Chapter 1

Synthesis of End-Functionalized Polynorbornenes *via* Ring-Opening Metathesis Polymerization (ROMP)

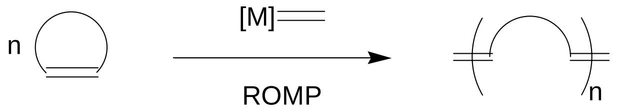
Abstract

The synthesis of a variety of polynorbornenes (PNB)s bearing acetoxy, hydroxy, and vinyl end-groups was accomplished. PNBs with an acetoxy group at one terminus and a vinyl group at the other were prepared using norbornene, ruthenium-based olefin metathesis catalyst $(PCy_3)_2Cl_2Ru{=}CHPh$, and allyl acetate as a chain transfer agent (CTA). Employing a more active catalyst, (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)$(PCy_3)Cl_2Ru{=}CHPh$, and 1,4-diacetoxy-2-butene as the CTA afforded telechelic PNBs bearing acetoxy groups at both ends of the polymer chains. Molecular weights were controlled by varying the initial monomer/CTA ratio and were in agreement with their theoretical values. Using a similar procedure, acetoxy end-functionalized PNBs were also obtained by degradation of high molecular weight PNB. Removal of the acetoxy groups afforded the corresponding hydroxy terminated polymers with number averaged functionalities close to two. Mechanisms are proposed for the formation of the end-functionalized polymers. Correction factors for characterizing PNBs by gel-permeation chromatography (GPC) are also suggested.

Portions of this chapter have been previously reported, see: Bielawski, C. W.; Benitez, D.; Morita, T.; Grubbs, R. H. *Macromolecules* **2001**, *34*, 8610.

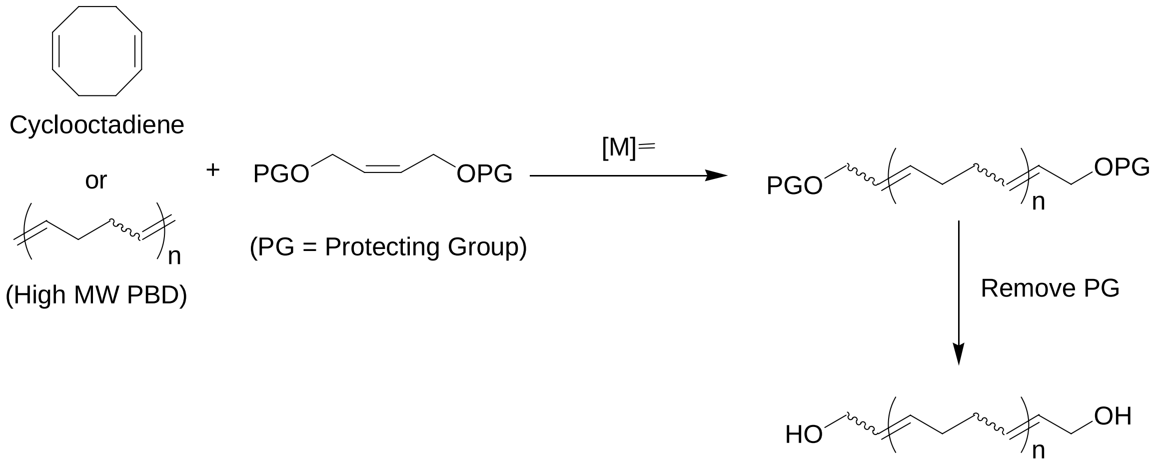
Introduction

Telechelic polymers, or polymers with functional groups selectively positioned at the termini of any given chain, have been extensively employed in a variety of applications including intermediates in the synthesis of block copolymers, use as cross-linking agents, and in the formation of polymeric networks.[1-4] Since these applications are often dependent on structural, mechanical, and thermal properties of the telechelic polymer, expanding the range of selectable monomers remains a synthetic goal in polymer chemistry. While most telechelic polymers are prepared using either free radical or ionic polymerization, there exists several classes of polymers that cannot be synthesized using either of these methods.[1] Ring-opening metathesis polymerization[5] (ROMP) is an attractive alternative which provides polyalkenamers capable of functioning as elastomers with low glass transition temperatures (T_g) (Eq. 1).



(1)

Previously, several metathetical approaches towards hydroxy-terminated telechelic polybutadienes (HTPBD) have been reported.[6-12] HTPBD has been extensively used in the polyurethane industry as a cross-linking agent for products ranging from rocket propellant binders to sealants and adhesives.[13] The approach generally involves using an olefin metathesis catalyst, an appropriate chain transfer agent (CTA) such as 2-butene-1,4-diacetate, and 1,5-cyclooctadiene (COD) or high molecular weight polybutadiene (PBD) as the butadiene equivalent (Scheme 1). The CTA not only provides the hydroxy functional group (which is usually protected to attenuate premature catalyst decomposition and therefore must be deprotected in a post-polymerization step) but also aids in regulating the molecular weight.[1,3,5] This approach has a distinct advantage over the free radical polymerization methods generally employed to prepare HTPBD as it provides polymers with an average of two functional groups per chain (F_n), as desired. Recently, we reported that the high functional group tolerance of $Cl_2(PCy_3)_2Ru{=}CHPh$ (Cy = cyclohexyl) (**1**)[14] allowed the approach to be extended to the synthesis of amino and carboxyl terminated telechelic PBDs.[15]



Scheme 1. General approach employed to prepare hydroxy end-functionalized telechelic polybutadienes *via* olefin metathesis.

Few reports exist on synthesis of telechelic polymers using highly strained cyclic olefins such as norbornene (bicyclo[2.2.1]hept-2-ene).[16-20] Polynorbornene (PNB) contains an expanded structure that can absorb large amounts of aromatic petroleum liquids or oils. This provides a convenient handle to tune the polymer's mechanical and thermal properties through plasticization. The material has successfully been used in sound barriers, oil spill recovery, and after cross-linking, in sealants and mechanical damping applications.[21] These properties make the material highly desirable for use in block copolymers and polymeric networks.[1] In addition, a wide variety of derivatives of norbornenes are available through simple Diels-Alder reactions. Unfortunately, placing functional groups at the end (or both ends) of the polymer chains remains challenging.

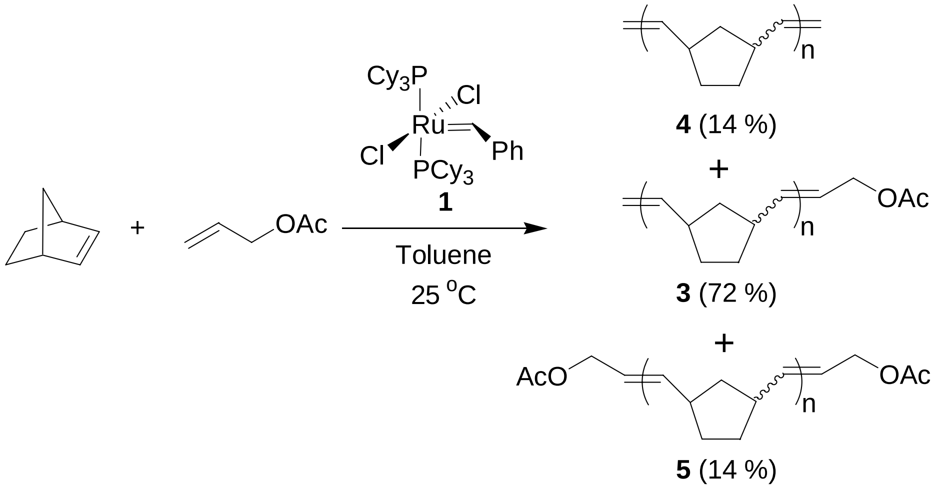
Fontanille and co-workers prepared ester-terminated telechelic PNBs using $WCl_6/Sn(CH_3)_4$ as the metathesis catalyst, unsaturated diesters as the CTAs, and norbornene as the monomer.[17] High catalyst loadings were necessary and ultimately lead to a depressed average of functional groups per polymer chain (1.7 to 1.9). In addition, poor agreement between the theoretical and experimental molecular weights was observed. Nevertheless, the ester functionality was successfully reduced to obtain hydroxy terminated telechelic PNBs. More recently, Gibson *et al.* extended this approach using Ru catalyst **1** to prepare hydroxy terminated telechelic *tert*-butyl ester functionalized PNBs.[19] While excellent control over molecular weight and end-functionality was achieved, carefully timed reagent additions were necessary and each polymer chain required an appropriately functionalized catalyst (as the initiator). Thus, there is a demand to increase the synthetic feasibility of preparing telechelic PNBs and reduce the catalyst loading.

The procedure described below for the synthesis of ester, hydroxy, and vinyl terminated telechelic and semi-telechelic (polymers possessing only one functional group per chain) PNBs is analogous to the approaches previously employed by our group to prepare telechelic PBDs from COD and an appropriate chain transfer agent.[11,12,15] The method uses low catalyst loadings, provides excellent end-group control, and permits the preparation of polymers with tunable molecular weights.

Results and Discussion

The ROMP of norbornene using Ru catalyst **1** has been previously shown to be extremely rapid and generally affords only high molecular weight material.[22] This result is observed even when high catalyst loadings are employed which would theoretically increase the number of polymer chains and therefore reduce molecular weight. This has been attributed to a slow rate of initiation (k_i) relative to propagation (k_p).[14] As discussed above, a well-known method for controlling molecular weight in ROMP is through the inclusion of acyclic olefins which effectively act as CTAs.[1,3,5] In addition, it has been previously shown that telechelic polymers can be obtained under certain conditions when symmetrically functionalized CTAs are employed.[6-12] When CTA 1,4-bis(acetoxy)-*cis*-2-butene (**2**) was included in the ROMP of norbornene (initiated by complex **1**), only high molecular weight polymer was obtained. Similar results were observed even when relatively high CTA loadings (CTA/monomer = 10) were employed. Congruent with an analogous system using COD as the monomer to form telechelic PBDs,[12] high molecular weight polymer was observed to form first. However, since the solvent extensively swelled the PNB, the reaction mixture became extremely viscous and further reaction between the growing polymer chains and the CTA was severely suppressed. In addition, the double bonds in PNB are less reactive in ROMP due to the steric hindrance of the adjacent centers.

Since Ru carbenes are known[23] to exhibit high rates of reactivity towards terminal olefins, efforts were shifted towards using allyl acetate as the CTA. When the polymerizations were performed in toluene ($[\text{monomer}]_0$ = 2.6 M, CTA/monomer = 5) using a monomer/catalyst loading = 4000 at 25 ºC, no polymer precipitation or swelling was observed. After 24 hours, the solvent was evaporated, and the resultant mixture of polymers was separated using column chromatography (silica gel, CH_2Cl_2 as eluent). Predominately (~72 %) PNB **3**, capped with allyl acetate on one terminus of the polymer chain and a vinyl group on the other, was obtained (Eq. 2) in addition to small amounts of bis-vinyl (**4**) (~14 %) and bis-acetoxy (**5**) (~14 %) end-functionalized PNBs. End-group analysis of PNB **3** using ^{1}H NMR spectroscopy indicated a perfect 1:1 stoichiometry between the acetate and vinyl end-groups with a number average molecular weight of 1800 g/mol. This result was in agreement with the theoretical value of 1500 g/mol (based on monomer and CTA consumption as determined by gas chromatography). Gel permeation chromatography (GPC) revealed the polymer distribution was monomodal (PDI = 1.8) with a molecular weight of 1700 g/mol (relative to polystyrene standards in THF). The PNB backbone contained *ca*. 85% *trans* olefin geometry, as expected for polymerizations of norbornene with **1**.[24] Similarly, end-group geometries were determined to be approximately 70% *trans*. The polymerizations were repeated in a similar fashion as described above using a variety of monomer/CTA ratios (Table 1) and afforded good yields (70 - 80%) of semi-telechelic polymer **3** over a wide range of molecular weights.



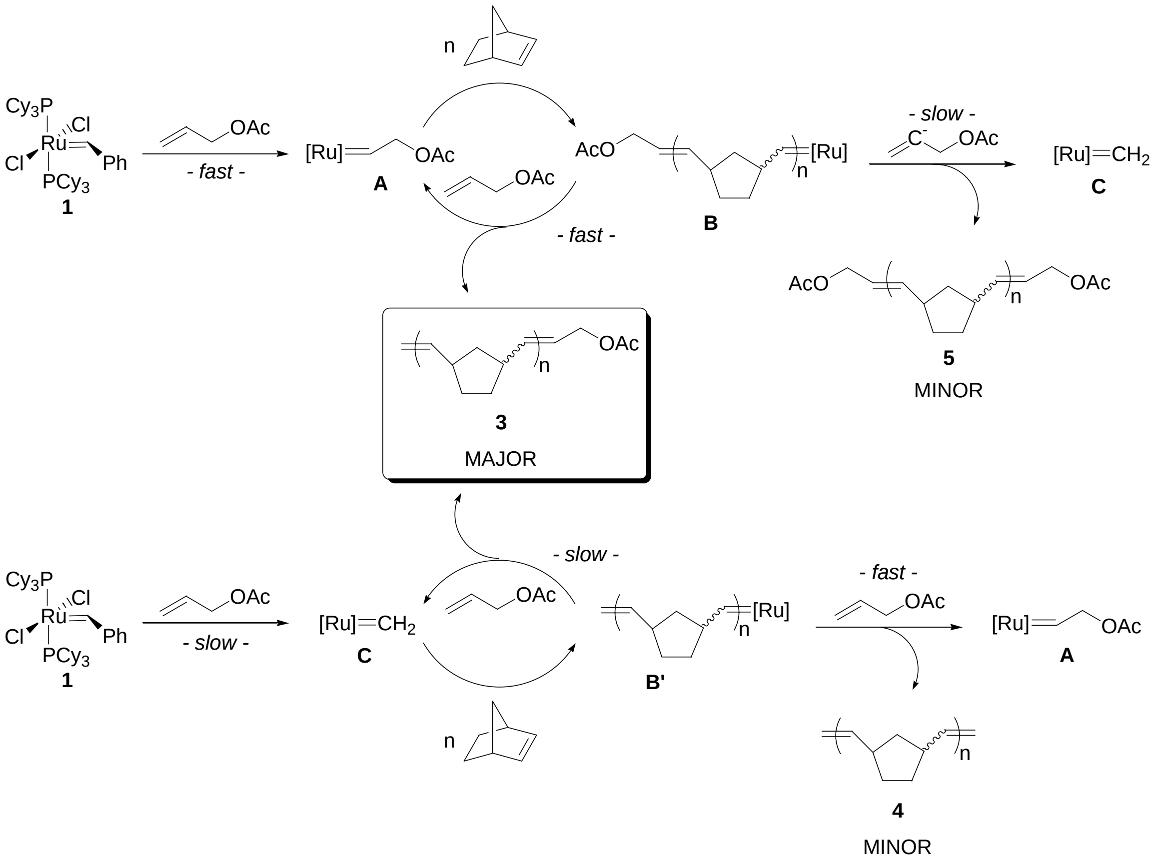
(2)

Table 1. Synthesis of a variety of acetoxy end-functionalized semi-telechelic poly-(norbornene)s **3**.[a]

M/CTA[b]	Yield[c] (%)	MW[d] (theo)	MW[e] (NMR)	M_n[f] (GPC)	PDI[f]	F_n[g]	Trans[h] (%)
5	72	1500	1800	1700	1.8	1.0	85
10	82	3400	3000	3600	1.7	1.0	82
25	75	8600	9400	8800	2.1	1.1	80

[a] Polymerizations conditions: Toluene as solvent, [Norbornene]$_0$ = 2.6 M, Temp = 23 ºC, Time = 12 h, Ar atmosphere, monomer/catalyst (**1**) = 4000, CTA = allyl acetate (**2**). [b] [Monomer]$_0$/[CTA]$_0$. [c] Isolated yield. [d] Theoretical MW based on residual monomer and CTA as determined by GC. [e] MW determined ^{1}H NMR end-group analysis. An average of one functional group per polymer chain was assumed. [f] Determined by gel permeation chromatography using THF as the eluent. The values are reported relative to monodispersed polystyrene standards. [g] Averaged ratio of ester groups to terminal olefins per polymer chain. [h] Percent *trans* olefin in the polymer backbone, as determined by ^{1}H and ^{13}C NMR spectroscopies.

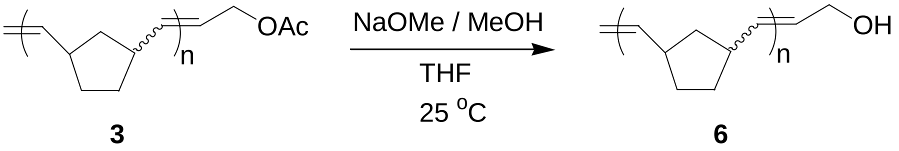
To gain a mechanistic understanding of how the end-functionalized polymers were formed, the polymerization (monomer/CTA = 5) was monitored over time using a combination of ^{1}H and ^{31}P NMR spectroscopies and the results are summarized in Scheme 2. Following rapid disappearance of initiator **1** from reaction with allyl acetate or monomer, three distinct carbene species were observed throughout the polymerization: acetate functionalized complex **A**, propagating species **B** (and **B´** which was indistinguishable from **B**), and to a lesser extent methylidene complex **C**.[25] Species **A** and **C** resulted from the cross-metathesis of **1** (or **B**) with allyl acetate, while **B** formed after the polymerization was initiated. Only a small amount of methylidene **C** was observed (signal intensity of **C** was <10% of **A**+**B**). The pathway in Scheme 2 leading to the formation of mono-functionalized PNBs **3** was that anticipated from the relative reactivities found in model systems.[26] In addition, the ratio of propagating species **B** to complex **A** was approximately 15:1 which was in agreement with the number of monomer units found in the resulting polymer chains ($X_n \approx 17$ by ^{1}H NMR spectroscopy, $X_n \approx 16$ by GPC). Thus, the molecular weight of the PNB appears to have been kinetically determined by the relative rates of reaction of the propagating species with CTA or monomer.[27,28] A similar mechanism has been recently proposed by Ozawa *et al.* in the ROMP of norbornene in the presence of heteroatom substituted vinyl substrates (using structurally similar Ru vinylidene initiators).[29]



Scheme 2. Proposed mechanistic pathways leading to the formation of end-functionalized polynorbornenes.[23,26]

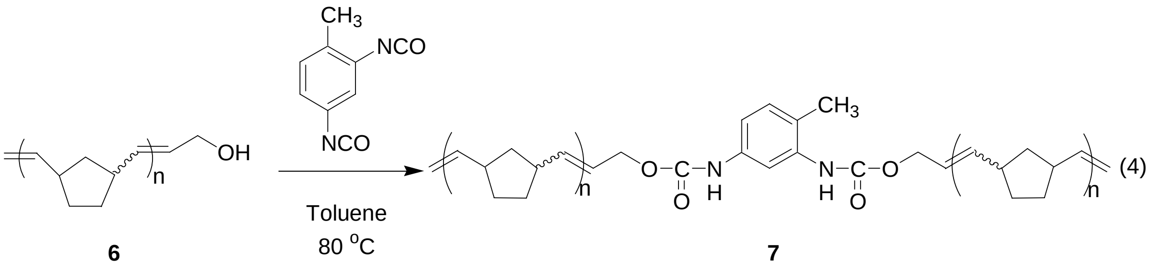
The kinetically controlled polymerization may stem from the lower reactivity of the propagating species towards olefins in the PNB backbone. For example, attempts to produce monofunctional PBD by the ROMP of COD in the presence of allyl acetate (using similar conditions as above) afforded a statistical mixture (1:2:1) of non, mono, and bis end-(acetoxy) functionalized polymers. In this case, the reactivities of the propagating species with monomer and olefins in the PBD backbone was similar and thus the reaction reached equilibrium. Furthermore, the reactivity of the propagating species appeared to depend on temperature as well. Performing the polymerizations described above (i.e., norbornene and CTA) at elevated temperatures (50 °C) also afforded statistical mixtures of end-functionalized PNBs.

Deprotection of the acetate group on PNB **3** using a mixture of sodium methoxide in methanol/THF gave hydroxy terminated PNB **6** in 86% isolated yield (Eq. 3). As expected, the molecular weight of **6** was slightly lower than **3** (M_n = 1500 g/mol by GPC) with no significant change in the polydispersity (PDI = 1.9) or polymer microstructure (85% *trans* olefin).

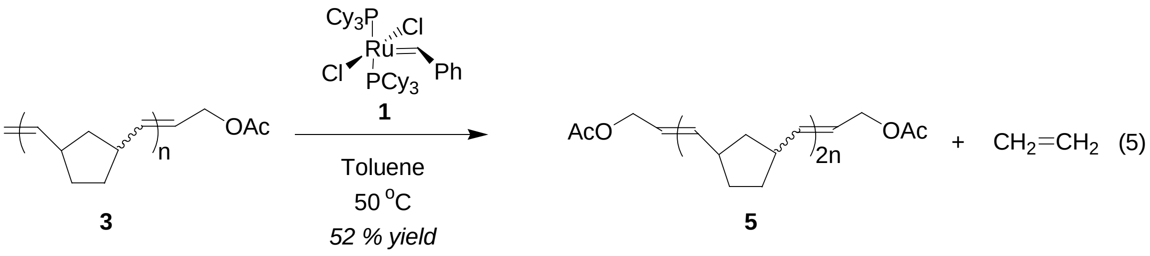


(3)

Reaction of two equivalents of PNB **6** with tolylene 2,4-diisocyanate in toluene at 80 ºC quantitatively afforded PNB **7** (Eq. 4). The presence of terminal vinyl groups and absence of hydroxy end-groups in the ^{1}H and ^{13}C NMR spectra indicated that the dimerization was complete. In addition, the ratio of the vinyl end-groups to the aromatic group on the diisocyanate was found to be 2:1. Accordingly, the molecular weight of the resulting polymer was nearly twice the starting material **6** by ^{1}H NMR spectroscopy (MW = 3100 g/mol) and GPC (M_n = 2900 g/mol, PDI = 2.5). Again, no change in the polymer backbone microstructure (85% *trans*) was observed during the deprotection or coupling reactions.

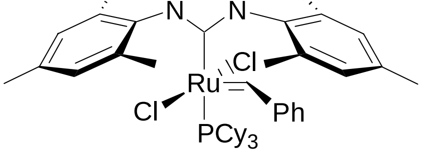


While the above procedure proved successful for preparing hydroxy mono-terminated (semi-telechelic) PNBs, the preparation of telechelic PNBs with hydroxy groups on *both* ends remained elusive and other synthetic protocols were explored. Cross-metathesis between two terminal olefins has become a powerful method for preparing complex organic substrates.[30] As shown in Eq. 5, dimerization of PNB **3** *via* cross-metathesis afforded a statistical mixture of PNBs **4**, **3**, and **5** (1:2:1). Elevated temperatures (50 °C) were necessary to achieve acceptable reaction rates, which as described above, may have resulted in extensive chain transfer which allowed the reaction to reach equilibrium.



Metathesis degradation of high molecular weight PBD (in the bulk or in solution) using Ru catalyst **1** and a CTA has been shown to be an alternative but powerful synthetic route to end-functionalized PBDs.[31] For example, bis(trimethylsilyl) end-functionalized telechelic PBD has been prepared through the metathetical degradation of high molecular weight PBD in the presence of an appropriately functionalized acyclic olefin.[8] The mechanism of degradation appears to proceed through (a catalyst mediated) chain transfer process between high molecular weight polymer chains and the CTA. This not only increases the number of chains (and concomitantly causes a reduction in the molecular weight) but also successfully transfers a functional group from the CTA to the end of the polymer chain.[5] Unfortunately, attempts at extending this methodology to PNB (in the bulk or solution) were unsuccessful. A possible explanation for the differential reactivity between PNB and PBD with **1** may be an increased steric hindrance around the olefins in the former polymer. Alternatively, in the case of bulk degradation, the difference may derive from the glass transition temperature (T_g) of the polymers. The T_g of 1,4-PBD is below -60 ºC, while the T_g of PNB is near 45 ºC (*vida infra*) which reflects depolymerizing a viscous liquid versus a solid polymer.[32] Performing the reaction at elevated temperatures (~60 ºC) resulted in only marginal degradation, which may be attributed to reduced catalyst lifetimes at higher temperatures.[33]

These barriers were overcome by employing catalysts with higher activity and thermal stability. Ruthenium complexes[34,35] **9** and **10,** which bear highly electron donating N-heterocyclic carbene ligands, have been shown to exhibit dramatically improved metathesis activity in ring-closing metathesis (RCM), cross-metathesis (CM), and ROMP when compared to the parent complex **1**.[34-38] In addition, these catalysts are thermally robust and are relatively inert towards oxygen and moisture.[34d]



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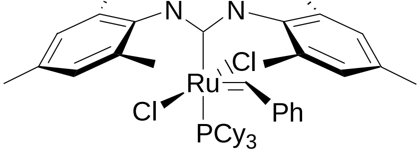
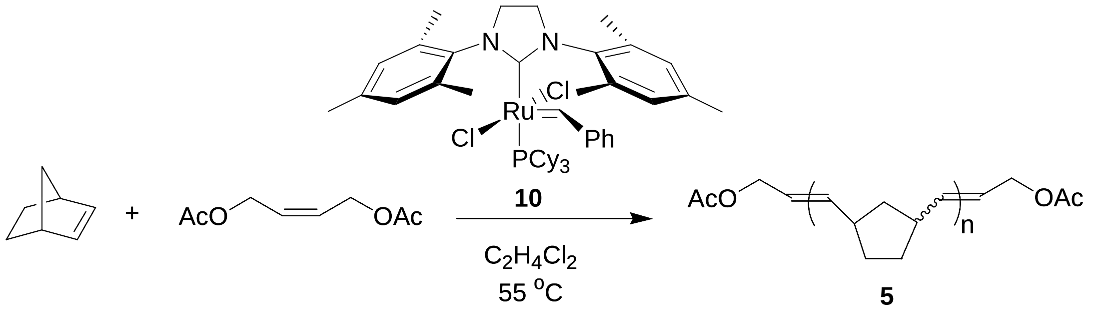


10

When the ROMP of norbornene was initiated by **10** (monomer/catalyst = 2000) and 1,4-bis(acetoxy)-*cis*-2-butene (**2**) was included as a CTA (monomer/CTA = 20), telechelic PNB **5** was obtained in 95% yield (Eq. 6). The polymerizations were performed in 1,2-dichloroethane at 55 ºC using $[\text{monomer}]_0 = 1.25$ M. After 12 h, the reaction mixture was poured into excess methanol and the precipitated polymer was collected by filtration. The molecular weight of the resulting PNB was determined by ^{1}H NMR spectroscopy to be 2000 g/mol by assuming an average of two functional groups per chain. This is in excellent agreement to the value expected (2100 g/mol) based on complete monomer and CTA incorporation. GPC indicated that the polymer had a polydispersity close to 2.0 and a molecular weight of 2100 g/mol (relative to polystyrene standards in THF). The T_g of the polymer was 45 ˚C as determined by differential scanning calorimetry (DSC). The *trans* olefin content in the polymer backbone was found to be between 60% and 65% by ^{1}H and ^{13}C NMR spectroscopy, which is lower than the *trans* content obtained when norbornene was polymerized with **1** and may reflect inherent *cis/trans* selectivities of the catalyst for norbornene. In addition, the stereochemistry of the polymer end-groups was determined to be approximately 65% *trans* olefin geometry. No vinyl end-groups olefins were observed.



(6)

The polymerizations were performed in a similar fashion as described above using a variety of monomer/CTA ratios (Table 2). The procedure afforded excellent yields (~90%) of telechelic polymer over a wide range of molecular weights. While most of the polymers prepared in Table 2 were isolated by simple precipitation (from methanol) and filtration procedures, the low molecular weight PNBs (MW < 1500 g/mol) remained soluble in the methanol/1,2-dichloroethane mixture. In these cases, solvent was simply evaporated after the polymerization was complete and residual catalyst was removed using silica gel chromatography. As shown in Figure 1, excellent agreement between the theoretical and experimental molecular weights was observed which reflects the high fidelity of this reaction. In addition, it is important to note that the PDI of each polymer described in Table 1 was near 2.0. Metathesis polymerizations with extensive chain transfer approximate a step-growth polymerization which yields polydispersity indices near two at high monomer conversion.[5]

Physical observations made throughout the polymerization provided strong mechanistic implications. High molecular weight PNB separated almost immediately when a 1,2-dichloroethane solution of norbornene (2.5 M) was added to a pre-heated (55 °C) solution of the catalyst **10** (1.3 mM) and CTA. This observation was analogous to when **1** was employed as the catalyst (*vide supra*). However, as the propagating Ru species (and any residual initiator) underwent chain transfer with the CTA, the molecular weight of the polymer decreased and therefore slowly dissolved over time. These observations are summarized in the mechanism proposed in Scheme 3. Monitoring the polymerization using GPC provided further evidence for this mechanism. As shown in

Figure 2, the molecular weight of the (soluble) polymer in the liquid phase of the reaction mixture was found to decrease over time.

Table 2. Synthesis of a variety of bis(acetoxy) end-functionalized telechelic polynorbornenes **5**.[a]

M/CTA[b]	Yield[c] (%)	MW[d] (theo)	MW[e] (NMR)	M_n[f] (GPC)	PDI[f]	F_n[g]	Trans[h] (%)
5	89	649	650	640	2.8	1.89	62
10	86	1120	1200	1100	2.3	1.90	62
20	86	2061	2100	2000	2.2	1.90	63
50	87	4886	4900	4800	2.0	1.93	65
100	91	9594	11000	11200	2.0	1.95	67
200	93	19010	20000	19500	2.0	1.95	67

[a] Polymerizations conditions: 1,2-dichloroethane as solvent, $[\text{Norbornene}]_0$ = 1.0 M, Temp = 55 ºC, Time = 12 h, Ar atmosphere, monomer/catalyst (**10**) = 2000, CTA = 1,4-diacetoxy-2-butene (**2**). [b] $[\text{Monomer}]_0/[\text{CTA}]_0$. [c] Isolated yield. [d] Theoretical MW based on complete monomer conversion and CTA incorporation. [e] MW determined by ^{1}H NMR end-group analysis. An average of two functional groups per polymer chain was assumed. [f] Determined by gel permeation chromatography using THF as the eluent. The values are reported relative to monodispersed polystyrene standards. [g] Average number of functional groups per polymer chain as determined by removal of the acetoxy groups followed by back-titration of the liberated acetate anion (see text for more details). [h] Percent *trans* olefin in the polymer backbone, as determined by ^{1}H and ^{13}C NMR spectroscopies.

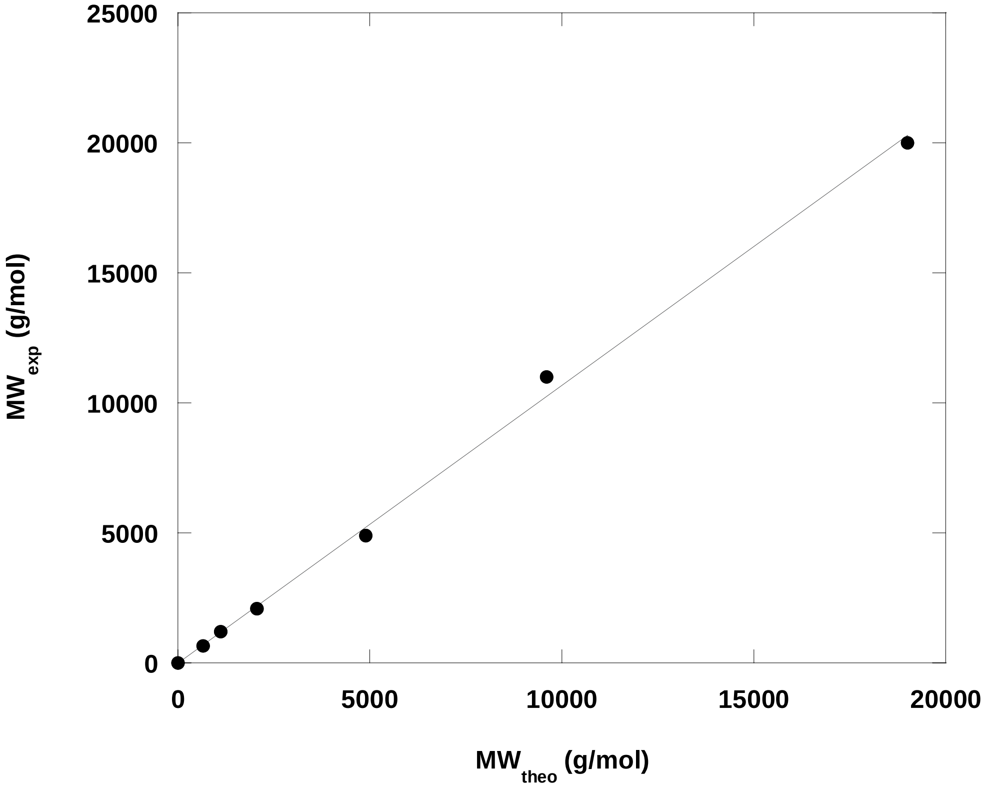


Figure 1. Comparison of theoretical molecular weights (based on complete monomer conversion and CTA incorporation) and their corresponding experimentally determined values (using ^{1}H NMR spectroscopy and assuming an average of two functional groups per polymer chain) for the synthesis of a variety of bis(acetoxy) end-functionalized telechelic polynorbornenes **5**. The values were taken from Table 2.

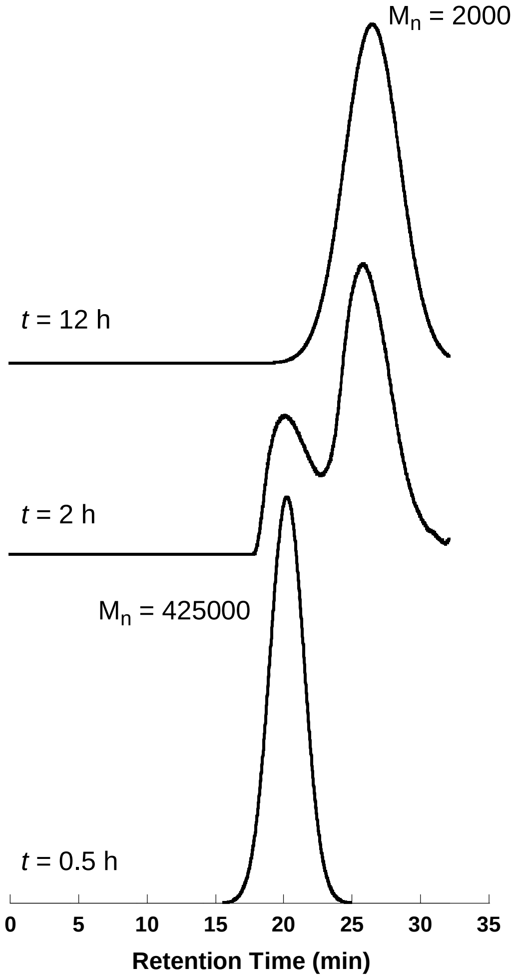
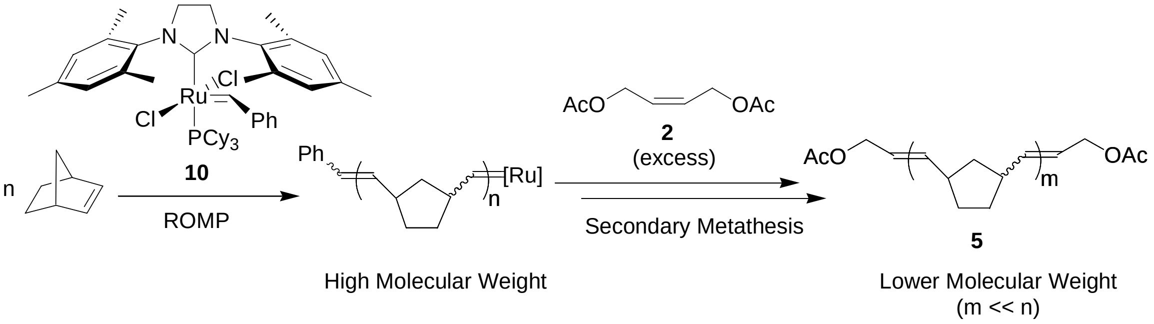


Figure 2. Molecular weight evolution of polynorbornene as a function of time. M_n was determined by GPC using THF as the eluent. The values are reported relative to monodispersed polystyrene standards. Conditions: 1,2-dichloroethane as solvent, Temp = 55 ºC, Ar atmosphere, $[\text{Norbornene}]_0$ = 1.0 M, monomer/catalyst (**10**) = 2000, CTA = 1,4-diacetoxy-2-butene (**2**), $[\text{Monomer}]_0/[\text{CTA}]_0$ = 20.



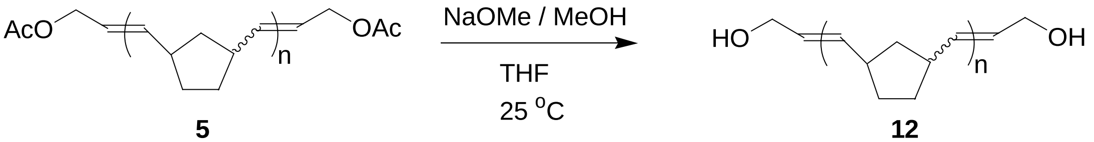
Scheme 3. Proposed mechanism leading to the formation of bis(acetoxy) end-functionalized telechelic polynorbornenes **5**.

As described above, an alternative approach to telechelic polymers prepared *via* olefin metathesis has been through the degradation of high molecular polymer in the presence of a symmetrically substituted CTA.[5] We attempted to extend this approach to the preparation of telechelic PNBs using the highly active Ru catalyst **10**. A benzene mixture of commercially available[39] high molecular weight PNB (MW 3,000 – 4,000 kg/mol), CTA **2** (monomer/CTA = 20), and catalyst **10** (monomer/catalyst = 2000) was heated to 55 ºC for 24 h. While a significant portion of the polymer dissolved, an unidentified contaminant in the commercial polymer separated from the liquid phase of the reaction mixture. The contaminant did not dissolve in boiling toluene and was probably cross-linked PNB. The dissolved polymer was precipitated into rapidly stirring methanol and examined by ^{1}H and ^{13}C NMR spectroscopies and GPC. While molecular weight reduction was observed (M_n = 3200 g/mol by GPC), the distribution of polymer chains was multi-modal. In addition, several unidentifiable resonances in both the aliphatic and olefin regions of the ^{1}H and ^{13}C NMR spectra were observed. These resonances may stem from a lightly (non-metathetical) cross-linked PNB network.

Nevertheless, allyl acetate end-groups were observed, suggesting that the reaction was successful to some extent.

To prove that a desired degree of degradation could be obtained in the absence of contaminants, high molecular PNB was prepared *via* the ROMP of norbornene using $(PPh_3)_2Cl_2Ru{=}CHPh$ (**11**), a catalyst capable of mediating the living polymerization of norbornene.[14] Combination of norbornene and **11** (monomer/catalyst = 10000) in toluene ($[\text{monomer}]_0$ = 0.5 M) at 25 ºC afforded PNB (M_n = 130 kg/mol by GPC, PDI = 1.3) in 90% yield. This PNB was subjected to the same degradation conditions as the commercial PNB described above. Complete dissolution was observed within 4 hours, and characterization of the resulting polymer indicated that the desired degree of degradation was achieved. GPC analysis revealed that the M_n was 1900 g/mol as expected, with a polydispersity of 2.1. Only allyl acetate end-groups were observed by ^1H and ^{13}C NMR spectroscopy and the polymer's molecular weight was calculated to be 2050 g/mol. In addition, the amount of *trans* olefin in the PNB backbone decreased from 80% (found in the starting PNB) to 65%. Thus, it appears in the absence of (possibly cross-linked) contaminants, telechelic PNBs can be obtained *via* the degradation of high molecular PNB.

Deprotection of the bis(acetoxy) end-functionalized telechelic PNBs **5** (i.e., removal of the acetate groups) was accomplished using a methanolic/THF solution of sodium methoxide followed by an acidic workup (Eq. 7). This afforded the corresponding hydroxy end-functionalized PNB **12** in quantitative yield. Potentiometric titration of the liberated acetate (generated using a slight modified deprotection procedure, see the experimental section for further details) on a range of PNB samples indicated an average of 1.9 ± 0.1 hydroxy groups per polymer chain (Table 2).[40] These numbers not only illustrated the success of the reaction but also justified the assumption (of using two functional groups per polymer chain) taken to determine MW by NMR spectroscopy. No change in the *cis*/*trans* ratio of the polymer backbone was observed.



5 **12** (7)

Since PNB standards are not commercially available to calibrate GPC instrumentation, it is common to report the molecular weight of the polymer relative to monodispersed polystyrene samples. The hydrodynamic volumes of these two polymers are not identical and therefore a correction factor has been generally applied to achieve agreement between experimental and theoretical molecular weights. Unfortunately, several inconsistencies in the factors are found throughout the literature, especially in the low molecular weight regime.[41] Since our titration experiments fully supported the assumptions taken to determine molecular weight by NMR end-group analysis (an independent method of determining molecular weight), we compared these values to those obtained *via* GPC (calibrated with polystyrene standards) in two different solvents. As shown in Figure 3, when THF was used at the GPC eluent, excellent agreement between the NMR spectroscopic and GPC determined molecular weights was observed. However, using CH_2Cl_2 as the GPC eluent, the molecular weights of the PNBs were approximately twice those obtained by NMR spectroscopy. Apparently, the hydrodynamic volume of a PNB chain in CH_2Cl_2 is approximately one-half of a comparable molecular weight poly(sytrene) chain, while in THF the hydrodynamic volumes of the two polymers are similar. Thus, when characterizing low molecular weight PNBs (MW < 25 kg/mol) by GPC against polystyrene standards, we suggest that no correction factor be applied when THF is used as eluent and 0.5 x M_n be applied when using CH_2Cl_2.

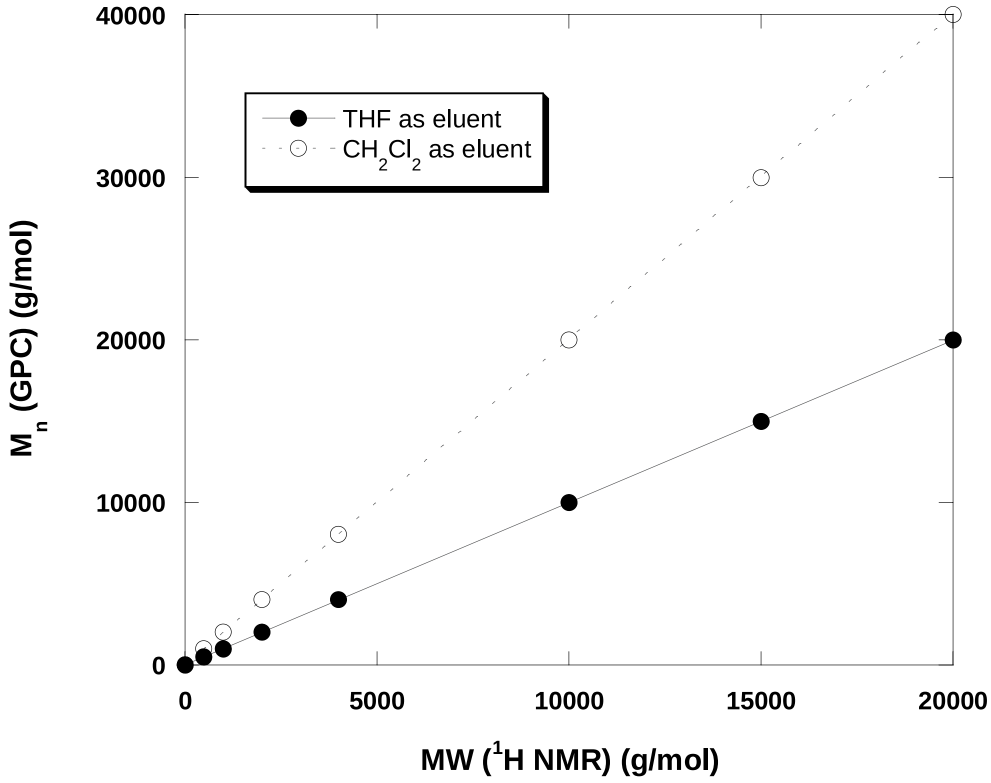


Figure 3. Comparison of molecular weights of a variety of bis(acetoxy) end-functionalized telechelic PNBs **5** determined by ^{1}H NMR spectroscopy and GPC. Standard end-group analysis procedures were employed for the ^{1}H NMR spectroscopic measurements. Either THF or CH_2Cl_2 was used the eluent in the GPC measurements and the values are reported relative to monodispersed polystyrene standards.

Conclusion

The synthesis of a variety of polynorbornenes bearing acetoxy, hydroxy, and vinyl end-groups was accomplished using ring-opening metathesis polymerization (ROMP). PNBs with an acetoxy group at one terminus and a vinyl group at the other were prepared using norbornene, $(PCy_3)_2Cl_2Ru{=}CHPh$ (**1**), and allyl acetate as a chain transfer agent (CTA). Molecular weight appears to be kinetically determined by the relative rates of reaction between the propagating species and monomer or CTA. Removal of the acetoxy groups was accomplished with sodium methoxide and afforded the corresponding hydroxy terminated polymers. Bis(vinyl) end-functionalized telechelic PNB was obtained by coupling the hydroxy end-functionalized to tolylene 2,4-diisocyanate. Attempts at preparing the bis(acetoxy) end-functionalized PNBs through dimerization of mono acetoxy end-functionalized semi-telechelic PNB afforded a statistical mixture of end-functionalized polymers.

An alternative and successful route to bis(acetoxy) end-functionalized PNBs was the result of using a more active olefin metathesis ruthenium based catalyst bearing an imidazolylidene ligand (**10**). Reaction of norbornene, 1,4-diacetoxy-2-butene as the CTA, and the highly active catalyst led to the formation of the desired bis(acetoxy) end-functionalized PNB. The mechanism appears to initially proceed through the formation of high MW PNB followed by polymer depolymerization from chain transfer reactions with the CTA. The experimentally determined molecular weights of the resulting telechelic polymers were in excellent agreement with their theoretical values and were easily controlled by simply varying the initial monomer/CTA ratio. Acetoxy end-functionalized PNBs were also obtained by degradation of high molecular weight PNB.

As with the mono end-functionalized polymers, the acetoxy groups were removed to obtained hydroxy terminated telechelic PNBs with number average functionalities close to 2.0.

Prior to this study, few routes to end-functionalized (especially telechelic) PNBs existed. In addition, these prior methods required high catalyst loadings and in some cases were unsuccessful in controlling molecular weight. The procedures outlined above provide several synthetically feasible, cost-effective routes to end-functionalized PNBs. Past experience has suggested that functionalized norbornenes will undergo similar reactions and will provide a wide range of telechelic functional materials. These polymers are expected to complement or substitute other telechelic polyalkenamers commonly employed in industry.

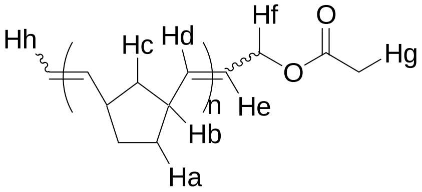
Experimental Section

General. Argon was purified by passage through columns of BASF R-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde).[42] NMR spectra were recorded in a GE QE-300 Plus (300.10 MHz ^{1}H ; 75.49 MHz ^{13}C) spectrometer or a JEOL GX-400 (399.65 MHz ^{1}H; 100.00 MHz ^{13}C; 161.85 MHz ^{31}P) spectrometer. Chemical shifts were recorded in parts per million (δ) and referenced to residual protio solvent. Coupling constants, *J*, are reported in hertz (Hz). Gel permeation chromatographs were obtained on either a HPLC system using an Altex model 110A pump, a Rheodyne model 7125 injector with a 100 μL loop, two American Polymer Standards, Inc. 10 μm mixed bed columns, and a Knauer differential refractometer using CH_2Cl_2 as eluent or on an analogous system using THF as the eluent. In either system, the flow rate was set to 1.0

mL/min and molecular weights and polydispersities were reported relative to monodispersed polystyrene standards (obtained from American Polymer Standards, Inc.). Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Pyris-7 calorimeter using a scan rate of 10 ˚C/min under an atmosphere of nitrogen.

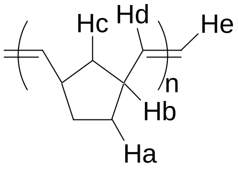
Materials. Catalysts **1**, **10**, and **11** were prepared as previously described.[14,35] Norbornene (Aldrich) was distilled from sodium metal. 1,4-Diacetoxy-2-butene and allyl acetate were purchased from TCI America, Inc. and distilled prior to use. 1,2-Dichloroethane was purged with Ar for 30 minutes. Toluene was purified by passage through a solvent column.[42] Tolylene 2,4-diisocyanate (Aldrich) was used as received. All other solvents were reagent grade and used without further purification.

Representative Procedure for Preparing Acetoxy End-functionalized Semi-Telechelic Polynorbornene 3. Inside a N_2 filled drybox, a small vial was charged with 10.9 mg (13.2 μmol) of catalyst **1** and a stir bar. A separate vial was charged with 5.00 g (53.1 mmol) of norbornene, 1.06 g (10.6 mmol) of allyl acetate, and 20 mL of toluene. Both vials were sealed and cooled to –30 ºC. The toluene solution was then transferred to the vial containing the catalyst via syringe and allowed to warm to room temperature under vigorous stirring. After 24 h at 25 °C, 0.6 mL (6.3 mmol, 500 equiv. relative to catalyst) of ethyl vinyl ether was added to quench the polymerization. The reaction mixture was then poured into excess stirring methanol (100 mL) causing precipitation of a white solid. The methanol was decanted away and the resulting solid was washed with fresh methanol (25 mL) three times. The material was collected and purified by silica gel chromatography to afford 3.9 g of semi-telechelic PNB **3** (72% yield, based on complete monomer conversion and 40% allyl acetate consumption as determined by GC analysis). GPC: $M_n = 1700$, $M_w = 3000$, PDI = 1.8. The ^{1}H NMR spectrum was assigned as follows:



^{1}H NMR ($CDCl_3$): δ 5.84-5.65 (bm, Hd + He), 5.28 (bd, Hd *trans*), 5.20 (bd, Hd *cis*), 5.01-4.82 (m, Hh), 4.62 (d, Hf, *cis*), 4.50 (d, Hf, *trans*), 2.74-2.65 (bs, Hb *cis*), 2.60-2.31 (bs, Hb, *trans*), 2.04 (s, Hg), 1.93 (bm, Hc), 1.77 (bm, Ha), 1.51-1.26 (bs, Ha), 1.18-0.97 (bm, Hc), MW = 1800 (end-group analysis).

Also recovered (0.81 g, 14%) from the reaction mixture was telechelic polynorbornene **4**. GPC: $M_n = 1500$, $M_w = 2400$, PDI = 1.6. The ^{1}H NMR spectrum was assigned as follows:

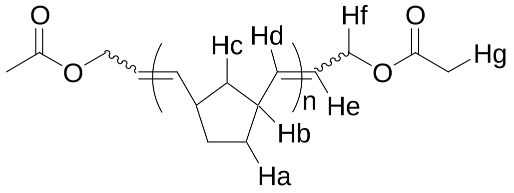


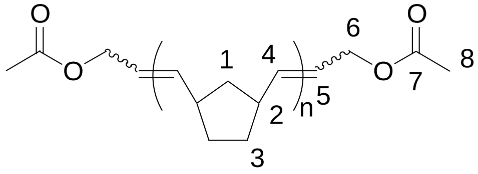
^{1}H NMR ($CDCl_3$): δ 5.86-5.74 (m, Hd), 5.40-5.33 (bm, Hd *trans*), 5.21 (bd, Hd *cis*), 5.00-4.85 (m, He), 2.79 (bs, Hb *cis*), 2.43 (bs, Hb, *trans*), 1.95-1.68 (bm, Hc), 1.47-1.29 (bm, Ha), 1.17-1.04 (bm, Hc), MW = 1400 (end-group analysis).

Acetoxy end-termined telechelic polynorbornene **5** (0.81 g, 14%) was also recovered from the reaction mixture. GPC: $M_n = 2100$, $M_w = 3800$, PDI = 1.8.

Assignment of its ^{1}H NMR spectrum can be found below; MW = 1900 (end-group analysis).

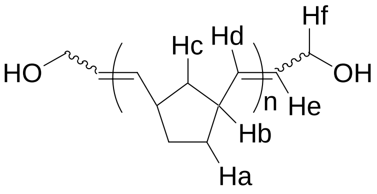
General Polymerization Procedure for Preparing Acetoxy End-functionalized Telechelic Polynorbornenes 5. Inside a N_2 filled drybox, a 5 dram vial was charged with catalyst **10** (5 mg, 6 μmol), 5 mL of 1,2-dichloromethane, and a stir bar. The vial was then capped with a rubber septum and removed from the drybox. After adding 1,4-diacetoxy-2-butene (0.1 mL, 0.6 mmol) *via* syringe, the vial was immersed in an oil bath thermostatted at 55 ºC. Under vigorous stirring, 5.12 mL (12.8 mmol) of norbornene (as a 2.5 M solution in 1,2-dichloroethane) was added via syringe. Separation of high molecular weight polynorbornene occurred almost immediately. The polymer then gradually dissolved over the next 2 hours. After 12 hours at 55 °C, the reaction was poured into excess stirring methanol (100 mL) causing precipitation of a white solid. The material was collected by filtration affording 1.2 g of telechelic PNB **5** (95 % yield). (In cases where low MW polymer was prepared, the reactions were passed through a short column of silica gel followed by evaporation of solvent under reduced pressure.) GPC: M_n = 2000, M_w = 4400, PDI = 2.2. DSC: T_g = 45 ºC. The ^{1}H and ^{13}C NMR spectra were assigned as follows:

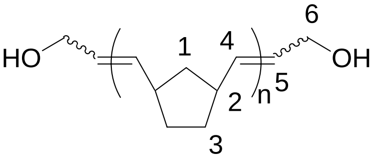




^{1}H NMR (CDCl$_3$): δ 5.81-5.94 (bm, Hd + He), 5.27 (bs, Hd *trans*), 5.13 (bd, Hd *cis*), 4.12 (bd, Hf, *cis*), 3.98 (bd, Hf, *trans*), 2.72 (bs, Hb, *cis*), 2.36 (bs, Hb, *trans*), 2.05 (bs, Hg), 1.78 (bm, Hc), 1.69 (bs, Ha), 1.28 (bs, Ha), 0.96 (bm, Hc). ^{13}C NMR (CDCl$_3$): δ 171.10 (C7), 141.08 (C5, t), 140.93 (C5, c), (134.46 (C4, tcc), 134.41 (C4, tct), 134.33 (C4, ccc), 134.28 (C4, ctc), 133.70 (C4, cct), 133.58 (C4, ttc), 133.58 (C4, ttt), 133.47 (C4, ctt), 65.67 (C6), 44.07 (C2, tc), 43.79 (C2, tt), 43.32 (C1, cc), 42.66 (C1, ct and tc), 41.93 (C1, tt), 38.73 (C2, cc), 39.22 (C2, ct), 33.62 (C3, cc), 33.45 (C3, ct), 32.91 (C3, tc), 32.76 (C3, tt), 21.37 (C8); MW = 2100 (end-group analysis).

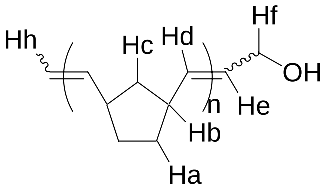
General Procedure for Removing the Acetoxy Groups from the End-functionalized Polynorbornenes. A 25 mL Erlenmeyer flask was charged with 500 mg (0.25 mmol) of acetate protected PNB **5** (MW = 2000) and 0.16 g (3 mmol) of NaOCH$_3$ (12 equiv. per polymer chain), 15 mL of THF, and 5 mL of CH$_3$OH. This mixture was stirred for 48 h at 45°C (higher temperatures appeared to result in cis/trans isomerization). Afterwards, residual base was quenched with a 1:3 methanol-water solution saturated with NH_4Cl and the resulting polymer was extracted (2 x 20 mL) into THF. The THF polymer solution was washed with water and evaporated under reduced pressure to afford 405 mg (88% yield) of hydroxy-terminated telechelic PNB **12** (as a highly viscous gel). GPC: M_n = 1900, M_w = 3900, PDI = 2.1. DSC: T_g = 43 ºC. The ^1H and ^{13}C NMR spectra were assigned as follows:





^1H NMR ($CDCl_3$): δ 5.82-5.91 (bm, Hd + He), 5.31 (bs, Hd *trans*), 5.17 (bd, Hd *cis*), 4.15 (bs, Hf, *cis*), 4.04 (bs, Hf, *trans*), 2.70 (bs, Hb, *cis*), 2.34 (bs, Hb, *trans*), 1.77 (bm, Hc), 1.73 (bs, Ha), 1.26 (bs, Ha), 0.95 (bm, Hc). ^{13}C NMR ($CDCl_3$): δ 140.83 (C5, t), 140.69 (C5, c), 134.04 (C4, tcc), 133.98 (C4, tct), 133.92 (C4, ccc), 133.87 (C4, ctc), 133.83 (C4, cct), 133.21 (C4, ttc), 133.09 (C4, ttt), 132.94 (C4, ctt), 60.98 (C6), 43.51 (C2, tc), 43.22 (C2, tt), 42.81 (C1, cc), 42.18 (C1, ct and tc), 41.45 (C1, tt), 38.73 (C2, cc), 38.48 (C2, ct), 33.15 (C3, cc), 32.98 (C3, ct), 32.42 (C3, tc), 32.27 (C3, tt); MW = 2000 (end-group analysis).

An similar procedure was employed to prepare acetoxy end-functionalized semi-telechelic PNB **6** (86% yield) via deprotection of PNB **3** (M_n = 1700, PDI = 1.8). GPC: M_n = 1500, M_w = 2850, PDI = 1.9. The ^1H NMR spectrum was assigned as follows:



^{1}H NMR (toluene-d_8): δ 5.80-5.63 (bm, Hd + He), 5.42 (bd, Hd *trans*), 5.28 (bd, Hd *cis*), 5.02-4.83 (m, Hh), 3.97 (bs, Hf, *cis*), 3.82 (bs, Hf, *trans*), 2.85-2.68 (bs, Hb *cis*), 2.59-2.25 (bs, Hb, *trans*), 2.02-1.83 (bm, Hc), 1.83-1.62 (bm, Ha), 1.58-1.25 (bs, Ha), 1.14-1.03 (bm, Hc); MW = 1600 (end-group analysis).

Titration Experiments. A 25 mL flask was charged with 500 mg (0.25 mmol) of bis(acetoxy)-functionalized telechelic PNB **5**, 100 mg (2.5 mmol) of crushed NaOH, and 15 mL of acetonitrile and then heated to reflux (under Ar) for 6 h. After cooling the solution to 0 ˚C (ice-bath), a 1.0 M solution (1.6 mL) of perchloric acid was slowly added to neutralize the excess base. The liberated acetate anion was then potentiometrically backtitrated with a freshly prepared pre-standarized[43] 0.1083 M perchloric acid solution in ethanol. The end point (and thus F_n) was determined using the Gran plot method.[44]

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(26) Previous studies have demonstrated that the reaction of **1** with a terminal olefin kinetically favors the formation of a substituted carbene complex (e.g., **A**) over methylidene (**C**).[14] In addition, the reaction of methylidene (**C**) with terminal olefins has been demonstrated[23] to be the formation of a substituted carbene (e.g., **A**). This combination of preferred reactivites favors the kinetic formation of end-functionalized PNB (**3**), as shown in Scheme 2.

(27) If the polymerization was thermodynamically controlled, a statistical formation (1:2:1) of non, mono, and bis (acetoxy) end-functionalized PNBs would be expected.

(28) Alternatively, production of **4** or **5** may have resulted from secondary metathesis, however it appears that such reactions only occur at elevated temperatures (*see text*).

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