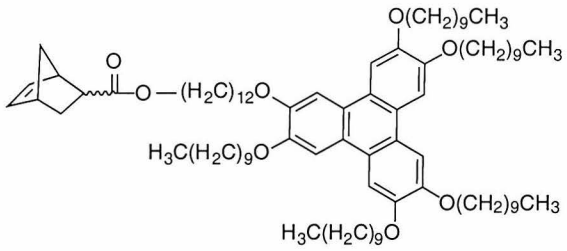
Synthesis of 11-(12'-hydroxydodecyloxy)-2,3,6,7,10-pentoxy-triphenylene (16):



16 was synthesized according to the procedure described above using **13** (0.7 g, 1.4 mmol) and **10** (0.7 g, 1.9 mmol) in dimethylformamide to give 0.38 g (32%) of a white crystalline solid.

^{1}H-NMR ($CDCl_3$) δ 7.82 (s, 6H), 4.22 (t, 12H, *J* = 6.6 Hz), 3.60 (t, 2H, *J* = 6.3 Hz), 1.94 (q, 12H, *J* = 6.9 Hz), 1.51 (m, 12H), 1.28 (m, 26H), 0.96 (t, 15H, *J* = 7.2 Hz); ^{13}C-NMR ($CDCl_3$) δ 148.8, 123.4, 107.2, 69.5, 62.8, 32.6, 32.3, 29.4, 29.3, 28.9, 28.1, 25.9, 25.5, 22.3, 13.8; IR (thin film on NaCl plate) 3104, 2925, 2857, 1617, 1518, 1468, 1453, 1389, 1341, 1263, 1172, 1054, 980, 894, 871, 836, 757, 730, 666, 616, 601 cm^{-1}; Anal. calcd. for $C_{55}H_{86}O_7$: C, 76.87; H, 10.09, found: C, 75.99; H, 9.82; HRMS (FAB) calcd. for $C_{55}H_{86}O_7$ $(MH)^+$ 858.6352, found 858.6366.

Synthesis of 5-{n-[-11-(12'-hydroxydodecyloxy)-2,3,6,7,10-decyloxy-triphenylene]-carbonyl}-bicyclo-[2.2.1]-hept-2-ene (17):

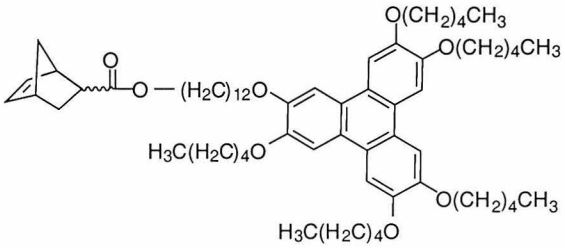


Norbornene-2-ene-5-carbonyl-chloride (50 mg, 0.3 mmol) in 10 mL dry tetrahydrofuran was added to a solution of **15** (190 mg, 0.16 mmol) and triethylamine (30 mg) in 50 mL dry tetrahydrofuran. The resulting solution was stirred under argon under reflux for 16

hours during which a white solid formed. The mixture was filtered, dried over magnesium sulfate and the solvent was removed *in vacuo*. Final purification was achieved by column chromatography (silica gel/dichloromethane) to yield 0.205 g of a white crystalline solid (96%).

^{1}H-NMR ($CDCl_3$) δ 7.82 (s, 6H), 6.17 (d of d, 1H, J = 3 Hz), 5.90 (dd, 1H, J = 3 Hz), 4.21 (t, 12H, J = 6.6 Hz), 3.99 (m, 2H), 3.18 (m, 1H), 2.95-2.88 (m, 2H), 1.92 (m, 14H), 1.55 (m, 12H), 1.27 (m, 78H), 0.87 (t, 15H, J = 5.1 Hz); ^{13}C-NMR ($CDCl_3$) δ 148.8, 137.5, 132.2, 125.3, 123.4, 107.2, 69.5, 64.0, 49.4, 45.5, 43.1, 42.3, 32.7, 30.1, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9, 28.5, 26.0, 25.7, 22.5, 13.9; IR (thin film on NaCl plate) 3044, 2922, 2852, 1842, 1738, 1617, 1517, 1468, 1435, 1388, 1262, 1174, 1072, 1048, 1033, 977, 835, 802, 722, 699, 602 cm^{-1}; Anal. calcd. for $C_{88}H_{144}O_8$: C, 75.52; H, 10.84, found: C, 75.41; H, 10.77. HRMS (FAB) calcd. for $C_{88}H_{144}O_8$ $(MH)^+$ 1330.1241, found 1330.1238.

Synthesis of 5-{n-[-11-(12'-hydroxydodecyloxy)-2,3,6,7,10-pentoxy-triphenylene]-carbonyl}-bicyclo-[2.2.1]-hept-2-ene (18):

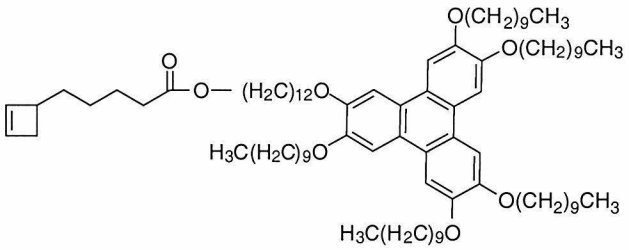


18 was synthesized according to the procedure described above using norbornene-2-ene-5-carbonyl-chloride (0.1 g, 0.64 mmol) and **16** (0.35 g, 0.41 mmol) to give 0.37 g (91%) of a white crystalline solid.

^{1}H-NMR ($CDCl_3$) δ 7.82 (s, 6H), 6.17 (d of d, 1H, J = 3.1 Hz), 5.91 (d of d, 1H, J = 3.1 Hz), 4.22 (t, 12H, J = 6.3 Hz), 3.99 (m, 2H), 3.19 (m, 1H), 2.95-2.88 (m, 2H), 1.94 (m, 14H), 1.55 (m, 12H), 1.29 (m, 28H), 0.97 (t, 15H, J = 7.2 Hz); ^{13}C-NMR

($CDCl_3$) δ 148.7, 137.5, 135.5, 132.1, 1223.4, 107.1, 69.4, 64.1, 49.4, 45.5, 43.1, 42.3, 31.4, 30.1, 29.5, 29.4, 29.3, 29.0, 28.9, 28.5, 28.2, 26.0, 25.7, 22.4, 13.9; IR (thin film on NaCl plate) 3048, 2934, 2857, 1842, 1733, 1619, 1510, 1468, 1430, 1389, 1262, 1174, 1071, 1033, 977, 938, 838, 774, 699, 605 cm^{-1}; Anal. calcd. for $C_{63}H_{94}O_8$: C, 77.26; H, 9.67, found: C, 76.81; H, 9.52; HRMS (FAB) calcd. for $C_{63}H_{94}O_8$ $(MH)^+$ 978.4468, found 978.6919.

Synthesis of [11-(12'-hydroxydodecyloxy)-2,3,6,7,10-decyloxy-triphenylene]-5-(2-cyclobutenyl)]pentanoate (19):

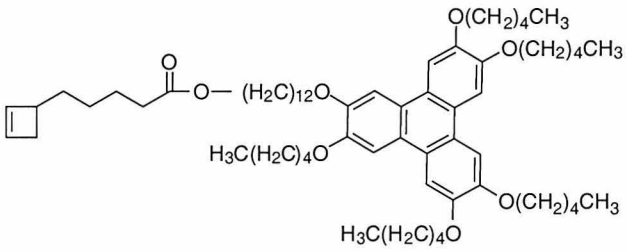


[5-(2-cyclobutenyl)]pentanoic acid[69] (0.26 g, 1.8 mmol) was combined with thionyl chloride (0.35 g) in a 25 mL round bottom flask. This mixture was heated to 45°C for 1.5 hours at which point gas evolution had ceased. The solution was then concentrated *in vacuo*. The resulting orange oil was added over a period of five minutes to a solution of **15** (0.35 g, 0.3 mmol) and 1 mL triethylamine in 50 mL tetrahydrofuran. The reaction was stirred under argon at room temperature for 16 hours during which a white solid precipitated. After filtration the solvent was removed *in vacuo*. Final purification was achieved by column chromatography (silica gel/dichloromethane) to yield 0.55 g of a white crystalline solid (99%).

^{1}H-NMR ($CDCl_3$) δ 7.82 (s, 6H), 6.04 (dd, 2H, J_1 = 3.2 Hz, J_2 = 10.2 Hz), 4.22 (t, 12H, J = 6.3 Hz), 4.04 (t, 2H, J = 6.6 Hz), 2.76 (m, 1H), 2.62 (dd, 1H, J_1 = 4.0 Hz, J_2 = 13.8 Hz), 2.29 (t, 2H, J = 7.5 Hz), 1.94 (m, 12H), 1.57-1.28 (m, 75H), 0.88 (t, 15H, J = 6.6 Hz); ^{13}C-NMR ($CDCl_3$) δ 148.9, 140.5, 134.9, 123.5, 107.5, 69.6, 64.1, 43.8,

36.6, 34.1, 34.0, 31.7, 31.3, 29.4, 29.3, 29.2, 29.1, 28.5, 27.3, 26.0, 25.7, 24.9, 22.4, 13.8; IR (thin film on NaCl plate) 3045, 2922, 2851, 1868, 1732, 1616, 1519, 1466, 1436, 1388, 1262, 1174, 1070, 1048, 977, 933, 836, 800, 774, 722, 699, 602 cm^{-1}; Anal. calcd. for $C_{89}H_{148}O_8$: C, 79.41; H, 10.99, found: C, 79.39; H, 10.61; HRMS (FAB) calcd. for $C_{89}H_{148}O_8$ $(MH)^+$ 1345.152, found 1345.117.

Synthesis of [11-(12'-hydroxydodecyloxy)-2,3,6,7,10-pentoxy-triphenylene]-5-(2-cyclobutenyl)]pentanoate (20):



20 was synthesized in analogy to **19** using [3-oxa-4-(2-cyclobutene)]butyric acid[42] (0.26 g, 1.8 mmol) and **16** (0.5 g, 0.05 mmol) to yield 0.54 g of **20** as a colorless liquid (93%).

^{1}H-NMR ($CDCl_3$) δ 7.82 (s, 6H), 6.05 (dd, 2H, J_1 = 3.2 Hz, J_2 = 10.4 Hz), 4.22 (t, 12H, J = 6.3 Hz), 4.04 (t, 2H, J = 6.6 Hz), 2.75 (m, 1H), 2.62 (dd, 1H, J_1 = 4.0 Hz, J_2 = 14.0 Hz), 2.28 (t, 2H, J = 7.5 Hz), 1.94 (m, 12H), 1.56-1.25 (m, 45H), 0.97 (t, 15H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$) δ 148.8, 140.6, 135.0, 123.4, 107.1, 69.5, 64.1, 43.7, 36.6, 34.1, 34.0, 31.4, 29.4, 29.3, 29.0, 28.9, 28.4, 28.2, 27.3, 26.0, 25.7, 25.0, 23.7, 22.3, 13.9; IR (thin film on NaCl plate) 3045, 2929, 2857, 1769, 1719, 1644, 1616, 1576, 1509, 1458, 1435, 1387, 1262, 1172, 1102, 1052, 837, 699 cm^{-1}; Anal. calcd. for $C_{64}H_{98}O_8$: C, 77.15; H, 9.92, found: C, 77.02; H, 9.63; HRMS (FAB) calcd. for $C_{64}H_{98}O_8$ $(MH)^+$ 994.7262, found 994.7281.

General polymerization procedure for norbornene monomers 17 and 18. Under an inert atmosphere, the catalyst and the monomer were weighed into vials and dissolved in dichloromethane (~1 mL dichloromethane for every 100 mg of monomer). The reaction was initiated by adding the catalyst solution to the vigorously stirred monomer solution. The reaction mixture was allowed to stir under argon for 6 hours. It was terminated by adding a small amount of ethyl-vinyl-ether and poured into ~50 mL methanol to precipitate the polymer. The resulting white polymer was purified by dissolving in dichloromethane, reprecipitation from methanol several times, and dried *in vacuo*. Isolated yields ranged from 90-99%.

Polymer (21): ^{1}H-NMR ($CDCl_3$) δ 7.78 (bs, 6H), 5.31 (bm, 2H), 4.20 (bs, 12H), 3.99 (bs, 2H), 2.89-2.44 (bm, 3H), 1.91 (bm, 14H), 1.56-1.25 (bm, 90H), 0.85 (bs, 15H); ^{13}C-NMR ($CDCl_3$) δ 149.1, 134.4-131.9 (Backbone C-*Olefine*), 123.6, 107.4, 69.8, 29.8-26.1 (Backbone C-*Alkyl*), 29.2, 28.3; IR (thin film on NaCl plate) 2929, 2856, 1730, 1617, 1509, 1468, 1437, 1389, 1263, 1174, 1052, 971, 836, 722, 605 cm^{-1}; Anal. calcd. for $C_{88}H_{144}O_8$: C, 75.52; H, 10.84, found: C, 76.02; H, 10.52.

Polymer (22): ^{1}H-NMR ($CDCl_3$) δ 7.78 (bs, 6H), 5.31 (bm, 2H), 4.19 (bs, 12H), 3.99 (bs, 2H), 2.87-2.46 (bm, 3H), 1.91 (bm, 14H), 1.57-1.26 (bm, 12H), 0.94 (bd, 28H, J = 5.1); ^{13}C-NMR ($CDCl_3$) δ 149.0, 134.5-132.1 (Backbone C-*Olefine*), 123.6, 107.3, 69.7, 29.8-26.0 (Backbone C-*Alkyl*), 29.2, 28.5; IR (thin film on NaCl plate) 2930, 2857, 1730, 1617, 1510, 1468, 1436, 1389, 1263, 1171, 1052, 971, 836, 730, 600 cm^{-1}; Anal. calcd. for $C_{63}H_{94}O_8$: C, 77.26; H, 9.67, found: C, 77.01; H, 9.61.

General polymerization procedure for cyclobutene monomers 19 and 20. Under an inert atmosphere, the catalyst and the monomer were weighed into vials and dissolved in dichloromethane such that the overall [M] was approximately 0.3M. The reaction

was initiated by adding the catalyst solution to the vigorously stirred monomer solution. The reaction mixture was allowed to stir under argon for 2 hours at room temperature. The reaction mixture was poured into methanol (~150 mL) containing 1N HCl (5% v/v) to precipitate the polymer, and left to stir for 30 minutes. The polymer was redissolved in dichloromethane and reprecipitated into methanol (~150 mL). The polymer was then isolated by filtration and dried *in vacuo*. Isolated yields ranged from 82 to 98% .

Polymer (23): ^{1}H-NMR ($CDCl_3$) δ 7.78 (s, 6H), 5.36-5.11 (bm, 2H), 4.23 (bs, 12H), 4.01 (bs, 2H), 3.44 (bs, 1H), 2.80-2.60 (bm, 2H), 2.25 (bm, 4H), 1.90 (bs, 14H), 1.57-1.29 (bm, 90H), 0.89 (bt, 15H, J = 6.7); ^{13}C-NMR ($CDCl_3$) δ 149.0, 134.0-126.0 (Backbone C-*Olefine*), 123.6, 107.3, 69.7, 64.5, 34.4-24.6 (Backbone C-*Alkyl*), 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 28.8, 26.3, 22.8, 14.2; IR (thin film on NaCl plate) 2922, 2852, 1739, 1617, 1518, 1468, 1436, 1388, 1262, 1174, 1071, 1033, 836, 802, 722, 602 cm^{-1}; Anal. calcd. for $C_{89}H_{148}O_8$: C, 79.41; H, 9.99, found: C, 79.33; H, 10.82.

Polymer (24): ^{1}H-NMR ($CDCl_3$) δ 7.80 (bs, 6H), 5.30-5.10 (bm, 2H), 4.20 (bs, 12H), 4.01 (bs, 2H), 3.46 (bs, 1H), 2.90-2.60 (bm, 2H), 2.25 (bm, 4H), 1.92 (bs, 14H), 1.56-1.27 (bm, 50H), 0.95 (bt, 15H, J = 6.9); ^{13}C-NMR ($CDCl_3$) δ 148.9, 134.7-127.8 (Backbone C-*Olefine*), 123.6, 107.6, 69.6, 64.1, 42.5-24.8 (Backbone C-*Alkyl*), 34.1, 29.4, 29.1, 29.0, 28.5, 26.0, 25.7, 22.3, 13.7; IR (thin film on NaCl plate) 2926, 2854, 1739, 1618, 1518, 1468, 1436, 1388, 1262, 1174, 1072, 1033, 836, 803, 722, 601 cm^{-1}; Anal. calcd. for $C_{64}H_{98}O_8$: C, 77.15; H, 9.92, found: C, 77.26; H, 10.04.

General procedure for the hydrogenation of polymers 23 and 24. Polymers **23** or **24** were dissolved in dichloromethane followed by the addition of a

catalytic amount of Crabtree's catalyst [Ir(COD)(Cy_3)(py)]PF_6. The flask was placed in a hydrogenation bomb and heated at 55°C for 16 hours under 120 psi of hydrogen pressure. The polymers were isolated by repeated precipitation from methanol.

Polymer (25): ^{1}H-NMR ($CDCl_3$) δ 7.80 (bs, 6H), 4.20 (bs, 12H), 4.03 (bs, 2H), 2.27 (bm, 4H), 1.92 (bs, 14H), 1.57-1.28 (bm, 95H), 0.89 (bt, 15H); ^{13}C-NMR ($CDCl_3$) δ 149.0, 123.6, 107.3, 69.7, 64.5, 34.5-26.1 (Backbone C-*Alkyl*), 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 26.3, 14.2; IR (thin film on NaCl plate) 2923, 2852, 1738, 1617, 1518, 1467, 1438, 1388, 1263, 1174, 1071, 1048, 836, 801, 722, 602 cm^{-1}; Anal. calcd. for $C_{89}H_{150}O_8$: C, 79.53; H, 11.14, found: C, 79.12; H, 11.30.

Polymer (26): ^{1}H-NMR ($CDCl_3$) δ 7.79 (bs, 6H), 4.20 (bs, 12H), 4.02 (bs, 2H), 2.25 (bm, 4H), 1.92 (bs, 14H), 1.54-1.18 (bm, 55H), 0.95 (bt, 15H, J = 6.9); ^{13}C-NMR ($CDCl_3$) δ 148.9, 123.6, 107.2, 69.7, 64.5, 51.0, 38.2-25.5 (Backbone C-*Alkyl*), 34.5, 29.8, 29.7, 29.6, 29.5, 29.2, 28.8, 28.5, 26.3, 26.0, 22.7, 14.2; IR (thin film on NaCl plate) 2923, 2852, 1738, 1617, 1518, 1467, 1436, 1387, 1262, 1173, 1071, 1033, 836, 802, 722, 602 cm^{-1}; Anal. calcd. for $C_{64}H_{100}O_8$: C, 77.11; H, 10.04, found: C, 76.87; H, 10.03.

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Chapter 4

Synthesis of Intertwined Structures Using Ring-Closing Metathesis

Abstract

This chapter presents three different synthetic strategies to obtain intertwined and interlocked architectures through ring-closing metathesis (RCM). The first approach is based on phenanthroline-based ligands containing terminal olefinic units which were designed to self-assemble around a copper atom. Treatment with ruthenium catalyst **1** resulted in [2]catenates in high yields of 88% to 92%. Demetallation produced the corresponding catenanes in nearly quantitative yields. Hydrogenation of the catenates was carried out to yield fully-saturated catenanes after demetallation. The second method introduces the self-assembly of a variety of crown ethers with dialkylammonium ions to yield rotaxane precursors. Alkylidine **1** proved to be incompatible with these complexes. However, using a Schiff-base-ligand-based ruthenium catalyst, it was possible to cyclize these complexes in 55% yield. The last part of this chapter describes the quantitative complexation of π-electron-deficient paraquat analogues with π-electron-rich crown ethers in acetonitrile. Macrocyclization of these complexes by RCM using ruthenium or molybdenum-based catalysts proved impossible. While the ruthenium catalyst is incompatible with acetonitrile, the molybdenum catalyst formed a stable acetonitrile-coordinated species thus preventing any cyclization.

Introduction

Physically linked molecules, rotaxanes, pseudorotaxanes, and catenanes[1] constitutes a major research field in supramolecular chemistry.[2] Catenanes, from the Latin *catena* meaning chain, are molecules which contain two or more interlocked ring systems. These rings are inseparable without breaking a covalent bond (Figure 1, A). Rotaxanes and pseudorotaxanes on the other hand, from the Latin *rota* meaning wheel, and *axis* meaning axle, are comprised of a dumbbell-shaped component, in most cases in the form of a rod and two bulky stoppers (Figure 1, C) around which are encircling macrocyclic components. These stoppers prevent the macrocycles from unthreading while if they are missing or too small, unthreading can occur. These resulting compounds are then called pseudorotaxanes (Figure 1, B).[3]

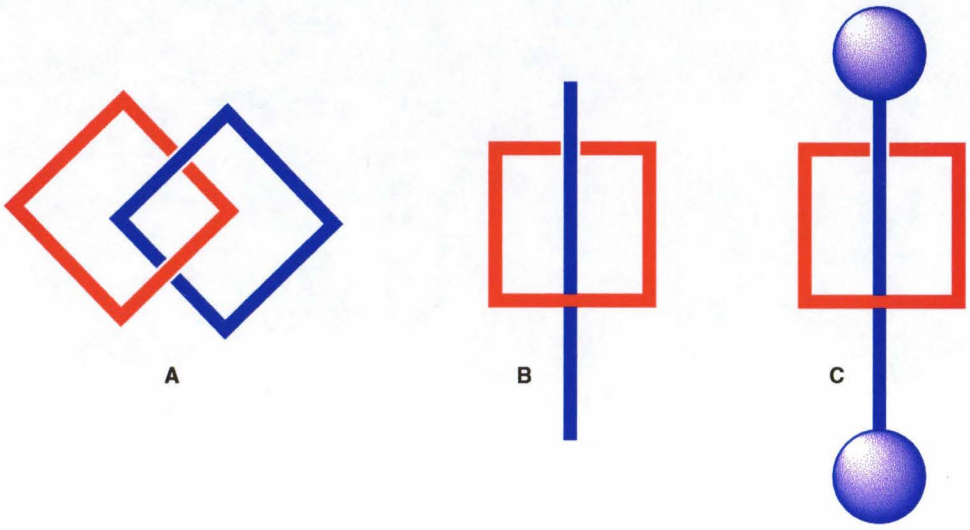


Figure 1. Schematic presentation of A) a catenand; B) a pseudorotaxane; C) a rotaxane.

Catenanes and rotaxanes started to attract considerable attention in the late 1960s because they presented a unique synthetic challenge. Also, they appeared to be promising chemical objects with novel physical properties and precursors to new materials. After the pioneering work of Schill[4] and Wasserman,[5] only a few research groups continued working on these kinds of systems. However, over the last 10 years the field has experienced a renaissance in response to the introduction of template strategies, thus

making the preparation of threaded and interlocked systems more accessible. Specifically, a significant number of catenane systems have been reported. Sauvage and coworkers used a copper-metal template based strategy to obtain catenanes,[6] knots, and rotaxanes.[7] In the last six years, Stoddart and his group have worked on the synthesis of interlocked systems based on secondary dialkylammonium salts and crown ethers[8] and on systems based on π-electron rich/π-electron deficient aromatic systems.[9] Figure 2 presents a schematic presentation of some common catenane systems.

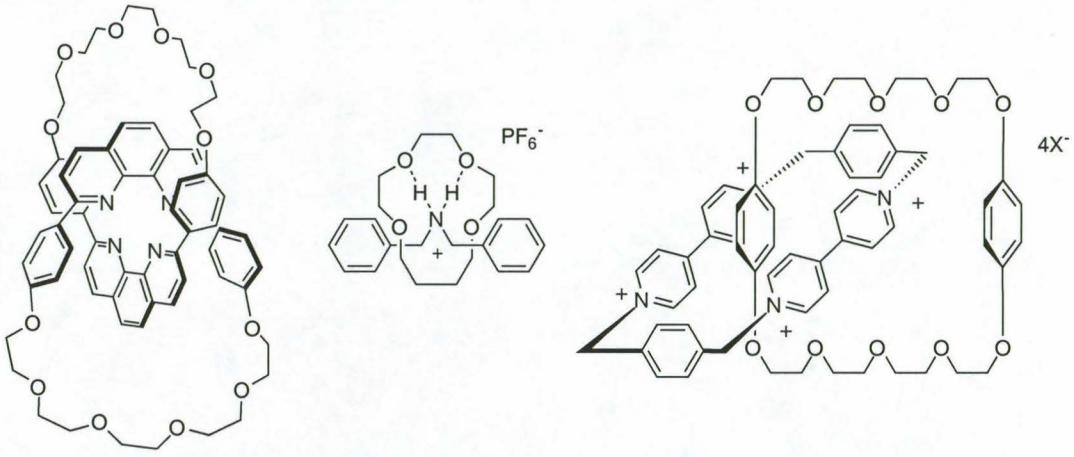


Figure 2. Schematic presentation of some catenane systems reported in the literature.

Catenane systems based on amines, as reported by Hunter and coworkers,[10] Vögtle and coworkers,[10] and Leigh and coworkers,[11] cyclodextrines as introduced by Wenz and coworkers,[12] and rotaxanes based on crown ethers frameworks presented by Gibson and coworkers,[13] have also been reported.[1,14-27]

In modern approaches, a large number of functional groups has been introduced into the catenanes and rotaxanes thus enabling these compounds to fulfill increasingly complex chemical and physical functions. Additionally, they display interesting physical properties, such as photo-induced intramolecular electron transfer, electrochemically triggered molecular motions, and photochemical dethreading processes. A number of these multicomponent systems have been named 'molecular machines'.[9]

For all the more recent supramolecular systems, the use of a template, or auxiliary linkage, is essential for an efficient synthesis. Figure 3 shows the principle behind this general approach. The components of the rings that are to be incorporated into the architecture are brought together in a specific orientation so that the most favorable outcome is interlocked rings.

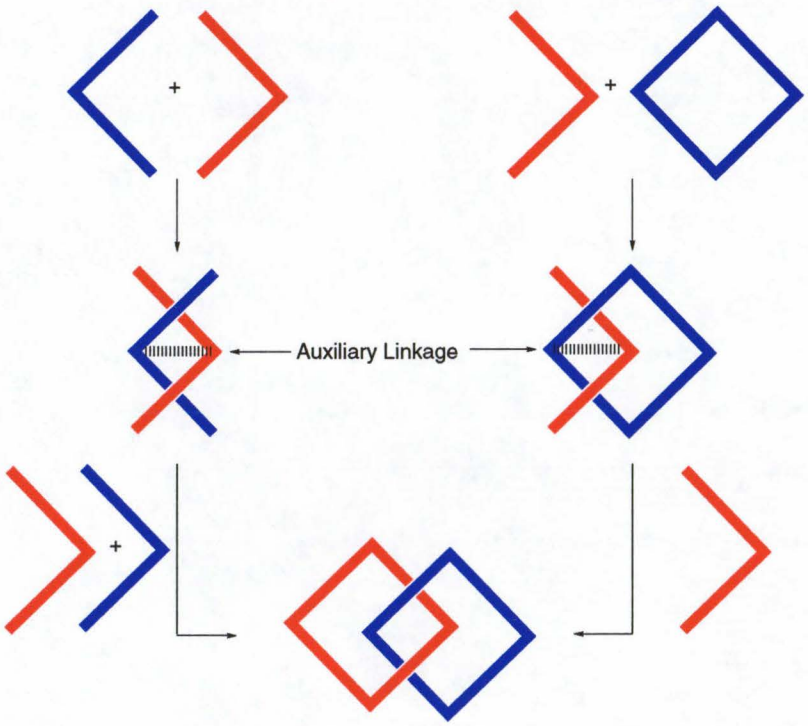
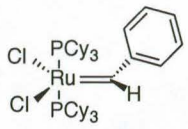


Figure 3. Approach to the synthesis of [2]catenanes employing auxiliary linkages.

Therefore, the synthesis relies on a quantitative self-assembly step followed by ring closure. In most cases, the cyclization reaction is restricted to the formation of ethers and amide bonds or quarternary ammonium salts by an intramolecular pathway.[1] However, this cyclization reaction also constitutes the biggest problem in the synthesis of catenanes and rotaxanes because the yield of the product is often times quite low.

Ring-closing metathesis (RCM) has been established as an efficient approach to macrocyclic systems *via* intramolecular formation of carbon-carbon double bonds.[5,28,29] Ruthenium benzylidene catalyst **1** has been shown to be highly effective in these reactions due to its high activity and tolerance to a wide array of functional groups.[30]

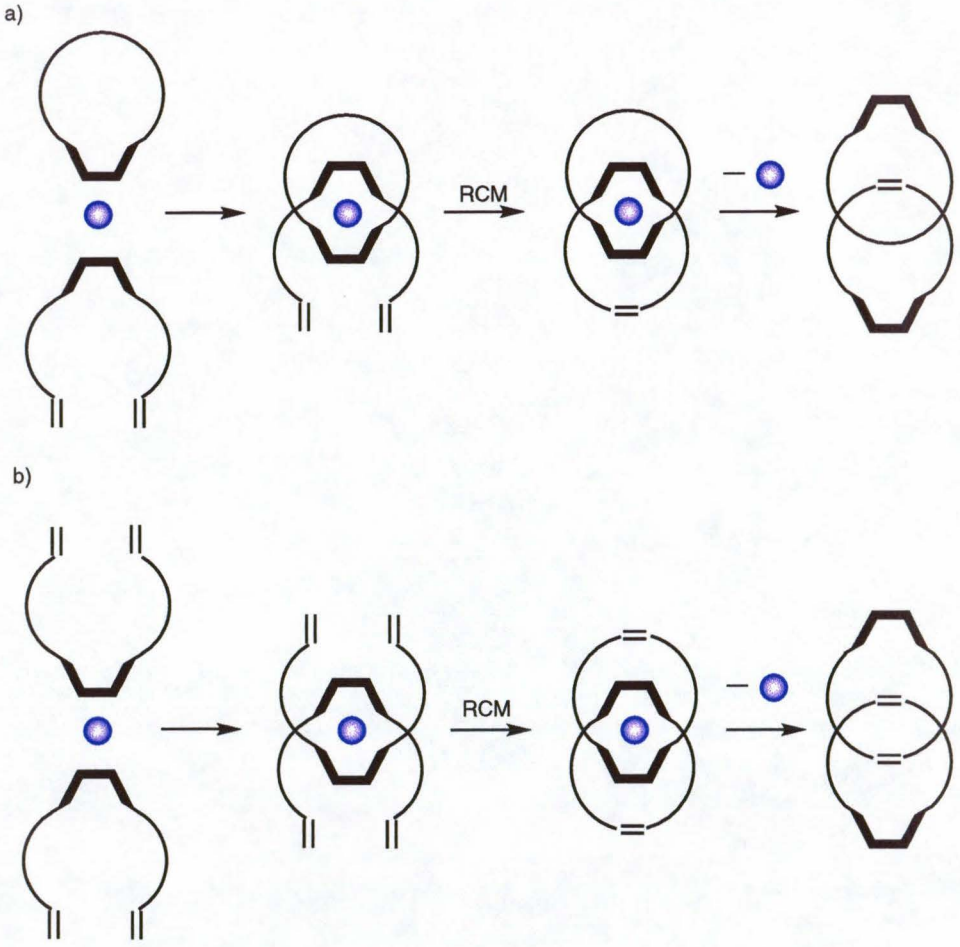


1

While RCM was initially applied to the synthesis of small -five to eight-membered rings-[29,31] this methodology has been recently extended to larger ring systems incorporating up to 38 atoms.[32] The approach presented herein utilizes a combination of s supramolecular template strategy and RCM to provide ready access to [2]catenanes and rotaxanes in high yields.

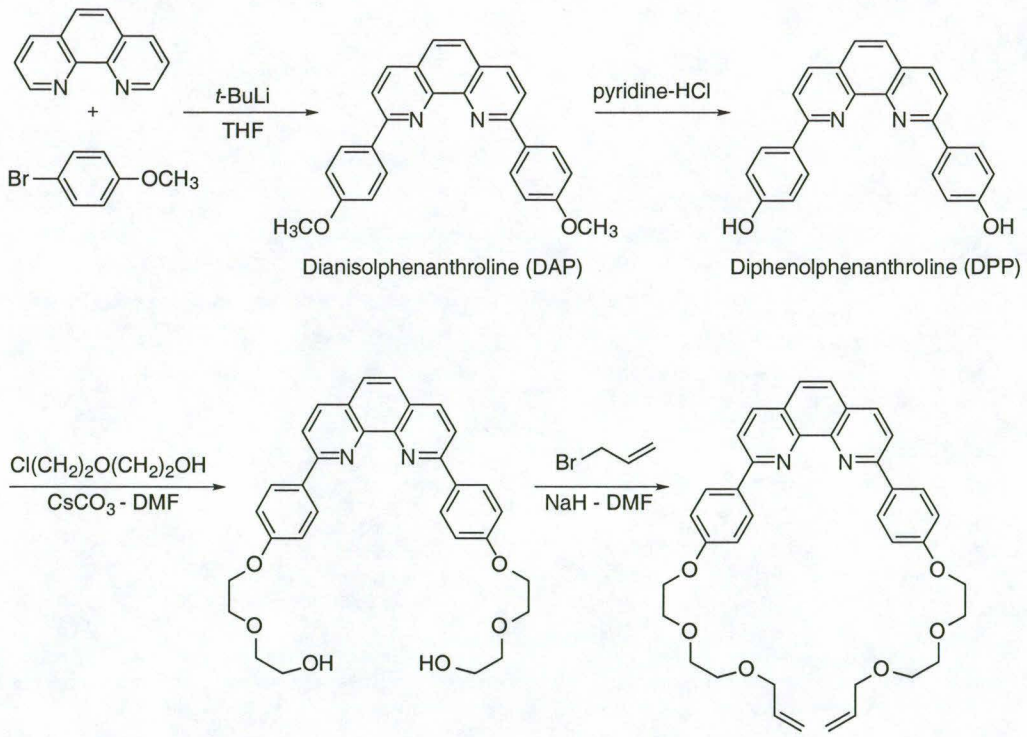
Results

Catenane strategies based on transition metals. Sauvage and coworkers pioneered the synthesis of interlocked molecules in which a transition metal ion was used as a template. This approach relied upon the tetrahedral coordination chemistry of metal ions, in most cases copper(I) or silver, and two 2,9-disubstituted 1,10-phenanthroline units. In their general strategy, a complex formed between 2,9-dianisyl-1,10-phenanthroline and copper(I) initiates the construction of the catenane. Reaction of this complex with a diiodide derived from pentaethylene glycol in the presence of cesium carbonate as base resulted in the [2]catenate in 27% yield with a variety of side products which were mostly not separable.[6g] In the first part of this chapter a new strategy for the synthesis of catenanes utilizing a combination of transition metal (copper) based preorganization and RCM will be described. Figure 1 presents a schematic presentation of the general approach.



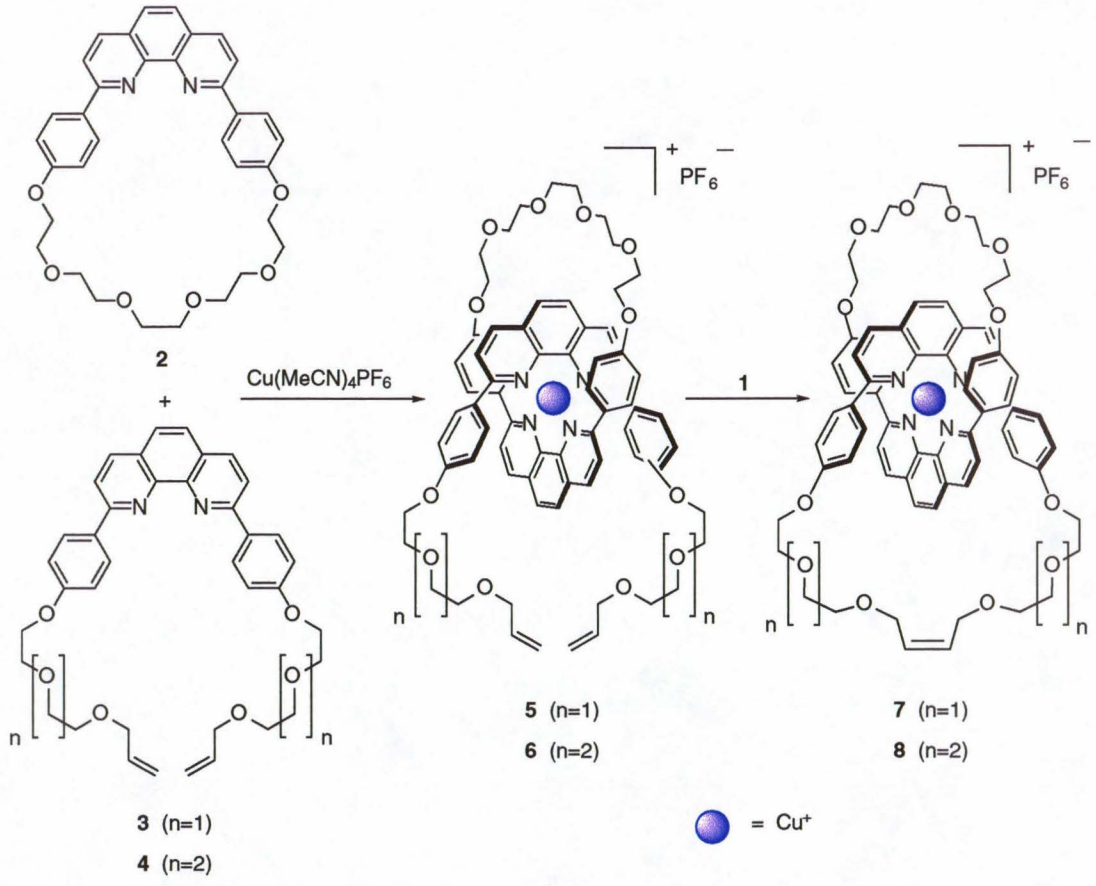
Scheme 1. Schematic drawing of the approach utilizing a combination of a transition metal based template strategy and RCM to provide access to [2]catenanes: a) formation of a threaded complex followed by RCM and decomplexation; b) formation of an intertwined complex followed by twofold RCM and decomplexation. The blue circle represents the transition ion.

The building blocks for this system are the 30-membered macrocycle **2**, bearing a 2,9-diphenyl-1,10-phenanthroline (DPP) bidentate in its backbone, and the acyclic ligands **3** and **4**, in which the dpp moiety was symmetrically substituted with ethylene oxide groups terminated with olefins in analogy to literature procedures (Scheme 2).[6g] The ligands were synthesized by coupling 4-lithio-anisole with 1,10-phenanthroline, followed by hydrolysis and oxidation to yield DAP in high yield. Deprotection yielded DPP which was reacted with chloro-ethyleneglycol and subsequently alkylated using allylbromide to yield the ligands in high yields.



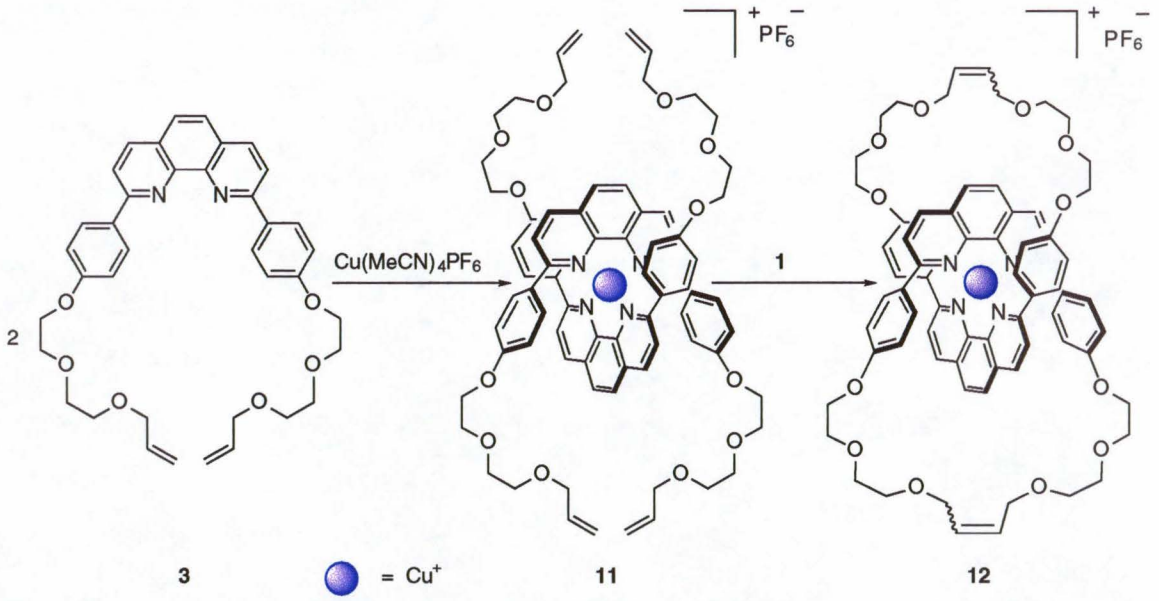
Scheme 2. General scheme for the synthesis of the catenanes building blocks. As an example the synthesis of **3** is shown here.

All building blocks were synthesized in the group of Prof. Sauvage by Dr. Bernhard Mohr. To ensure the compatibility of these building blocks with the ruthenium catalyst **1**, several NMR experiments were carried out in which the different building blocks, both with and without copper, were added to a dichloromethane solution of **1** at room temperature under argon. No decomposition of the catalyst over a period of several hours was detected, which indicated the compatibility of these compounds with **1**.



Scheme 3. Synthesis of [2]catenates **7** and **8** using RCM.

Threaded complexes **5** and **6** assembled instantly and quantitatively by the reaction of **2** with a stoichiometric amount of $[Cu(MeCN)_4]PF_6$ in dichloromethane/methanol followed by the addition of diolefins **3** and **4** (Scheme 3).[6] In a similar manner, the intertwined complex **11** was obtained in quantitative yields by complexation of two equivalents of **3** with $[Cu(MeCN)_4]PF_6$ in dichloromethane/methanol (Scheme 4). The full complexation of these compounds could be easily followed by NMR since specific aromatic proton resonances in the NMR were charateristically shifted.[6]



Scheme 4. Synthesis of [2]catenate **12** using RCM.

After complexation, complexes **5**, **6**, and **11** were subjected to intramolecular RCM with catalyst **1** to yield the corresponding catenates **7**, **8**, and **12** through the formation of 32- (**7**, **12**) and 38-membered (**8**) rings. All reactions were carried out at room temperature under argon for several hours. A total of 10 mol% catalyst was used, which was added to the reaction in 5 mol% portions: once at the beginning of the reaction and again after 6 hours. Because ethylene is also a product of the RCM, it was removed from the reaction by opening the reaction vessel for a short period of time every 2 hours to a weak vacuum, acting to drive the RCM reactions closer to completion.

Twofold RCM of **11** led exclusively to systems with two interlocked rings. The twisted product, formed by the intramolecular reaction between the olefins of different ligands, was not detected. The formation of catenates **7**, **8**, and **12** could be unequivocally shown by ^{1}H NMR spectroscopy and fast atom bombardment (FAB-MS) mass spectroscopy. Figure 4 presents the FAB-MS spectra of catenates **7** and **12**.

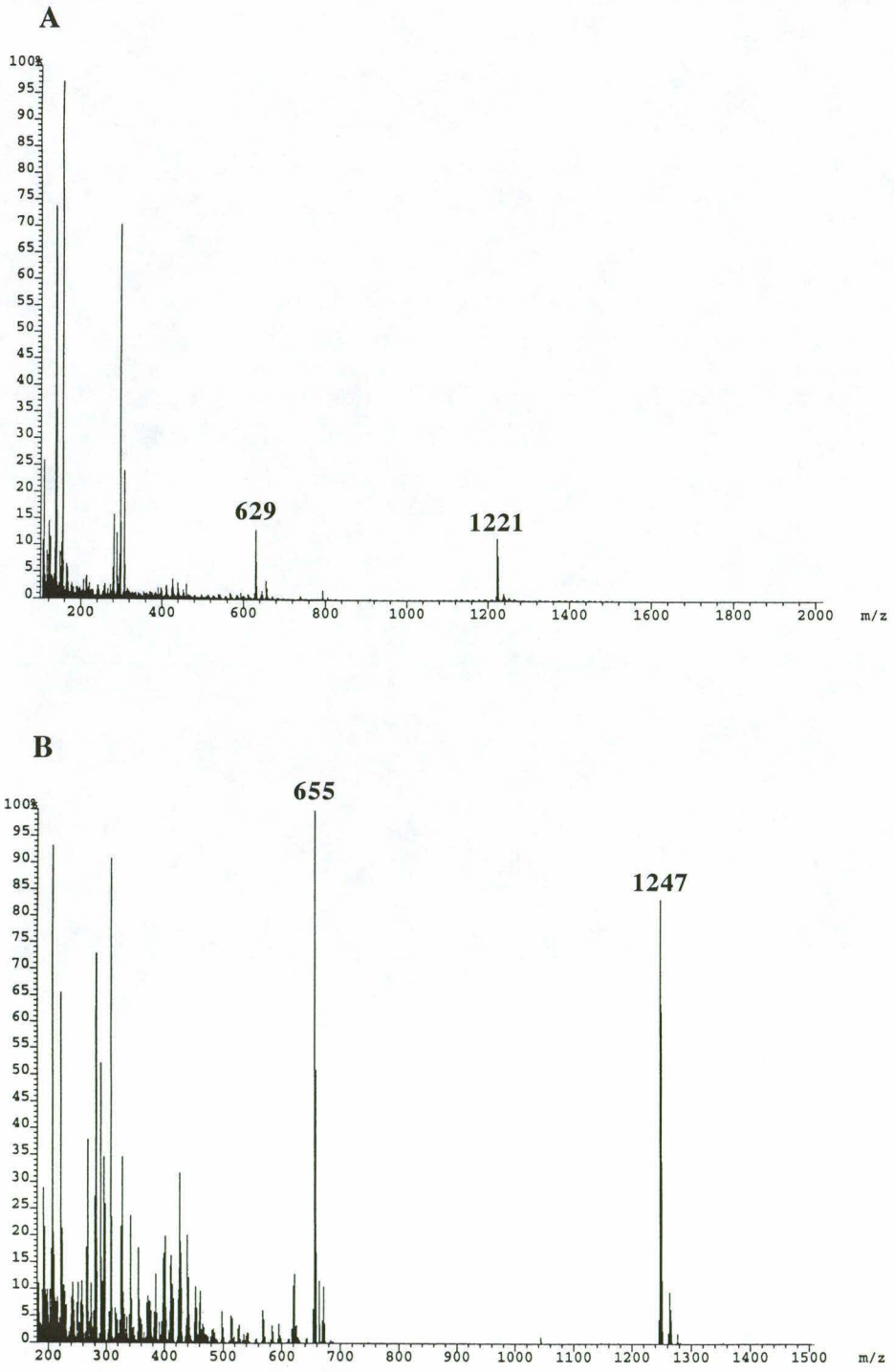


Figure 4. Positive FAB-MS spectra of a) catenate **7** and b) catenate **12** in a *p*-nitrobenzyl alcohol matrix. The peaks at *m/z* = 1221 and 1247 correspond to catenates **7** and **12**, respectively. The absence of peaks between the molecular ion peak and the peaks corresponding to the individual macrocycles is characteristic of catenate species.[6n]

Yields of these cyclization reactions ranged from 88 to 92% and are summarized in Table 1. The cyclization yields for these systems exceeded those for most other medium or large ring systems, where hydrogen bonding,[28,32] conformational constraints[32] or template effects[33] are present to facilitate the reaction. It is believed that the remarkable efficiencies of these RCM reactions stemmed, at least in part, from a preorganization of the olefins due to electrostatic interactions and hydrogen bonding between the oxygen atoms and the phenanthroline systems,[34] in combination with a locked conformation of the phenyl rings (π-donors) and phenanthroline systems (π-acceptor).[35] This assumption is supported by the exclusive formation of the interlocked species in the RCM of **11**, and the observation that RCM of the free ligands **3** and **4** proceeds in lower yields between 70-75%.

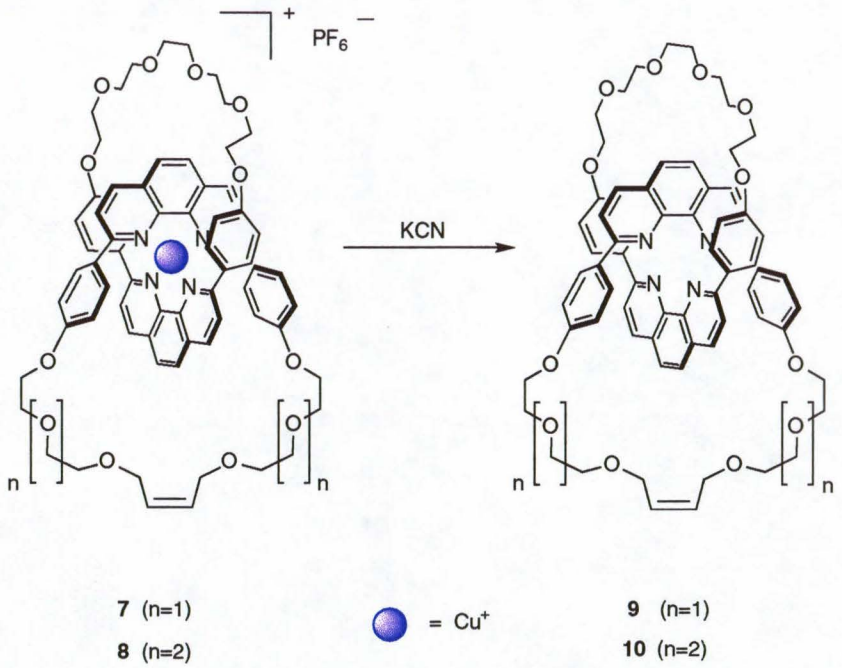
Table 1. Results of the ring-closing metathesis and demetallation reactions.

Catenate	Yield (%) [a]	*trans/cis* [b]	Catenand	Yield (%) [a]
7	92	97/3	**9**	92
8	88	95/5	**10**	93
12	92	98/2	**13**	90

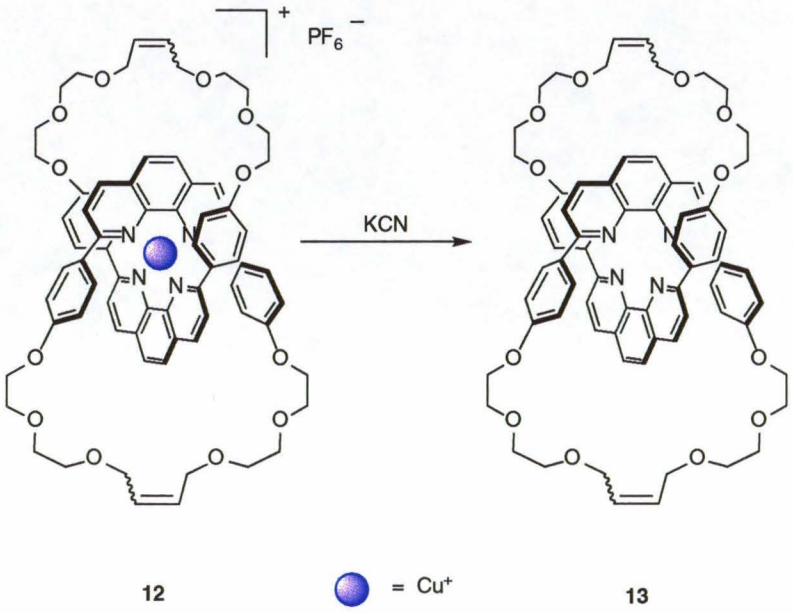
[a] Yield of isolated product. [b] Determined by integration of the ^{1}H-NMR signals of the isomeric olefin protons.

For all catenates, the energetically favored *trans* configuration at the double bond prevailed, which is commonly reported for macrocycles made *via* RCM.[28,32,33] The olefin E/Z ratio could be determined by the integration of the ^{1}H-NMR signals of the isomeric olefin protons.

Demetallation of catenates **7**, **8**, and **12** with potassium cyanide in aqueous acetonitrile in analogy to literature procedures[6,7] afforded [2]catenanes **9**, **10**, and **13** in high yields. Schemes 5 and 6 show the demetallation of catenates **9**, **10**, and **13**.



Scheme 5. Demetallation of [2]catenates **7** and **8** to yield [2]catenanes **9** and **10**.



Scheme 6. Demetallation of [2]catenate **12** to yield [2]catenand **13**.

In analogy to the catenates, the composition of catenanes **9**, **10**, and **13** was confirmed by ^{1}H-NMR and FAB-MS. Figure 5 shows the FAB-MS spectra of catenanes **9** and **13**. Both spectra display the characteristic patterns for catenated species, the absence specifically of peaks between the molecular ion peaks and the peaks corresponding to the

individual macrocycles.[6n] If an intramolecular RCM reaction between the olefins of different ligands had occurred, peaks in the region between the molecular ion peak and the peaks corresponding to the individual macrocycles would be expected. Therefore, these FAB-MS provide further proof for the exclusive formation of catenates **7**, **8**, and **12** in the RCM steps.

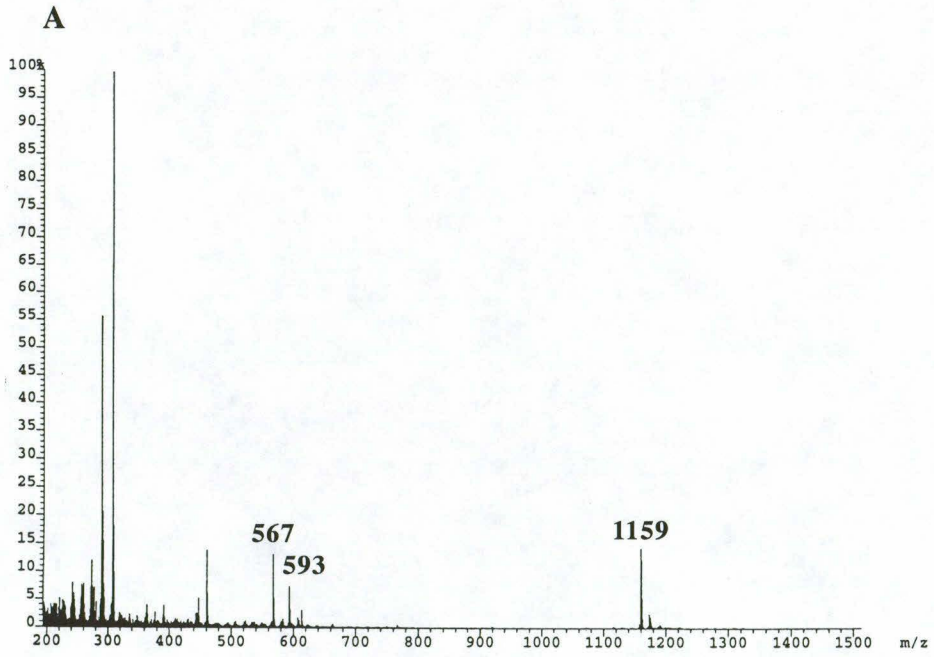


Figure 5a. Positive FAB-MS spectra of catenand **9** in a *p*-nitrobenzyl alcohol matrix. The peak at m/z = 1159 corresponds to catenand **9**. The absence of peaks between the molecular ion peak and the peaks corresponding to the individual macrocycles is characteristic for catenate species.[6z]

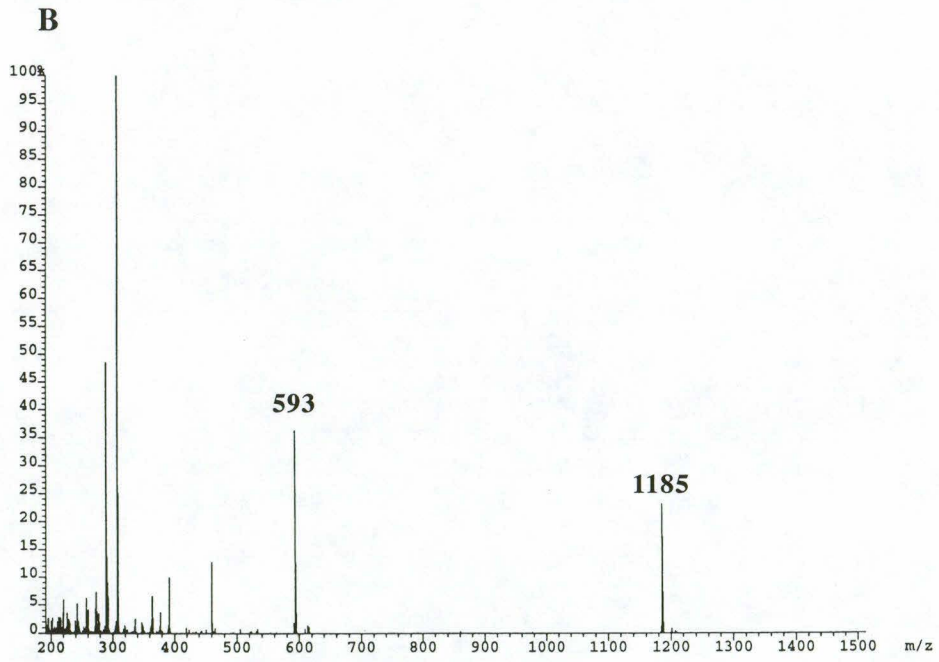
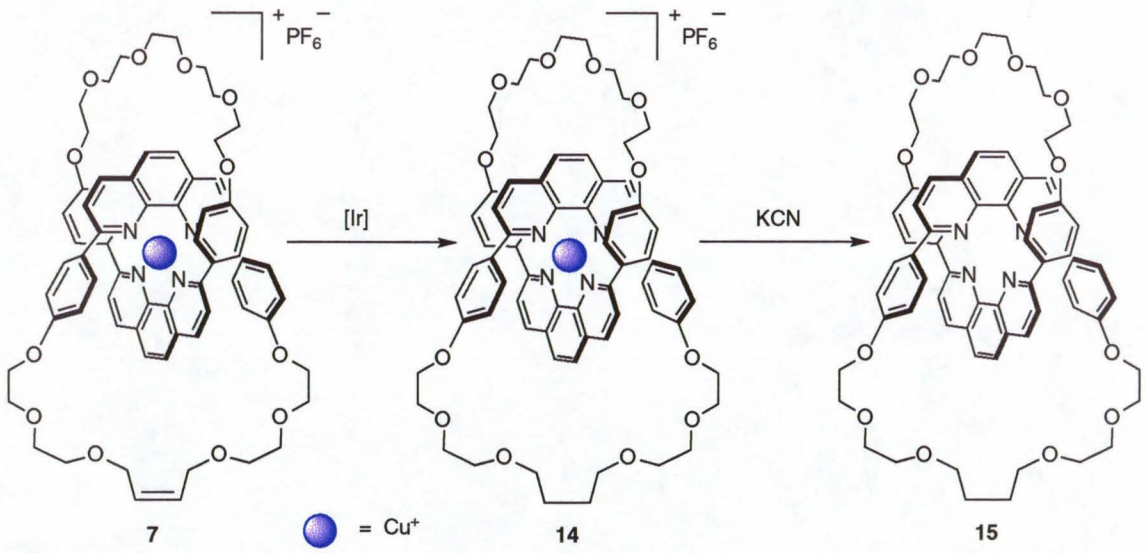


Figure 5b. Positive FAB-MS spectra of catenand **13** in a *p*-nitrobenzyl alcohol matrix. The peak at *m/z* = 1185 corresponds to catenand **13**. The absence of peaks between the molecular ion peak and the peaks corresponding to the individual macrocycles is characteristic for catenate species.[6z]

Upon standing at room temperature under argon for 4-5 months, catenanes **9**, **10**, and **13** changed in color from white to yellow, indicating decomposition. This decomposition seems to occur at least partially at the double bonds which were formed during the RCM. Therefore, a selective hydrogenation of these double bonds has been carried out using Crabtree's iridium-based catalyst as outlined in Scheme 7. In a general procedure, the catenate was dissolved in dichloromethane, a catalytic amount of the iridium catalyst was added, and the reaction was stirred overnight under 200 psi hydrogen pressure. The hydrogenated catenate **14** was obtained in quantitative yield. As described above, demetallation was carried out using potassium cyanide to yield the free catenand in 96% yield (Scheme 7).



Scheme 7. Hydrogenation of [2]catenate **5** using Crabtree's iridium-based catalyst to yield the double-bond-free [2]catenate **14** followed by demetallation to yield [2]catenand **15**.

Catenand **15** was characterized by ^{1}H-NMR and FAB-MS. Figure 6 shows the positive FAB-MS of **15**.

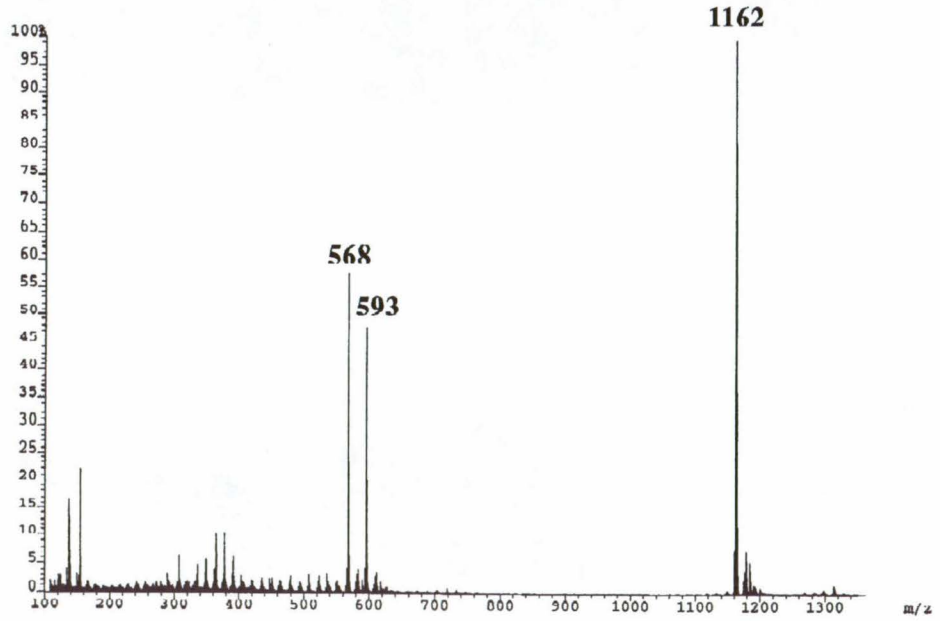
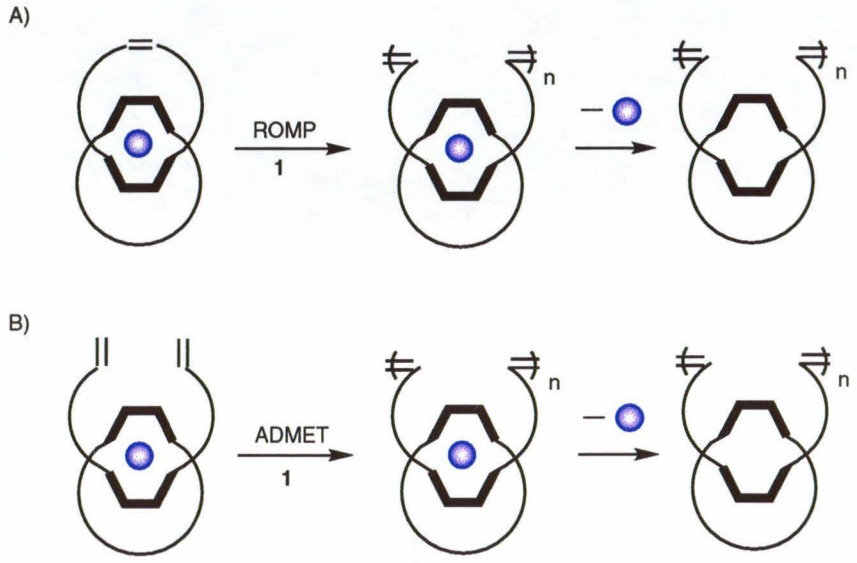


Figure 6. Positive FAB-MS spectra of catenand **15** in a *p*-nitrobenzyl alcohol matrix. The peak at *m/z* = 1221 corresponds to catenand **15**. The absence of peaks between the

molecular ion peak and the peaks corresponding to the individual macrocycles is characteristic for catenate species.[6z]

To further investigate the possibility of these materials to form polymeric materials such as (poly(rotaxane)s and poly(pseudorotaxane)s), several potential strategies can be envisioned. Recently, one strategy to polymerize large ring-systems was introduced by Grubbs and coworkers who reported the metal-template assisted RCM of crown ethers using catalyst **1**.[33] In a second step, they were able to demonstrate the ROMP of these cyclic materials through treatment of their concentrated solutions with catalyst **1**. Dilution of the polymeric material and subsequent treatment with another catalyst solution resulted in depolymerization *via* RCM. Another possible route to polymerize diolefinic compounds using olefin metathesis is acyclic diene metathesis (ADMET) as described in Chapter 1.[36] Both polymerization methods could potentially be used for catenates **7** and **8** or the unclosed complexes **5** and **6** (Scheme 8).



Scheme 8. Schematic drawing of the approach utilizing a combination of a transition metal based template strategy and ROMP or ADMET to provide access to polyrotaxanes: A) ROMP of the closed catenate and decomplexation to yield the polyrotaxane; B) ADMET of the open catenate precursor and decomplexation to yield the polyrotaxane. The blue circle represents the transition ion.

Pathway A shows the possible ring-opening metathesis polymerization of the closed catenantes. To investigate this approach several catenates were dissolved in a minimum of dichloromethane, a small amount of **1** (5 mol%) in dichloromethane was added, and the reaction was stirred under argon for several hours at room temperature. However, no polymerization was observed. Even heating the reaction mixture up to 60°C did not yield any polymer.

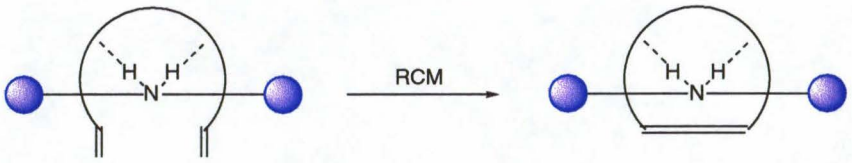
In Figure 8, pathway B displays the ADMET strategy to obtain poly(rotaxane)s and poly(pseudorotaxane)s. Threaded complexes **5** and **6** were subjected to standard ADMET conditions. The complexes were dissolved in a minimum of dichloromethane and a catalytic amount of **1** was added. However, no polymerization was observed. Varying the solvent and temperature did not facilitate ADMET polymerization of complexes **5** and **6**.

Several explanations for the failure of these polymerization reactions are imaginable. First, all interlocked catenanes are charged species. Therefore, some solubility problems of the monomers as well as for potential polymers can be expected since a critical concentration of monomer is required for ADMET or ROMP. Second, ROMP is driven exclusively by the release of ring-strain. It is possible that the ring-strain of these large rings is too small to polymerize the catenanes *via* ROMP. Similarly, the solubility problems of the monomers are likely to be the limiting factor in the ADMET polymerization.

Catenane and rotaxane strategies based on dialkylammonium salts. Since Pedersen's discovery in 1967 that crown ethers form complexes with a variety of cations,[37] numerous investigations of the binding of primary alkylammonium ions (RNH_3^+) and ammonia ions (NH_4^+) to macrocyclic polyethers have been reported.[38] The mode of binding of these ions to the crown ethers is face-to-face in character, and usually 1:1 in its stoichiometry, although occasionally a 1:2 complexation occurs. However, until five years ago, reports of the complexation of dialkylammonium ions ($R_2NH_2^+$) by crown

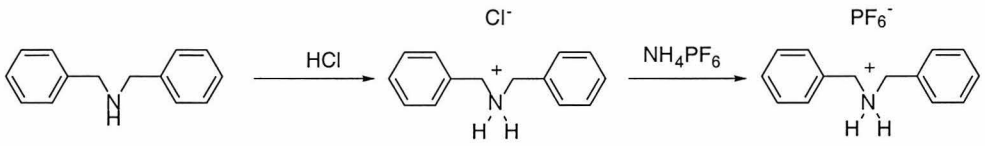
ethers were relatively sparse.[39] More recently, it has been shown that suitably chosen $R_2NH_2^+$ ions can thread through the cavities of appropriately constituted crown ethers to give inclusion complexes with pseudorotaxane-like geometries, as outlined in the introduction.[8,22] Stoddart and coworkers have recently reported a large variety of different inclusion complexes based on $R_2NH_2^+$ ions and crown ethers, including pseudorotaxanes, poly(pseudorotaxane)s and cages.[8] However, because the dialkylammonium ion has to thread through the crown ether before the self-assembly step, it is not possible to synthesize rotaxane-like structures using Stoddart's strategy.

An approach combining a hydrogen-bonding template strategy and RCM could be able to overcome this obstacle (see Scheme 9). RCM could be applied to the ring-closure of a crown-ether precursor self-assembled around a dialkylammonium ion containing a stopper to yield a rotaxane. It could also be possible to synthesize a catenane-like structure by utilizing a cyclic dialkylammonium ion species.



Scheme 9. Schematic drawing of the approach utilizing a combined strategy of a hydrogen bonding template and RCM to provide access to rotaxanes. The blue circle represents a bulky end-group to prevent the dethreading of the ring-system.

To test this approach a variety of dialkylammonium ions and crown ether precursors containing terminal olefins for ring-closure were synthesized. The advantage of dibenzylammonium salts is that they are readily synthesized and the nature of the complexation to crown ethers can be compared to the literature.[8a] Scheme 10 shows the synthesis of dibenzylammonium hexafluorophosphate **17**.

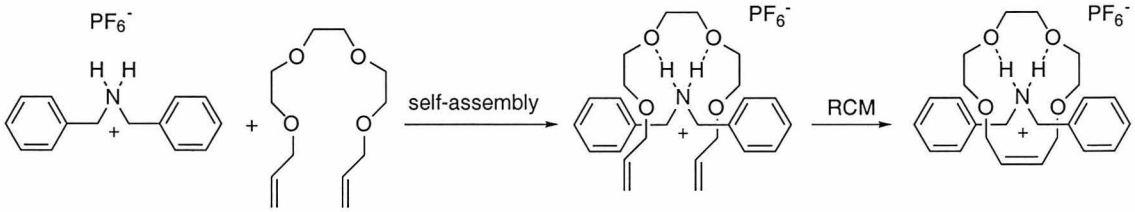


Scheme 10. Synthesis of the secondary dialkylammonium ion **17**.

Compound **17** can be easily synthesized by treating dibenzylamine with hydrochloric acid followed by the addition of a saturated aqueous solution of ammonium hexafluorophosphate. Dibenzylammonium tetrabenzylborane can be synthesized analogously. To verify the compatibility of the alkylammonium salts with **1**, ^{1}H NMR experiments were performed by adding **1** to a solution of the dialkylammonium salts in methanol or dichloromethane. In all cases, a solid precipitated immediately after addition of the catalyst, the solution turned brown, and after 10 minutes turned green. However, a carbene signal could still be observed by NMR. Addition of diethyl-allylmalonate to the solution yielded 95% closed product after 24 hours. Therefore it can be concluded that, while a reaction of the salts with **1** is likely, the product is still catalytically active for RCM.

In an initial experiment a 1:1 mixture of a crown-4-ether precursor and **17** were dissolved in acetonitrile and stirred for 2 days. However, full complexation was not observed by NMR (complexation ranged from 50 - 90%). Based on this result, several different solvents were examined to obtain full complexation. While neither methanol nor acetonitrile nor benzene allowed full complexation, a 1:1 mixture of the crown-ether precursor and **17** in dichloromethane resulted in full complexation after 24 hours (Scheme 11). Although **17** is virtually insoluble in dichloromethane, solubility was achieved by addition of one equivalent of the crown-ether precursor. This observation was the first evidence of a strong 1:1 complexation of some type. As described in literature,[8] the nature of the self-assembly of dialkylammonium salts and crown ethers was confirmed by ^{1}H-NMR spectroscopy: the ^{1}H-NMR spectrum of a 1:1 mixture of **17** and the crown ether precursor in CD_2Cl_2 clearly displayed shifts of all protons which reflected the change of the

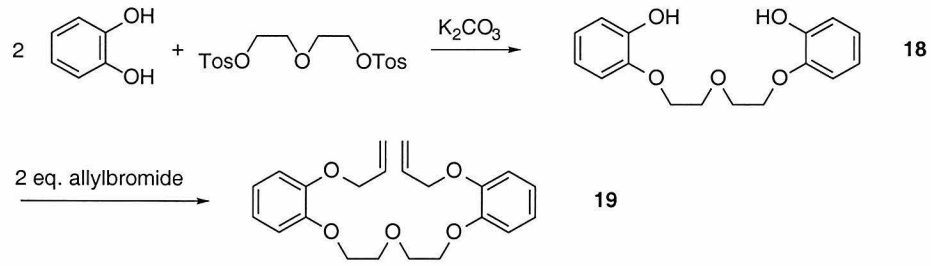
electron density. The N-H protons of **17** were shifted over 4 ppm downfield, and the CH_2-protons of the crown ether displayed downfield shifts of up to 0.5 ppm. A small excess of one of the two complexation partners was clearly visible in the ^{1}H-NMR spectrum in the appearance of signals characteristic for the uncomplexed species.



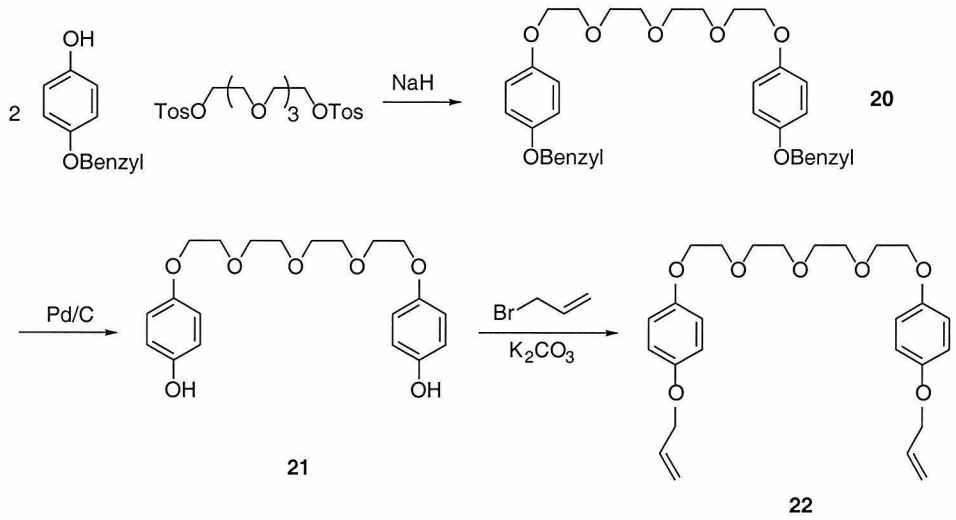
Scheme 11. Synthetic strategy to obtain rotaxanes based on **17** and crown ethers.

When **1** was added to the 1:1 complex of **17** and the crown ether, no cyclization was observed. It was anticipated that the olefins of the crown-4-ether precursor could be sterically too hindered after complexation to react with **1**. Therefore, a 1:1 complex of a crown-5-ether precursor was synthesized and added to a dichloromethane solution of **1**. However, no cyclic product was detected using the larger crown ether precursor. To eliminate the possibility of the hexafluorophosphate counterion being the reason for the closure failure, an RCM experiment was carried out using a dialkylammonium ion with a tetraphenyl borane counterion instead of **17**. No cyclic product was observable in this case, either.

After neither of the two crown ether precursors yielded any cyclic product after complexation, a new crown ether framework was employed which was based on Stoddart's recent reports that dibenzocrown ethers do not only self-assemble with dialkylammonium salts *via* hydrogen bonding but by π-π stacking interactions instead. Therefore, to further stabilize the self-assembly complex for ring-closure using π-π stacking interactions, crown ether precursors **19** and **22** were synthesized as outlined in Schemes 12 and 13.



Scheme 12. Synthesis of dibenzo-crown ether precursor **19**.



Scheme 13. Synthesis of dibenzo-crown ether precursor **22**.

In analogy to above, a 1:1 complex of **17** and **19** or **22** was obtained by mixing **17** and **19** or **22** in dichloromethane and stirring them for 24 hours. The complexes were fully soluble in dichloromethane and characterized by ^{1}H NMR. Similar to the results above, self-assembly resulted in a shift of most proton resonance of the complex. Figure 7 presents the NMR spectra of **17**, **22** and the 1:1 complex.

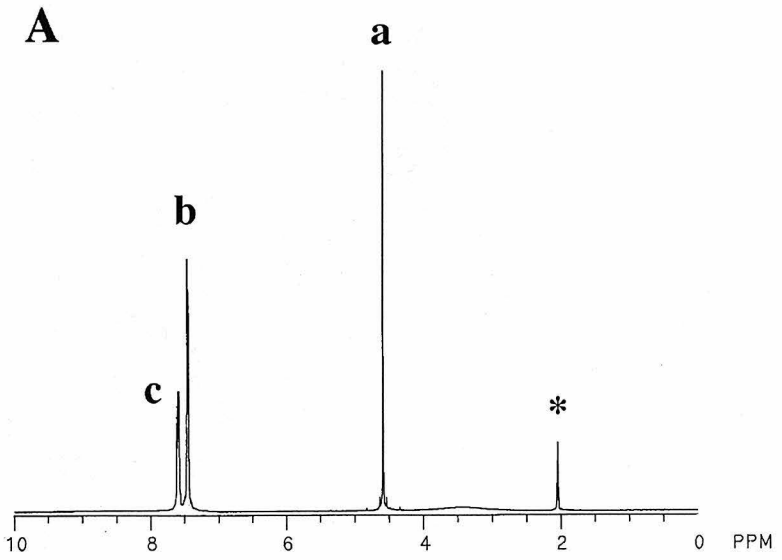


Figure 7a. Partial ^{1}H-NMR spectra of salt **17** recorded in acetone at 300 MHz at room temperature (* results from the solvent).

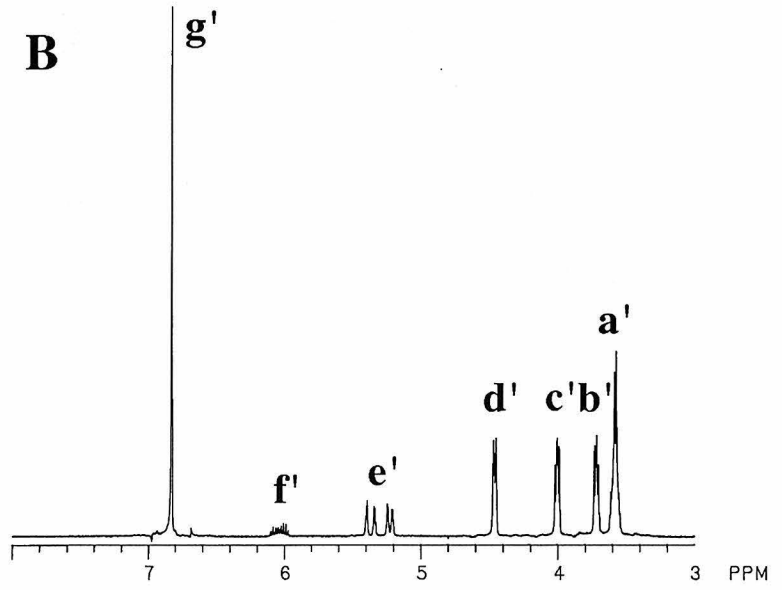


Figure 7b. Partial ^{1}H-NMR spectra of crown ether precursor **22** recorded in dichloromethane at 300 MHz at room temperature.

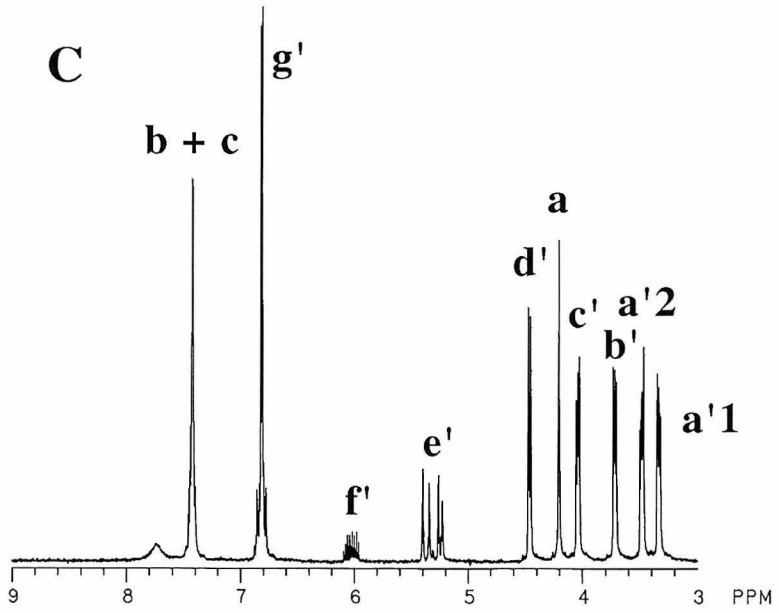


Figure 7c. Partial ^{1}H-NMR spectra of an equimolar mixture of **17** and **22** recorded in dichloromethane at 300 MHz at room temperature.

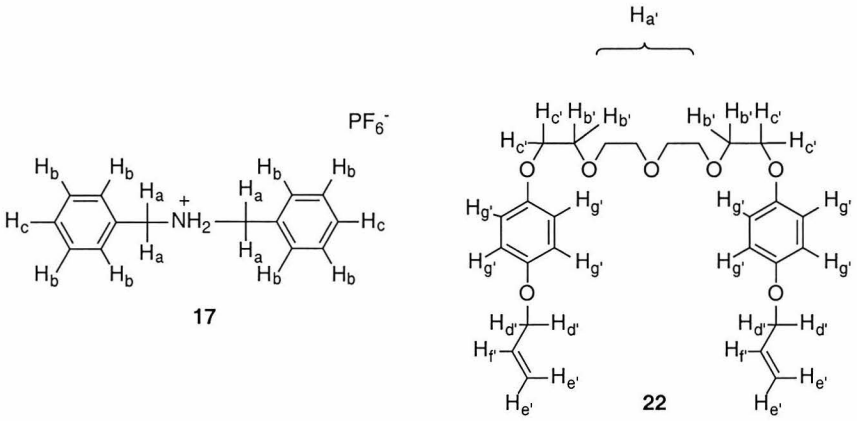
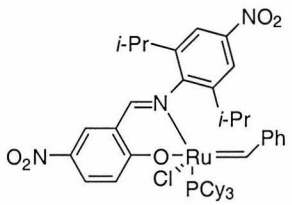


Figure 7d. Proton assignments for compounds **17** and **22**.

However, addition of **1** to the above complexes did not result in high yields of cyclic product. After 10 minutes, a small percentage (approximately 10-20%) of the ring-closed product was observed. However, after 15 more minutes the terminal olefins started to isomerize to the vinyl-ethers and no further ring-closure was detected. Changing the concentration of the catalyst or the reaction temperature did not result in a higher yield of ring-closed product.

One potential problem could be the stability of catalyst **1**. However, in 1997, Grubbs *et al.* developed a new ruthenium catalyst **23** which is based upon a Schiff base ligand,[40] which is more stable than **1** in a variety of solvents and at higher temperatures. Therefore, a solution of **23** in dichloromethane was added to a 1:1 complex of **17** and the crown-5-precursor. In contrast to the ring-closure experiments of **17** and the crown-5-precursor with **1**, a small percentage of closed product (10%) was observed after 20 hours. After 2 days, however, the crown ether started to isomerize and no further closed product was detected.



23

Nonetheless, addition of **23** to a 1:1 complex of **17** and **22** resulted in closed product in 55% yield as detected by NMR. Surprisingly, catalyst loadings of more than 10% did not increase the yield. Furthermore, it was not possible to isolate the closed complex. Precipitation into hexanes or pentane resulted only in an insoluble solid.

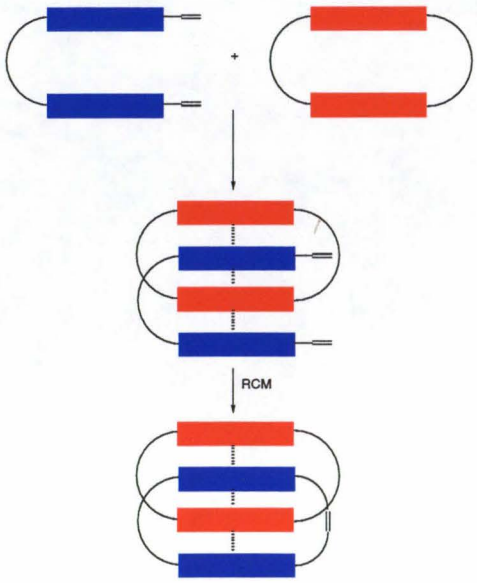
Several explanations are possible for the failure of most RCM reactions of 1:1 complexes of dialkylammonium salts with crown ethers. One could be the incompatibility of the catalyst with these dialkylammonium salts. Furthermore, it is possible that the catalyst is too bulky after initiation to 'swing around' and close the crown ether precursor.

Catenane and rotaxane strategies based on π-electron acceptor and π-electron donor molecules. In 1992, Stoddart and coworkers introduced a new supramolecular synthon for the synthesis of catenanes and rotaxanes based on π-electron-deficient units (tetracationic cyclophane cyclobis(paraquat-*p*-phenylene)) and hydrochinone-based polyethers which contain π-electron rich aromatic rings.[9a] A large number of reports from Stoddart's group followed this result by describing the self-

assembly of a number of interlocked and intertwined structures, such as rotaxanes, catenanes, pseudorotaxanes and oligomeric structures based on these π-electron deficient/π-electron rich units and related building blocks.[9]

Similar to the dialkylammonium ion-based synthon, self-assembly of these building blocks resulted in full complexation. To obtain rotaxanes and catenanes an intramolecular cyclization must take place after the self-assembly step. For this cyclization, Stoddart and coworkers used a double quaternization reaction to obtain the corresponding catenanes and rotaxanes in 20-70% yield after several days.

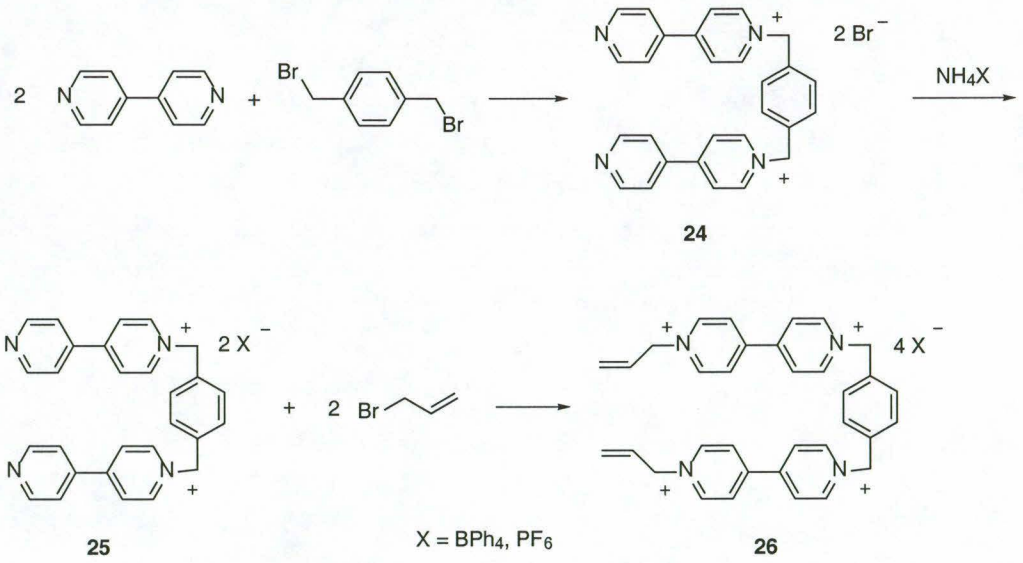
The research presented below describes a general approach to synthesize catenanes and rotaxanes through a combination of the π-electron deficient/π-electron rich template strategy with RCM. Scheme 14 shows the general strategy for this approach.



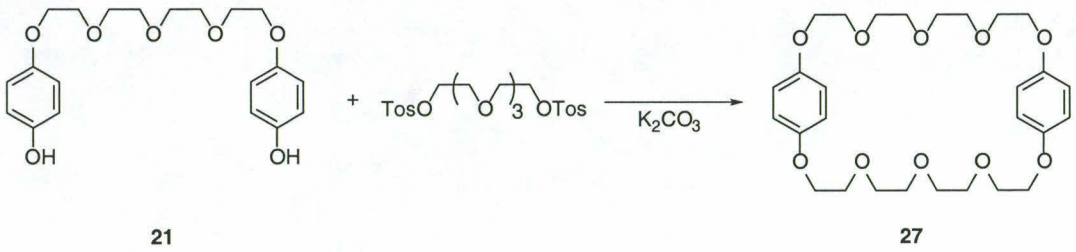
Scheme 14. Schematic drawing of a combination of a π-π interaction based template-strategy and RCM to provide access to catenanes: self-assembly followed by RCM.

Several new compounds were synthesized which contain terminal olefinic groups so as to implement RCM as the cyclization reaction. In analogy to literature procedures, salt **26** was prepared in two steps as shown in Scheme 15. Reaction of 4,4'-bipyridine and 1,4-bis(bromomethyl)benzene yielded **25** after anion exchange in approximately 50 % yield. Compound **25** was functionalized with allylbromide to afford **26** in low yield after

another ion exchange. Crown ether **27** was synthesized as described in literature[9a] through treatment of **21** in 21 % yield with one equivalent of tetraethylene glycol bistosylate in DMF (Scheme 16) over 6 days.



Scheme 15. Synthesis of **26**.



Scheme 16. Synthesis of **27**.

Complexation of salts **25** and **26** with crown ethers **22** and **27** was performed in acetonitrile at room temperature. It was not possible to induce complexation between these substrates in any other solvent. Complexations were followed by a solution color change from clear to deep orange. In analogy to the previously mentioned complexations, ^{1}H NMR chemical shift data indicated the formation of the inclusion complexes. In all complexes, a significant shift upfield was observed for the protons of the bipyridinium rings, while the *p*-phenylene protons were shifted downfield. The upfield shift of the former and the downfield shift of the latter correspond to the relative orientation of the

hydrochinol ring inside the cavity of the tetracationic cyclophane precursor, as described in literature.[9] This conclusion is further supported by the dramatic upfield shift of the hydrochinol ring protons, at least two of which were simultaneously involved in stabilizing edge-to-face interactions with the *p*-phenylene ring in the tetracation.[9a] Figure 8 presents as representative example the NMR spectra of **25**, **22** and the 1:1 complex of both.

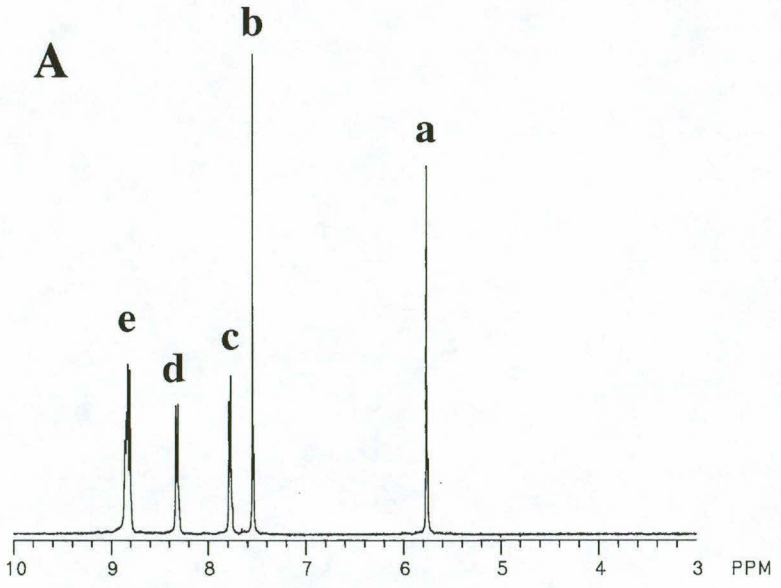


Figure 8a. Partial ^{1}H-NMR spectra of salt **25** recorded in acetonitrile at 300 MHz at room temperature.

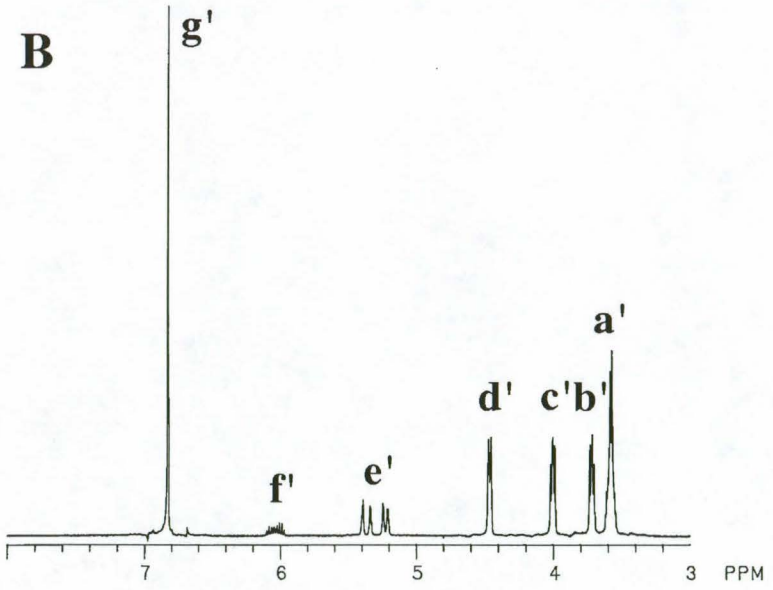


Figure 8b. Partial ^{1}H-NMR spectra of crown ether precursor **22** recorded in acetonitrile at 300 MHz at room temperature.

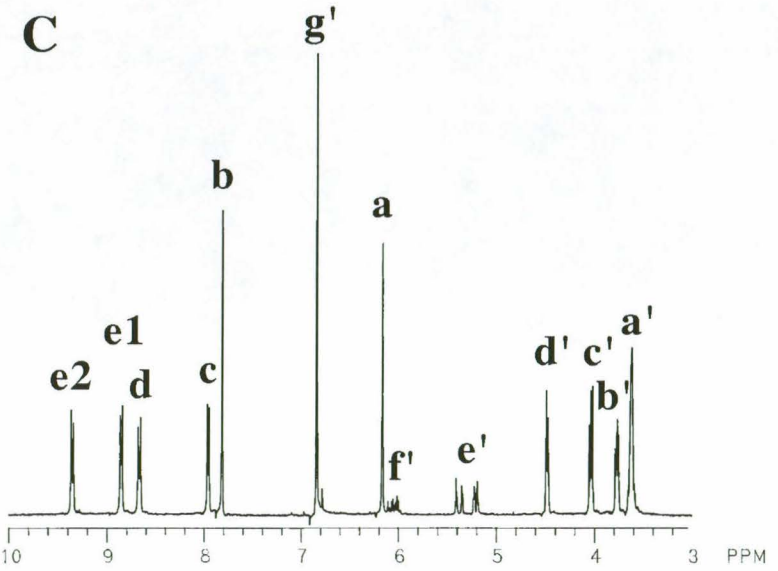


Figure 8c. Partial ^{1}H-NMR spectra of an equimolar mixture of **25** and **22** recorded in acetonitrile at 300 MHz at room temperature.

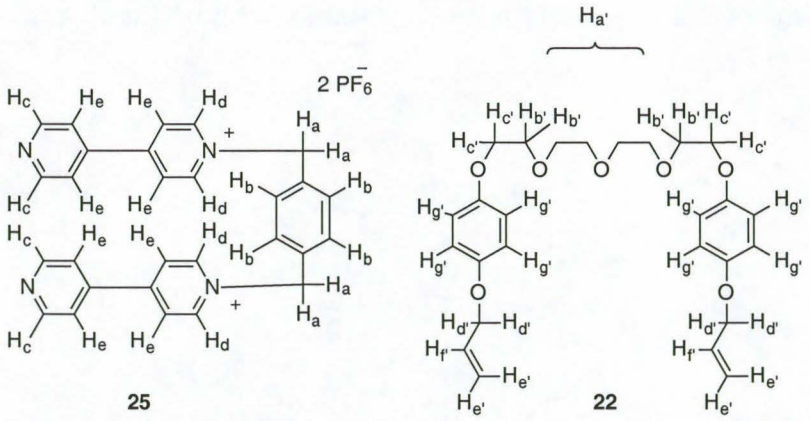
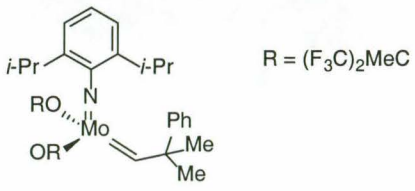


Figure 8d. Proton assignments for compounds **25** and **22**.

Because these complexes were only soluble in acetonitrile, ruthenium catalysts **1** or **23** could not be used for RCM due to their incompatibility with this solvent. However, Schrock and coworkers have used molybdenum catalyst **28** for the synthesis of liquid crystalline polymers containing a cyano-group.[41] Therefore, the compatibility of **28** with acetonitrile as solvent was investigated by dissolving it in acetonitrile and observing the carbene signal by ^{1}H NMR. After five hours the carbene signals at 12.84 and 13.72 ppm were still visible. However, a new species started to grow in after seconds which was hypothesized to be an acetonitrile-coordinated molybdenum species.



28

Based on this result, **28** was added to 1:1 solutions of **26** with crown ethers **22** or **27**. However, in all cases the reactions turned dark green, which is generally an indication for the decomposition of the molybdenum catalyst. The reason for the decomposition of the catalyst is unknown at this point. Though in most cases the appearance of a new carbene species indicated that some initiation took place, no cyclic product was observed by

NMR. Most likely the acetonitrile-coordinated molybdenum species is too stable to allow for any cyclization to take place.

Conclusion

Three different approaches to obtain intertwined and interlocked architectures through RCM were presented. RCM based on a metal template preorganization by intramolecular cyclization was established as a highly efficient protocol for the synthesis of [2]catenanes. Since its first report in 1997, Sauvage and coworkers have extended this methodology to the synthesis of knots and topologically related structures.[6b]

A variety of crown ethers were shown to self-assemble with dialkylammonium ions to yield rotaxane precursors. However, catalyst **1** proved to be incompatible with these complexes. However, a Schiff-base-based ruthenium complex **23** successfully catalyzed the ring-closure of these complexes in 55% yield.

Finally, a number of π-electron-deficient compounds and π-electron-rich crown ethers were synthesized which are able to quantitatively complex in acetonitrile. However, since ruthenium catalyst **1** is incompatible with acetonitrile and molybdenum-based catalysts formed a stable acetonitrile-coordinated species, it was not possible to cyclize these complexes by ring-closing metathesis using any olefin metathesis catalysts.

Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4Å molecular sieves (Linde). NMR spectra were recorded on a GE QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane and referenced to residual protio solvent. Coupling constants are reported in Hertz (Hz). IR spectra for the characterization of the samples were recorded on a Perkin-Elmer 1600 series FT-IR

spectrometer. Elemental analyses were performed by Fenton Harvey at the California Institute of Technology Elemental Analysis Facility.

Materials. Dichloromethane was distilled from calcium hydride and degassed by repeated freeze-pump-thaw cycles. All other solvents were used without further purification unless otherwise noted. All chemicals were purchased from the Aldrich Chemical Company and used without further purification. The ruthenium complex **1** was graciously provided by Dr. Peter Schwab. Compounds **2**, **3**, **4**, **5**, **6** and **11** were synthesized by Dr. Bernhard Mohr in Prof. Jean-Pierre Sauvage's group in Strasbourg, France.

General procedure for the metal complexation to form the pre-catenates 5,6 and 11. In a Schlenk flask, one equivalent of **2** (for the synthesis of **5** or **6**) or **3** (for the synthesis of **11**) was dissolved under argon in a 1:1 mixture of dichloromethane and acetonitrile. After addition of one equivalent of $[Cu(MeCN)_4$ the reaction was stirred at room temperature under argon for 15 minutes. In a second Schlenk flask, one equivalent of **3** (for the synthesis of **5** and **11**) or **4** (for the synthesis of **6**) was dissolved in dichloromethane and cannula filtered into the first solution. The solution was stirred under argon at room temperature for an additional 30 minutes, followed by removal of the solvent *in vacuo*. Final purification was achieved by silica gel column chromatography to yield a dark red, crystalline solid in quantitative yield.

General procedure for the ring-closing metathesis of the copper-based catenates 7,8 and 12. Under exclusion of air and moisture, **1** (5 mol%) was added in dichloromethane to a 0.01M solution of the diolefin (typically 200 to 900 mg) in dichloromethane. After the mixture was stirred for 6 hours at room temperature, additional catalyst (5 mol%) was added, and stirring continued for an additional 6 hours. The solvent

was then removed *in vacuo*, and the crude reaction mixture purified by repeated silica gel column chromatography using dichloromethane/methanol (96:4) to yield the [2]catenates as burgundy solids.

Catenate (7): yield: 92%; ^{1}H-NMR ($CDCl_3$) δ 8,62 (d, 2H, *J* = 8.4 Hz), 8.52 (d, 2H, *J* = 8.4 Hz), 8.23 (s, 2H), 8.14 (s, 2H), 7.80 (m, 4H), 7.32 (m, 8H), 6.09 (m, 2H), 6.00 (m, 8H), 4.16 (m, 4H), 3.80-3.48 (m, 36H); ^{13}C-NMR (acetone d^6) δ 159.0, 158.9, 155.9, 143.3, 143.2, 137.7, 137.3, 132.1, 131.7, 129.5, 129.4, 129.3, 128.1, 127.1, 126.8, 123.7, 123.6, 112.7, 112.6, 71.5, 71.1, 70.8, 70.7, 70.5, 69.1, 68.8, 67.4, 66.9; Anal. calcd. for $C_{70}H_{70}N_4O_{12}CuPF_6$: C, 61.41; H, 5.16; N, 4.09, found: C, 60.82; H, 5.05; N, 3.96; HRMS (FAB) calcd. for $C_{70}H_{70}N_4O_{12}Cu$ $(MH)^+$ 1221.4, found 1221.4.

Catenate (8): yield: 88%; ^{1}H-NMR ($CDCl_3$) δ 8,62 (d, 2H, *J* = 8.4 Hz), 8.55 (d, 2H, *J* = 8.4 Hz), 8.22 (s, 2H), 8.12 (s, 2H), 7.84 (m, 4H), 7.47 (d, 4H, *J* = 8.7 Hz), 7.30 (d, 4H, *J* = 8.7 Hz), 6.09 (d, 4H, *J* = 8.7 Hz), 5.98 (d, 4H, *J* = 8.7 Hz), 5.83 (m, 2H), 4.16 (m, 4H), 3.80-3.48 (m, 44H); ^{13}C-NMR (acetone d^6) δ 159.2, 158.9, 156.3, 155.9, 143.4, 143.3, 137.7, 137.3, 132.4, 132.1, 131.4, 129.5, 129.4, 129.3, 129.2, 128.2, 128.1, 127.3, 126.8, 126.4, 124.4, 123.7, 123.6, 113.0, 112.8, 112.6, 71.1, 71.0, 70.9, 70.8, 70.7, 70.5, 70.3, 69.7, 69.4, 68.8, 67.6, 66.9; Anal. calcd. for $C_{74}H_{78}N_4O_{14}CuPF_6$: C, 61.05; H, 5.40; N, 3.85, found: C, 61.05; H, 5.28; N, 3.95; HRMS (FAB) calcd. for $C_{74}H_{78}N_4O_{14}Cu$ $(MH)^+$ 1309.1, found 1309.3.

Catenate (12): yield: 92%; ^{1}H-NMR ($CDCl_3$) δ 8,51 (d, 4H, *J* = 8.4 Hz), 8.13 (s, 4H), 7.81 (d, 4H, *J* = 8.4 Hz), 7.41 (d, 8H, *J* = 8.7 Hz), 6.11 (m, 4H), 6.02 (d, 8H, *J* = 8.7 Hz), 4.18 (m, 8H), 3.80-3.67 (m, 32H); ^{13}C-NMR (acetone d^6) δ 159.0, 155.9, 143.3, 137.5, 131.7, 129.5, 129.3, 128.1, 126.8, 123.7, 112.7, 71.5, 70.8, 70.6, 69.1, 67.5; Anal. calcd. for $C_{72}H_{72}N_4O_{12}CuPF_6$: C, 61.83; H, 5.48; N, 3.88, found: C,

62.04; H, 5.21; N, 4.00; HRMS (FAB) calcd. for $C_{72}H_{72}N_4O_{12}Cu$ $(MH)^+$ 1247.2, found 1247.1.

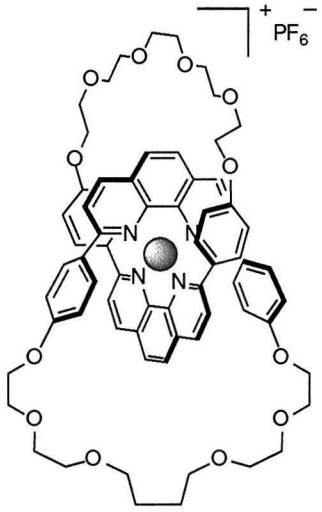
General procedure for the demetallation of the copper based catenates 7,8 and 12. The catenate was dissolved in acetonitrile followed by addition of an excess potassium cyanide in water. The mixture was stirred for 30 minutes at room temperature during which the dark burgundy color vanished and a brown solid precipitated. The solution was decantated and the precipitate dissolved in dichloromethane. The dichloromethane phase was washed several times with water and dried over magnesium sulfate. The solvent was removed *in vacuo* to yield a slightly milky solid. Final purification was achieved by silica gel column chromatography to yield a white solid.

Catenand (9): yield: 92%; ^{1}H-NMR ($CDCl_3$) δ 8,48 (m, 8H), 8.19 (d, 2H, J = 2.7 Hz), 8.17 (d, 2H, J = 2.7 Hz), 8.05 (s, 2H), 8.02 (s, 2H), 7.67 (m, 4H), 7.16 (t, 8H, J = 8.7 Hz), 5.96 (m, 2H), 4.19-3.56 (m, 40H); ^{13}C-NMR ($CDCl_3$) δ 161.5, 160.0, 156.3, 156.2, 146.1, 146.0, 136.7, 132.5, 132.4, 129.7, 129.3, 129.2, 127.4, 125.5, 119.2, 115.3, 115.2, 71.6, 71.1, 70.9, 70.7, 70.1, 68.8, 68.4, 66.8, 66.5; Anal. calcd. for $C_{70}H_{70}N_4O_{12}$: C, 72.52; H, 6.09; N, 4.83, found: C, 72.43; H, 5.95; N, 4.69; HRMS (FAB) calcd. for $C_{70}H_{70}N_4O_{12}$ $(MH)^+$ 1159.5, found 1159.5.

Catenand (10): yield: 93%; ^{1}H-NMR ($CDCl_3$) δ 8,48 (m, 8H), 8.18 (m, 2H), 8.17 (m, 2H), 8.07 (s, 2H), 8.03 (s, 2H), 7.67 (m, 4H), 7.16 (t, 8H, J = 8.7 Hz), 5.99 (m, 2H), 4.17-3.54 (m, 48H); ^{13}C-NMR ($CDCl_3$) δ 160.0, 159.8, 156.4, 156.2, 146.2, 146.0, 136.8, 132.5, 132.4, 129.7, 129.2, 129.1, 127.4, 125.6, 119.2, 114.9, 114.8, 71.3, 70.9, 70.8, 70.7, 69.8, 69.6, 68.4, 67.4, 66.8, 66.4; Anal. calcd. for $C_{74}H_{78}N_4O_{14}$: C, 71.47; H, 6.00; N, 4.51, found: C, 71.22; H, 5.96; N, 4.41; HRMS (FAB) calcd. for $C_{74}H_{78}N_4O_{14}$ $(MH)^+$ 1242.5, found 1242.5.

Catenand (13): yield: 90%; ^{1}H-NMR ($CDCl_3$) δ 8,47 (d, 8H, *J* = 2.7 Hz), 8.21 (d, 4H, *J* = 8.4 Hz), 8.05 (d, 4H, *J* = 8.4 Hz), 7.70 (s, 4H), 7.16 (d, 8H, *J* = 9.6 Hz), 5.93 (m, 4H), 4.18-3.56 (m, 40H); ^{13}C-NMR ($CDCl_3$) δ 160.0, 155.9, 146.0, 136.6, 132.4, 129.5, 129.1, 127.5, 125.6, 119.1, 115.1, 71.5, 70.9, 70.1, 68.8, 66.9; Anal. calcd. for $C_{72}H_{72}N_4O_{12}$: C, 72.94; H, 6.13; N, 4.73, found: C, 72.51; H, 6.12; N, 4.69; HRMS (FAB) calcd. for $C_{72}H_{72}N_4O_{12}$ $(MH)^+$ 1185.5, found 1185.5.

Synthesis of catenate (14):

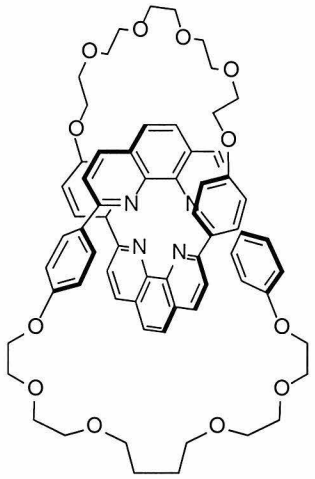


In a Schlenk flask, **7** was dissolved under argon in dichloromethane and cannula-filtered into a Schlenk flask containing Crabtree's iridium catalyst dissolved in dichloromethane. The reaction was stirred at room temperature under argon under 200 psi hydrogen pressure for 2 hours. After filtration of the reaction over a plug containing celite and the solvent was removed *in vacuo* to yield a dark burgundy solid. Final purification was achieved by silica gel column chromatography (dichloromethane/methanol (95:5)) to afford a burgundy solid in quantitative yield.

^{1}H-NMR ($CDCl_3$) δ 8.68 (d, 2H, *J* = 8.4 Hz), 8.59 (d, 2H, *J* = 8.4 Hz), 8.27 (s, 2H), 8.21 (s, 2H), 7.85 (t, 4H, *J* = 7.5 Hz), 7.35 (m, 8H), 6.04 (t, 8H, *J* = 8.1 Hz), 3.86-3.48

(m, 44H); ^{13}C-NMR ($CDCl_3$) δ 158.8, 158.7, 155.8, 155.7, 143.0, 142.9, 137.6, 137.1, 131.8, 131., 128.9, 128.8, 127.9, 127.8, 126.8, 126.5, 123.6, 123.5, 112.7, 71.3, 70.8, 70.7, 70.4, 70.3, 68.8, 68.7, 67.4; Anal. calcd. for $C_{70}H_{72}N_4O_{12}CuPF_6$: C, 61.39; H, 5.30; N, 4.09, found: C, 61.52; H, 5.11; N, 4.05; HRMS (FAB) calcd. for $C_{70}H_{72}N_4O_{12}Cu$ $(MH)^+$ 1223.4, found 1223.4.

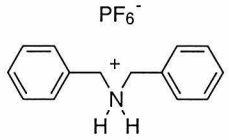
Synthesis of catenand (15):



15 was synthesized in analogy to **14** in 96% yield.

^{1}H-NMR (CD_2Cl_2) δ 8.53 (d of d, 8H, *J* = 9 Hz), 8.24 (d, 2H, *J* = 12.6 Hz), 8.21 (d, 2H, *J* = 12.6 Hz), 8.09 (s, 2H), 8.07 (s, 2H), 7.71 (d, 4H, *J* = 10.5 Hz), 7.27 (d, 4H, *J* = 8.7 Hz), 7.16 (d, 4H, *J* = 9 Hz), 4.36-3.48 (m, 46H); ^{13}C-NMR (CD_2Cl_2) δ 158.8, 158.7, 155.8, 155.7, 143.0, 142.9, 137.6, 137.1, 131.8, 131., 128.9, 128.8, 127.9, 127.8, 126.8, 126.5, 123.6, 123.5, 112.7, 71.3, 70.8, 70.7, 70.4, 70.3, 68.8, 68.7, 67.4; Anal. calcd. for $C_{70}H_{72}N_4O_{12}$: C, 72.38; H, 6.25; N, 4.83, found: C, 72.22; H, 6.17; N, 4.62; HRMS (FAB) calcd. for $C_{70}H_{72}N_4O_{12}$ $(MH)^+$ 1161.5, found 1161.5.

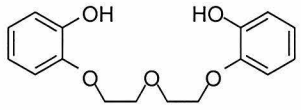
Synthesis of *N*,*N*-dibenzylammonium hexafluorophosphate (17):



HCl (2M, 250 mL) was added to *N*,*N*-dibenzylamine and the solution stirred for 5 hours. The solvent was removed *in vacuo* and the residue dissolved in 500 mL hot water. Saturated aqueous ammonium hexafluoruphosphate solution was added until no further precipitation occurred. The white solid was filtered off and dried to afford the title compound in 89% (7.6 g) yield.

^{1}H-NMR ($CDCl_3$) δ 7.60-7.43 (m, 10H), 4.58 (s, 4H); HRMS (FAB) calcd. for $C_{14}H_{16}N$ $(MH)^+$ 198.1283, found 198.1283.

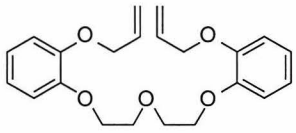
Synthesis of (18):



Catechol (3.1 g, 0.028 mol) was dissolved in dry dimethyl formamide (80 mL). Potassium carbonate (4.3 g, 0.031 mol) was added and the reaction was stirred for 30 minutes under argon at 120°C. Diethyl glycol ditosylate (4.8 g, 0.011 mol) was added in one portion and the reaction was further stirred at 120°C under argon for an additional 36 hours. The reaction was then poured into water and extracted several times with ether and ethyl acetate. The combined organic phases were washed with water and dried over magnesium sulfate. The solvent was removed *in vacuo*. Final purification was achieved by silica gel column chromatography using ethyl acetate/hexane (4:6) as eluents to yield a white solid in 36% yield (1.11 g).

^{1}H-NMR ($CDCl_3$) δ 7.47 (bs, 2H), 7.00-6.78 (m, 8H), 4.18 (t, 4H, *J* = 4.5 Hz), 3.83 (t, 4H, *J* = 4.5 Hz); Anal. calcd. for $C_{16}H_{18}O_5$: C, 66.18; H, 6.25, found: C, 65.91; H, 6.16; HRMS (FAB) calcd. for $C_{16}H_{18}O_5$ $(MH)^+$ 290.1154, found 290.1154.

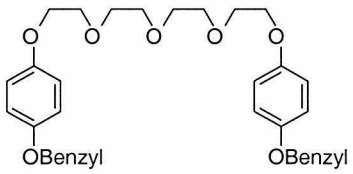
Synthesis of (19):



Potassium carbonate (1 g, 0.0065 mol) was added to a solution of **18** (0.85, 0.003 mol) in acetone (80 mL) and stirred for 20 minutes under argon at 50°C. Allylbromide (0.85 g, 0.0065 mol) was added and the reaction stirred under argon at 50°C for an additional 16 hours. The reaction was cooled down to room temperature, filtered and dried under dynamic vacuum. Final purification was achieved by silica gel column chromatograhy using hexane/ethyl acetate (8:2) as eluents to yield a yellow oil (0.87 g,78%) which solidified after several days.

^{1}H-NMR ($CDCl_3$) δ 6.90 (m, 8H), 6.05 (m, 1H), 5.31 (m, 2H), 4.57 (m, 4H), 4.12 (t, 4H, *J* = 5.4 Hz), 3.96 (t, 4H, *J* = 5.4 Hz); ^{13}C-NMR ($CDCl_3$) δ 149.3, 134.2, 122.1, 122.0, 118.0, 115.3, 115.0, 70.5, 69.5; IR (thin film on NaCl plate) 3065, 3017, 2927, 2873, 1648, 1592, 1504, 1453, 1424, 1409, 1361, 1327, 1255, 1213, 1126, 1055, 1020, 997, 928, 830, 785, 743, 645 cm^{-1}; Anal. calcd. for $C_{22}H_{26}O_5$: C, 71.32; H, 7.08, found: C, 70.98; H, 7.16; HRMS (FAB) calcd. for $C_{22}H_{26}O_5$ $(MH)^+$ 370.1780, found 370, 1780.

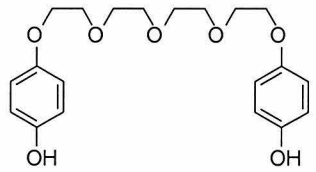
Synthesis of 1,11-bis[4-(benzoyloxy)phenoxy]-3,6,9-trioxaundecane (20):



A solution of 4-(benzyloxy)phenol (8.7 g, 44 mmol) in dry dimethyl formamide (70 mL) was added over a period of 20 minutes to a suspension of sodium hydride (2.16 g, 45 mmol) in dry dimethyl formamide (60 mL) and stirred under an argon atmosphere. After 15 minutes, tetraethylene glycol bistosylate (11.4 g, 22.7 mmol) dissolved in dry dimethyl formamide (100 mL) was added over a period of 2.5 hours and the temperature was raised to 80°C. Stirring and heating were continued for 2 days. After the reaction was cooled down to room temperature, the slight excess of sodium hydride was quenched by a few drops of water. The solvent was removed *in vacuo*, and the residue was partitioned between dichloromethane and water. The organic phase was washed with water and dried over magnesium sulfate. Evaporation of the solvents afforded a residue, which was purified by silica gel column chromatography (ethyl acetate/hexane (1:1); then ethyl acetate/dichloromethane/hexane (5:3:2)) to yield the title compound as a pale yellow oil that quickly solidified in 96% yield (11.6 g).

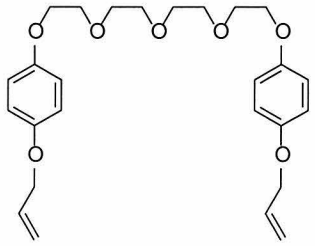
^{1}H-NMR ($CDCl_3$) δ 7.38 (m, 10H), 6.87 (m, 8H), 4.99 (s, 4H), 4.04 (t, 4H, J = 4.8 Hz), 3.81 (t, 4H, J = 4.5 Hz), 3.68 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 152.9, 152.8, 137.0, 128.3, 127.6, 127.2, 115.5, 115.3, 70.5, 70.4, 70.3, 69.6, 67.8; IR (thin film on NaCl plate) 2871, 1591, 1508, 1454, 1382, 1351, 1286, 1230, 1110, 1065, 1026, 916, 826, 771, 740, 697, 523 cm^{-1}; Anal. calcd. for $C_{34}H_{38}O_7$: C, 73.10; H, 6.86, found: C, 73.08; H, 6.88; HRMS (FAB) calcd. for $C_{34}H_{38}O_7$ $(MH)^+$ 558.2617, found 558.2618.

Synthesis of 1,11-bis[4-hydroxyphenoxy]-3,6,9-trioxaundecane (21):



A solution of **20** (10 g, 18 mmol) in dichloromethane/methanol (1:1, 160 mL) was subject to hydrogenolysis over 10% palladium on charcoal (1 g) for 24 hours. After filtration of the catalyst, the solvent was evaporated to give **21** as a viscous pale yellow oil in quantitative yield, which was employed in the next step without further purification. ^{1}H-NMR ($CDCl_3$) δ 6.71 (m, 8H), 3.96 (m, 4H), 3.71 (m, 4H), 3.57 (m, 8H); ^{13}C-NMR (acetone d^6) δ 152.8, 151.8, 117.1, 116.1, 71.0, 70.9, 70.1, 68.6; IR (thin film on NaCl plate) 3364, 2922, 2879, 1690, 1644, 1514, 1454, 1352, 1297, 1236, 1105, 1065, 951, 829, 756 cm^{-1}; Anal. calcd. for $C_{20}H_{26}O_7$: C, 63.46; H, 6.93, found: C, 63.22; H, 6.77; HRMS (FAB) calcd. for $C_{20}H_{26}O_7$ $(MH)^+$ 378.1678, found 378.1674.

Synthesis of 1,11-bis[4-(allyloxy)phenoxy]-3,6,9-trioxaundecane (22):



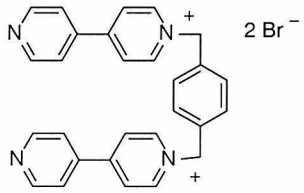
21 (0.9 g, 0..0024 mol) was dissolved in acetone (100 mL). After the addition of potassium carbonate (3.5 g) the suspension was heated at 50°C for 1 hour. Allylbromide (4 mL) was added and the reaction was stirred at 50°C under argon for 24 hours. After the reaction cooled down to room temperature it was filtered and the solvent removed *in vacuo* to yield a brown solid. Final purification was achieved by silica gel column

chromatography using ethyl acetate and hexane as eluents (1:1) to yield 790 mg (73%) of a white solid.

^{1}H-NMR ($CDCl_3$) δ 6.81 (s, 8H), 6.03 (m, 2H), 5.30 (m, 4H), 4.49 (m, 4H), 4.05 (t, 4H, J = 4.8 Hz), 3.81 (t, 4H, J = 5.4 Hz), 3.68 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 134.1, 118.1, 116.1, 116.0, 71.3, 71.2, 70.4, 70.0, 68.5; IR (thin film on NaCl plate) 3019, 2955, 2873, 1648, 1592, 1505, 1455, 1426, 1352, 1286, 1228, 1109, 1065, 1025, 997, 925, 823, 770, 738 cm^{-1}; Anal. calcd. for $C_{26}H_{34}O_7$: C, 68.09; H, 7.48, found: C, 67.99; H, 7.23; HRMS (FAB) calcd. for $C_{26}H_{34}O_7$ $(MH)^+$ 458.2304, found 458.2304.

General procedure for the complexation of crown ethers with secondary dialkylammonium ions. A 1:1 mixture of crown ether and dialkylammonium ion was mixed together in dichloromethane at room temperature. The salt dissolved instantly as a result of total complexation, which could be proved by ^{1}H-NMR spectroscopy.

Synthesis of 1,1'-[1,4-phenylenebis(methylene)]bis-4,4'-bipyridinium bis(bromine) (24):

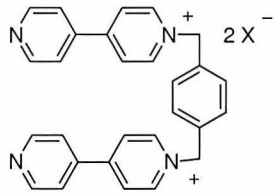


A solution of 1,4-bis(bromomethyl)benzene (17.5 g, 66 mmol) in dry acetonitrile (350 mL) was added over 6 hours to a solution of 4,4'-bipyridine (25 g, 160 mmol) in dry acetonitrile (250 mL). This mixture was heated under reflux under argon for 16 hours. After the solution cooled down to room temperature, the yellow precipitate was filtered off and washed with acetonitrile and ether before being dissolved in water (2 L). The aqueous solution was washed with ether, after which the water was removed *in vacuo* to leave a

solid residue. This residue was recrystallized three times from water to give a pale, slightly brownish solid in 47% yield.

^{1}H-NMR ($CDCl_3$) δ 8.98 (m, 4H), 8.65 (m, 4H), 8.34 (m, 4H), 7.81 (m, 4H), 7.57 (s, 4H), 5.87 (s, 4H); HRMS (FAB) calcd. for $C_{28}H_{24}N_4Br$ $(MH)^+$ 495.1185, found 495.1184.[42]

Synthesis of 1,1'-[1,4-phenylenebis(methylene)]bis-4,4'-bipyridinium bis(hexa-fluorophosphate) or 1,1'-[1,4-phenylenebis(methylene)]bis-4,4'-bipyridinium bis(tetraphenyl-borane) (25):

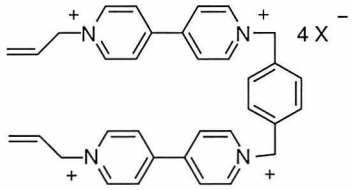


The dibromide salt **24** was dissolved in hot water (2 L). Ammonium hexaflourophosphate or ammonium tetraphenyl borane in methanol were added until no further precipitation was observed. The precipitate was filtered off and washed with water, methanol and ether, and used without further purification.

BPh_4-salt: ^{1}H-NMR ($CDCl_3$) δ 8.98 (m, 4H), 8.65 (m, 4H), 8.34 (m, 4H), 7.81 (m, 4H), 7.57 (s, 4H), 5.87 (s, 4H); HRMS (FAB) calcd. for $C_{52}H_{44}N_4B$ $(MH)^+$ 735.3659, found 735.3659.[42]

PF_6-salt: ^{1}H-NMR ($CDCl_3$) δ 8.98 (m, 4H), 8.65 (m, 4H), 8.34 (m, 4H), 7.81 (m, 4H), 7.57 (s, 4H), 5.87 (s, 4H); HRMS (FAB) calcd. for $C_{28}H_{24}N_4PF_6$ $(MH)^+$ 561.1643, found 561.1643.[42]

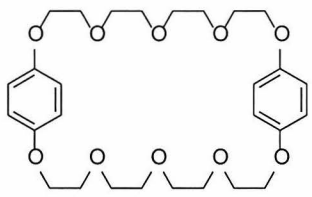
Synthesis of 1,1'-[1,4-phenylenebis(methylene)],-8,8'-[bisallyl]-bis-4,4'-bipyridinium bis(hexa-fluorophosphate) (26):



25 (1.4 g, 0.002 mol) was dissolved in dry acetonitrile (300 mL) and heated for 30 minutes under argon to 80°C. Allylbromide (0.18 mL, 25 mg, 0.002 mol) was added, and the reaction stirred at 80°C for an additional 24 hours. Then a second portion of allylbromide (0.18 mL, 25 mg, 0.002 mol) was added and the reaction refluxed for 36 hours. The reaction was cooled down to room temperature, the yellow precipitate filtered off and washed with acetonitrile. The residue was dissolved in water and washed with acetonitrile and ether, and the solvent was removed *in vacuo* to yield a yellow/green precipitate which was used without further purification.

^{1}H-NMR (acetone d^6) δ 9.47 (m, 4H), 9.38, m, 4H), 8.80 (m, 8H), 7.80 (s, 4H), 6.32 (m, 2H), 6.22 (s, 4H), 5.61 (m, 8H); HRMS (FAB) calcd. for $C_{34}H_{34}N_4P_3F_{18}$ $(MH)^+$ 933.1709, found 933.1709.[42]

Synthesis of 1,4,7,10,17,20,23,26,28,32-decaoxa[13.13]paracyclophane (27):



A solution of **21** (1.12 g, 0.003 mol) in dry tetrahydrofuran (60 mL) and a solution of tetraethylene glycol bistosylate (1.51 g, 0.003 mol) in dry tetrahydrofuran (50 mL) were added simultaneously over 2 hours to a stirred suspension of sodium hydride (0.22 g,

0.009 mol) in refluxing dry tetrahydrofuran (50 mL) under argon. The mixture was refluxed for 5 days before being cooled down to room temperature. Excess sodium hydride was quenched by the addition of a small amount of water and the solvent was removed *in vacuo*. The residue was partitioned between water and dichloromethane, the organic phase washed several times with 2N hydrochloric acid, and water, dried over magnesium sulfate and then concentrated *in vacuo*. Silica gel column chromatography (ether/chloroform/methanol (68:30:2)) afforded **27** as a white solid in 21% yield (340 mg). ^{1}H-NMR ($CDCl_3$) δ 6.73 (s, 8H), 3.96 (t, 8H, J = 4.5 Hz), 3.82 (t, 8H, J = 5.1 Hz), 3.69 (m, 16H); ^{13}C-NMR ($CDCl_3$) δ 154.2, 116.3, 71.5, 71.4, 70.5, 69.0; IR (thin film on NaCl plate) 2929, 2868, 1638, 1511, 1454, 1348, 1281, 1234, 1135, 1114, 1068, 952, 846, 821, 750, 524cm^{-1}; Anal. calcd. for $C_{28}H_{40}O_{10}$: C, 62.66; H, 7.52, found: C, 62.33; H, 7.38; HRMS (FAB) calcd. for $C_{28}H_{40}O_{10}$ $(MH)^+$ 536.2621, found 536.2614.

General procedure for the complexation of π-electron acceptors with π-electron donors. A 1:1 mixture of the π-electron acceptor and the π-electron donor was mixed together in acetonitrile at room temperature. The salt dissolved instantaneously and the color changed to yellow as a result of total complexation, which could be proved by ^{1}H-NMR spectroscopy.

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Chapter 5

Ring-Opening Metathesis Polymerization from Surfaces

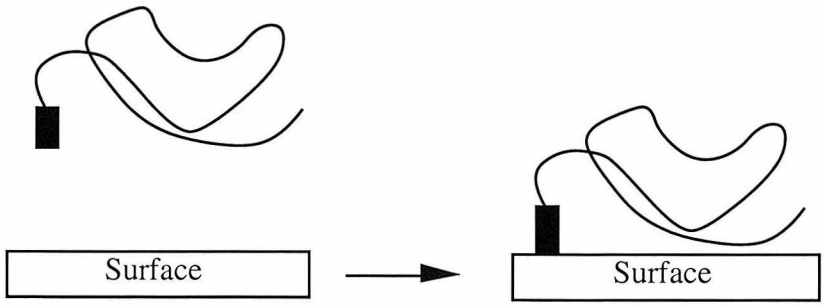
Abstract

Two strategies to initiate ring-opening metathesis polymerization (ROMP) from surfaces have been developed. The first approach is based on the covalent attachment of an olefin metathesis catalyst to a gold surface. However, since the newly-synthesized ruthenium catalyst decomposed rapidly, no attachment to the surface was possible. For the second approach, a molecular wire-type molecule containing a norbornene-functionality on one end and a thiol on the other was synthesized. Using a two-step self-assembly process, the single molecular wire molecules were attached to the gold surface surrounded by a dodecanethiol matrix. Treatment of the mixed-functionalized surface with a ruthenium catalyst followed by addition of monomer resulted in ROMP. The polymers were characterized by STM, AFM, and SEM. Most of the polymerizations took place on the gold step-edges and the domain boundaries of the terraces resulting in polymers of several hundred Angstroms in diameter. Moreover, it could also be shown that larger polymer brushes exist in large defect areas on the surface. These results constitute the first successful ROMP from surfaces.

Introduction

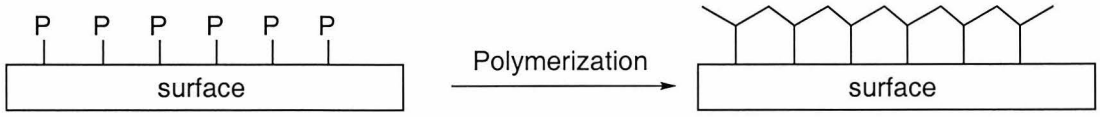
The organization of well-defined molecular assemblies on solid surfaces provides a rational basis for the fabrication of interfaces with well-defined structures and compositions, such as organized mono- and multilayer assemblies.[1,2] In particular, ultrathin ordered polymeric layers on inorganic surfaces exhibit potential for a variety of advanced technological applications such as microlithography,[3] biocompatible materials, biosensors,[4] ion sensors,[5] chemical separations,[6] multilayer light emitting diodes (LEDs), modification of electrode surfaces, catalysis, corrosion, surface protection, lubrication, and adhesion.[1,2,7] Furthermore, experimental verification of theoretical models describing the adsorption of polymeric structures on surfaces is of fundamental interest.[8] In particular, experimental proof of the theoretical descriptions of polymer brushes, polymers which are confined to a small volume of a surface and, due to steric requirements, stretch away from their grafting point toward the polymer edges, by Alexander and deGennes would be desirable since these describe the difference between a free polymer chain system and a chain in a grafted brush.[8c-e]

Currently the most widely used methods to obtain ordered polymeric films are Langmuir-Blodgett deposition,[9] vapor deposition, non-specific adsorption,[10] spin-coating and spin-casting.[11] However, several applications require the covalent attachment of the polymeric layer to the surface. In recent years, the most widely studied method to covalently attach polymers to surfaces was the use of polymers with functional groups which are able to react with the surface (Scheme 1).[12]



Scheme 1. Strategy for linking polymers to a surface *via* terminal functional groups.

Other surface polymer functionalization techniques include the decomposition of CH_2N_2 onto the surface,[13] physisorption onto the surface,[14-16] and molecular recognition.[17] Beside all these commonly employed techniques, polymer layers on surfaces can also be prepared *via* a direct surface initiation of the polymerization reaction (Scheme 2). Surface-initiated polymerization techniques have been used for a variety of monomers and different polymerization methods, including radical,[18] cationic,[19] and anionic polymerization methods.[20]



P = polymerizable unit

Scheme 2. Surface initiated polymerization.

However, the polymerizations from surfaces known to date are mostly ill-defined and proceed in a non-living fashion as a result of side-reactions, impurities, and incompatibilities with the surface.[18] Therefore, controlled polymer growth off the surface would be of great interest since a living polymerization from the surface would result not only in a well-defined system on the surface but would also allow the construction of multilayer structures and the introduction of a well-defined number of functional groups on the surface.

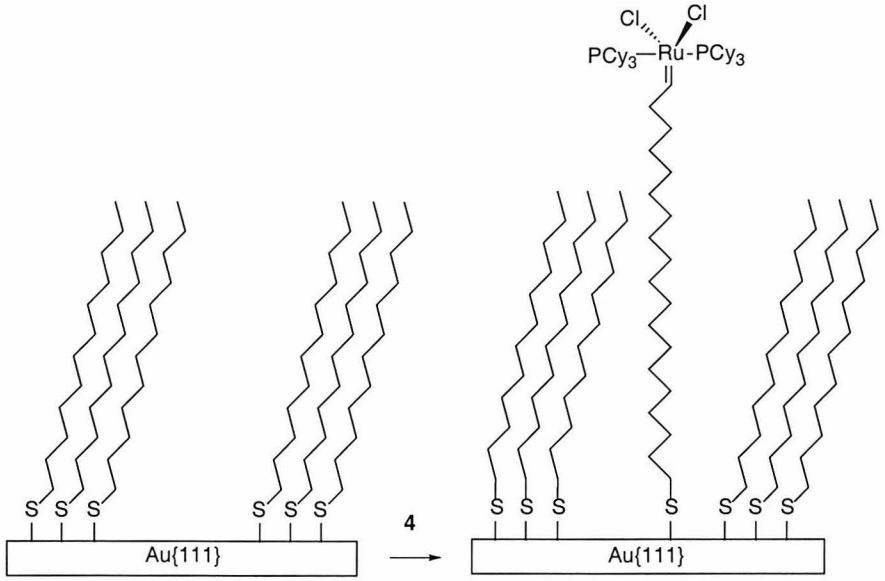
In the last decade, ring-opening metathesis polymerization (ROMP) catalyzed by well-defined metal-alkylidines has been established as an efficient method to control a polymer's molecular structure, size, and bulk properties.[21] Ruthenium-based ROMP initiators, in particular, have been shown to polymerize a large variety of monomers in a living fashion in a number of solvents, ranging from benzene to water.[22] With these recent advances in catalyst design, ROMP is capable of overcoming the problems associated with surface polymerization.

This chapter describes the synthesis of a number of difunctionalized compounds which can self-assemble on a gold surface and which are able to initiate ROMP after addition of a ruthenium initiator. Subsequent addition of monomer resulted in ROMP. The polymerized surfaces were characterized using scanning tunneling microscopy (STM), atomic force microscopy (AFM) and scanning electron miscroscopy (SEM).

Results

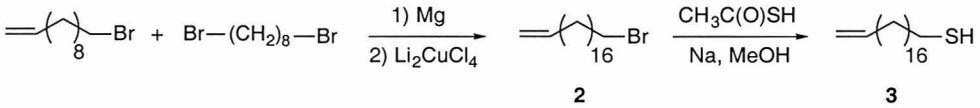
In the last decade, self-assembled monolayers (SAMs) prepared by adsorbing alkanethiols or dialkyl sulfides onto Au{111} (binding energy is approximately 120 KJ/mol) have attracted widespread interest because they can be prepared easily and have a number of potential applications.[1,2,4-7,23-25] Moreover, numerous surface analytical techniques have been successfully used to study and characterize Au{111}-supported alkanethiol SAMs.[1,2,4-7,23-25] Because many properties of Au{111}-supported alkanethiols and dialkyl sulfides are well-established,[1,2,23-25] the research presented in this chapter is based on these compounds.

I. Surface polymerization strategy based on a surface-bound initiator. The easiest way to initiate a ROMP from a surface is to covalently attach an olefin metathesis catalyst to the surface. Addition of monomer should result in full initiation of the catalyst followed by polymerization from the surface. Scheme 3 shows the general strategy to anchor a ruthenium catalyst to the surface.



Scheme 3. General strategy for anchoring an olefin metathesis catalyst to a gold surface.

The synthesis of a surface-bound metathesis catalyst has not yet been accomplished. However, based on literature procedures[22d] simple cross-metathesis using a surface-bound molecule containing a terminal olefin should result in an active catalyst. Therefore, a molecule containing a surface-active group, in this case a thiol on one end and an olefinic group on the other, was synthesized as outlined in Scheme 4.



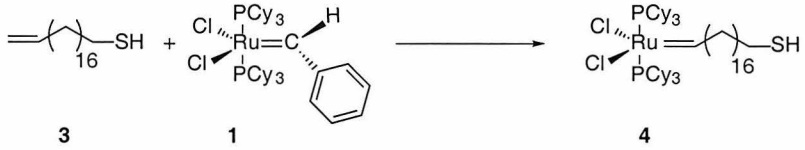
2 **3**

Scheme 4. Synthesis of precursor **3** for the synthesis of the initiator species **4**.

A Grignard reaction using 11-bromo-1-undecene and 1,8-dibromooctane furnished 19-bromo-1-nonadecene **2** in 40% yield. Introduction of the thiol group was achieved by treating **2** with thiolacetic acid followed by quenching with ammonium chloride solution to yield 18-nonadecene-1-thiol **3** in 68% yield.

It has been shown that ruthenium catalyst **1** can be quantitatively converted into an alkylidine-substituted complex *via* cross metathesis by treating **1** with a large excess of a terminal olefin such as propene or hexene.[22d] Although cross-metathesis is an equilibrium process, the kinetic product can be quantitatively isolated under such conditions.

Therefore, in analogy to literature procedures,[22d] a thirty-fold excess of **3** in benzene was added *via* a cannula to a solution of **1** in benzene as outlined in Scheme 5.



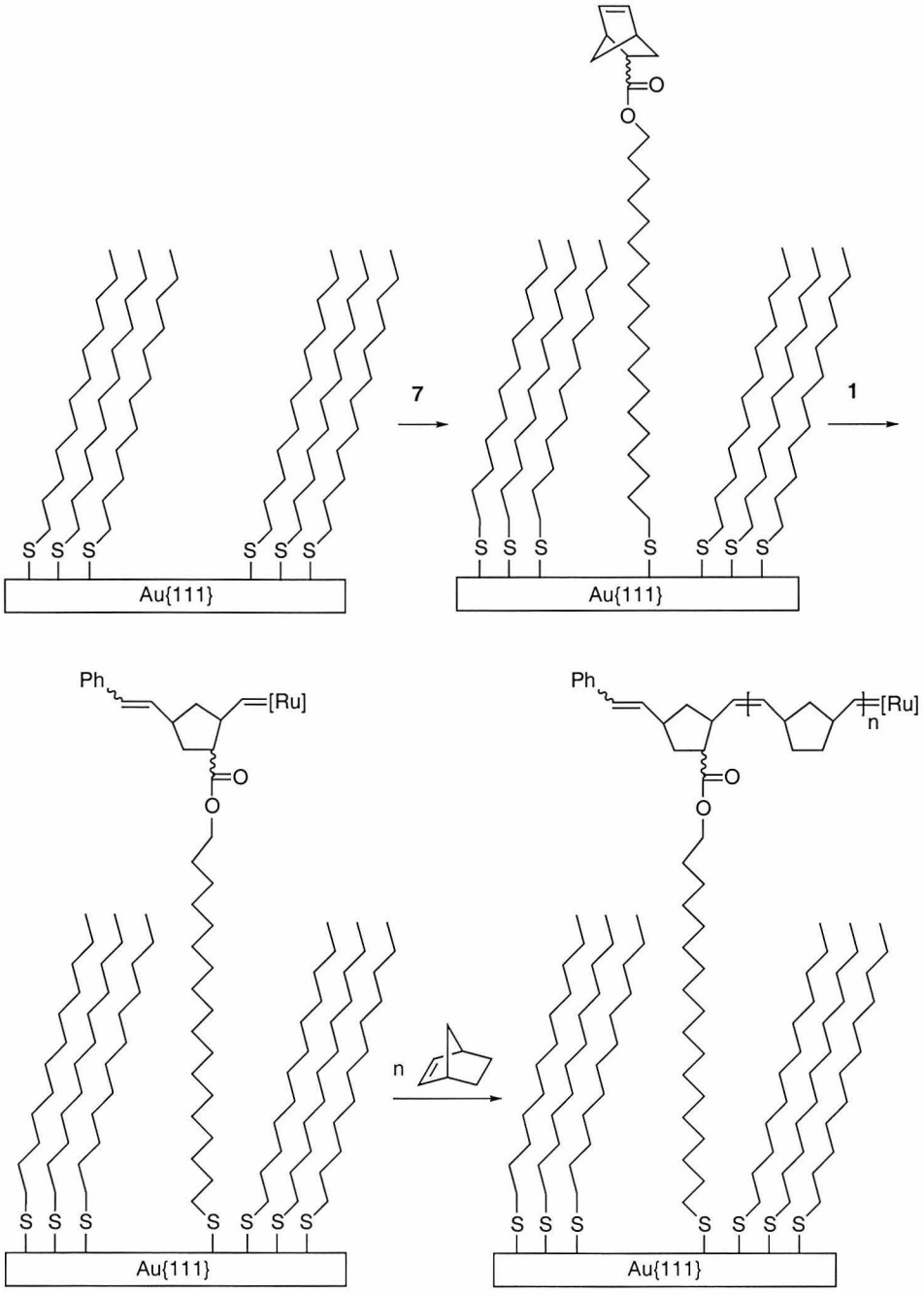
3 1 4

Scheme 5. Synthesis of initiator species **4** containing a thiol functionality.

Two minutes after the addition of **3** to the catalyst solution, the formation of a new carbene species at 19.25 ppm (triplet) was observed by NMR indicating the generation of a new complex. After 30 minutes the formation of the new catalytic species was complete. This new complex was stable in solution for several hours after which it started to decompose accompanied by the formation of a methylidine species. However, it was not possible to separate the catalyst from the excess of **3** since both compounds are soluble in the same solvents. No solvent was found in which only one of the two components was soluble. Therefore, this approach was not investigated any further.

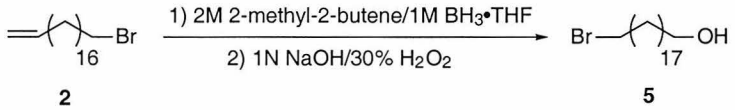
II. Surface polymerization strategy based on surface-bound monomers. An alternate strategy to initiate a ROMP from the surface is to anchor a ROMP-active monomer to the surface. This strategy requires one additional step compared to the catalyst-anchoring approach described above. However, since it does not require the modification of a ruthenium catalyst the main problem encountered above can be avoided.

For the purpose of anchoring an initiating unit to the surface, a difunctional molecule containing an anchor-group such as a thiol for a gold surface on one end and a monomeric unit on the other must be synthesized. This molecule can both self-assemble on a gold surface and initiate ROMP after addition of a ruthenium initiator. The initiated surface can be cleaned from excess catalyst and be exposed to monomer which should result in polymerization. Scheme 6 illustrates the general outline of this approach.



Scheme 6. General strategy for anchoring a monomer unit to a gold surface, followed by initiation and polymerization.

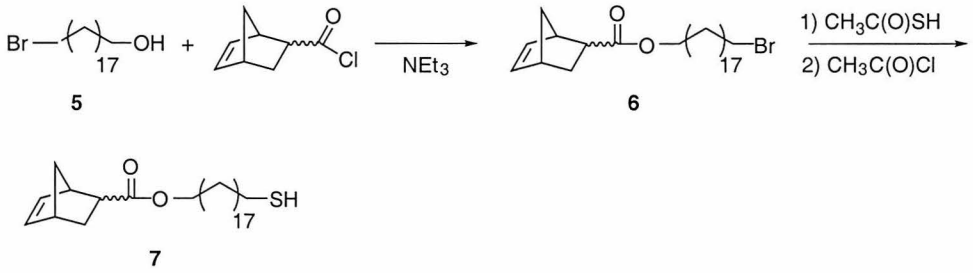
A polymerization- and surface-active molecule for this approach can be synthesized from compound **3** by treating it with disiamylborate followed by the addition of hydrogen peroxide to yield 19-bromo-1-nonadecanol **5** in 56% yield as outlined in Scheme 7.



2 5

Scheme 7. Synthesis of precursor **5** for the synthesis of norbornene lipid **7**.

Esterfication of **5** using norborn-2-ene-5-carbonyl-chloride[26] afforded compound **7** as a white solid in 63% yield (Scheme 8).

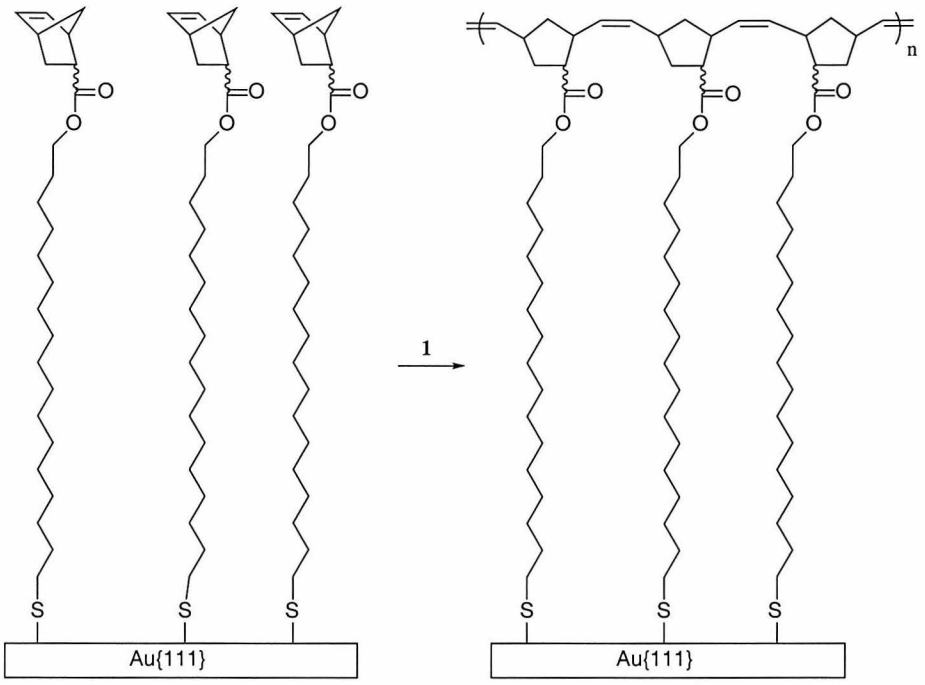


5 6 7

Scheme 8. Synthesis of the flexible thiol **7** containing a norbornene functionality.

However, in comparison to the catalyst-anchoring approach presented above, another problem can be foreseen. Coverage of the entire surface with the monomer-containing molecule could, after addition of the catalyst, result not only in polymerization from the surface but also in polymerization between initiating units as outlined in Scheme 9. Since this type of polymerization would only result in a surface covered by a 'single polymer layer' but not in a polymerization which leads to multilayer structures, the self-assembly process must be modified.

To resolve this problem, several modifications are possible. The most common approach to resolve this problem is the co-self-assembly of a functionalized molecule with alkylthiolates.[23] This results in a mixed monolayer with separate areas on the surface containing the functionalized molecules while other areas are only covered with the alkylthiolates. This approach, however, also allows a partial polymerization between initiating units.

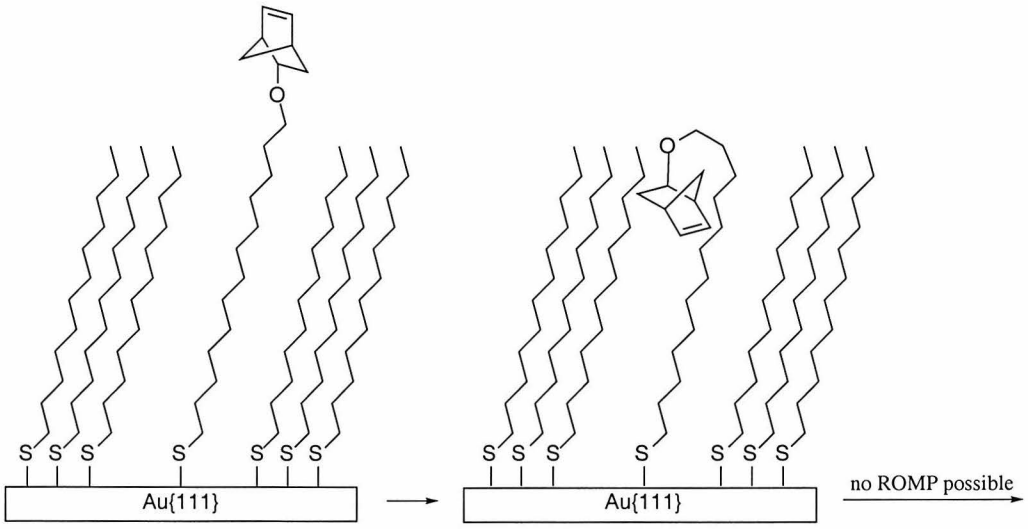


Scheme 9. Schematic presentation of a possible polymerization between initiating units.

Another possible solution was introduced in 1996 by Tour, Allara, and Weiss, describing a new method for the insertion of single molecules into a monolayer consisting of alkylthiolates on gold.[27] This method is based on two different self-assembly steps. Initially the surface is functionalized using an alkylthiolate SAM (in most cases dodecanethiol). Alkylthiolate SAMs on gold form flat and ordered terraces with steps of single gold atom height. These terraces are distinguished by domains of ordered lattices which frequently neighbor single-gold atom deep pits. These pits contain alkylthiolates bound in the same close-packed conformation as on the terraces. The gold-atoms in the terraces are therefore chemically isolated from the environment by the monolayer of close-packed alkyl-chains except at boundary areas such as step edges and alkyl thiol orientational domains. These boundaries and holes constitute the easiest access to the gold surface and thus may offer the most favored site for further chemisorption. Therefore, in a second self-assembly step, the monofunctionalized surface can be exposed to a functionalized molecule which can self-assemble in these pitholes and boundaries. The molecules of interest are then diluted and isolated by the alkylthiol SAM matrix.

However, this two step self-assembly technique yielded no efficient initiation or polymerization after the functionalization of the gold surface with dodecanethiol and **7**. To further investigate this result a model system was synthesized. It is known that aqueous gold can be reduced in the presence of an alkylthiol to produce nanometer-scale gold particles stabilized by a surface monolayer of alkylthiolates.[28] The resulting nanoclusters are stable in air at room temperature and can be handled and characterized as single chemical substances. In contrast to SAMs on surfaces, these nanoclusters can be investigated by simple techniques such as NMR. Therefore, gold nanoclusters stabilized by a monolayer of dodecanethiol and **7** (5 - 20% coverage of **7**) were synthesized. However, after adding **1** to these nanoclusters, again no efficient initiation or polymerization was observed by NMR. Changing the content of **7** in the monolayer to 50% did not result in significant initiation over a period of several days, either. After this time the catalyst started to decompose.

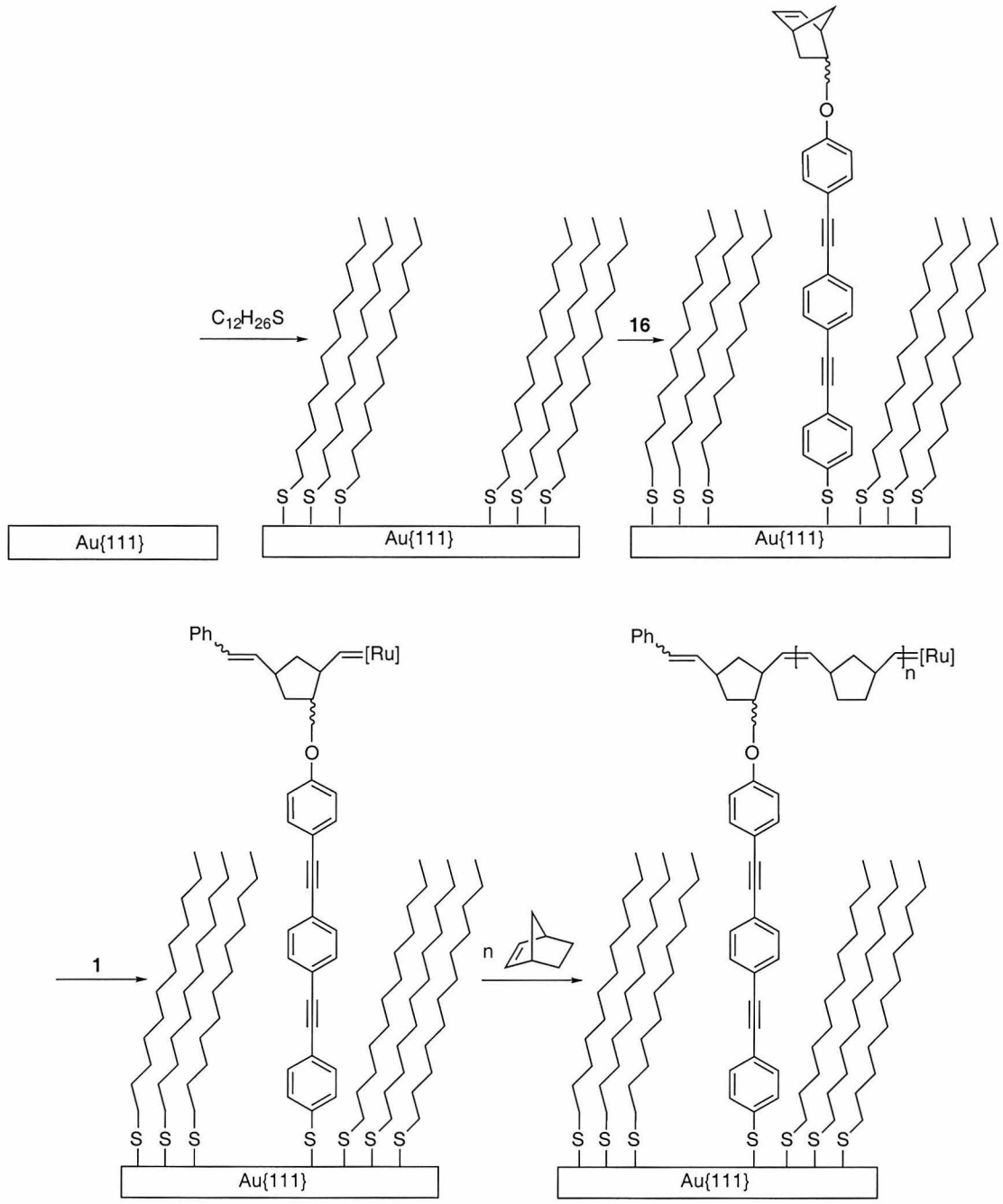
The non-initiation of the monomeric units in the monolayer cannot be explained in its entirety at this point. However, it is possible that the norbornene-functionalized molecule is too flexible thereby causing the monomeric unit to fall into the dodecanethiol monolayer. This could prevent the catalyst from initiating the monomer as a result of its steric demand. Scheme 10 outlines the potential problem of the strategy based on a flexible, norbornene-functionalized molecule.



Scheme 10. Possible explanation for the non-initiation of the surface-bound thiol **7** using catalyst **1**.

To eliminate the possibility of the norbornene functionality falling into the dodecanethiol monolayer matrix, thereby preventing the catalyst from initiating polymerization, a new synthetic strategy based on a stiff molecular wire-type molecule was developed. This kind of molecule has the advantage of being more rigid and longer than the surrounding dodecanethiol matrix. Therefore, the norbornene functionality is easily accessible for the catalyst. Furthermore, the molecular wire molecule would be highly conjugated thus making a characterization of the surfaces through microscopy methods, such as STM, easier.

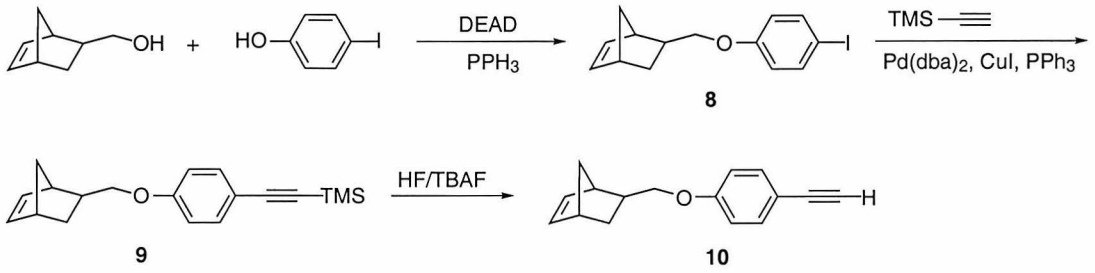
This latter strategy is also based on a two-step self-assembly method to insure insertion of a single molecule into the dodecanethiol SAM matrix. Exposure of the functionalized surface to a catalyst solution followed by addition of monomer should result in a polymerization from the surface. Scheme 11 outlines the general strategy for a polymerization from surfaces using a molecular wire-type molecule.



Scheme 11. General strategy for anchoring a molecular wire type molecule to a gold surface followed by initiation and polymerization.

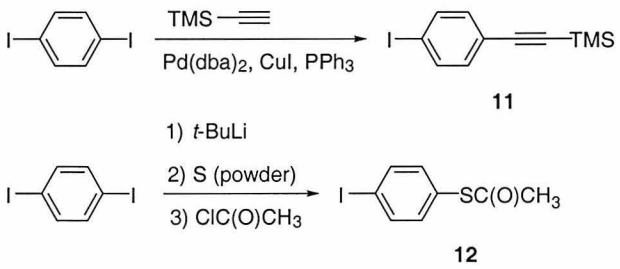
The stiff molecular wire-type molecule used in these studies is based on phenyl-ethynylenes and was synthesized in analogy to literature procedures[27] by sequential addition of acetylene units to aryl-iodides. The norbornene-containing precursor **10** was synthesized *via* a Mitsunobu reaction followed by a palladium-catalyzed coupling of a

protected acetylene. Deprotection of the acetylenes using buffered HF/TBAF conditions afforded **10** in nearly quantitative yields (Scheme 12).



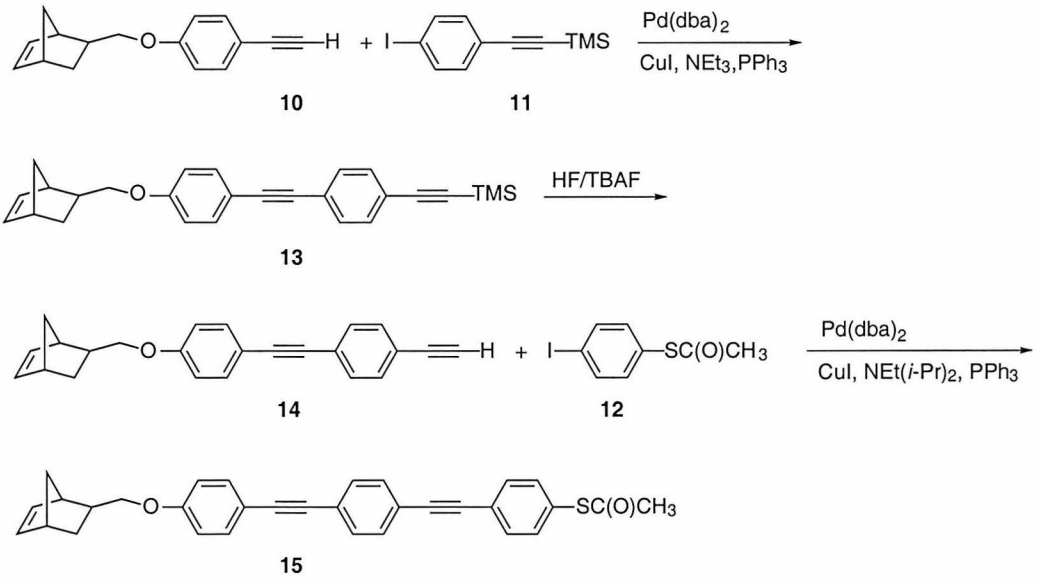
Scheme 12. Synthesis of molecular wire precursor **10**.

The middle building block of the molecular wire was synthesized in a straightforward fashion, again using palladium-catalyzed coupling of a protected acetylene to an aryl halide to yield **11** in 40 % yield (Scheme 13). It was anticipated that a non-protected thiol endgroup functionality could easily be oxidized. Therefore, the thiol functionality in the end building-block was protected as a thioester which can be easily deprotected under basic conditions. The protected thiol building-block of the molecular wire was synthesized in 32 % yield as outlined in Scheme 13.[27]



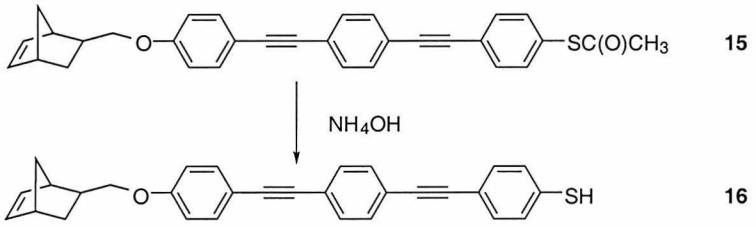
Scheme 13. Synthesis of molecular wire precursors **11** and **12**.

Having all the different building blocks for the synthesis of the molecular wire in hand, several sequential palladium-catalyzed couplings after deprotection of the acetylenes afforded the thioester-protected molecular wire **15**. Scheme 14 describes the different coupling and deprotection steps of the sequential synthesis of **15**.



Scheme 14. Step-by-step synthesis of the protected molecular wire **15**.

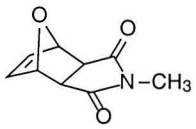
Addition of NH_4OH to compound **15** resulted in the quantitative formation of the unprotected molecular wire **16** (Scheme 15).



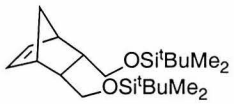
Scheme 15. Deprotection of **15** to yield molecular wire **16**.

General sample preparation and polymerization conditions. Functionalization of the gold surfaces was achieved as outlined in Scheme 11. 1000 Å of gold were deposited onto a freshly cleaved mica wafer through evaporation.[29] The freshly prepared mica/gold wafers were then immersed into a 1 mM solution of dodecanethiol in ethanol at room temperature under a nitrogen atmosphere for 12-24 hours. Subsequently, the wafers were rinsed with hexane, acetone, and ethanol. The dodecanethiol functionalized wafers were then placed into a 0.1-0.3 mM solution of **15** in freshly distilled tetrahydrofuran at room temperature under a nitrogen atmosphere with a slight excess of NH_4OH to generate the deprotected species **16** *in situ*. The samples were kept in the

solution for 30 minutes, and were subsequently washed with tetrahydrofuran, acetone, and ethanol. After characterization, the wafers were immersed into a solution of **1** in dichloromethane for 5-15 minutes to initiate the monomeric units on the surface. After rinsing the wafers with dichloromethane several times to remove excess catalyst, the initiated samples were immersed into a monomer solution in dichloromethane. Monomers **17** and **18** were used in this study because of their documented ability to polymerize in a living fashion with ruthenium catalysts under a variety of conditions.[30]



17



18

The polymerizations were allowed to run between 2 minutes to one hour. Afterwards, the wafers were again rinsed several times with dichloromethane, acetone, and ethanol, and were stored under nitrogen.

Surface characterization. A variety of analytical tools are currently available for the characterization of organic thin films on surfaces.[1] Contact angles are measured to evaluate wetting properties, uniformity, and surface-free energy. Ellipsometry is used to measure the thickness and uniformity of a prepared film. Fourier transform infrared spectroscopy (FTIR) can be used to learn about coverage, packing, and molecular orientation. However, none of these techniques is able to characterize films on the molecular level.

In recent decades, microscopy methods including scanning tunneling microscopy (STM), atomic force microscopy (AFM), and scanning electron microscopy (SEM) developed rapidly.[31] These methods are not only able to provide information on coverage and molecular orientation but are also able to probe individual arrangements of atoms and map the surface with sub-Angstrom accuracy (STM and AFM) using strongly distant

dependent currents (STM) or forces (AFM). These scanning probe techniques reveal surface structures in unprecedented detail, which is particularly useful for the elucidation of locations, disclinations, and defects on the surface.

Ellipsometry measurements of the functionalized surfaces after the two-step self-assembly process gave an average SAM thickness of 15-17Å. These values are consistent with those reported for a mixed SAM prepared of dodecanthiol and a stiff molecular wire molecule.[27] However, neither ellipsometry nor X-ray photoelectron spectroscopy (XPS) measurements on the polymer-functionalized wafers gave any conclusive data. The ellipsometry measurements yielded no reliable information on the thicknesses of the samples which can be explained by the different sizes of the polymerized material on the surface since ellipsometry averages over a relatively large area on the surface.

XPS experiments were carried out to determine the concentration of polymer-specific atoms, such as silicon (for polymers based on monomer **18**) or nitrogen (for polymers based on monomer **17**), on the surface. However, as a result of the relatively low concentration of the nitrogen and silicon atoms compared to the gold, carbon and silicon atoms of the mica and the overlap of the nitrogen and silicon signals with other signals, it was not possible to determine the exact concentration of the polymer on the surface. In the case of the silicon-containing polymer, several peaks characteristic of a silicon-containing species could be seen. However, it was not possible to establish if the peaks resulted from the silicone bound in the mica or from the silicon-containing polymer. As for the nitrogen-containing polymer, a small peak corresponding to nitrogen on the surface could be identified. However, the signal was too small to allow any conclusions.

Scanning tunneling microscopy measurements. In recent years, STM measurements have yielded molecular resolution images of both single and mixed composition SAMs.[27,31-33] In these studies, it was possible to determine the position of

individual molecules in the film and individual molecules have been differentiated. Therefore, this technique permits the characterization of a thin film on the molecular level.

To analyze the coverage of the surface with the functionalized lipid **16**, especially to ascertain whether the lipids are sufficiently separated to prevent the polymerization between initiating units, STM studies on the non-polymerized wafers were carried out in collaboration with Prof. Paul Weiss and his group at Penn State University. Figures 1 and 2 are representative images of a Au{111} surface covered by a dodecanethiol monolayer with inserted **16**. These images are characteristic of a large number of analyses taken on SAM films.

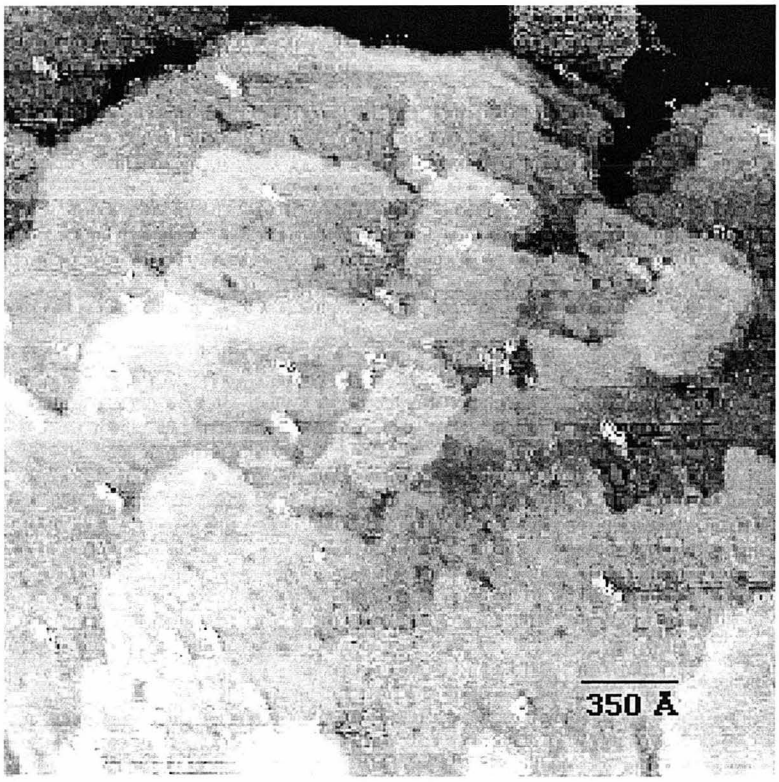


Figure 1. A constant-current STM topograph showing a 2000 Å x 2000 Å area of an Au{111} surface covered by a dodecanethiol monolayer with inserted **16** (tip bias = +1.0 V, tunneling current = 10 pA). The molecules of **16** appear as peaks in the topography (displayed as bright spots). **16** inserts at the structural domain boundaries in terraces of dodecanethiolate SAMs. The apparent average size of **16** on the surface in this image is 65 x 30 Å. Note that the features of **16** appear larger than their physical size because its protruding molecules image the tip structure as reported previously for single inserted molecules.[27]

Figure 1 shows a representative STM image of a 2000 Å x 2000 Å area of a mixed monolayer of dodecanethiol and **16** synthesized in two self-assembly steps. Pit defects and terrace domain boundaries in the films as well as gold terraces are clearly visible. Protruding several Angstroms from the film (6-7 Å) are features (displayed as bright spots) which were assigned as **16** and which are absent in pure dodecanethiol SAMs. It must be noted that these features appear broad because the protruding molecules image the tip structure as discussed in the literature.[27] The average size of the features ranges from 60 Å x 30 Å to 70 Å x 30Å. While the appearance of the feature is comparable when scanned with the same tip, the size and shape of the feature vary with the structure of different tips (Figure 2).

Figure 2. A constant-current STM topograph showing a 1000 Å x 1000 Å area of an Au{111} surface covered by a dodecanethiol monolayer with inserted **16** (tip bias = +1.0 V, tunneling current = 10 pA). Arrows point to the molecules of **16** which appear as peaks in the topography and are displayed as bright spots. Molecule **16** inserts at the structural domain boundaries in terraces of dodecanethiolate SAMs. The apparent average size of **16**

on the surface is 60 x 30 Å. Note that the features of **16** appear larger than their physical size because its protruding molecules image the tip structure as reported previously for single inserted molecules.[27]

Analyses of the images containing dodecanethiol and **16** clearly show that single inserted molecules of **16** are on average separated by several hundred Angstroms from each other. Therefore, no polymerization between initiating units is possible.

Figures 3 to 4 show representative constant-current STM images of mixed polymer/dodecanethiol monolayers. These images were obtained after exposure of the initiated functionalized monolayers to a solution of monomer in dichloromethane at room temperature for 2-20 minutes. The polymerizations were carried out in very dilute monomer solutions to yield only oligomers instead of long-chain polymers, as it was anticipated that longer polymer chains would prevent tunneling through the polymer.

In analogy to Figures 1 and 2, protrusions (displayed as bright spots) are visible. However, in contrast to Figures 1 and 2, the protrusions have different sizes. Several larger features are visible which were assigned as oligomers and polymer brushes on the surface. However, these features appear as non-uniform peaks. This can be explained by the polymer brushes being pushed on the surface by the microscope tip thereby making it impossible to determine their actual size. Furthermore, in some images smaller features are still visible which were attributed to non-initiated **16**.

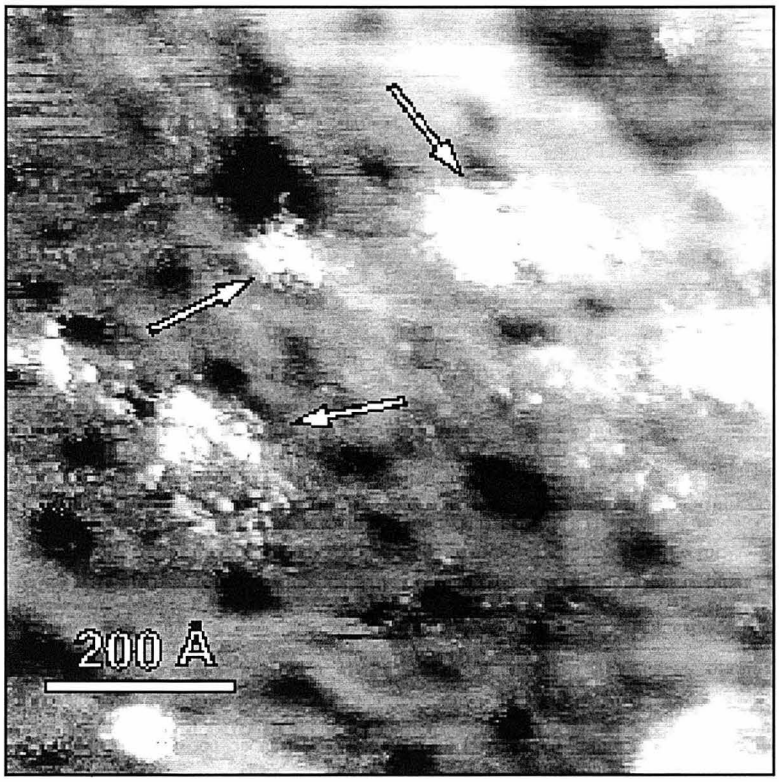


Figure 3. A constant-current STM topograph showing a 800 Å x 800 Å area on an Au{111} surface displaying multiple terraces covered by a dodecanethiol monolayer with inserted polymers after polymerization using **17** (tip bias = +1.0 V, tunneling current = 10 pA). Polymer brushes appear as non-uniform bright peaks in the topography. The polymers may be pushed on the surface by the microscope tip making it impossible to determine their actual sizes.

Figure 3 is a representative constant-current STM image of an 1000 Å x 1000 Å area of polymer brushes inserted into the dodecanethiol monolayer matrix. Again, the polymer brushes are located at both step edges and terrace domain boundaries. Most non-initiated molecules of **16** can be found at the domain boundaries within the terraces. This shows that the step edges are more open towards insertion of **16** and initiation of **1** and polymer propagation. Furthermore, since the defects are usually larger at the step edges than at the domain boundaries within the terraces, it is possible to insert molecular wire molecules into the dodecanethiol SAM next to each other, thus resulting in faster propagation and more polymer growth after initiation.

Figure 4 shows a molecular resolution constant current image of the crystalline order of the dodecanethiol monolayer and a polymer brush inserted into the dodecanethiol monolayer. The polymer brush is located at a step edge. However, the image shows some streaking of the polymer brushes in the scanning direction. This is noteworthy, since it is possible that larger polymers protrude significantly from the dodecanethiol monolayer and, as a result of their greatly reduced tunneling properties, interfere with the tip thus causing those streaks.

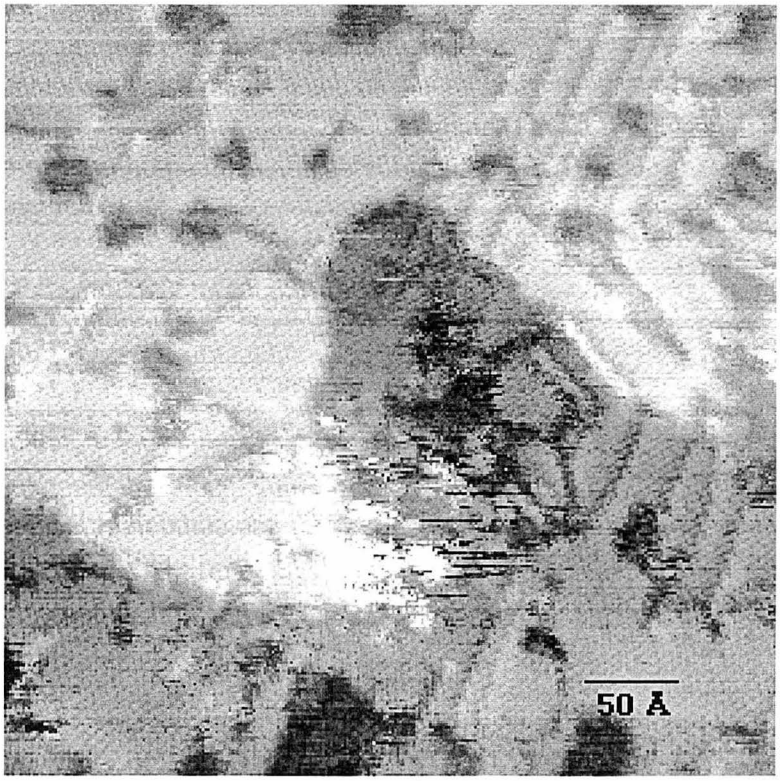


Figure 4. A constant-current STM topograph showing a 400 Å x 400 Å area on an Au{111} surface covered by a dodecanethiol monolayer with inserted polymer (tip bias = +1.0 V, tunneling current = 10 pA). The polymer appears as a non-uniform peak in the topography (displayed as bright spots).

These measurements clearly show that polymer propagation on the surface took place after initiation with catalyst **1** and addition of monomer. However, since large polymer brushes have greatly reduced tunneling properties, it was not possible to image larger polymers on the surface.

Atomic force microscopy measurements. To further investigate the nature of the surface polymerization, tapping mode AFM (TMAFM) was employed to image the polymer on the surface. While it was not possible to obtain molecular resolution images, this method, in contrast to STM, can be used for the morphological characterization of non-conductive films thus making the imaging of longer polymer chains on the surface possible.

Figures 5 and 6 are typical TMAFM images of the mixed monolayers containing dodecanethiol and **16** on the gold surface. In contrast to the STM images, no domain formation is obvious in these TMAFM images as a result of the low resolution of the AFM instrument. Furthermore, no obvious protrusions which could stem from the molecular wire molecule **16** are identifiable in these images.

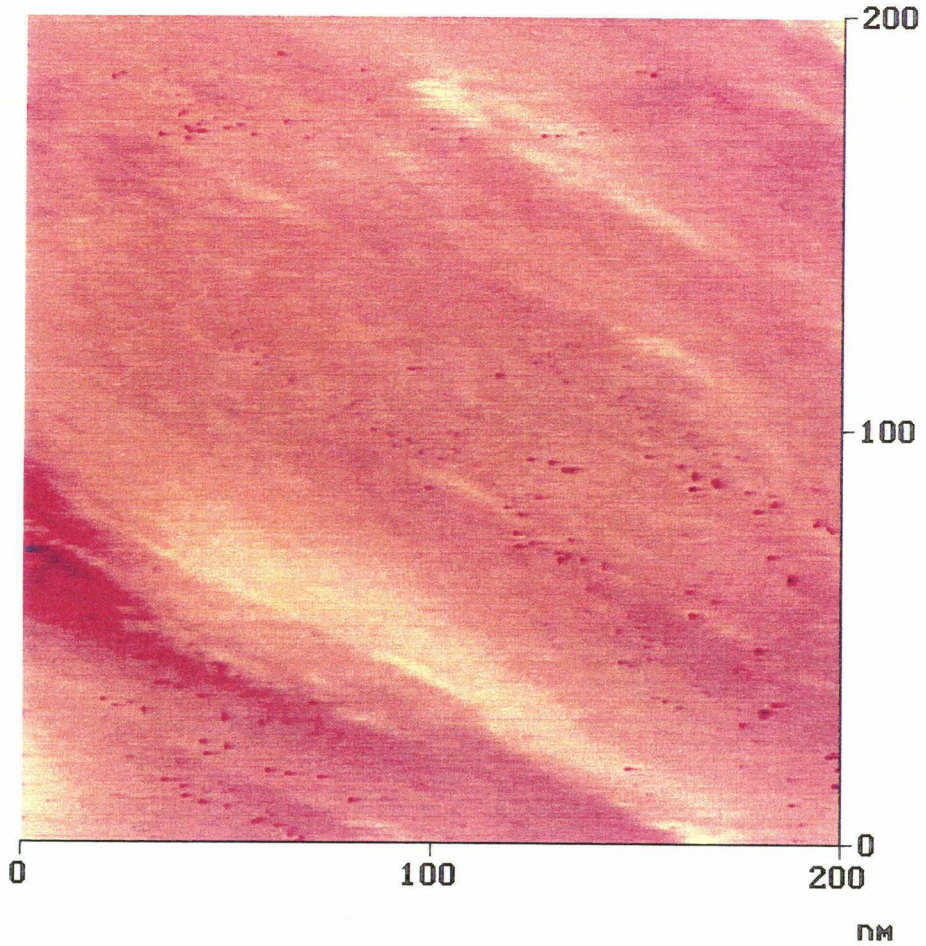


Figure 5. A 200 nm x 200 nm TMAFM image of a mixed monolayer of dodecanethiol and **16** on gold. The image was obtained at a 45° scan angle, a scan rate of 1 Hz, and a set point of 2.08 V (number of samples 256, integral gain = 0.106, proportional gain 2.00). A first-order planefit was applied to the image and several problematic scan lines were erased. In the image only small step edges and no protrusions can be identified.

Figure 6 is a three-dimensional presentation of the TMAFM image shown in Figure 5. This image clearly shows that there are no obvious protrusions on the surface. Although small features are visible on the surface it is not possible to assign them unambiguously to **16** since it is conceivable that they result from instrument distortions.

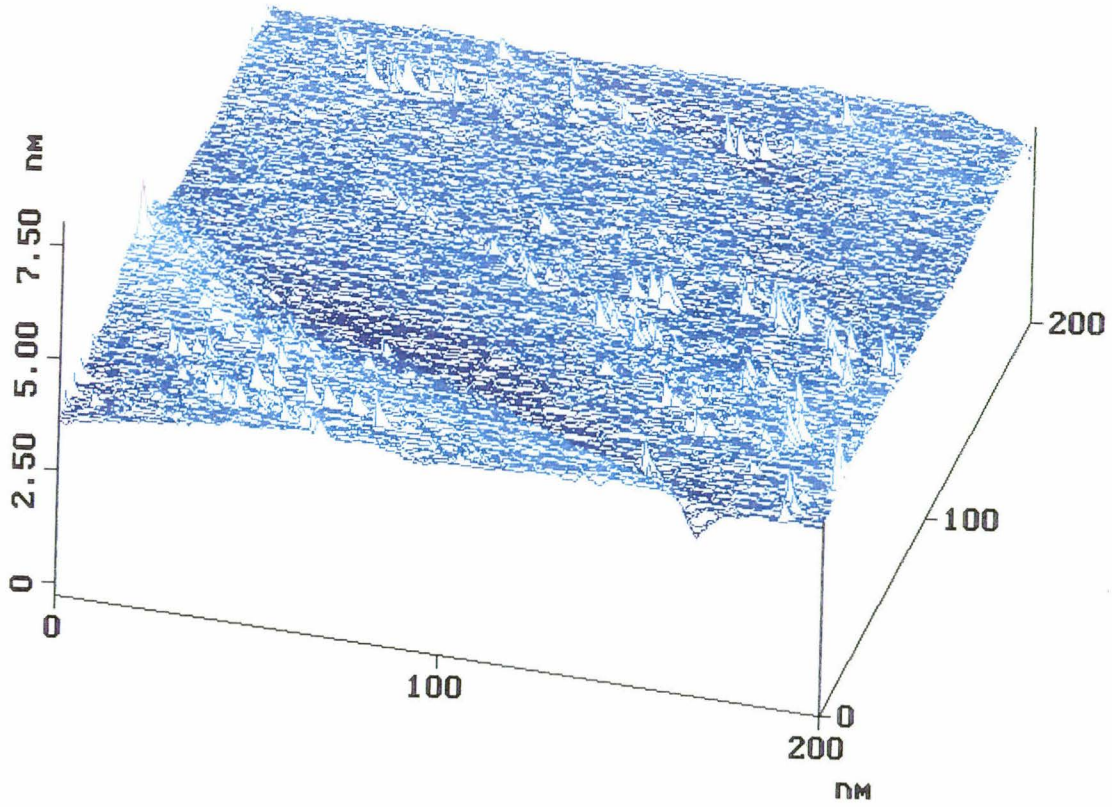


Figure 6. 3-Dimensional 200 nm x 200 nm x 8 nm presentation of the TMAFM image shown in Figure 5. The image was obtained at a 45° scan angle, a scan rate of 1 Hz, and a set point of 2.08 V (number of samples 256, integral gain = 0.106, proportional gain 2.00). A first-order planefit was applied to the image and several problematic scan lines were erased. In the image only small step edges and protrusions can be identified.

Figures 7 to 10 are images taken from samples after the mixed-monolayer functionalized surface was initiated with catalyst **1** followed by the addition of monomers **17** or **18**. In all three images a number of protrusions are visible which were assigned to polymer brushes on the surface.

Figure 7 shows a 200 nm x 200 nm area of a polymerized surface. Two different kinds of protrusions are clearly visible. One large polymer brush with extremely irregular size is shown in the middle part of the image, while a number of smaller features are visible around it. The larger polymer brush is located in a very large defect area in the monolayer.

In contrast, the smaller polymer brushes which are between 100 Å and 200 Å in size are located primarily in the boundary domains of the terraces.

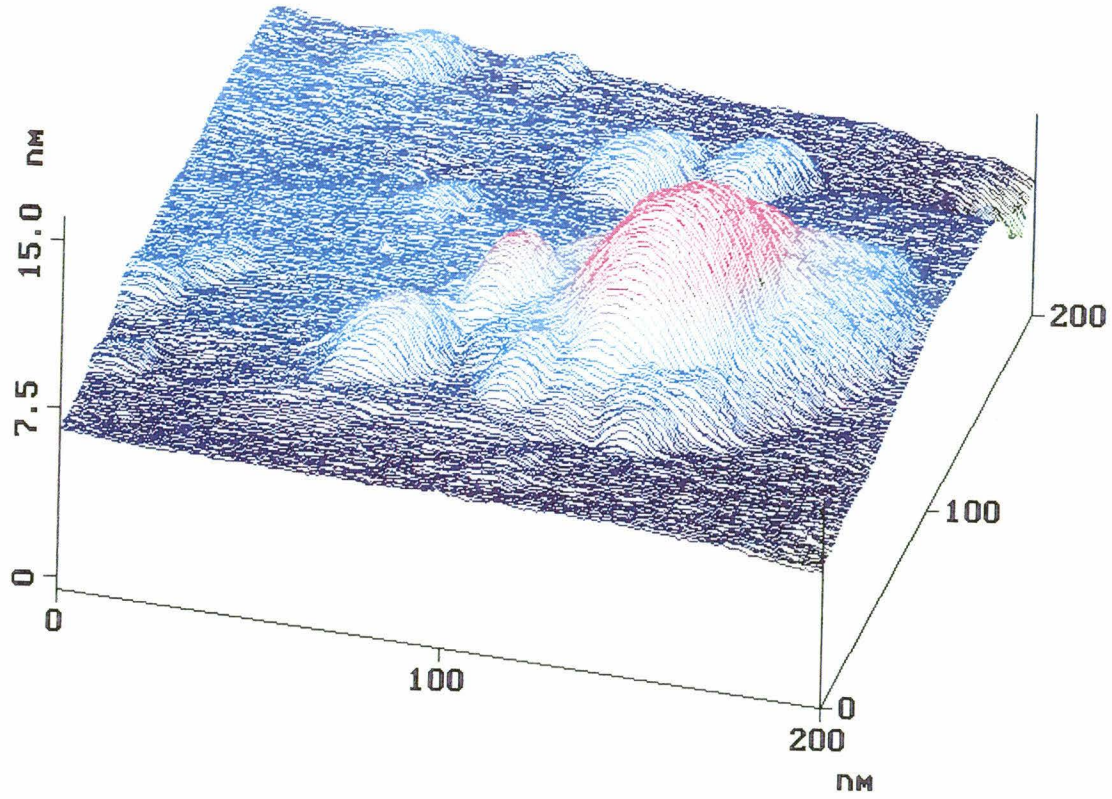


Figure 7. 3-Dimensional 200 nm x 200 nm x 18 nm AFM image of polymer brushes on gold. The image was obtained at a 60° scan angle, a scan rate of 0.803 Hz, and a set point of 2.08 (number of samples 512, integral gain = 0.131, proportional gain 2.74). The image was first order flattened before analysis. In contrast to Figures 5 and 6 a number of differently sized polymers are clearly visible.

Figure 8 shows a 200 nm x 200 nm image of another SAM after polymerization. In contrast to Figure 7, only smaller polymer brushes are visible. However, Figure 8, as well as Figure 9, clearly show the preferred insertion and polymerization along the step edges, since only a few polymer brushes are visible inside the boundary domains of the terraces compared to the relatively large number along the gold step edges. Again, this can be

explained by the larger defects of the monolayer along the step edges compared to the boundary domains of the terraces.

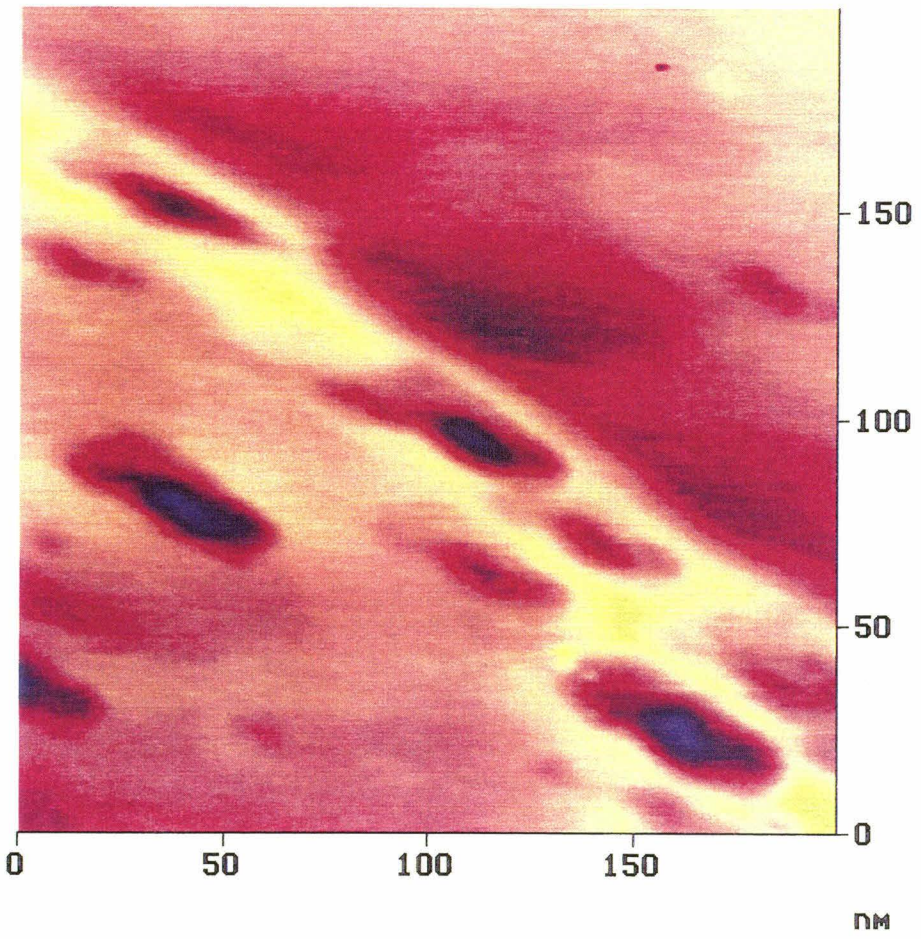


Figure 8. A 200 nm x 200 nm TMAFM image after polymerization using **17** on gold. The image was obtained at a 60° scan angle, a scan rate of 0.803 Hz, and a set point of 2.08 V (number of samples 512, integral gain = 0.131, proportional gain 2.74). A first-order planefit was applied to the image and several problematic scan lines were erased. In contrast to Figures 7 only one type of protrusions is visible.

Figure 9 is a three-dimensional presentation of the image shown in Figure 8. This image clearly shows the preferred insertion and polymerization along the step edges.

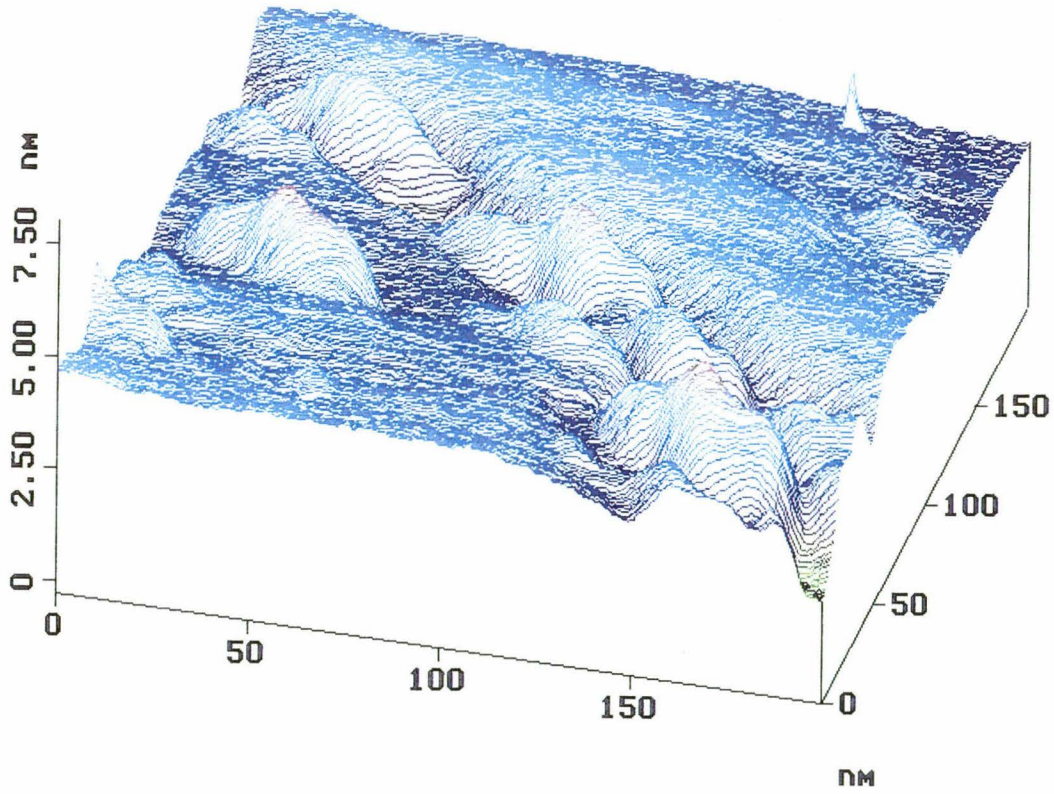


Figure 9. Three-dimensional 200 nm x 200 nm x 8 nm TMAFM image after polymerization using **17** on gold. The image was obtained at a 60° scan angle, a scan rate of 0.803 Hz, and a set point of 2.08 V (number of samples 512, integral gain = 0.131, proportional gain 2.74). A first-order planefit was applied to the image and several problematic scan lines were erased. In contrast to Figures 7 only one kind of protrusions is visible.

These AFM images support the STM results, which indicated that a polymerization took place after immersion of the mixed monolayer-functionalized surfaces into a catalyst solution of **1** followed by their treatment with monomers **17** and **18**. To obtain further proof of the surface polymerization several wafers were characterized by SEM.

Scanning electron microscopy measurements. SEM has been widely used for the visualization of organic surfaces, especially for the study of surface morphology, domains, pinholes, defects, and patterns. Therefore, it is likely that only SEM pictures of larger polymer brushes can be taken.

Figures 10 to 12 are SEM images of mixed monolayer-functionalized wafers after polymerization using monomers **17** or **18**. In all three cases, several polymer brushes (they are displayed in white or as protrusions), pitholes, as well as gold terraces can be seen on the surface. The polymer brushes visible by SEM are separated by large distances which can be explained by the very low resolution of the SEM in comparison to the AFM, and, even more so, the STM. It is likely that the large polymer brushes in these figures are the same as the very large protrusions visible in the AFM image of Figure 7.

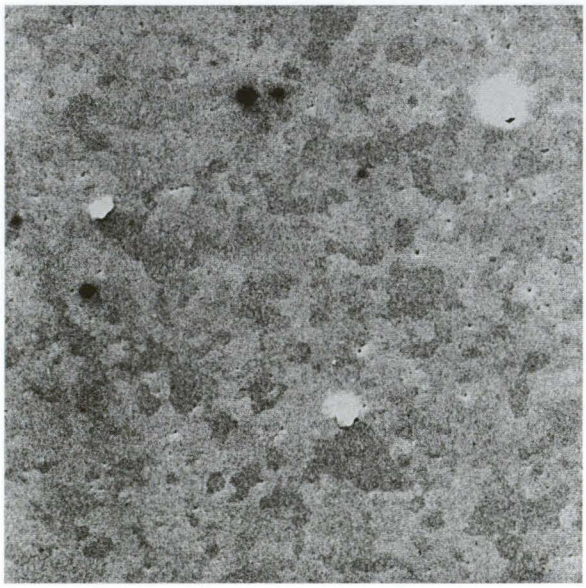


Figure 10. SEM picture of a polymerized surface (magnification 4 x 10^3). The picture was taken at a 90° angle.

Figure 11 is the only SEM picture taken from a 90° angle, which not only shows large polymer brushes but also smaller white features which could be assigned as smaller polymer brushes in the monolayer matrix. It is also possible to identify the large defect in the mixed monolayer into which the large polymer brush (several 1000 Angstroms in size) is inserted. As discussed above, it is very likely that several molecular-wire type molecules

inserted into this large defect, therefore resulting in strong polymer growth after initiation and addition of monomer.

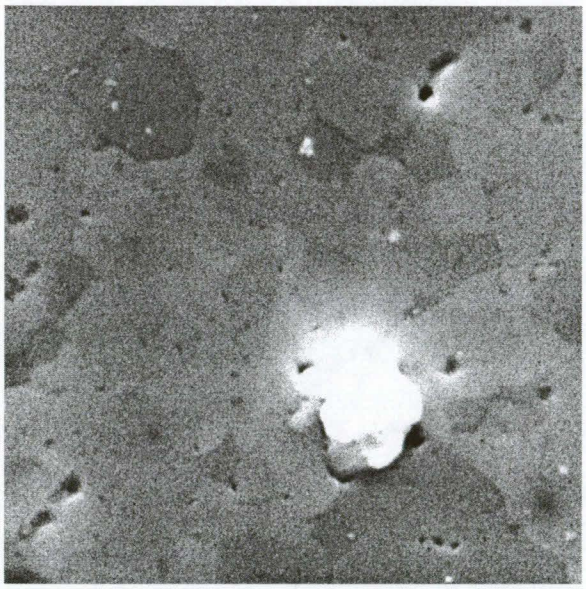


Figure 11. The same SEM picture of the polymerized surface as shown in Figure 10, although in a significantly higher magnification (3×10^4). The picture was taken at a 90° angle.

Figure 12 is an SEM picture taken from a 60° angle. In this picture the heights of the polymer brushes are clearly visible. Like in Figure 11, the identification of smaller polymer brushes is possible.

Figure 12. SEM picture of a polymerized surface (magnification 3 x 10^3). In contrast to Figures 10 and 11, this picture was taken at a 60° angle.

Results from all three microscopy measurements show that a ring-opening metathesis polymerization occurred after treatment of the mixed monolayer-functionalized surfaces with catalyst **1** and the addition of monomer. Although STM results show small polymer brushes of up to 110 Å in diameter, AFM and SEM results show that more highly-polymerized features exist on the surface as well.

Conclusion

Two strategies for ROMP from surfaces based on alkylthiolates on gold have been investigated. The first strategy was based on the covalent attachment of an olefin metathesis catalyst to a gold surface. For this approach, a ruthenium catalyst containing a thiol which is able to self-assemble on gold surfaces was synthesized. However, it was not possible to purify the catalyst from the excess starting material, and it started to decompose after several hours.

The second strategy was based on the attachment of a cyclic olefin to a gold surface. This cyclic olefin can be initiated by an olefin metathesis catalyst to propagate

polymerization upon addition of monomer. Two different kinds of anchor molecules containing a norbornene-functionality on the one end and a thiol on the other were synthesized. A norbornene-functionalized molecule based on a flexible alkyl-chain did not initiate polymerization efficiently. A possible explanation could be that as a result of its flexibility the norbornene functionality could fall into the monolayer matrix thereby preventing initiation.

To eliminate this problem, a stiff molecular wire molecule was synthesized through repeated palladium-catalyzed coupling reactions. This molecule has the advantage of being longer than the surrounding monolayer matrix and can therefore be easily imaged by STM due to its conjugation.

Using a two-step self-assembly approach, the gold surfaces were functionalized with a dodecanethiol monolayer followed by single insertion of the molecular wire into defects in the dodecanethiol SAM. The mixed-functionalized monolayers were characterized by ellipsometry and STM, showing that the molecular wire molecules were inserted along the gold step edges and in the domain boundaries of the terraces.

Addition of catalyst to the mixed-functionalized surfaces followed by addition of monomer resulted in polymerization from the surface. The polymerized surfaces were characterized by STM, AFM, and SEM. While STM only imaged smaller polymer brushes on the surface as a result of the poor tunneling properties of larger polymers, AFM and SEM images showed two different kinds of polymer brushes on the surface. While in most cases only smaller polymer brushes with sizes of several hundred Angstroms were identified, the polymerization did in fact also result in very large polymer brushes with diameters of several thousand Angstroms which exist only in very large defects on the surface.

This is the first successful ring-opening metathesis polymerization from surfaces. Investigations are currently under way to prove the living character of the polymerization

by synthesizing **16**-functionalized gold-nanoclusters and observing any carbene species during initiation and propagation.

Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4Å molecular sieves (Linde). NMR spectra were recorded on a GE QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane and referenced to residual protio solvent. Coupling constants are reported in Hertz (Hz). IR spectra for the characterization of the samples were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. GPC analyses in dichloromethane were obtained on a HPLC system utilizing an Altex Model 110A pump, a Rheodyne model 7125 injector with a 100μl injection loop, through two American Polymer Standards 10 micron mixed bed columns, and a Knauer differential-refractometer. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. Elemental analyses were performed by Fenton Harvey at the California Institute of Technology Elemental Analysis Facility.

Surface Sample Preparation. Substrates for STM and AFM studies were prepared by resistive evaporation of gold (99.999%) onto the surface of freshly cleaved mica which was preheated to 380°C in a vacuum. The base pressure in the chamber during evaporation was maintained at $\leq 2 \times 10^{-7}$ Torr. After 120 nm of gold were deposited at a rate of 0.1 nm/s, the substrate temperature was cooled down to <30°C while still under vacuum.

Scanning Tunneling Microscopy. The STM images were recorded using two different beetle-style scanning tunneling microscopes.[35] Both microscopes are housed in chambers that were purged with dry N_2 or argon gas to minimize air exposure and to

eliminate capillary condensation. All the samples studied were sufficiently conductive to permit the use of a DC tunneling current to control the tip-sample separation. All images were recorded at large tunneling gap impedances, 10^{11} Ω or higher, to reduce perturbations to the monolayers caused by imaging. Such high impedance measurements have recently been shown to open the possibility of imaging lattices of the shorter chain alkylthiolate monolayers.[33] Controlled geometry Pt/Ir STM tips were used as the scanning probes.[34] All images were recorded in constant tunneling current mode. STM piezoelectric scanner calibrations were performed by recording atomic resolution images of surfaces of known crystallography. One of the microscopes was a microwave frequency alternating current STM (ACSTM), the design and operation of which have been previously described.[27,35]

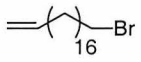
Atomic Force Microscopy. The AFM system used in this chapter was a commercially available NanoScope III Multimode AFM using TESP probes (Digital Instrument, Inc., Santa Barbara, CA). The measurements were performed in air at room temperature. The tapping mode oscillation amplitude was set to 3 V (near the tip's resonance frequency of 312 kHz) before moving near the surface, and the oscillation setpoint used for imaging was around 2 V. All images were taken at scan rates between 1.50 - 0.50 Hz and were processed using a 'plane fit' or 'flatten' program in Nanoscope III.

Scanning Electron Microscopy. The SEM pictures were obtained on an ETEC Autoscan equipped with a Zeiss camera.

Materials. Dichloromethane was destilled from calcium hydride and degassed by repeated freeze-pump-thaw cycles. All other solvents were used without further purification unless otherwise noted. All chemicals besides 1-undecanebromide were

purchased from the Aldrich Chemical Company and used without further purification. The ruthenium complex **1** was graciously provided by Dr. Peter Schwab.

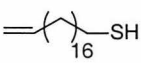
Synthesis of 19-bromo-1-nonadecene (2):



11-bromo-1-undecene (0.95 g, mol) was added dropwise to a solution of magnesium (1.15 g) in 100 mL tetrahydrofuran containing a catalytic amount of I_2. The solution was stirred for 12 hours until 95% of the magnesium had reacted. Then 85 mL of this solution was added to a mixture of 1,8-dibromooctane (11 mL, 16.3 g, 60 mmol) and 0.1M Li_2CuCl_4 (5 mL) in 50mL tetrahydrofuran at 0°C over a period of 6 hours. After stirring the solution for an additional 90 minutes at 0°C it was slowly warmed up to room temperature, quenched with 75 mL saturated ammonium chloride solution, and allowed to stand for 12 hours to let the copper salt pass into the aqueous layer. The clear organic layer was decantated and the aqueous layer extracted with ether several times. The organic fractions were combined, washed three times with brine and dried over magnesium sulfate. The solvent was removed *in vacuo*. Final purification was achieved by distillation (0.09 Torr, 145°C) to afford 19-bromo-1-nonadecene as a clear liquid in 40% (8.2 g).

^{1}H-NMR ($CDCl_3$) δ 5.79 (m, 1H), 4.93 (m, 2H), 3.37 (t, 2H, J = 7.5 Hz), 2.01 (m, 2H), 1.82 (m, 2H), 1.36 (m, 2H), 1.24 (bs, 28H). ^{13}C-NMR ($CDCl_3$) δ 138.9, 113.8, 33.6, 32.6, 29.5, 29.4, 29.3, 29.0, 28.8, 28.6, 28.0.

Synthesis of 18-nonadecene-1-thiol (3):

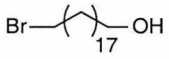


Sodium (500 mg) was dissolved in 80 mL degassed methanol. Thiolacetic acid (1.72 mL, 24 mmol) and **2** (3.28 g, 10 mmol) were added and the reaction stirred under reflux under

argon for 2 hours. Then sodium methoxide (1 g) was added and reflux continued for 1 hour. The reaction mixture was quenched with a degassed, half saturated ammonium chloride solution (200 mL) and dichloromethane (80 mL). The aqueous phase was extracted several times with dichloromethane and the combined organic phases were washed with water and dried over magnesium sulfate. Removal of the solvent *in vacuo* and flash column chromatography using hexane as eluant yielded 18-nonadecane-1-thiol as a colorless liquid (1.93 g, 68%).

^{1}H-NMR ($CDCl_3$) δ 5.79 (m, 1H), 4.93 (m, 2H), 2.48 (q, 2H, J = 10.8 Hz), 2.0 (q, 2H, J = 9.6 Hz), 1.57 (m, 2H), 1.23 (bs, 28H); ^{13}C-NMR ($CDCl_3$) δ 139.2, 114.1, 34.2, 34.0, 29.8, 29.7, 29.3, 29.2, 29.1, 28.5, 24.7; IR (thin film on NaCl plate) 3077, 2998, 2914, 2858, 2683, 1821, 1641, 1468, 1439, 1415, 1370, 1352, 1257, 993, 909, 802, 722, 647, 565 cm^{-1}; Anal. calcd. for $C_{19}H_{38}S$: C, 76.43; H, 12.83, found: C, 76.86; H, 13.01; HRMS (FAB) calcd. for $C_{19}H_{38}S$ $(MH)^+$ 297.2620, found 297.2620.

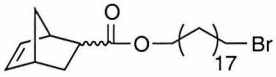
Synthesis of 19-bromo-1-nonadecanol (5):



Disiamylborate was produced by addition of 2M 2-methyl-2-butene (18 mL) in tetrahydrofuran to 18 mL of 1M BH_3•THF at 0°C. The solution was slowly warmed up to room temperature and after 30 minutes cooled back to 0°C. Then 19-bromo-1-nonadecene (**2**) was added dropwise. The solution was stirred at 0°C for 15 minutes followed by the addition of 1N sodium hydroxide (6 mL) and 30% hydrogen peroxide (6 mL). The solution was allowed to warm up to room temperature and stirred for an additional 30 minutes. The reaction was extracted several times with dichloromethane. The organic phase was washed with water and dried over magnesium sulfate. Removal of the solvent *in vacuo* and flash column chromatography using hexane/ethyl acetate (3:1) as eluant yielded 19-bromo-1-nonadecanol as white needles (3.05 g, 56%).

^{1}H-NMR ($CDCl_3$) δ 3.62 (t, 2H, J = 6.6 Hz), 3.39 (t, 2H, J = 6.9 Hz), 1.83 (m, 2H), 1.53 (m, 2H), 1.39 (m, 2H), 1.23 (bs, 28H); ^{13}C-NMR ($CDCl_3$) δ 70.9, 62.9, 33.8, 32.6, 29.4, 29.3, 29.2, 28.5, 27.9, 25.5; IR (thin film on NaCl plate) 3444, 2917, 2848, 1639, 1470, 1057, 718, 647 cm^{-1}; Anal. calcd. for $C_{19}H_{39}BrO$: C, 62.97; H, 10.82, found: C, 62.62; H, 10.50; HRMS (FAB) calcd. for $C_{19}H_{39}BrO$ $(MH)^+$ 362.2183, found 362.2152.

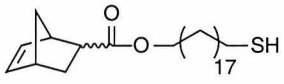
Synthesis of 5-{n-[-19-bromo-nonadecane]carbonyl}-bicyclo-[2.2.1]hept-2-ene (6):



Norborn-2-ene-5-carbonyl-chloride (0.5 g, 0.0032 mol) in tetrahydrofuran (50 mL) was added dropwise to a solution of **5** (1.2 g, 0.003 mol) and triethylamine (0.3 g) in dry tetrahydrofuran (20 mL). The resulting solution was stirred under argon under reflux for 18 hours during which a white solid formed. The mixture was filtered, dried over magnesium sulfate and the solvent removed *in vacuo*. Final purification was achieved by column chromatography (silica gel/CH_2Cl_2) to yield 0.9 g of a white crystalline solid (63%).

^{1}H-NMR ($CDCl_3$) δ 6.17 (d of d, 1H, J = 2.7 Hz), 5.90 (d of d, 1H, J = 2.7 Hz), 3.99 (m, 4H), 3.39 (t, 2H, J = 6.9 Hz), 3.18 (m, 1H), 2.98-2.87 (m, 2H), 1.83 (m, 2H), 1.56 (m, 2H), 1.39 (m, 2H), 1.23 (bs, 30H); ^{13}C-NMR ($CDCl_3$) δ 137.5, 132.1, 64.1, 49.4, 45.5, 43.1, 42.3, 33.8, 32.6, 29.4, 29.3, 29.2, 29.0, 28.9, 28.5, 28.4, 27.9, 25.7; IR (thin film on NaCl plate) 2917, 2849, 1727, 1472, 1393, 1272, 1232, 1174, 1111, 1062, 1024, 941, 918, 838, 779, 718, 642 cm^{-1}; Anal. calcd. for $C_{27}H_{47}BrO_2$: C, 67.06; H, 9.80, found: C, 67.53; H, 9.81; HRMS (FAB) calcd. for $C_{27}H_{47}BrO_2$ $(MH)^+$ 482.2759, found 482.2792.

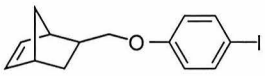
Synthesis of 5-{n-[-19-mercapto-nonadecane]carbonyl}-bicyclo-[2.2.1]hept-2-ene (7):



Sodium (43 mg) was dissolved in dry methanol (25 mL). After the sodium was completely dissolved, thiolacetic acid (0.134 mL, 0.0019 mol) and **6** (530 mg, 0.0011 mol) were added and the mixture was stirred under argon under reflux for 2.5 hours. The reaction was cooled down to 0°C and acetyl chloride (2 mL) was added to generate anhydrous hydrochloric acid *in situ*. The reaction was refluxed for an additional 15 minutes during which a white solid precipitated. After cooling down, water was added to dissolve all salts. The reaction was filtered, the precipitate washed with methanol and dried. Final purification was achieved by recrystallization from hexane to yield **7** as a white crystalline solid (320 mg, 66%).

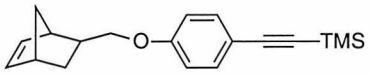
^{1}H-NMR ($CDCl_3$) δ 6.17 (d of d, 1H, J = 2.7 Hz), 5.90 (d of d, 1H, J = 2.7 Hz), 3.99 (m, 4H), 3.62 (t, 2H, J = 6.6 Hz), 3.18 (m, 1H), 2.98-2.87 (m, 2H), 2.47 (t, 2H, J = 7.2 Hz), 1.83 (m, 2H), 1.55 (m, 2H), 1.39 (m, 2H), 1.23 (bs, 28H); ^{13}C-NMR ($CDCl_3$) δ 137.5, 132.1, 64.1, 49.4, 45.5, 43.1, 42.3, 32.0, 29.5, 29.3, 29.0, 28.9, 28.8, 28.5, 25.7; IR (thin film on NaCl plate) 3425, 2918, 2850, 1731, 1644, 1472, 1463, 1390, 1272, 1238, 1188, 1111, 1067, 1025, 911, 731, 720 cm^{-1}; Anal. calcd. for $C_{27}H_{48}SO_2$: C, 74.25; H, 11.09, found: C, 73.45; H, 11.14; HRMS (FAB) calcd. for $C_{27}H_{48}SO_2$ $(MH)^+$ 436.3375, found 436.3302.

Synthesis of 5-{4-[-1-iodo-benzene]methyl-ether}-bicyclo-[2.2.1]hept-2-ene (8):



DEAD (3.58 mL, 3.96 g, 0.0227 mol) in dry tetrahydrofuran (50 mL) was added dropwise to a mixture of 4-iodophenol (5 g, 0.0227 mol), norbornene-2-ene-5-methanol (2.82 g, 0.0227 mol) and triphenyl phosphine (7.14 g, 0.02724 mol) in 150 mL tetrahydrofuran under argon at 0°C. The reaction was slowly heated up to room temperature and stirred for an additional 12 hours. The mixture was then poured into water and extracted several times with ether. The combined organic phases were washed with water, saturated brine solution and again with water and dried over magnesium sulfate to yield a brown liquid after removal of the solvent. Final purification was achieved by silica gel column chromatography using hexane/ethyl acetate (98:2) to yield 4.68 g of a clear liquid (66%). ^{1}H-NMR ($CDCl_3$) δ 7.52 (m, 2H), 6.65 (M, 2H), 6.15 (exo, d of d, 1H, J = 3 Hz), 6.09 (endo, m, 2H), 5.91 (exo, d of d, 1H, J = 3 Hz), 3.96 (endo, m, 1H), 3.77 (endo, t, 1H, J = 9 Hz), 3.63 (exo, m, 1H), 3.47 (exo, t, 1H, J = 9.3 Hz), 2.99 (endo, bs, 2H), 2.83 (exo, bs, 2H), 2.52 (m, 2H), 1.88 (m, 2H), 1.47-1.17 (m, 6H), 0.59 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 159.6, 138.8, 138.7, 138.2, 137.5, 137.0, 83.1, 83.0, 72.9, 72.1, 50.0, 45.6, 44.4, 44.3, 42.8, 39.1, 38.8, 30.2, 29.6; IR (thin film on NaCl plate) 2966, 2866, 1646, 1586, 1486, 1466, 1282, 1241, 1174, 1021, 999, 818, 721 cm^{-1}; Anal. calcd. for $C_{14}H_{15}IO$: C, 51.55; H, 4.64, found: C, 51.67; H, 4.60; HRMS (FAB) calcd. for $C_{14}H_{15}IO$ $(MH)^+$ 326.0169, found 326.0166.

Synthesis of 5-{1-[-4(2'-(trimethylsilyl)ethynyl)benzene]methyl-ether}-bicyclo-[2.2.1]hept-2-ene (9):

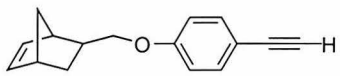


To a stirring solution of 5-{4-[-1-iodo-benzene]methyl-ether}-bicyclo-[2.2.1]hept-2-ene (2.1 g, 0.00644 mol), bis(dibenzylideneacetone)palladium (0) or bis(triphenylphosphino)-palladium(2)chloride (2 mol%), triphenylphosphino (2.5 equivalents based on Pd) and copper(I)iodide (2 mol%) in tetrahydrofuran trimethylsilyl acetylene (1.3 mL, 0.86 g, 0.0083 mol) and dry triethyl amine (7 mL) were added at room temperature under argon. The reaction was stirred under nitrogen for 24 hours. The reaction mixture was subject to an aqueous work-up and the aqueous layer was extracted several times with ether. The combined organic phases were washed with water, dried over magnesium sulfate and the solvent was removed *in vacuo*. Final purification was achieved using column chromatography on silica gel (hexane/ethyl acetate (98:2)) to yield a slightly yellow liquid in 79% yield (1.505 g).

^{1}H-NMR ($CDCl_3$) δ 7.37 (m, 2H), 6.77 (M, 2H), 6.15 (exo, d of d, 1H, J = 2.7 Hz), 6.09 (endo, m, 2H), 5.92 (exo, d of d, 1H, J = 2.7 Hz), 3.99 (endo, m, 1H), 3.80 (endo, t, 1H, J = 9 Hz), 3.67 (exo, m, 1H), 3.51 (exo, t, 1H, J = 9 Hz), 3.00 (endo, bs, 2H), 2.83 (exo, bs, 2H), 2.53 (m, 2H), 1.89 (m, 2H), 1.47-1.17 (m, 6H), 0.59 (m, 1H), 0.21 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 159.9, 138.2, 137.4, 137.0, 134.0, 132.9, 115.5, 114.9, 105.9, 92.8, 72.9, 72.1, 50.0, 45.6, 44.4, 44.3, 42.8, 42.1, 39.1, 38.9, 30.2, 29.6, 0.7; IR (thin film on NaCl plate) 3059, 2961, 2869, 2156, 1606, 1569, 1507, 1468, 1409, 1390, 1347, 1304, 1287, 1248, 1170, 1108, 1024, 932, 866, 841, 780, 760, 722, 636, 589, 541 cm^{-1}; Anal. calcd. for $C_{19}H_{24}SiO$: C, 76.99; H, 8.17, found: C, 76.67; H, 8.02; HRMS (FAB) calcd. for $C_{19}H_{24}SiO$ $(MH)^+$ 296.1596, found 296.1601.

General Procedure for the Deprotection of Silylated Alkynes. (a) The silylated alkynes were dissolved in pyridine (0.5M) in a plastic container. A pre-formed solution of concentrated hydrofluric acid (1.1 eq.) in tetrabutylammonium fluoride (2.2 eq., 1.0M in tetrahydrofuren) was added at room temperature and allowed to stir for 15 to 30 minutes before being quenched with silica gel. The reaction mixture was then subject to an aqueous work-up and the aqueous layer was extracted several times with ether. After drying the combined organic layers with magnesium sulfate, the solvent was removed *in vacuo*. The crude product was then fast purified by column chromatography (silica gel) yielding the free alkyne which was immediately taken to the next step. (b) The silylated alkyne was dissolved in methanol, and in some cases, methanol and dichloromethane. Potassium carbonate (2 equivalents) was added and the reaction was stirred overnight. The reaction mixture was subject to an aqueous work-up and the aqueous layer was extracted several times with ether. After drying the combined organic layers over magnesium sulfate, the solvent was removed *in vacuo*. The crude product was fast purified by column chromatography (silica gel) yielding the free alkyne which was immediately taken to the next step.

Synthesis of 5-{1-[-4-ethynyl-benzene]methyl-ether}-bicyclo-[2.2.1]hept-2-ene (10):

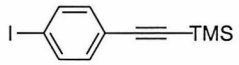


10 was synthesized in analogy to above (method b) from 5-{1-[-4(2'-(trimethylsilyl)ethynyl)benzene]methyl-ether}-bicyclo-[2.2.1]hept-2-ene (1.1 g, 0.0037 mol) to yield 830 mg (100%) of the title compound as a yellow liquid.

^{1}H-NMR ($CDCl_3$) δ 7.40 (m, 2H), 6.78 (M, 2H), 6.15 (exo, d of d, 1H, J = 2.7 Hz), 6.09 (endo, m, 2H), 5.93 (exo, d of d, 1H, J = 2.7 Hz), 4.00 (endo, m, 1H), 3.81 (endo, t, 1H, J = 9 Hz), 3.68 (exo, m, 1H), 3.52 (exo, t, 1H, J = 9 Hz), 3.00 (endo, bs, 2H),

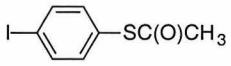
2.99 (endo, s, 1H), 2.98 (exo, s, 1H), 2.84 (exo, bs, 2H), 2.53 (m, 2H), 1.89 (m, 2H), 1.48-1.17 (m, 6H), 0.59 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 160.1, 138.2, 137.4, 137.0, 134.1, 132.9, 115.5, 84.3, 76.2, 72.9, 72.1, 50.0, 45.6, 44.5, 44.3, 42.8, 42.2, 39.1, 38.9, 30.2, 29.6.

Synthesis of 1-iodo-4-(2'-(trimethylsilyl)ethynyl)benzene (11):



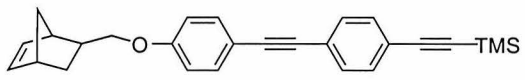
To a stirring solution of diiodobenzene (5 g, 0.015 mol), bis(dibenzylideneacetone)-palladium (0) or bis(triphenylphosphino)-palladium(2)chloride (2 mol%), triphenyl-phosphino (2.5 equivalents based on Pd) and copper(I)iodide (2 mol%) in toluene trimethylsilyl acetylene (2.2 mL, 1.5 g, 0.0145 mol) and dry triethyl amine (15 mL) were added dropwise at room temperature under argon. The solution was stirred for 24 hours under argon at room temperature. The reaction was then subject to an aqueous work-up. The aqueous layer was extracted several times with ether. Then the combined organic layers were washed with water, brine and again with water, dried over magnesium sulfate followed by removal of the solvent *in vacuo*. Final purification was achieved by silica gel column chromatography using hexane as eluent to yield 1.8 g (40%) of a white solid. ^{1}H-NMR ($CDCl_3$) δ 7.61 (d, 2H, J = 8.7 Hz), 7.16 (d, 2H, J = 8.4 Hz), 0.22 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 137.1, 133.1, 122.4, 103.7, 95.6, 94.1, 0.4; Anal. calcd. for $C_{11}H_{13}IO$: C, 44.04; H, 4.37, found: C, 43.85; H, 4.27; HRMS (FAB) calcd. for $C_{11}H_{13}IO$ $(MH)^+$ 299.9833, found 299.9817.

Synthesis of 1-iodo-4-(thioacetyl)benzene (12):



1,4-Diiodobenzene (9.9 g, 30 mmol) in tetrahydrofuran (30 mL) in a 100 mL 3-neck round bottom flask equipped with a mechanical stirrer and an argon inlet and*t*-butyllithium (30.10 mL, 59 mmol, 1.96M in hexanes) were added at -78°C over 39 minutes. The milky-green mixture was allowed to stir for 30 minutes before powdered sulfur (1,15 g, 36 mmol) was added in one portion. After stirring for an additional 30 minutes, the temperature was allowed to rise to 0°C for 10 minutes, then to recool to -78°C, and acetyl chloride (3.2 mL, 45 mmol) was added dropwise. The mixture was then warmed up to room temperature over 1 hour and poured into water (25 mL). The aqueous layer was extracted several times with ether, and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (hexane/ether (24:1)) to afford 2.6 g (32%) of the title compound as a clear liquid which solidified upon standing into a white flaky solid.
^{1}H-NMR ($CDCl_3$) δ 7.70 (d, 2H, *J* = 8.1 Hz), 7.10 (d, 2H, *J* = 8.1 Hz), 2.38 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 193.4, 138.5, 136.1, 127.8, 102.6, 30.4; Anal. calcd. for C_8H_7IOS: C, 34.54; H, 2.54, found: C, 34.83; H, 2.58; HRMS (FAB) calcd. for C_8H_7IOS $(MH)^+$ 299.9833, found 299.9817.

Synthesis of 5-{1-[-4-(Phenylethynyl-[2'-(trimethylsilyl)])benzene]methyl-ether}-bicyclo-[2.2.1]hept-2-ene (13):

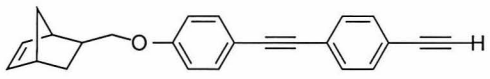


To a stirring solution of 5-{1-[-4-ethynyl-benzene]methyl-ether}-bicyclo-[2.2.1]hept-2-ene (0.83 g, 37 mmol), bis(dibenzylideneacetone)palladium (0) or bis(triphenylphosphino)-palladium(2)chloride (2 mol%), triphenylphosphino (2.5 equivalents based on Pd) and

copper(I)iodide (2 mol%) in tetrahydrofuran 1-iodo-4-(2'-(trimethylsilyl)ethynyl)benzene (1.11 g, 37 mmol) and dry triethyl amine (10 mL) were added at room temperature under argon. The reaction was stirred under nitrogen for 24 hours. The reaction mixture was subject to an aqueous work-up and the aqueous layer was extracted several times with ether. The combined organic phases were washed with water, dried over magnesium sulfate and the solvent was removed *in vacuo*. Final purification was achieved using column chromatography on silica gel (hexane/ethyl acetate (98:2)) to yield a white solid in 45% yield (0.65 g).

^{1}H-NMR ($CDCl_3$) δ 7.43 (m, 6H), 6.83 (M, 2H), 6.17 (exo, d of d, 1H, J = 3 Hz), 6.09 (endo, m, 2H), 5.95 (exo, d of d, 1H, J = 3 Hz), 4.00 (endo, m, 1H), 3.82 (endo, t, 1H, J = 9 Hz), 3.69 (exo, m, 1H), 3.53 (exo, t, 1H, J = 9 Hz), 3.03 (endo, bs, 2H), 2.85 (exo, bs, 2H), 2.56 (m, 2H), 1.91 (m, 2H), 1.47-1.17 (m, 6H), 0.59 (m, 1H), 0.26 (s, 9H); ^{13}C-NMR ($CDCl_3$) δ 159.9, 138.2, 137.5, 137.2, 133.6, 132.9, 132.5, 131.8, 124.4, 123.0, 115.3, 115.2, 105.4, 96.6, 92.2, 88.3, 72.9, 72.1, 50.0, 45.6, 44.5, 44.3, 42.8, 42.1, 39.1, 38.9, 30.2, 29.6, 0.6; Anal. calcd. for $C_{27}H_{28}SiO$: C, 81.78; H, 7.12, found: C, 80.98; H, 7.09; HRMS (FAB) calcd. for $C_{27}H_{28}SiO$ $(MH)^+$ 396.1909, found 396.1907.

Synthesis of 5-{1-[-4-(Phenylethynyl)phenylethynyl]methyl-ether}-bicyclo-[2.2.1]hept-2-ene (14):

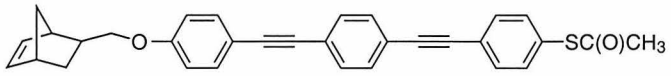


13 was synthesized in analogy to method A as outlined above from **12** (640 mg, 0.0016 mol) to yield 520 mg (100%) of the title compound as a slightly orange solid.

^{1}H-NMR ($CDCl_3$) δ 7.45 (m, 6H), 6.85 (M, 2H), 6.17 (exo, d of d, 1H, J = 3 Hz), 6.09 (endo, m, 2H), 5.96 (exo, d of d, 1H, J = 3 Hz), 4.01 (endo, m, 1H), 3.83 (endo, t, 1H, J = 9 Hz), 3.69 (exo, m, 1H), 3.54 (exo, t, 1H, J = 9.3 Hz), 3.17 (s, 1H), 3.04 (endo,

bs, 2H), 2.85 (exo, bs, 2H), 2.56 (m, 2H), 1.91 (m, 2H), 1.47-1.17 (m, 6H), 0.59 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 160.1, 138.2, 137.5, 137.0, 133.7, 132.9, 132.6, 131.9, 124.8, 122.0, 115.2, 92.3, 88.2, 84.0, 79.4, 72.9, 72.1, 50.1, 45.7, 44.5, 44.3, 42.8, 42.2, 39.1, 38.9, 30.3, 29.7.

Synthesis of compound (15):



To a stirring solution of **13** (0.81 g, 25 mmol), bis(dibenzylideneacetone)palladium (0) or bis(triphenylphosphino)-palladium(2)chloride (2 mol%), triphenylphosphino (2.5 equivalents based on Pd) and copper(I)iodide (2 mol%) in tetrahydrofuran 1-iodo-4-(thioacetyl)benzene (0.9 g, 33 mmol) and dry *N*,*N*-diisopropylethylamine (8 mL) were added at room temperature under argon. After stirring the reaction under nitrogen for 24 hours, the reaction mixture was subjected to an aqueous work-up and the aqueous layer was extracted several times with ether. The combined organic phases were washed with water, dried over magnesium sulfate and the solvent was removed *in vacuo*. Final purification was achieved using column chromatography on silica gel (hexane/ethyl acetate (90:10)) to yield a white solid in 48% yield (0.57 g).

^{1}H-NMR ($CDCl_3$) δ 7.47 (m, 10H), 6.83 (M, 2H), 6.16 (exo, d of d, 1H, J = 2.7 Hz), 6.09 (endo, m, 2H), 5.94 (exo, d of d, 1H, J = 2.7 Hz), 4.02 (endo, m, 1H), 3.84 (endo, t, 1H, J = 9 Hz), 3.70 (exo, m, 1H), 3.54 (exo, t, 1H, J = 9 Hz), 3.02 (endo, bs, 2H), 2.84 (exo, bs, 2H), 2.56 (m, 2H), 2.42 (s, 3H), 1.91 (m, 2H), 1.49-1.23 (m, 6H), 0.60 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 193.9, 174.2, 138.2, 134.8, 133.6, 132.9, 132.7, 132.1, 131.9, 131.7, 128.8, 115.2, 92.3, 88.2, 84.0, 79.4, 72.2, 50.0, 44.5, 42.8, 42.2, 38.9, 32.0, 30.8, 29.6; IR (thin film on NaCl plate) 2961.4, 1706, 1597, 1516, 1466, 1397, 1351, 1284, 1243, 1174, 1108, 1017, 950, 833, 722, 614 cm^{-1}; Anal. calcd.

for $C_{32}H_{26}SO_2$: C, 80.98; H, 5.52, found: C, 80.93; H, 5.44; HRMS (FAB) calcd. for $C_{32}H_{26}SO_2$ $(MH)^+$ 474.1653, found 474.1654.

General procedure for the synthesis of the gold nanoparticles. $HAuCl_4$ (0.355 g, 0.0009 mol) was dissolved in 30 mL degassed water. When trioctylamino bromide (2.187 g, 0.004 mol) in 80 mL was added, the mixture turned dark red. The mixture was stirred for 1 hour at room temperature under argon followed by the addition of hexadecanethiol (1 mL) or dodecanethiol (1 mL). The reaction was stirred for an additional hour during which the reaction turned clear. Then sodium borohydride (0.38 g, 0.01 mol) in 25 mL degassed water was added, and the reaction was stirred for another 3 hours. The organic phase was decantated and the solvent removed *in vacuo*. The black residue was dissolved in as little toluene as possible and precipitated in ethanol. This procedure was repeated several times until no starting material was present anymore to yield a gray powder.

^{1}H-NMR ($CDCl_3$) δ 2.66 (t, 2H, J = 7.2 Hz), 1.67 (m, 2H), 1.23 (m, 26 or 18H), 0.86 (t, 3H, J = 4.5 Hz).

General Procedure for the Functionalization of the Gold Nanoparticles. (a) During the initial formation of the monolayer a small amount of functionalized thiol was added to the reaction. The reaction was worked-up as described above to yield a partially functionalized gold nanoparticle. (b) In analogy to the surface functionalization, the pre-formed nanoparticle was dissolved in a small amount of dichloromethane. Then a small amount of the functionalized thiol was added and the reaction was stirred at room temperature for 24 hours. The reaction was worked-up in the same manner as described above to yield the partially functionalized gold nanoparticle. In both cases the functionalization of the nanoparticles ranged from 10% to 40%.

References

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