

Chapter 3

Direct Synthesis of Soluble, End-Functionalized Polyenes and Polyacetylene Block-Copolymers

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3.1 Abstract

The ring-opening metathesis polymerization (ROMP) of 1,3,5,7-cyclooctatetraene (COT) in the presence of a chain transfer agent (CTA) with a highly active ruthenium olefin metathesis catalyst resulted in the formation of soluble polyenes. Small molecule CTAs containing an internal olefin and a variety of functional groups resulted in soluble telechelic polyenes with up to 20 double bonds. Use of polymeric CTAs with an olefin terminus resulted in polyacetylene block copolymers. These materials were subjected to a variety of solution and solid phase characterization techniques including ^1H NMR, UV/vis, and FT-IR spectroscopies, as well as MALDI-TOF MS and AFM.

3.2 Introduction

Intrinsically conducting polymers (ICP)s are of great interest due to their potential use in a wide variety of applications such as polymer light-emitting diodes (PLED)s, electrostatic dissipation (ESD) materials, and charge storage devices. As a consequence of their rigidity, most ICPs are insoluble materials, preventing thorough characterization and thereby slowing the development of this field. Moreover, the inherent instability of ICPs and associated processing difficulties create a large barrier for commercialization. In an effort to overcome these obstacles, the development of a practical synthesis of relatively stable and soluble conducting polymers with a controlled architecture is important.

The field of conducting polymers was founded upon the discovery of polyacetylene (PA), the simplest ICP, in the 1970s.¹⁻⁵ There have since been numerous accounts on the synthesis of PA including the Ziegler-Natta polymerization of acetylene,⁶ the synthesis of precursor polymers followed by thermal evolution of a small molecule,^{7, 8} and the ring-opening metathesis polymerization (ROMP) of 1,3,5,7-cyclooctatetraene (COT).⁹⁻¹² Despite these developments, applications of PA remain particularly elusive. Unlike PA, however, three decades of research involving other

ICPs such as polyaniline, poly(1,4-phenylenevinylene) (PPV), polypyrrole (PPy), and polythiophene (PTh) has resulted in their commercialization in applications such as anti-fouling coatings¹³ and electrodes in batteries and capacitors.¹⁴

Since most ICPs are completely insoluble in organic solvents, several strategies have been employed to address this problem. One common approach is to add substitution along the polymer backbone thereby disturbing alignment between polymer chains and allowing for the penetration of solvating molecules. This approach has worked well for improving the solubilities of PPV and PTh in the forms of poly[2-(2-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene](MEH-PPV),¹⁵ ester-substituted PPVs,¹⁶ and poly(3-alkylthiophene).¹⁷ While the materials' solubilities are greatly enhanced, they also maintain a suitable level of conductivity; unfortunately, this strategy is not amenable to PA. Both alkyl- and aryl-acetylene (R-acetylenes) derivatives have been polymerized to produce the corresponding soluble poly(R-acetylene)s. Although the disorder stemming from the substituents aids in solubilizing the R-PA, it simultaneously disrupts the π -conjugation along the polymer backbone. As a result, these materials exhibit substantially decreased conductivities in comparison to the parent PA.

Another synthetic method used to solubilize ICPs is to produce copolymers by introducing a second monomer with good solubility properties. Typically, in order to keep the conductive characteristics of the ICP, block copolymers are necessary. PA block copolymers have been previously synthesized via two approaches. In the first approach, using sequential addition of monomers, a soluble PA-precursor polymer such as poly(phenyl vinyl sulfoxide) is prepared as one of the blocks.¹⁸ Upon heating, an elimination reaction converts the precursor polymer to PA. This method has been adapted both to anionic polymerization and, through the Durham route, to ROMP.⁷ The second approach involves sequential addition copolymerization of COT and another ROMP-active monomer.¹⁹ In both approaches, however, block copolymer composition is limited because both monomers must be polymerizable by the same method.

As many of the desirable characteristics of ICPs and PA are realized with a rela-

tively small number of repeat units, several groups have endeavored to produce soluble polyenes with up to 20 double bonds.^{20, 21} Furthermore, the areas of natural product synthesis²² and network polymer formation²³ would benefit if functional end groups were built into these soluble polyenes. It has been demonstrated that heating of a ROMP polymer, prepared from a Durham precursor monomer using highly active molybdenum and tungsten olefin metathesis catalysts, leads to polyenes with alkyl end groups.^{19, 21, 24, 25} For polyenes with less than 16 double bonds, these alkyl groups enhance solubility and allow for more detailed characterization.²⁰ One drawback to producing polyenes via the Durham route is the need for a subsequent deprotection step.

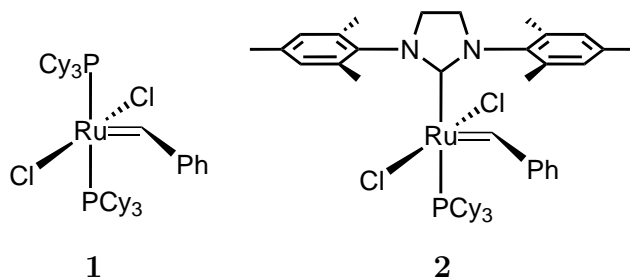


Figure 3.1: Ruthenium olefin metathesis catalysts.

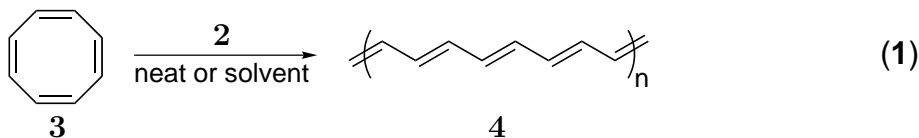
Recently, we reported the direct synthesis of PA via the ROMP of COT with the highly active ruthenium catalyst **2**.¹² This reaction is not possible with the less active catalyst **1** as the ring strain of COT (2.5 kcal/mol) is extremely low.²⁶ Catalyst **2** has also been shown to form telechelic polymers with a variety of functional end groups when utilized in conjunction with a chain transfer agent (CTA).^{27–29} Building upon this work, we report herein a method of forming telechelic polyenes by the ROMP of COT in the presence of a CTA. Furthermore, these polyenes are soluble in common organic solvents allowing for extensive solution-phase characterization. We also describe here the ROMP of COT in the presence of an olefin-terminated polymer, which allows PA block copolymers to be formed with a variety of commodity polymers such as polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(ethylene glycol) (PEG). Indeed, nearly any monomer that is polymerizable by living anionic or controlled radical techniques can be used as the solubilizing block. Furthermore, no elim-

ination step is necessary in forming the PA block, thus reducing synthetic complexity and material waste. Since the ROMP of COT forms PA directly without the need for deprotection steps,^{11, 12} and olefin-terminated polymers are commercially available, this represents the first one-step synthesis of PA-containing block copolymers from commercially available materials.

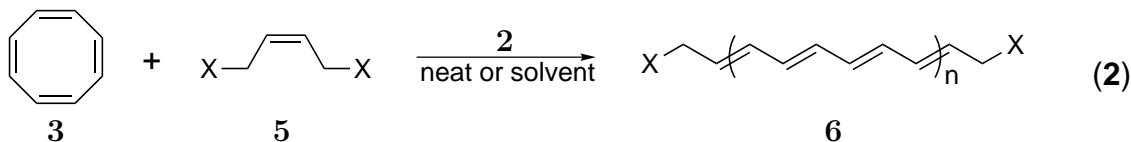
3.3 Results and Discussion

3.3.1 Synthesis of Soluble Polyenes

We recently published a report detailing the ROMP of COT (**3**) to form PA with catalyst **2** (Equation 1).¹² The characteristics of the PA produced by **2** proved to



be very similar to PA produced by previous synthetic routes.¹² Unfortunately, the characteristic insolubility of PA was also observed. The functional group tolerance of catalyst **2**, however, suggests the possibility of placing solubilizing functional groups at the chain ends by utilizing a chain transfer agent (CTA). It has been previously shown that the use of a CTA with **2** can produce telechelic oligomers and polymers from CTAs containing functional groups such as alcohols, halides, and esters.^{27, 28} The same strategy can now be applied for the direct formation of telechelic PA. Furthermore, if the PA chain length can be controlled by this method, it would provide for the direct formation of soluble polyenes as outlined in Equation 2.



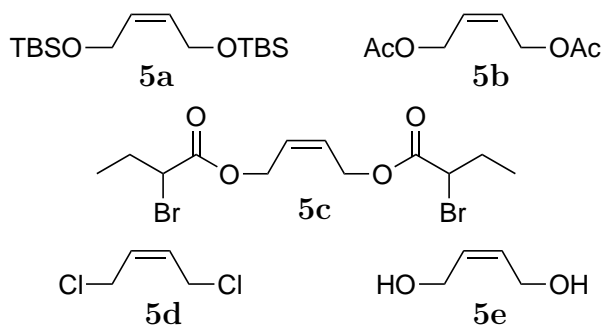
The synthesis of telechelic PA was successfully carried out both neat and in solution via the ROMP of COT with a CTA using catalyst **2** (see Table 3.1). Upon

Table 3.1: Effects of Monomer/CTA and Monomer/Catalyst Ratio on Yield of Polyenes

Entry	CTA	[COT]/[CTA]	[COT]/[2]	% yield
1 ^a	5a	1	500	76
2 ^a	5a	2	500	83
3 ^b	5a	1	540	78
4 ^b	5a	2	480	69
5 ^b	5a	3	520	49
6 ^b	5a	1	980	40
7 ^b	5a	3	1050	9
8 ^c	5b	2	490	5
9 ^c	5b	4	490	18
10 ^d	5c	4	800	12
11 ^a	5d	1	5000	0
12 ^e	5e	1	500	0

^aReaction carried out in 1 mL of CH₂Cl₂. ^bReaction carried out neat.^cReaction carried out in 1 mL of toluene. ^dReaction carried out in 3 mL of toluene. ^eReaction carried out in 1 mL of THF.

addition of **2**, the yellow COT solution turned light orange and then became progressively darker over the next 5 min depending on the ratio of COT to CTA. After 24 h, only a small amount of solid was observed to precipitate on the container walls. This result was visibly different from the large amount of solid (metallic in appearance) produced when a CTA was omitted from the reaction. After isolation, the resulting polymer was completely soluble in common organic solvents, enabling characterization by ¹H NMR, UV-vis, and FT-IR spectroscopies, as well as MALDI-TOF MS.

**Figure 3.2:** CTAs **5a**–**5e**.

Attempts to use CTAs such as **5d** and **5e** were not successful (Figure 3.2). While no solids precipitated during the ROMP of COT with CTA **5d**, ^1H NMR spectroscopy of the crude reaction mixture showed very little polyene and no material could be isolated (entry 11). Immiscibility of COT and **5e** prevented neat polymerization and required solvents such as THF for ROMP in solution. Unfortunately, THF has been shown to dramatically decrease the rate of ROMP,¹¹ and no desired polyene product was observed in the ^1H NMR spectrum of the crude reaction mixture (entry 12).

As a consequence of the loss of material at each stage of preparation, obtaining the polyenes in high yield was somewhat difficult. Some polyene product was simply lost upon repetitive centrifuge/decant/wash cycles, while shorter polyene chains were most likely soluble in the MeOH washes. Entries 1 and 2 in Table 3.1 show that for ROMP carried out in solution, increasing the amount of COT relative to CTA **5a** has a very minimal effect on the yield of polyene **6a**. When the corresponding reactions are carried out neat (entries 3-5, Table 3.1), a decrease in yield of **6a** is observed with a decrease in the amount of CTA **5a**. This trend is likely due to insoluble PA chains precipitating out of solution when too few chain transfer groups are present to attenuate the molecular weight. When the amount of COT relative to catalyst **2** is increased to 1000:1 (entries 6 and 7, Table 3.1), the yields decrease substantially. This observation is likely due to the incomplete initiation of catalyst **2**³⁰ which would result in a “true” monomer to catalyst ratio far in excess of 1000. Finally, although it does not lead to chain termination, backbiting of catalyst **2** onto the growing polyene chain has previously been shown to eliminate benzene.¹² As benzene is not metathesis active, backbiting essentially removes monomer from the reaction.

3.3.1.1 Characterization of Soluble Polyenes

The loss of monomer over the course of the reaction because of backbiting also evidently hinders our attempt to control the molecular weight of the polyenes by adjusting the ratio of COT to CTA. Previous reports of ROMP reactions with catalyst **2** and a CTA have shown that molecular weight is dictated by the ratio of [monomer]:[CTA] if the reaction is allowed to reach thermodynamic equilibrium.^{27, 28, 31} This result was

not found to be the case for COT. While accurate molecular weights and distributions could not be obtained for the polyenes, ^1H NMR spectroscopy as well as MALDI-TOF MS data indicated average chain lengths of around 10–13 double bonds for all reactions and did not vary with the ratio of COT:CTA. The average chain length of the isolated polyenes, however, may be misleading. When a higher COT to CTA ratio is employed, more polyene chains reach lengths that render them insoluble. For lower ratios, shorter, MeOH-soluble polyene chains are favored. As a result of likely fractionation of smaller and longer chains during workup, regardless of the starting COT to CTA ratio, the isolated polyene chains are heavily weighted to an average of 10–13 double bonds. Of course, the backbiting of **2** might be attenuated by decreasing the reaction temperature; however, if the polymerization of COT occurred without significant backbiting with a CTA molecule, an insoluble PA chain would result. Hence, in the direct synthesis of polyenes **6** with catalyst **2**, the ability to control molecular weight is limited.

The solution phase ^1H NMR spectrum of polyene **6a** (Figure 3.3) clearly shows signals corresponding to the backbone protons of the telechelic polyene between $\delta=6$ –7 ppm, which are characteristically shifted downfield due to the highly conjugated segment of olefins. The allylic CH_2 protons give rise to peaks around $\delta=4.2$ ppm and the *tert*-butyl and methyl protons of the silane protecting group (from CTA **5a**) correspond to singlets at $\delta=0.9$ and 0.05 ppm, respectively. The absence of a singlet at $\delta=5.79$ ppm suggests that all of the unreacted COT was successfully removed from the polyene product. Integration of the methylene and polyene backbone peaks suggests an average of 10 double bonds for the sample, which is consistent with the MALDI-TOF MS data presented below.

Previous reports have provided very detailed UV-vis spectroscopy data on soluble polyenes containing up to 15 double bonds.^{20, 21} As the number of conjugated double bonds increases, the absorption shifts to longer wavelengths and some detail of the higher energy transitions is lost. UV-Vis spectroscopy was carried out on polyene **6a** in both THF and CH_2Cl_2 . Figure 3.4 shows the UV-vis spectrum in CH_2Cl_2 with 4 distinct transitions between 355 and 450 nm and a smooth absorption profile

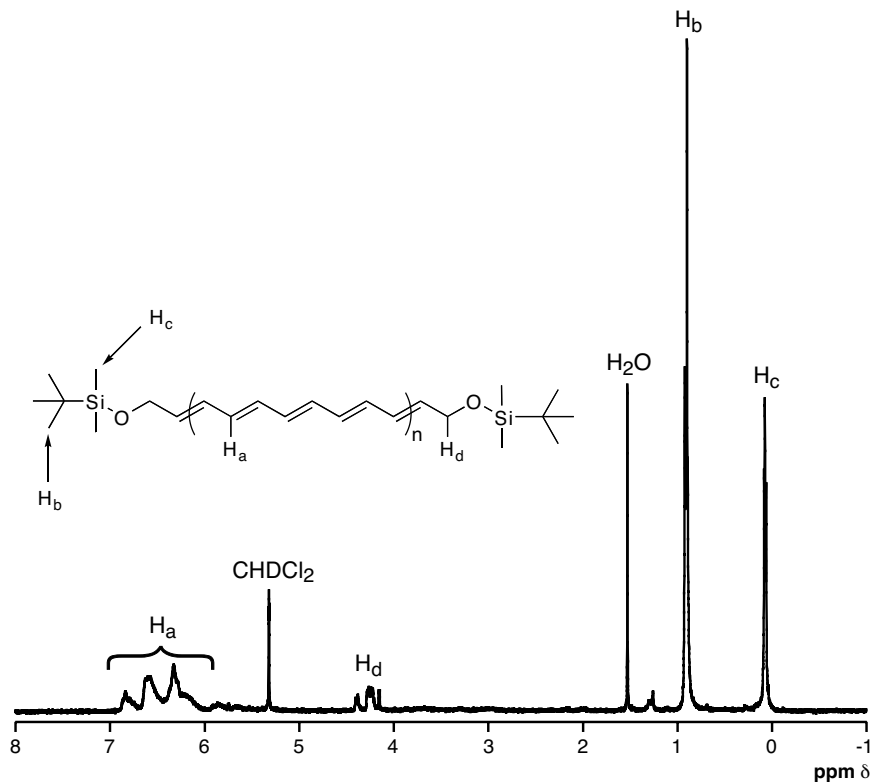


Figure 3.3: ^1H NMR spectrum of telechelic polyene **6a** in CD_2Cl_2 .

extending past 500 nm. These transitions are consistent with a polyene composed of 10 to 20 double bonds.²⁰

Infrared spectroscopy was also carried out on telechelic polyenes **6a** and **6b**. Figure 3.5 displays the FT-IR spectra for both telechelic polyenes. The bands at 745, 773, and 1011 cm^{-1} are visible in both polyene spectra and are conserved from the IR spectrum of poly(COT).¹² The peak at 743 cm^{-1} can be attributed to the *cis* C-H out-of-plane vibrational mode while the peak 1011 cm^{-1} is due to the *trans* C-H mode.³² The presence of a much larger *trans* peak at 1011 cm^{-1} supports the mechanism of *trans*-selective catalyst **2** backbiting into the polymer chain to attach the endgroups and form telechelic polymers or to simply isomerize *cis* olefins to their *trans* counterparts.

Finally, mass spectrometry was carried out on the telechelic polyenes. Figure 3.6 shows the MALDI-TOF spectrum for **6a** acquired from a dithranol matrix. The first labeled peak with a mass of 628.9 Da corresponds exactly to telechelic polyene **6a**

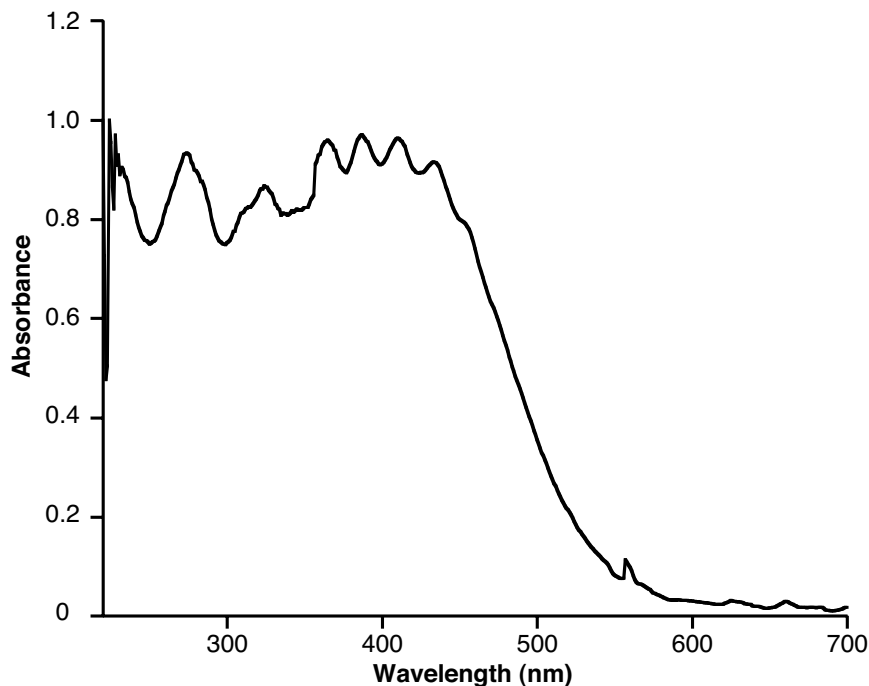


Figure 3.4: UV-Vis spectrum of telechelic polyene **6a** in CH_2Cl_2 .

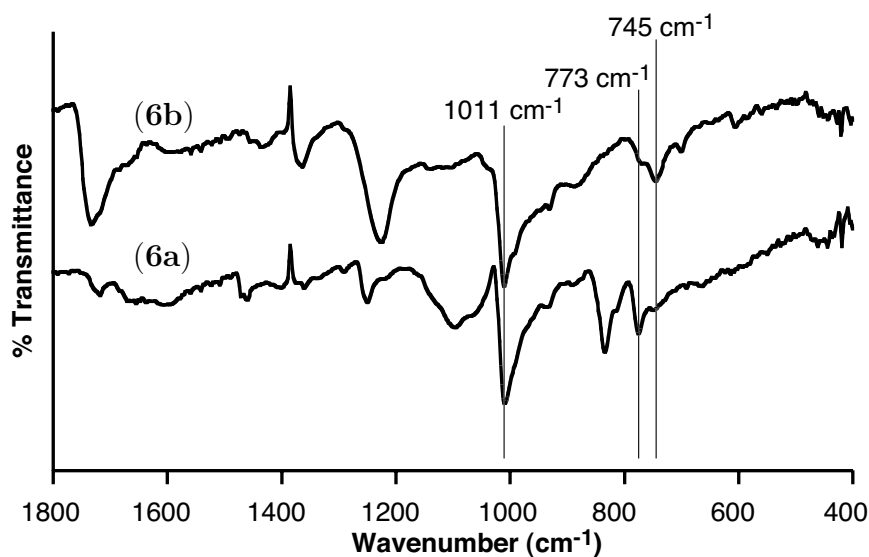


Figure 3.5: FT-IR % transmittance spectra of polyenes **6a** and **6b** in KBr pellets.

with 13 double bonds. There is a difference of 26.0 amu between each peak in the series corresponding to a C_2H_2 unit. The series is easily visible out to a mass peak of 811.0 amu, corresponding to a species with 20 double bonds. Furthermore, no other series with 26.0 amu mass differences are observed suggesting that all of the polyene

chains are capped at *both* ends.

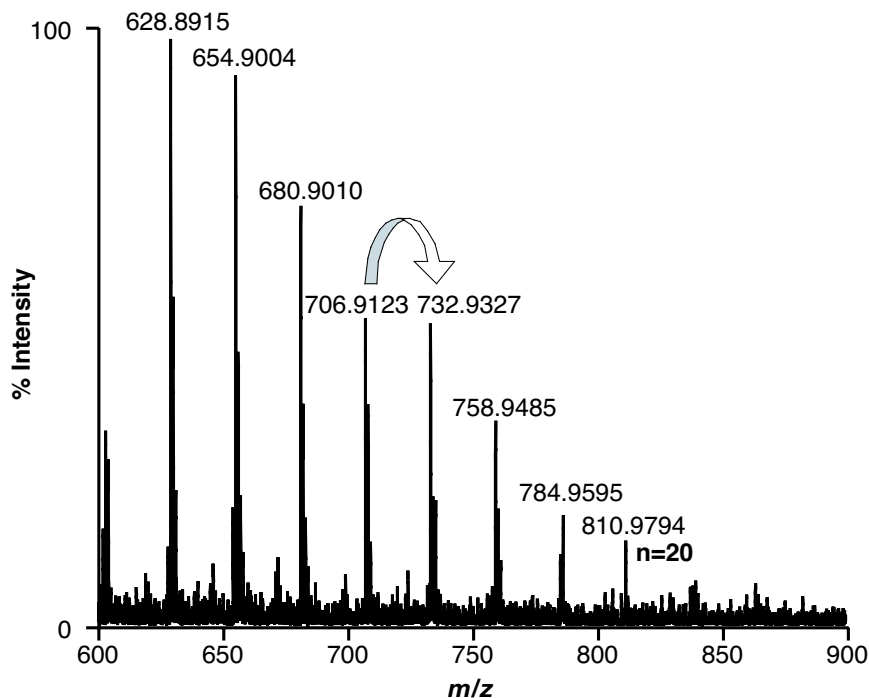


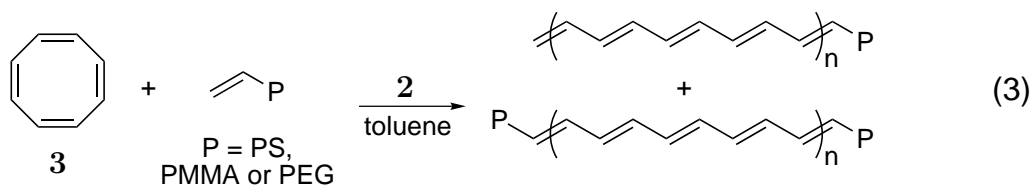
Figure 3.6: MALDI-TOF MS of polyene **6a** ionized from a dithranol matrix.

These data provide evidence for the formation of a telechelic polyene with the CTA functionality successfully placed onto both ends of each polyene chain. It also shows that catalyst **2** is capable of backbiting into a growing polyene chain in order to mediate chain transfer. Furthermore, the materials produced are completely soluble in common organic solvents and allow for much more detailed characterization of polyenes. These results encouraged us to further explore the use of CTAs as a method for producing soluble and processable PA-based materials. We anticipated difficulties, however, using telechelic PA as macroinitiators (e.g. entry 10, Table 3.1). An alternative route to PA block copolymers was therefore sought.

3.3.2 Synthesis of PA-containing Block Copolymers

CTAs containing terminal olefins have been previously used with catalyst **2** to form mixtures of monofunctionalized and difunctionalized (i.e., telechelic) polymers.²⁸ Furthermore, only difunctional materials result when a large excess of a CTA containing

an internal olefin is used. Extending this concept, olefin-terminated *polymers* were found to control the ROMP of COT by forming block copolymers containing PA as one of the blocks (see Equation 3). As in the case with small molecule CTAs, a polymer with an olefin in the middle of the chain should lead exclusively to tri-block copolymers containing PA as the middle block. We are currently investigating this possibility, but due to difficulties in obtaining *absolutely* pure polymers containing an internal olefin, we have limited this report to include only end-functionalized polymers.



The use of olefin-terminated polymers as CTAs allows for a wide variety of block copolymer compositions, as polymers containing olefin endgroups can be prepared using numerous techniques.^{33–36} Atom transfer radical polymerization (ATRP) was chosen for this work principally for its synthetic ease. Recent advances in ATRP allow these reactions to be performed without the exclusion of oxygen, and with monomers that have not been rigorously purified.³⁷ Allyl bromide and 5-bromo-1-pentene were convenient ATRP initiators for forming PMMA and PS functionalized with a terminal olefin.³⁴ ¹H NMR spectroscopic and MALDI-TOF MS analysis of the polymers confirmed the presence of olefin endgroups, and molecular weights were determined by GPC and NMR. As with previous reports in the literature, mass spectral analysis showed that the halogen endgroups were replaced by hydrogen atoms for many of the polymer chains after long polymerization times.^{38, 39} Since ruthenium-based catalysts have been shown to successfully catalyze ATRP,⁴⁰ however, the loss of the halogen endgroup was considered advantageous, reducing the possibility of unwanted side reactions during the subsequent ROMP step. Indeed, no reaction was observed when the olefin-terminated polymer was subjected to ATRP conditions in the presence of COT.

Formation of PA block copolymers was accomplished via the ROMP of COT in the

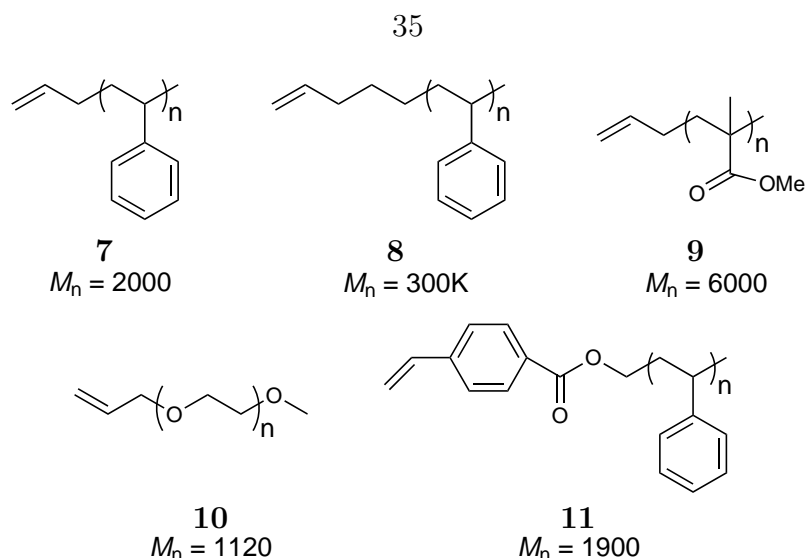


Figure 3.7: Olefin-terminated polymers.

presence of olefin-terminated polymers **7–11**.⁴¹ Typically, the amount of solvent was adjusted to ensure an initial monomer concentration, $[\text{COT}]_0$, of approximately 0.2 M. When large amounts of olefin-terminated polymer were used, however, additional solvent was added to ensure complete dissolution. Monomer-to-catalyst ratios were typically maintained at 1000:1, although ratios of up to 21000:1 were found to be viable. After completely dissolving the olefin-terminated polymers in toluene, COT was added, followed by the catalyst (either in solid form or from a stock solution). Within minutes, a color appeared that varied depending on the relative proportions of COT and olefin-terminated polymer, as well as the molecular weight of the latter. For low proportions of COT, the color of the reaction was light orange, while for medium proportions it was deep orange or red and for high proportions it was deep red or black. This color was maintained throughout the reaction. Isolation of the block copolymer product was accomplished by precipitation in a non-solvent for the olefin-terminated polymer such as MeOH or hexanes. Table 3.2 shows the colors of the final polymer products from various reactions. A solution of product polymer, when left on the benchtop, became clear over the period of many weeks, indicating eventual decomposition of the conjugated structure. However, the solid polymers maintain their color for months if protected from light and oxygen.

For most block copolymer compositions, solubility of the final product was iden-

Table 3.2: Variation in composition of PA block copolymers.

CTA	[COT]/[CTA]	[COT]/[2]	product color	% yield ^a	polymer ^b
7	4	900	orange	18	7a
7	20	4000	dark rust	26	7b
7	100	21000	brown/black	13	7c ^c
8	200	800	dark grey	82	8a ^d
8	1000	4000	faded black	71	8b
9	2	1000	light orange	44	9a ^d
9	5	1000	orange	20	9b
9	20	1000	deep red	58	9c
9	40	1000	black	52	9d
10	1	500	dark red	62	10a
10	4	1600	brown/black	39	10b
10	7	1400	brown/black	28	10c
10	20	4000	brown/black	22	10d
11	20	4000	brown	36	11a

^aCalculated based on total mass of reactants and recovered product. ^bAll reactions were carried out in toluene with [COT]₀=0.2 M unless otherwise noted. ^c[COT]₀=1.1 M. ^d[COT]₀=0.03 M.

tical to that of the olefin-terminated polymer. All of the entries in Table 3.2 yielded completely soluble block copolymers. When very large amounts of COT were used in conjunction with a low molecular weight non-conjugated block (for example, samples **7c**, **9d** and **10d**), some solid product was deposited on the walls of the reaction flask. This material was redissolved upon sonication, indicating that the solubilizing effect of the nonconjugated block is sufficient to keep the block copolymers soluble, even in cases where significant crystallization of the PA blocks is possible.

Yields of the block copolymer products varied widely depending on the proportions of COT and olefin-terminated polymer, as well as the molecular weight of the latter (see Table 3.2). Yields exceeded 80% when higher molecular weight olefin-terminated polymers were used, or if lower proportions of COT were used. As the proportion of COT was increased, however, a corresponding increase in the ratio of [COT]/[**2**] led to decreased yields (see, for example, sample **7c**). Thus, as described for small molecule CTAs, the generally low yields reported in Table 3.2 are likely due to incomplete incorporation of COT. This observation is further supported by the ¹H NMR spectra of the block copolymers (vida infra).

3.3.2.1 Characterization of Block Copolymers

Characterization of the block copolymers by UV-vis spectroscopy provided the clearest evidence for the presence of extended PA blocks. Figure 3.8 shows the UV spectra for three types of block copolymers—PS-*b*-PA, PMMA-*b*-PA, and PEG-*b*-PA. For comparison, the absorption spectra of the homopolymers (i.e., the olefin-terminated polymer) are also shown. The absorbance bands previously seen for polyenes containing 10–15 double bonds²⁰ were observed in block copolymers made from small amounts of COT (e.g., sample **9a**). These details are lost, however, when larger amounts of COT are used. The smooth spectra that result indicate the presence of a wide range of conjugation lengths. In addition, as the proportion of COT is increased, the absorption region corresponding to the PA block shifts to longer wavelengths, while the absorption due to the nonconjugated block remains unchanged. These data indicate that increasing the amount of COT in the reaction produces PA blocks with longer conjugation lengths.

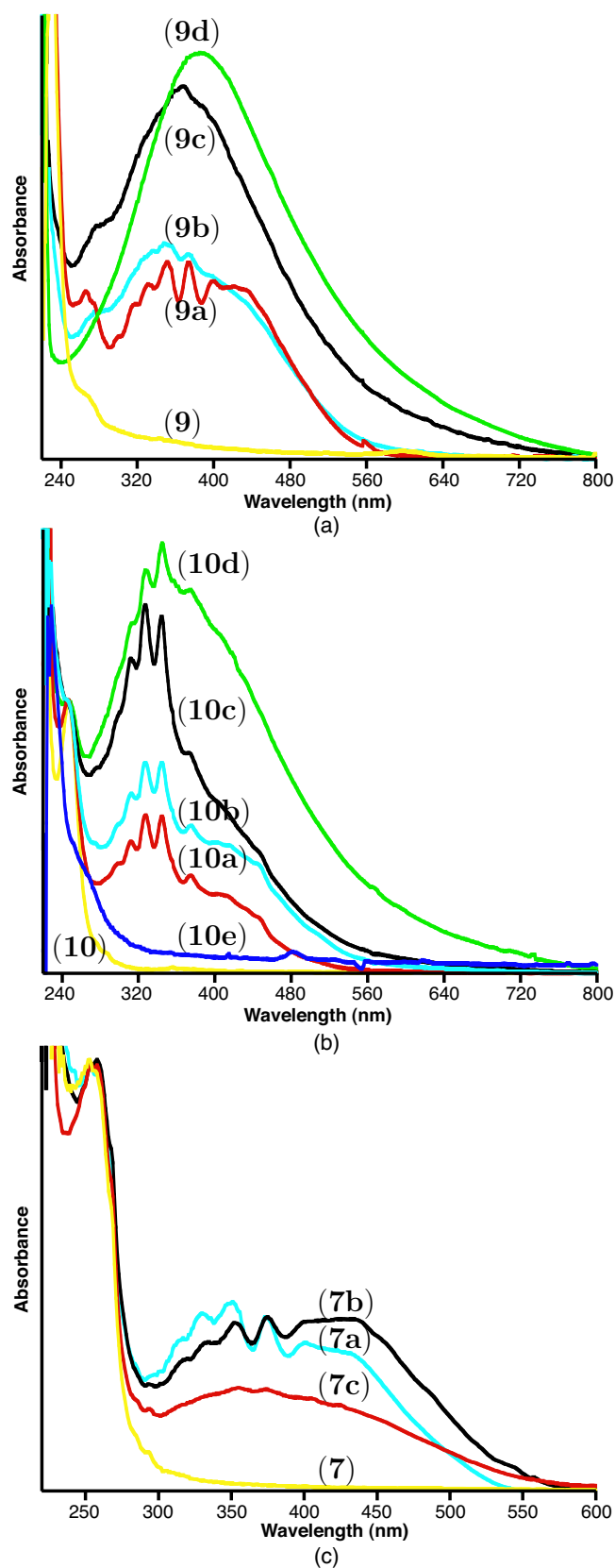


Figure 3.8: UV-vis spectra of PA-containing block copolymers in CH_2Cl_2 solution. (a) PMMA (9), PMMA-*b*-PA (9a-d). (b) PEG (10), PEG-*b*-PA (10a-d), bis(hydroxy)-terminated PEG reaction product (10e). (c) PS (7), PS-*b*-PA (7a-c).

To show that PA is covalently attached to the olefin terminated polymers in these reactions, the ROMP of COT was carried out in the presence of a bis(hydroxy)-terminated PEG. A significant amount of insoluble, black solid formed during the reaction. This solid was removed by filtration, and the remaining polymer product (white) was isolated by precipitation. The UV-vis spectrum of the resulting polymer is shown in Figure 3.8b (sample **10e**). The lack of absorbance above 320 nm indicates that no PA was present in the product.

Characteristic IR absorption bands of polyCOT produced with catalyst **2** include 1010, 992, 930, 773, and 745 cm^{-1} .¹² Unfortunately, absorption from the nonconjugated polymer segments often obscured these absorption bands in the PA block copolymers. For PMMA-*b*-PA, however, absorption of the PA segment at 1012 cm^{-1} is clearly visible and overlays with the absorption spectra of the olefin-terminated homopolymer (see Figure 3.9).

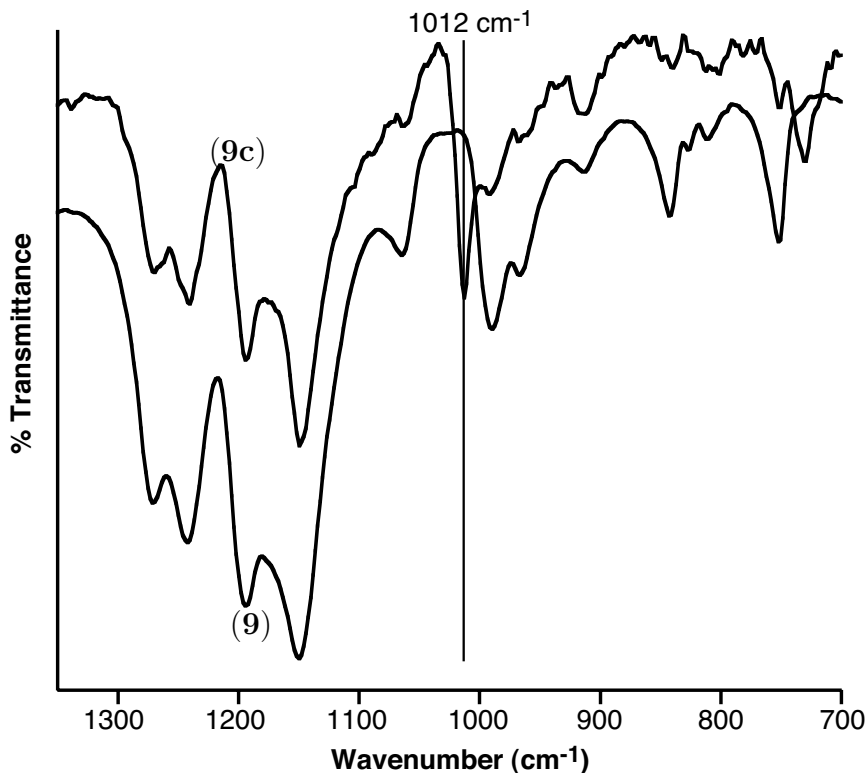


Figure 3.9: FT-IR spectra of **9** and **9c**.

For samples of PMMA-*b*-PA and PEG-*b*-PA, it was possible to observe characteristic peaks in the polyene region of the ^1H NMR spectra that appeared very similar to the peaks shown in Figure 3.3.⁴² In general, integration of the polyene region indicated far smaller PA blocks than would be expected from the ratio of COT to olefin-terminated polymer. For example, integration for sample **9b** showed an average of four or fewer ($-\text{C}=\text{C}-$) units per polymer chain, whereas 20 ($-\text{C}=\text{C}-$) units would be expected from the initial reactant ratio. As discussed previously, this low incorporation can be attributed to two likely sources: the ROMP of COT does not reach completion, and/or benzene formed from backbiting leads to an effective loss of monomer. In all NMR spectra, however, a significant amount of unreacted olefin endgroups remained visible after block copolymer formation, indicating that some polymer chains have no attached PA blocks. This observation makes it very difficult to speculate on the average conjugation length of the PA blocks.

Along with the trends observed in UV-vis spectra, AFM afforded a method for observing changes in the relative sizes of conjugated segments between samples. Phase separation in PA-containing block copolymers has been observed previously.^{19, 43–45} Tapping Mode (TM) AFM images of PS-*b*-PA films show a phase separated morphology consisting of isolated domains against a uniform background. These domains, which were absent in films formed from the olefin-terminated homopolymer, were randomly distributed in space, but fairly regular in size and shape. Furthermore, the sizes of the domains exhibited a dependency on the relative proportions of COT and olefin-terminated polymer used in the preparation of the block copolymers. Figure 3.10 shows TM AFM height images of films made by spin coating 0.4 wt% toluene solutions of **8a** and **8b**. Clearly, the domains (appearing as white spots) are larger for **8b** which contains a greater percentage of conjugated material, implying that the white spots in Figure 3.10 represent PA domains. As shown by the side views of these images (Figure 3.10b and d), the domains appear to be directed perpendicular to the film surface. These domains are highly stable: annealing the polymer films under vacuum at 130 °C for 24+ hours only reduced their height and spatial density. Furthermore, the domains could also be observed using contact mode.⁴⁶ We

believe that these images, the UV spectra of the two copolymers, and the fact that the solution of **8b** was darker in color than that of **8a** are evidence for a variation in the conjugation length of the PA blocks that relates to the relative amount of COT used in the polymerizations. It should be reiterated, however, that these polymers remained completely soluble in common organic solvents.

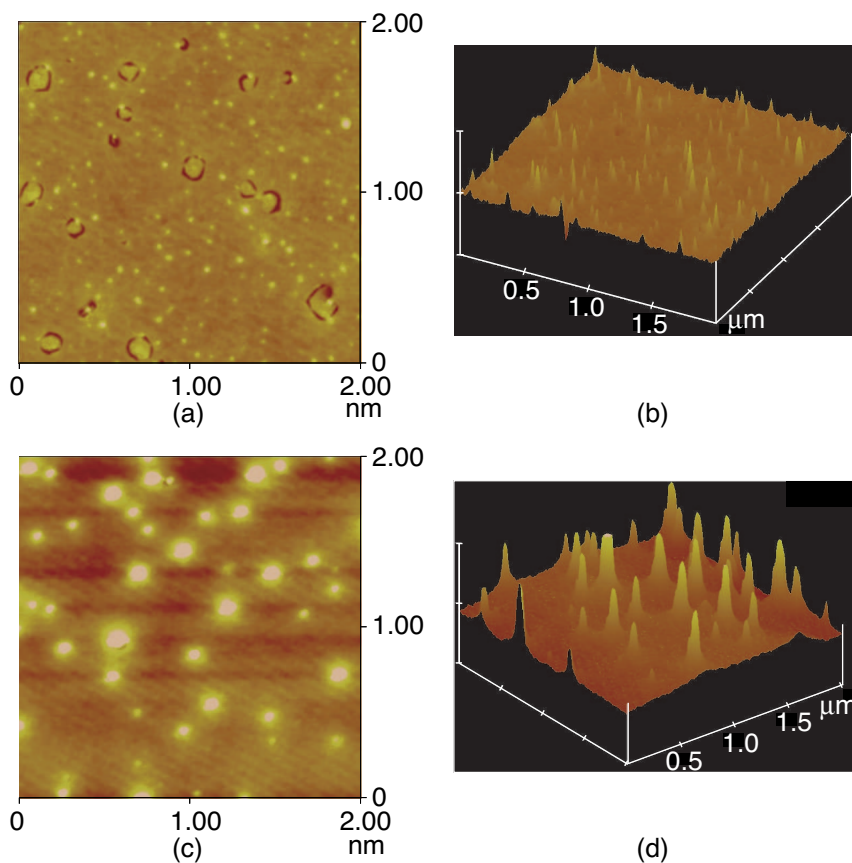


Figure 3.10: TM AFM height images. (a, b) Sample **8a**, produced from **8** and 200 equivalents of COT. (c, d) Sample **8b**, produced from **8** and 1000 equivalents of COT. In (a), (b), and (c) the same height scale applies (0–15 nm), while in (d) the height scale is 0–20 nm.

3.4 Conclusions

The synthesis of telechelic polyenes via the direct ROMP of COT in the presence of a CTA with catalyst **2** has been demonstrated. The telechelic polyenes remained

completely soluble in common organic solvents and were characterized in detail using solution and solid-state spectroscopic methods. Furthermore, PA block copolymers were synthesized in one step from olefin-functionalized commodity polymers. As a consequence of their solubility, all of these block copolymers were amenable to spin coating and subsequent AFM investigation. We hope that the tunability and improved processability of these materials may soon lead to their commercialization; investigations of their electronic properties are currently underway.

3.5 Experimental Section

General Procedures. NMR spectra were recorded on a Varian Mercury 300 (300 MHz for ^1H and 75 MHz for ^{13}C). All NMR spectra were recorded in CD_2Cl_2 or CDCl_3 and referenced to residual proteo species. Gel permeation chromatography (GPC) was carried out on three AM GPC Gel columns, 15 μm pore size, (American Polymer Standards Corp.) connected in series with a Type 188 differential refractometer (Knauer). Molecular weights were calculated relative to polystyrene standards. MALDI-TOF mass spectra were recorded using an Applied Biosystems (ABI) Voyager DE-PRO time-of-flight mass spectrometer. A 20 Hz nitrogen laser (337 nm, 3 ns pulse width) was used to desorb the sample ions that were prepared in a dithranol matrix. Mass spectra were recorded in linear (or reflector) delayed extraction mode with an accelerating voltage of 20 kV and a delay time of 100 ns. The low mass cut-off gate was set to 500 Da to prevent the lower mass matrix ions from saturating the detector. Calibration was external using a peptide mixture provided by the instrument manufacturer covering the mass range of interest. Raw spectra were acquired with an internal 2 GHz ACQIRIS digitizer and treated with Data Explorer software provided by ABI. Tapping Mode atomic force microscopy images were obtained in air using a Nanoscope IIIa AFM (Digital Instruments, Santa Barbara, CA) with silicon cantilever probes (Veeco Metrology, Santa Barbara, CA). To improve image quality, height and amplitude images were flattened using commercial software (also from Digital Instruments). AFM samples were prepared using dilute solutions of polymer

(either 0.4 or 1 wt/wt %) in either toluene or CH_2Cl_2 . A 35 μL aliquot of the solution was spin coated onto freshly cleaved mica substrates (1 cm^2) at 3000 rpm. FT-IR Spectra (KBr pellet) were recorded on a Perkin-Elmer Paragon 1000 or on a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Win-IR Pro software. UV-Vis spectra were obtained on a Beckman DU 640 Spectrophotometer in either THF or CH_2Cl_2 .

Materials. Toluene and CH_2Cl_2 were dried by passage through solvent purification columns.⁴⁷ 1,3,5,7-Cyclooctatetraene (COT) (**3**) (generously donated by BASF) was dried over CaH_2 and distilled prior to use. Cis-1,4-diacetoxy-2-butene (96%) (**5b**) (Aldrich) was dried over CaH_2 and distilled prior to use. Cis-2-butene-1,4-diol (95%) (**5d**) (Aldrich) was distilled prior to use. Cis-Cyclooctene (Aldrich) was degassed by freeze/pump/thaw cycles before use. Vinyl-terminated PS (**11**) ($M_n = 1900$, $M_w/M_n = 1.11$), and vinyl terminated PEG (**10**) ($M_n = 1120$, $M_w/M_n = 1.17$) were purchased from Polymer Source, Inc. $(\text{PCy}_3)_2(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**1**)⁴⁸ and $(\text{IMesH}_2)(\text{PCy}_3)(\text{Cl})_2\text{Ru}=\text{CHPh}$ (**2**)⁴⁹ [Mes = 2,4,6-trimethylbenzene] as well as CTAs **5a**⁵⁰ and **5c**⁵¹ were synthesized according to literature procedure. All other materials were used as received.

Procedure for the ROMP of COT (3**) with CTA **5a** (in solution).** A stir bar was placed in an oven-dried small vial with a teflon screw cap. Under an argon atmosphere, 0.5 mL (4.44 mmol) of COT and 1.6 mL (4.34 mmol) of CTA **5a** were added by syringe. Subsequently 1.0 mL (8.84×10^{-3} mmol) of a 7.5 mg/mL solution of **2** in CH_2Cl_2 was added by syringe. The vial was placed in a 55 °C oil bath. The yellow solution turned dark orange within 5 min. After 24 h, the reaction vial was removed from the heating bath and the solution was precipitated into 100 mL of stirring MeOH and filtered through a Büchner funnel to yield a red solid. The solid was dried under reduced pressure, yielding 91 mg of polymer (20%). Alternatively, the precipitate in MeOH solution was placed in centrifuge tubes and a number of centrifuge-decant-wash with MeOH cycles were performed until the decanted liquid was colorless. The red solid was then dissolved in CH_2Cl_2 , transferred to an amber vial, and the solvent was removed under reduced pressure.

Procedure for the ROMP of COT with CTA **5a (neat).** An oven-dried

small vial with a teflon screw cap was charged with a stirbar and 7.3 mg (8.61×10^{-3} mmol) of catalyst **2**. Under an argon atmosphere, 0.5 mL (4.44 mmol) of COT and 0.55 mL (1.49 mmol) of the CTA **5a** were added by syringe. The vial was placed in an aluminum heating block set to 55 °C. The yellow solution immediately turned dark reddish-orange. After 24 h, the solution was removed from the heating block and dissolved in CH₂Cl₂. The solution was precipitated into 100 mL of stirring MeOH and filtered through a Büchner funnel to yield a purple solid. The solid was then dried under reduced pressure, yielding 124 mg of polymer (27%).

Synthesis of vinyl-terminated polystyrene (7). To a small round bottom flask containing a stirbar was added 0.365 g (4.62 mmol) 2,2'-dipyridyl, 0.299 g (4.70 mmol) copper powder, 0.114 g (0.511 mmol) CuBr₂, 0.4 mL (4.62 mmol) allyl bromide, and 3.0 mL (44.6 mmol) styrene. The flask was sealed with a rubber septum, purged with argon for 5 min, and heated to 110 °C. After 15 min, the reaction mixture turned bright green. The reaction was terminated after 24 h by cooling down to room temperature, dissolving the mixture in THF, and precipitating in MeOH. The resulting solid was isolated by filtration, dissolved in THF, and passed through a plug of alumina before reprecipitating in MeOH. The isolated white product was dried in vacuo.

Synthesis of vinyl-terminated polystyrene (8). As for **7**, but with 5-bromo-1-pentene as initiator.

Synthesis of vinyl-terminated polymethylmethacrylate (9). As for **7**. To maintain lower reaction viscosity, however, an amount of diphenylether equivalent to the amount of methyl methacrylate monomer (by mass) was added.

Synthesis of PA block copolymers. In a typical procedure, the olefin terminated polymer chain transfer agent was added to a small vial containing a stirbar. The vial was purged with argon for 10–15 min, toluene was added, and the mixture was stirred to completely dissolve the polymer. COT was then added, followed by the appropriate amount of a stock solution of catalyst in toluene. The solution was heated up to 55 °C and left stirring under an argon atmosphere for 24 h. The reaction mixture was cooled down to room temperature and precipitated in a nonsolvent

such as MeOH or hexane. The resulting solid was isolated by filtration, dried under reduced pressure, and stored in an amber vial under an atmosphere of argon.

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Rather, a highly disordered morphology with large, randomly placed crystal-like structures was seen.

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