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Polymerization of Functionalized Norbornenes Employing $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ as the Initiator

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ABSTRACT: Norbornenes containing esters, cyano, acetate, and related functionalities can be polymerized in a living manner employing $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ as the initiator, especially in THF, to give polymers with polydispersities as low as 1.04. Poly(*exo-cis*-2,3-norbornenediol diacetate) (poly-**6**), poly(*exo-syn*-2,7-norbornenediol diacetate) (poly-**7**), and poly(*exo-cis-O,O'*-isopropylidene-2,3-norbornenediol) (poly-**8**) can be hydrolyzed to give polymers containing hydroxyl groups in place of acetates. Poly-**6** and poly-**7** lose 2 equiv of acetic acid above 300 °C to give black intractable films; the analogous diols lose 2 equiv of water under similar conditions. Addition of *exo-cis*-2,3-dichloro-*endo-cis*-2,3-(carbonyldioxy)norbornene (**12**) to $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ yields an isolable square-pyramidal molybdacyclobutane complex, ~50% of which loses **12** at room temperature to re-form $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$. A block copolymer of 5-cyanonorbornene (**5**) and norbornene (100/100 equiv) was prepared. Living polymers containing molybdenum alkylidene end groups have been characterized by ^1H NMR methods.

Introduction

Metathesis catalysts that will tolerate functionalities have been sought ever since the discovery of the olefin metathesis reaction.[1] Since the metal center in metathesis catalysts shows electrophilic character, there may be some direct correlation between the rate at which a metal–carbon double bond reacts with a carbon–carbon double bond and the rate at which it reacts with donor functionalities such as the carbonyl group. Therefore, a given metal–carbon double bond could react relatively selectively with an especially reactive double bond (e.g., in a strained cyclic olefin) relative to a functionality elsewhere in the molecule. Indeed there seem to be many more examples of polymerizations of norbornenes that contain functional groups remote from the double bond than ordinary olefins that contain remote functional groups.[1] However, since details concerning the structure and reactivity of classical metathesis catalysts are virtually nonexistent, their reactivities cannot be controlled systematically. In contrast, a well-defined catalyst could be "deactivated" in a systematic fashion to the extent that it does not react with the functionality but still will react with the strained carbon–carbon bond on the time scale of the polymerization.

Recently well-characterized molybdenum[2] and tungsten[3] alkylidene complexes of the type $M(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ ($Ar = 2,6$-diisopropylphenyl) have been synthesized whose reactivities toward carbon–carbon double bonds can be varied dramatically by varying the nature of the alkoxides. Complexes containing *tert*-butoxides do not react readily with internal olefins but will react readily with the double bond in norbornenes.[4] This results in a process where no chain termination or chain transfer occurs on the time scale of initiation and propagation, i.e., one that has all the characteristics of a living polymerization. Preliminary[5] and more recent[6] results have suggested that $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ is more tolerant of functional groups than $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$. Furthermore, some intermediate alkylidene complexes that contain molybdenum seem to be more stable toward decomposition and side reactions.[7] In this paper we report the polymerization of a variety of functionalized norbornenes by $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$. The development of living ring-opening metathesis polymerization (ROMP[8]) catalysts that tolerate functionalities should create the possibility of preparing a wide variety of functionalized polymers of this general type and perhaps also create the possibility of attaining a significant degree of control over the polymer structure.[6]

Results

Survey of Functionalities Tolerated by $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$. Monomers that have been polymerized successfully by $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (Mo(CH-*t*-Bu)) are shown in Table I. A polymerization is termed successful if the monomer is consumed quantitatively according to proton NMR studies, the polymer can be cleaved from the metal in a Wittig-like reaction with aldehydes, and the polymer can be isolated quantitatively and has a narrow polydispersity (PDI). All of the polymers we have prepared are soluble in toluene or dichloromethane in the molecular weight range indicated. The preferred aldehydes that are used in the termination step do not have β protons (e.g., pivaldehyde or benzaldehyde). All polymerizations were carried out at room temperature under a nitrogen atmosphere in toluene or THF (~10 mL), with typical catalyst concentrations being 5–20 mM.

Norbornene (NBE) is polymerized rapidly in toluene, benzene, or THF. The alkylidene resonance for Mo(CH-*t*-Bu) at 11.23 ppm in C_6D_6 is replaced by one new H_α doublet resonance at 11.53 ppm that broadens slightly as the chain lengthens. There is no evidence for formation of a mixture of syn and anti rotamers about the Mo=C bond in living polynorbornene.[2,3] By use of 10 equiv of norbornene and measurement of the amount of residual initiator, the ratio k_p/k_i has been determined in toluene.[6b]

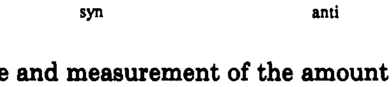

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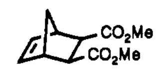
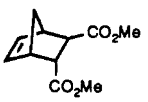
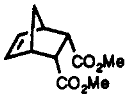
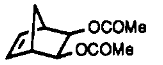
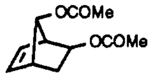
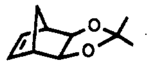
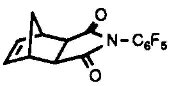
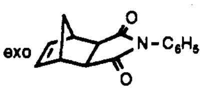
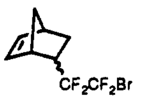
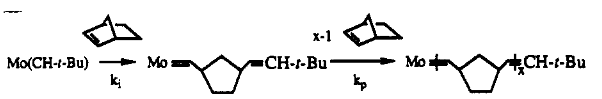
Table I
Monomers Polymerized by Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$

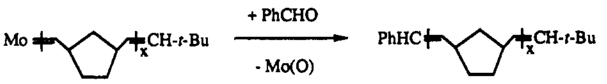
 1	 2	 3
50[b]/1.07[c] 100/1.06 200/1.04	50/1.06 100/1.07	50/1.05 100/1.04 200/1.04
 4	 5 (THF)	 6 (THF)
50/1.11 100/1.12 200/1.22	50/1.06 100/1.07 200/1.07	50/1.14 100/1.19
 7 (THF)	 8 (THF)	 9
50/1.13 100/1.11 200/1.09	50/1.12 100/1.07	50/1.05
 10		 11
100/1.07		100/1.06

[a] For reaction conditions, refer to the Experimental Section; solvent = toluene, unless specified otherwise. [b] Equivalents of monomer added. [c] Polydispersity index (vs polystyrene in dichloromethane).

The result ($k_p/k_i = 12.1$ (5))[9] is within the range that allows low polydispersities to be achieved for polymers containing 50 or more monomer units.[10] Olefinic proton resonances characteristic of cis and trans double bonds in the polymer chain are observed in the ratio of 2:3. Living polynorbornene reacts with benzaldehyde rapidly and quantitatively to yield benzylidene-capped polynorbornene (approximately 65% trans configuration).



(1)



(2)

Polymerization of norbornene in THF is not as satisfactory, owing to the sporadic appearance of some doubled molecular weight polynorbornene. The origin is uncertain. Only freshly distilled norbornene gives the expected results consistently.

Comparison of the polymers from **4** (PDI = 1.12, 100 equiv), **2** (PDI = 1.07, 100 equiv), and **3** (PDI = 1.04, 100 equiv) suggests that monomers that contain two endo functionalities behave less ideally than those that contain one or two exo substituents. In general, polymerizations employing classical catalysts have been less successful if substituents (especially two) are in endo positions.[1] To our knowledge, this is the first successful report of the polymerization of **2** and **4**. Polymerization of **3** by classical catalysts has been reported,[1a] but this polymerization, like the vast majority of those involving tungsten-based and molybdenum-based classical catalysts, did not show characteristics of a living system. Classical catalysts based on later transition metals such as ruthenium appear to tolerate functionalities to a greater degree,[1] and recent studies have shown that functionality-tolerant ruthenium catalysts can be prepared that are active in water and that have some living characteristics.[11]

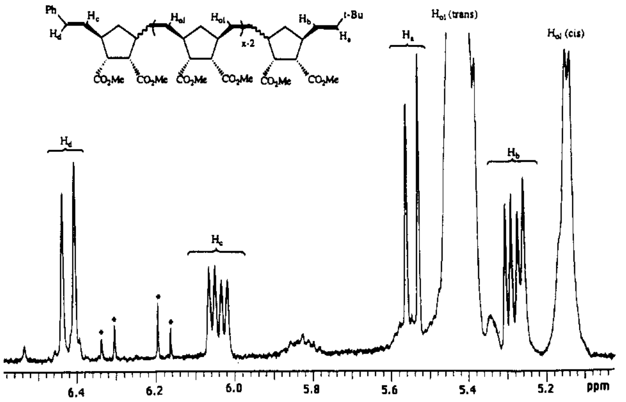


Figure 1. 500-MHz ^{1}H NMR spectrum (CDCl$_3$, 40 °C) in the olefinic region of the organic products resulting from adding 20 equiv of **2** to Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ followed by a benzaldehyde quench. (Asterisks = *trans*-PhCH═CH-*t*-Bu.)

The ^{1}H NMR spectrum of poly-**2** suggests that propagation is ~95% trans selective and that the trans to cis ratio does not change in several days in living poly-**2** containing 20 equiv of monomer; i.e., secondary metathesis is slow. The ^{1}H NMR spectrum of an oligomer made by adding 20 equiv of **2** to Mo(CH-*t*-Bu) followed by capping with benzaldehyde is shown in Figure 1. The configuration about the first double bond in the polymer is >98% trans (the error is ~2%), as shown by the patterns for the resonances ascribable to H$_b$ at 5.29 ppm (dd, J_{HH} = 15 and 7 Hz) and H$_a$ at 5.53 ppm (d, J_{HH} = 15 Hz). The double bond that is formed in the Wittig-like reaction with benzaldehyde is also all-trans with resonances at 6.02 ppm for H$_c$ (dd, J_{HH} = 16 and 7.5 Hz) and 6.42 ppm for H$_d$ (d, J_{HH} = 16 Hz). (The resonances at 6.18 and 6.32 ppm are olefinic resonances in *trans*-PhCH═CH-*t*-Bu that is formed upon reaction of residual Mo(CH-*t*-Bu) with benzaldehyde.) Presumably the greater bulk of the substituent in the alkylidene ligand forces an *all-trans*-2-oxamolybdacyclobutane intermediate to form.[12] Integration of the four olefinic protons on the two terminal double bonds versus the resonance for the *tert*-butyl capping group at 0.97 ppm shows the ratio to be close to 1:1:1:1:9, consistent with quantitative yields in each of the proposed steps. If the polymerization is terminated by adding pivaldehyde, then only the resonances due to the olefinic protons near the *tert*-butyl end group (at 5.53 and 5.28 ppm) are observed. The ^{1}H and ^{13}C NMR spectra can be assigned by a combination of homonuclear and heteronuclear correlation experiments. The two alkylidene proton resonances that are observed in the living oligomers at 11.51 and 11.45 are assigned to syn and anti rotamers (not necessarily respectively), the syn rotamer referring to that in which the alkylidene substituent points toward the nitrogen atom of the imido ligand. (See the Experimental Section for details.) Rotamers have been observed in polymers made from functionalized norbornadienes,[6] and there is no reason why they could not be present in these circumstances.

In ^{1}H NMR spectra of oligomers made from **4** the resonances due to cis olefinic protons overlap with those

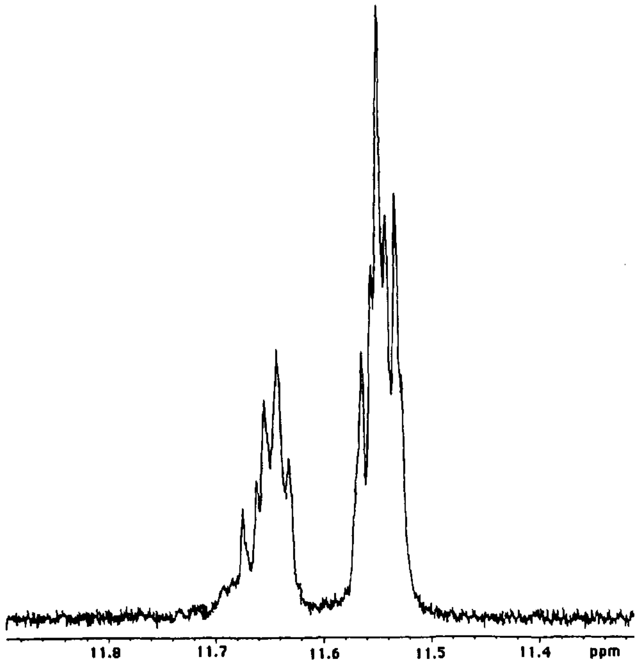


Figure 2. 500-MHz ^1H NMR spectrum (C_6D_6) in the alkylidene region of a living 20-mer of poly-3.

due to trans olefinic protons, but the trans content can be estimated to be ~80% on the basis of the ratio of the allylic protons next to a cis or a trans olefinic bond. Resonances that could be ascribed to olefinic protons in the first and last double bond that arise in the initiation or termination steps cannot be discerned clearly.

Polymerization of **3** is expected to yield head-to-tail, tail-to-tail, and head-to-head sequences. ^1H and ^{13}C NMR spectra of the isolated polymers are broad and complex, consistent with a complex and random microstructure. Little information can be obtained. The alkylidene region of the ^1H NMR spectrum of living poly-**3** is shown in Figure 2. The two groups of alkylidene resonances can be assigned to isomers in which the carbomethoxy functionality nearest the alkylidene carbon atom is either exo (H_α at 11.55 ppm) or endo (H_α at 11.65 ppm) in a ratio of approximately 2:1 by comparison with alkylidene resonances in living poly-**2** and living poly-**4**. Two resonances for the *tert*-butyl group from the initiator are observed at 0.964 and 0.935 ppm, depending on whether the carbomethoxy group is syn or anti relative to the trans olefinic bond. Addition of 10 equiv of norbornene to living poly-**3** produces an alkylidene resonance typical of living polynorbornene at 11.53 ppm. The two resonances for the *tert*-butyl group are unchanged, and, furthermore, these solutions are stable for days; only the alkylidene resonance for living polynorbornene is observed with its original intensity.

Addition of 100–200 equiv of 5-cyanonorbornene (**5**) to Mo(CH-*t*-Bu) in toluene does not yield polymer; the reason is not known. However, in THF as many as 200 equiv of **5** are polymerized smoothly to give polymers with polydispersities of 1.06–1.07. The alkylidene proton region of the ^1H NMR spectrum in THF-d_8 for living poly-**5** is shown in Figure 3. The three main groups of resonances that are observed can be rationalized in terms of the three basic isomers that are possible upon opening this unsymmetric monomer (eq 3). The resonance at 11.53 ppm is assigned to the alkylidene resonance that most resembles that in living polynorbornene (eq 3). We can only speculate as to the source of the doubling of this resonance. Possibilities are that the chemical shift of H_α is sensitive to exo or endo orientation of the cyano group relative to the C_α–C_β bond or cis or trans configuration of the first C=C bond, or syn and anti rotamers are present. Whatever the explanation, the ratio of the two H_α types is approximately 1:1. The two other resonances at ~11.29 and ~11.39 ppm are assigned to H_α protons in propagating alkylidene complexes in which the cyano group (either exo or endo) is on a γ carbon atom with respect to the metal. Their ratio is ~2:1, as observed for poly-**3** (Figure 2). Further complexity within each group of resonances could arise from a sensitivity to the nature of adjacent monomers in the chain as well as from the presence of syn and anti rotamers. The identification of these resonances is further supported by the observation of only two complex envelopes of resonances in the living polymer prepared from *trans*-5,6-dicyanonorbornene.[13]

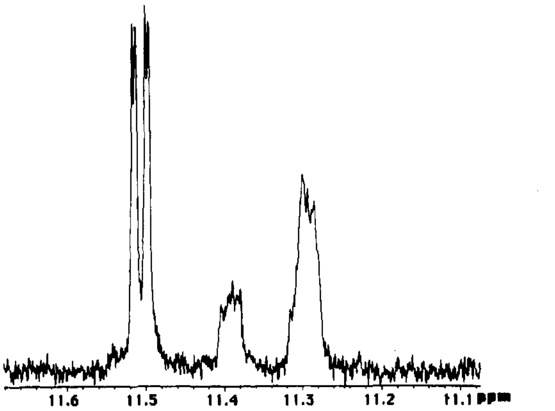
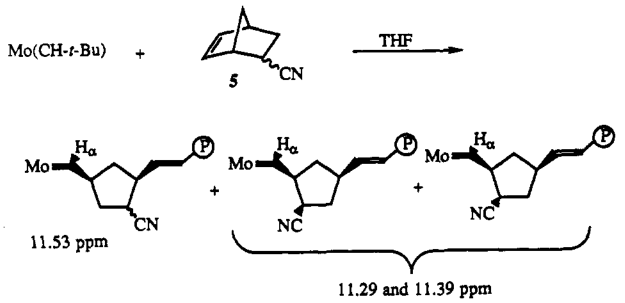
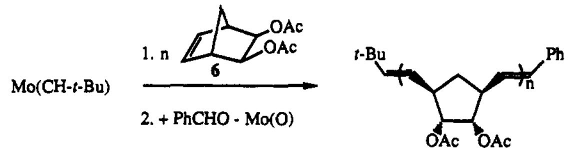


Figure 3. 500-MHz ^1H NMR spectrum (THF-d_8) in the alkylidene region of a living 20-mer of poly-**5**.



(3)

6 (eq 4) is polymerized quantitatively in THF to give a polymer with a polydispersity of 1.19 (100-mer). In aromatic solvents (toluene, chlorobenzene, or benzene) **6** is not consumed completely (~85%) and broader molecular weight distributions are found (PDI = 1.3–2). The reason why polymerization was not successful in aromatic solvents is not known. The IR spectrum of the polymer shows the characteristic ester carbonyl absorption at 1740 cm^{-1}. By ^1H NMR the trans olefinic content was determined to be 60%.



(4)

Poly-6 is a white powder that is insoluble in methanol and can be cast from toluene as a flexible transparent film. The tensile strength of the film at the breaking point is 370 kg/cm^2, a value that is comparable to that of acrylonitrile/butadiene/styrene (ABS) resin (380 kg/cm^2).[14] A DSC measurement showed only a glass transition temperature (T_g) at 102 °C. TGA suggests that the polymer is stable up to 300 °C. Above 300 °C 2 equiv of acetic acid

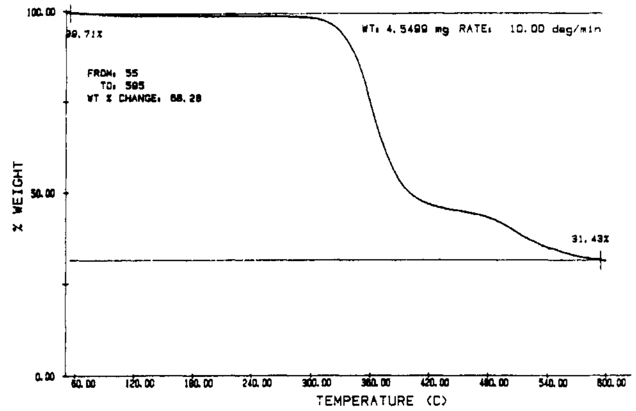
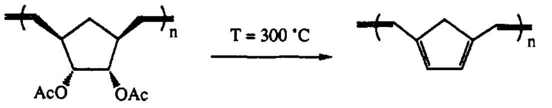


Figure 4. TGA analysis of poly-**6**.

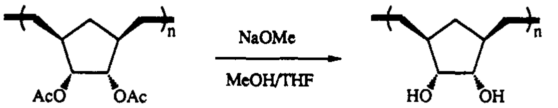
are lost (Figure 4; eq 5) followed by polymer decomposition



(5)

at higher temperatures. Isothermal pyrolysis showed that at 300 °C 56% of the mass is lost in 2 h while at 350 °C 61% is lost in 1 h. (Loss of 2 equiv of acetic acid corresponds to a 57% mass loss.) Heating a strip of polymer at 300 °C for 2 h in a temperature-programmable furnace yielded a red-black insoluble film. Its IR spectrum showed that the carbonyl absorption characteristic of the precursor polymer has decreased and the 1600 cm^{-1} (C=C) absorption has increased. Therefore, pyrolysis appears to be incomplete. When the black polymer is left exposed to air, an absorption band at 1730 cm^{-1} appears, characteristic of oxidation, the nature of which remains undetermined.

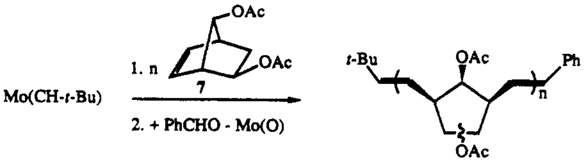
Hydrolysis of poly-**6** gives the polydiol shown in eq 6 quantitatively. Since hydroxyl groups are incompatible



(6)

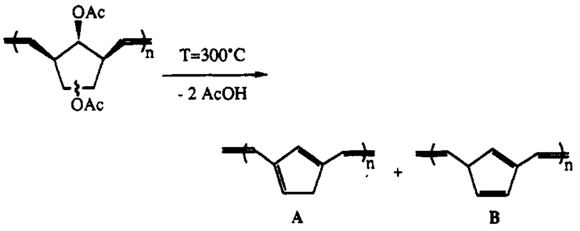
with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$, this polymer cannot be made directly from the corresponding monomer. The polydiol is insoluble in standard solvents (THF, chloroform, aromatics, methanol, or water), but it dissolves completely in acidic chloroform ($CF_3CO_2H/CDCl_3$). The solid polymer absorbs strongly in the region between 3100 and 3500 cm^{-1}; the absorption at 1740 cm^{-1} in the precursor polymer is absent. No glass transition was found by DSC up to 220 °C. The TGA displayed a two-stage degradation, the first step of which (at ~300 °C) corresponds to a dehydration analogous to the loss of acetic acid (eq 5).

exo-syn-5-Norbornene-2,7-diol diacetate (**7**; eq 7) is



(7)

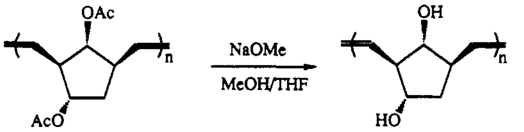
polymerized quantitatively to yield a polymer with a PDI = 1.09 in THF and 2.17 in chlorobenzene (200-mer). Poly-**7** can be purified by precipitation into methanol and can be cast from toluene to give flexible, transparent thin films. Its tensile strength at the breaking point is 420 kg/cm^2. DSC analysis indicates that it is amorphous with a T_g at 110 °C and that it is stable up to 300 °C. The TGA for poly-**7** resembles that for poly-**6**, consistent with loss of 2 equiv of acetic acid from the polymer backbone (eq 8). Structure A is likely to be more favorable as a result of



(8)

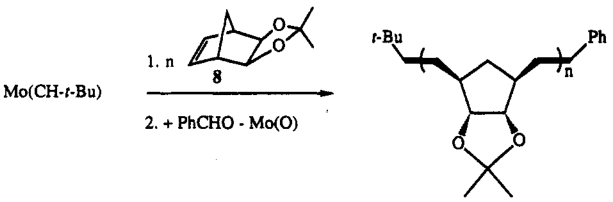
cross conjugation. The pyrolysis product made from poly-**7** is brittle and oxidizes readily in air.

Poly-7 can be hydrolyzed to yield the polydiol shown in eq 9. The IR spectrum of the polydiol shows a broad



(9)

OH absorption at 3100–3500 cm^{-1} and a vinyl stretch at 1590 cm^{-1} but no carbonyl absorption. A ^1H NMR spectrum in a 1:1 mixture of CF_3CO_2H and $CDCl_3$ showed the hydroxyl protons as a broad resonance at 2.8 ppm. This polymer also is soluble in *aqueous* acidic media (CF_3CO_2H/H_2O). The TGA is similar to that of the polydiol shown in eq 6, the first stage of which can be attributed to loss of 2 equiv of water to give the polymers shown in eq 8, most likely with structure A. Isothermal pyrolysis at 270 °C shows the loss of mass to be 26% in 2 h (theoretical mass loss for dehydration = 29%).

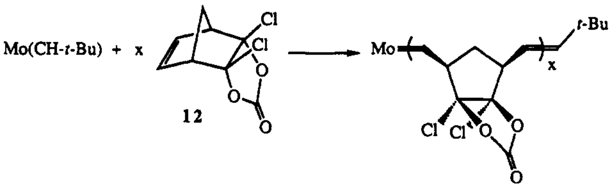


(10)

8 (eq 10) can be polymerized in THF straightforwardly. ^1H NMR spectra of poly-**8** show it to contain 60% trans olefinic linkages. DSC analysis reveals a T_g at 108 °C and decomposition starting at 300 °C. Hydrolysis of poly-**5** yields the polydiol obtained by hydrolysis of poly-**6** mentioned earlier.

Monomers **9**–**11** were polymerized smoothly in toluene to give the homopolymers shown in Table I, but the polymer properties were not investigated. It is interesting to note that the endo isomer analogous to **10** could not be polymerized by Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$. As mentioned earlier, this type of result has been ascribed to steric problems associated with the approach of an endo-substituted monomer to an alkylidene that has just been formed from that monomer.[1]

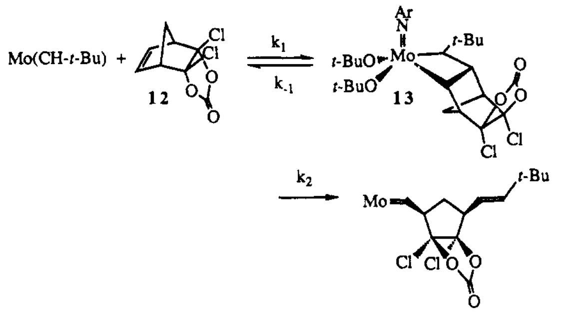
Reversible Formation of a Square-Pyramidal Molybdacycle with *exo-cis*-2,3-Dichloro-*endo-cis*-2,3-carbonatonorbornene. Researchers have been interested in polymerizing *exo-cis*-2,3-dichloro-*endo-cis*-2,3-carbonatonorbornene (*endo*-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one) (**12**) because poly-**12** is a potential precursor to conjugated materials. **12** has been polymerized using classical catalysts, but the polydispersity was large.[15,16] Reaction of 10 equiv of **12** with Mo(CH-*t*-Bu) in C_6D_6 at room temperature for approximately 60 min yields living oligomers (eq 11),



(11)

judging from the broad alkylidene doublet at 11.57 ppm, but unreacted **12** remained. The monomer (10 equiv) was completely consumed in 24 h at room temperature. The intensity of the alkylidene resonance for the living species appears to decrease slowly with time and attempts to polymerize 100 equiv of **12** in toluene in the standard fashion failed, both of which are believed to be the consequence of some decomposition of the living species. Increasing the reaction time at a catalyst concentration of 0.02 M up to 24 h at room temperature also did not yield any polymer.

Closer examination of the polymerization reaction by ^{1}H NMR showed that only ~2 equiv of **12** were consumed over a 2-h period ([Mo(CH-*t*-Bu)] = 0.02 M, 4 equiv of **12**, 25 °C). At −30 °C the neopentylidene and olefin resonances decreased, but no new alkylidene resonances were found. However, broad resonances appeared, which resembled those of well-characterized square-pyramidal tungstacyclobutane complexes.[17] Therefore, we propose that the square-pyramidal molybdacycle (**13**; eq 12) forms at this temperature and does not open readily. Mo(CH-*t*-Bu) was not completely converted to **13** in the presence of **12** at −30 °C.



(12)

A solution containing Mo(CH-*t*-Bu) and **12** was prepared at −30 °C and stored at −40 °C for 2–3 days. The bright red crystals that formed were dissolved in toluene-d_8 at −45 °C. At that temperature a mixture of 4 parts **13** and 1 part a 1:1 mixture of Mo(CH-*t*-Bu) and **12** was observed. Only a trace of the propagating alkylidene was observed (Table II). As the temperature was raised, the amount of propagating alkylidene, Mo(CH-*t*-Bu), and **12** increased relative to **13**. At 0 °C the ratio of **13** to Mo(CH-*t*-Bu) was 2:1. Finally at 25 °C only traces of **13** were observed, and **12** was regenerated to give approximately 60% Mo(CH-*t*-Bu). These results indicate that **13** is unstable at 25 °C, but it "decomposes" either by ring opening to yield a new propagating alkylidene or degeneratively to yield the original reactants (eq 12); i.e., $k_{-1} \approx k_2$. At low temperatures **13** is in equilibrium with Mo(CH-*t*-Bu) and **12** ($K = k_1/k_{-1} = 4$ at −45 °C) while formation of new alkylidene is negligible (k_2 is small). At 0 °C, $K \approx 2$.

Similar results were observed in THF. A total of 5 equiv of **12** was added to Mo(CHCMe$_2$Ph) in THF-d_8. After 30 min at 25 °C the relative ratio of initiator, metallacycle **13**, and propagating alkylidene is 59:34:7; more than 4.5 equiv of **12** remains. This result eliminates any possibility that THF plays any magical role in this case, as it apparently does in other cases, e.g., cyano derivatives.

Table II
Distribution of Products as a Function of Temperature after Dissolving 13 in Toluene-d_8

temp, °C	Mo(CH-*t*-Bu)	13	14	FIP[a]	SIP[b]
−45	1	4	1	trace	
0	1	2	0.9	0.2	
25	1	0.1	0.9	0.3	0.06

[a] Alkylidene due to first insertion product. [b] Second insertion product. Equilibration time at each temperature was 20 min.

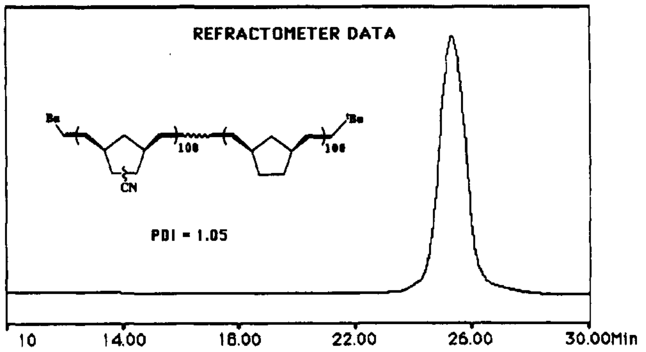
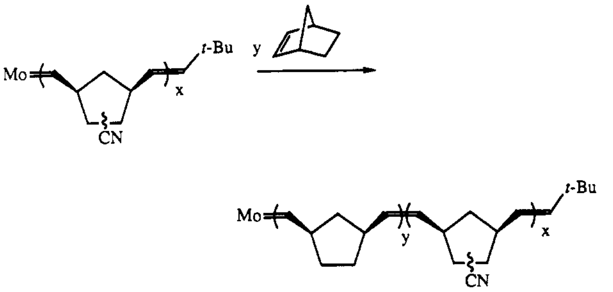


Figure 5. GPC trace of poly-**1**/**5**.

Failure to polymerize **12** can be attributed to the slow rate of its reaction with either Mo(CH-*t*-Bu) or the propagating alkylidene complex. In this case, the rate of catalyst deactivation, most likely in a reaction involving the carbonyl bond in the carbonate, is approximately the same as the rate of polymerization.

Block Copolymers. Analysis by ^{1}H NMR shows that 15 equiv of norbornene is consumed upon addition to a solution of living poly-**5**, and the complex set of alkylidene resonances characteristic of poly-**5** (Figure 3) are replaced by the doublet characteristic of living polynorbornene. This implies that poly-**5** reacts with norbornene to give a living block copolymer (eq 13). Addition of **5** to living polynorbornene yields the resonances ascribed to poly-**5**. If $x = y = 100$ and the block copolymer is cleaved from the metal by addition of benzaldehyde, then a block copolymer (poly-**1**/**5**) whose GPC is shown in Figure 5 is obtained. Inverting the order of addition of the two monomers produces a virtually identical polymer (poly-**5**/**1**) provided that more time is allowed for polymerization of **5**. Note that the PDI = 1.05 and the peak is symmetric, indicative of a process in which there is no chain transfer or termination on the time scale of either polymerization.



(13)

The ^{1}H NMR spectrum of poly-**1**/**5** is a superposition of those of polynorbornene and poly-**5** homopolymers. The olefinic region of the ^{13}C NMR spectrum of poly-**1**/**5** is compared with that of poly-**5** in Figure 6. The complexity of the olefinic resonances in poly-**5** can be attributed to the many variations of monomer sequences for this material. The resonances are broad since the olefinic protons are likely to be sensitive to the stereochemistry

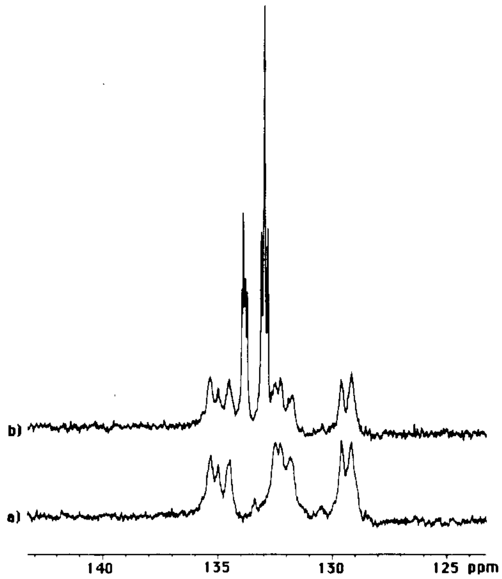


Figure 6. 125-MHz ^{13}C NMR ($CDCl_3$) spectra in the olefinic region of (a) poly-**5** and (b) poly-**1**/**5**.

of the monomers on both sides of the olefinic bond. In poly-**1**/**5** the resonances at 133.8 (cis olefin) and 132.9 (trans olefin) ppm can be ascribed to the polynorbornene block.

Discussion

Narrow dispersities and the formation of block copolymers indicate that norbornenes containing the variety of functionalities shown in Table I are polymerized in a living manner by Mo(CH-*t*-Bu). For example, the preparation of a 200-mer of **3** suggests that the catalytic site is stable in the presence of 400 equiv of ester functionality over the time period of the polymerization. Solvent plays an important role, although the precise nature of that role remains to be determined. One possibility is that THF competes successfully with the functionality for the metal. Another possibility is a bulk solvent effect that keeps the polar groups pointed away from the metal into the solution. A third possibility is that THF is intimately involved in opening the intermediate metallacycles formed in these reactions. Finally, traces of oxygen or other impurities might vary from one solvent to another and lead to significant differences that cannot be traced to the nature of the solvent itself.

Liberation of **12** from **13** represents the first example of the reversible formation of a metallacyclobutane ring involving a norbornene derivative. This situation is likely to be rare and probably encountered only when the monomer is bulky and relatively electron poor. The high stability of **13** suggests that a considerable amount of intramolecular rearrangement is necessary in order to lose the olefin from this metallacycle in a productive fashion. Similar conclusions have been reached recently in related circumstances.[6b,17a]

Ejection of small molecules in a precursor polymer to yield a conjugated polymer is a fairly mature subject in polymer chemistry.[18] Poly(vinyl acetate),[19], poly(vinyl chloride),[20] and poly(vinyl alcohol)[21] lose acetic acid, HCl, and water, respectively, to yield conjugated polyene sequences at high temperatures, but pyrolysis of poly-**6** and poly-**7** and the analogous diols appear to be the first reports of such a reaction for polymers prepared by ring-opening metathesis. This circumstance can be ascribed to the previous paucity of catalysts for preparing suitably functionalized polymers.

Transformation of poly-**6**, poly-**7**, and poly-**8** to polydiols is interesting because of the unusual solubility properties of these materials and unobservable (presumably high) T_g. Poly(*exo*-5-hydroxynorbornene)[22] has been prepared by polymerizing an organoborane derivative of norbornene using classical catalysts followed by alkaline oxidation of the resulting polymer. The final polymer displays bulk characteristics similar to the ones reported here, but the polydispersity was 2.3 and only 65% of the monomer was consumed. An unsuccessful attempt to dehydrate the polymer was attributed to the unfavorable introduction of ring strain.

Conclusion

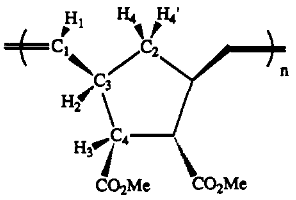
We have shown that several functionalized norbornenes can be polymerized in a living manner by Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ in toluene or THF, depending on the monomer, and that polymerization proceeds via molybdacyclobutane and alkylidene intermediates. Success can be attributed to deactivation of the electrophilic metal toward metathesis of ordinary olefins by *tert*-butoxide ligands, to the lower electrophilicity of Mo compared to W, and to the relatively high reactivity of the norbornene double bond. These results suggest that norbornenes that contain a variety of other functionalities (none, however, that contain active protons) may be polymerized in a controlled manner under these conditions.

Experimental Section

General Details. All polymerizations were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Tetrahydrofuran was predried over calcium chloride and distilled from sodium benzophenone ketyl under nitrogen immediately prior to usage. Toluene was distilled from molten sodium and stored over sodium potassium alloy. All deuterated NMR solvents were passed through a column of activated alumina. Norbornene was doubly distilled from molten sodium. Commercially available **5** (60:40 mixture of exo and endo isomers) was distilled under nitrogen, passed through a column of activated alumina, and stored under nitrogen. **4** was prepared by adding methanol to the commercially available endo anhydride.[23] Commercially available aldehydes were purified by distillation under nitrogen. **2**,[11,24] **3**,[25], **6**,[26], **7**,[27] and **8**[28] were prepared by literature procedures.

NMR data are listed in parts per million downfield from TMS for both proton and carbon. Coupling constants are quoted in hertz. Obvious multiplicities and routine coupling constants usually are not listed. Gel permeation chromatographic (GPC) analyses were carried out at room temperature employing a Rheodyne Model 7125 sample injector, a Kratos Spectroflow 400 pump, Shodex KF-802.5, 803, 804, 805, 800P columns, a Knauer differential refractometer, and a Spectroflow 757 absorbance detector on samples 0.1–0.3% w/v in dichloromethane, which were filtered through a Millex-SR 0.5-μm filter in order to remove particulates. GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories, Ltd.) ranging from 1206 to 1.03×10^6 MW. Thermal analysis (TGA) was done on a Perkin-Elmer TGS-2 thermogravimetric analyzer. Differential scanning calorimetry was performed on a Perkin-Elmer instrument at a heating rate of 30 °C/min. Tensile strengths of polymer films (0.35 mm × 3 mm: thickness × width) were measured by use of an Instron 4201 at an extension rate of 10 mm/min.

Typical Polymerization of *exo-cis*-2,3-Dicarbomethoxynorbornene (2). A solution of **2** (431 mg, 2.05 mmol, 100 equiv) in toluene (10 mL) was added dropwise quickly to a rapidly stirring solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 0.0205 mmol) in toluene (5 mL) over a period of 1–2 min. The solution was allowed to stir for an additional 20–30 min, quenched by addition of excess benzaldehyde (10 μL, ~0.1 mmol), and stirred for an additional 20 min. The solution was brought out of the drybox and added dropwise to 500 mL of vigorously stirred hexane. The

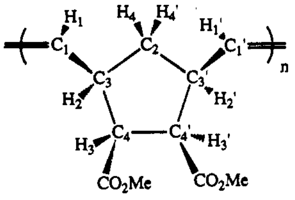


poly-2

resulting precipitate was isolated by centrifugation, washed with hexane or pentane, and placed under vacuum overnight. The final product was a white powder (380 mg, 88%) soluble in toluene, CH_2Cl_2, or benzene: ^{1}H NMR ($CDCl_3$) δ 5.37 (br, 2, H_1), 3.62 (s, 6, $CO_2\mathit{Me}$), 2.93 (br, 2, H_2), 2.79 (br, 2, H_3), 2.06 (br, 1, H_4 or H_4'), 1.25 (br, 1, H_4 or H_4'), 0.96 (s, *t*-Bu); ^{13}C NMR δ 173.1 ($\mathit{C}O_2Me$), 132.0 (C_1), 52.4 (C_4), 51.7 ($CO_2\mathit{Me}$), 45.1 (C_3), 39.1 (C_2), 29.5 (*t*-BU). GPC data are found in Table I.

Living oligomers were prepared by adding the monomer (65 mg, 0.31 mmol, 15 equiv) in C_6D_6 (300 μL) to a rapidly stirred solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 0.0205 mmol) in C_6D_6: ^{1}H NMR δ 11.51 and 11.45 (H_α, $J_{H_\alpha H_\beta}$ = 7 Hz), 4.61 (H_β, $J_{H_\alpha H_\beta}$ = 7 Hz), 3.97 (C*H*Me$_2$). Resonances due to the oligomer protons are similar to those of the polymer; other resonances due to the ligands on the metal center could not be assigned due to overlap with oligomer resonances. Assignment of resonances from H_2, H_3, and H_4 along with C_2, C_3, and C_4 is ambiguous on chemical shift arguments alone. H_2 is assigned to the resonance at 2.93 ppm since it couples with H_1 (5.37 ppm). C_2 (39.1 ppm) is split into a triplet in a gated ^{13}C experiment, which allows the assignment of H_4 and H_4' ($J_{C_2H_4'}$) to the resonances at 1.25 and 2.06 ppm since both are shown to be coupled in a HETCOR (^{13}C–^{1}H correlation) experiment to C_2. The same experiment shows that the resonance at 45.1 ppm is coupled to H_2 and therefore belongs to C_3. By elimination, C_4 (52.4 ppm) and H_3 (2.79 ppm) can be assigned.

Typical Polymerization of *trans*-2,3-Dicarbomethoxynorbornene (3). A solution of 3 (431 mg, 2.05 mmol, 100 equiv) in toluene (10 mL) was added dropwise but quickly to a rapidly stirring solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 0.0205 mmol) in toluene (5 mL) over a period of 1–2 min. The solution was allowed to stir for an additional 20–30 min, quenched by addition of excess benzaldehyde (10 μL, ~0.1 mmol) (or pivalaldehyde), and stirred for an additional 20 min. The solution was brought out of the box and added dropwise to 500 mL of hexane under vigorous stirring; the resulting precipitate was isolated by centrifugation, washed with hexane or pentane, and placed under vacuum overnight. The polymer was obtained as white flakes (405 mg, 94%); ^{1}H NMR δ ($CDCl_3$, 500 MHz) 5.08 and 5.25 (br, 2, H_1 and H_1'), 3.43 (s, 3, $CO_2\mathit{Me}$), 3.40 (s, 3, $CO_2\mathit{Me}$), 3.00 (br, 1, H_2 or H_2' or H_3'), 2.73 (br, 2, H_2 or H_2' or H_3 or H_3'), 2.46 (br, 1, H_2 or H_2' or H_3 or H_3'), 1.76 (br, 1, H_4 or H_4'), 1.27 (br, 1, H_4 or H_4'), 0.935 and 0.962 (s, C*Me*$_3$); ^{13}C NMR 174.3 (CO_2Me), 173.5 (CO_2Me), 132.2 (C_1), 131.2 (C_1), 129–131.2 (C_1), 51-53 (C_4 and $CO_2\mathit{Me}$), 44.5 (C_3 or C_3'), 46.7 (C_3 or C_3'), 29.5 (C*Me*$_3$). All resonances are extremely broad consistent with the many stereochemical configurations possible. GPC data are found in Table I.



poly-3

Living oligomers were prepared by addition of the monomer (65 mg, 0.31 mmol, 15 equiv) in C_6D_6 (300 μL) to a rapidly stirring solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 0.0205 mmol) in C_6D_6. Oligomer resonances are similar to the polymer; for resonances due to H_α see Figure 2.

Polymerization of *exo-cis-N*-Phenyl-5-norbornene-2,3-dicarboximide (10). A solution of 10 (239 mg, 1.03 mmol, 50 equiv) in THF (15 mL) was added dropwise over a period of 2–3 min to a rapidly stirring solution of Mo(CH-*t*-Bu) (10 mg) in THF (4 mL) and stirred an additional 30 min. The polymer was quenched with benzaldehyde and isolated as described above. The product was obtained as a gummy solid (213 mg, 90%): ^{1}H NMR δ ($CDCl_3$) 6.9–7.2 (br, 5, H_{Ar}), 5.55 (br, 2, C*H*=CH), 2.87 (br, 2, C*H*CO or allylic C*H*), 2.55 (br, 2, C*H*CO or allylic C*H*), 1.90 (br, 1, C*H*H), 1.41 (br, 1, C*H*H); GPC M_n = 21 000 (vs polystyrene), PDI = 1.06.

Polymerization of *endo-cis-N*-(Pentafluorophenyl)-5-norbornene-2,3-dicarboximide (9). 9 was prepared as described above for the protio analogue using 329 mg of monomer. The product was obtained as a white powder: ^{1}H NMR δ 5.61 (br, 2, C*H*=CH), 2.6–2.8 (br, 4, C*H*O and allylic C*H*), 1.82 (br, 1, C*H*H), 1.30 (br, 1, C*H*H).

Preparation of 13 and Observation of Its Decomposition. A solution of **12** (68 mg, 0.31 mmol) in ether (2 mL, –30 °C) was layered over a solution of Mo(CH-*t*-Bu) (150 mg, 0.31 mmol) in pentane (2.0 mL, –30 °C) and immediately stored at –40 °C for 48 h. Bright red crystals (98 mg, 45%) were isolated by decanting the solution and briefly placed under vacuum. Analysis by ^{1}H NMR was done by dissolving 20 mg of the product in toluene-d_8 (800 μL, [**13**] = 3.5×10^{-5} M) at low temperature: ^{1}H NMR (–45 °C) 7.02 (m, 3, H_{Ar}), 4.02 (br, 1 C*H*Me$_2$), 3.83 (br, 1, C*H*Me$_2$), 3.55 (s, 1, bridgehead H), 3.41 (dd, 1, H_β, $J_{H_{\alpha'}H_\beta}$ = 8 $J_{H_\alpha H_\beta}$ = 8), 2.62 (s, 1, bridgehead H), 1.85 (d, 1 H, C*H*H bridgehead (H_γ)), 1.68 (d, 1 C*H*H bridgehead (H_γ)), 1.32 (br, 12, CH*Me*$_2$), 1.29 (s, 9, OC*Me*$_3$), 1.17 (s, 9, OC*Me*$_3$), 0.92 (s, 9, CHC*Me*$_3$).

Typical Polymerization of *exo-cis*-2,3-Norbornenediol Diacetate (6). A solution of 6 (431 mg, 2.05 mmol) in THF (10 mL) was added dropwise but quickly to a vigorously stirring solution of Mo(CH-*t*-Bu) (10 mg, 2×10^{-5} mol) in THF (5 mL) over a period of 1–2 min. The resulting solution was allowed to stir for 1 h, quenched with benzaldehyde (15 μL, approximately 0.15 mmol), and allowed to stir for an additional 30 min. The polymer was purified by dropwise addition of the resulting solution into a large excess of methanol, filtration, subsequent precipitation from chloroform into methanol, and placement under vacuum for 24 h. The yield of isolated polymer (410 mg, 95%) was essentially quantitative: ^{1}H NMR ($CDCl_3$) δ 5.42 (br, C*H*=CH, trans), 5.33 (br, C*H*=CH, cis), 4.96 (br, C*H*OAc), 4.87 (br, C*H*OAc), 3.03 (br, allylic C*H*), 2.66 (br, allylic C*H*), 2.08 (br, C*H*H bridgehead), 2.01 (s, O*Me*), 1.98 (s, O*Me*), 1.17 (br, C*H*H bridgehead); ^{13}C NMR ($CDCl_3$) 170.9, 170.6, 133.0, 132.2, 76.8, 76.5, 45.3, 40.6, 35.2, 34.3, 33.4, 20.9; IR (Nujol) 1750 cm^{-1} (strong, C=O stretch). DSC analysis reveals a reversible T_g at 102 °C. TGA is shown in Figure 4; isothermal pyrolysis determined the amount of loss to be 55.7% (300 °C, 2 h). GPC data are found in Table I.

Typical Polymerization of *exo-syn*-2,7-Norbornenediol Diacetate (7). A solution of 7 (431 mg, 2.05 mmol) in THF (10 mL) was added dropwise but quickly to a vigorously stirring solution of Mo(CH-*t*-Bu) (10 mg, 2×10^{-5} mol) in THF (5 mL) over a period of 1–2 min. The resulting solution was allowed to stir for 1 h, quenched with benzaldehyde (15 μL, ~0.15 mmol), and allowed to stir for and additional 30 min. The polymer was purified by dropwise addition of the resulting solution into a large excess of methanol, filtration, subsequent precipitation from chloroform into methanol, and placement under vacuum for 24 h. The polymer was obtained as a white powder (388 mg, 90%): ^{1}H NMR ($CDCl_3$) δ 5.2–5.4 (br m, 2, C*H*CH), 4.6–4.8 (br m, 2, C*H*OAc), 2.6 (br, 1, allylic C*H*), 2.5 (br, 1, allylic C*H*), 1.95 (s, 3, O*Me*), 1.77 (m, 3, O*Me*); ^{13}C NMR ($CDCl_3$) 171.3 and 171.0 (*C*=O), 133.1 and 132.0 and 131.3 and 130.2 (*C*HCH, resonances are split due to cis and trans isomers (~50:50) and their relation to the acetate group in the 2-position), 79.3, 76.7, 54.2, 46.1, 36.3, 21.3, 21.0; IR (Nujol) 1730 cm^{-1} (strong, C=O stretch). DSC analysis shows a T_g at 110 °C. A TGA thermogram is similar to Figure 4 with a 56.2% mass loss observed on heating at 300 °C for 2 h (calculated for loss of 2 equiv of acetic acid: 57.2%). GPC data are found in Table I.

Typical Polymerization of *exo-cis-O,O'*-Isopropylidene-2,3-norbornenediol (8). A solution of 8 (344 mg, 2.05 mmol) in THF (5 mL) was added quickly but dropwise to a solution of Mo(CH-*t*-Bu) (10 mg, 2.05×10^{-5} mol) in THF (3 mL) over a period of 1–2 min. The color of the solution changed immediately from light yellow to red. The solution was allowed to stir for an additional 30 min, quenched with benzaldehyde (15 μL), and stirred for an additional 30 min to yield a yellow solution. The polymer was obtained free of impurities by precipitation from the above solution into a large excess of methanol followed by three consequent precipitations from chloroform into methanol and removal of solvent in vacuo for 24 h. The polymer was obtained as a white flaky solid (327 mg, 95%): ^{1}H NMR (CDCl$_3$) δ 5.51 (br, trans C*H*=CH), 5.28 (br, cis C*H*CH), 5.2–5.3 (br m, C*H*O), 2.95 (br, allylic C*H*), 2.55 (br, allylic C*H*), 2.94 (br, C*H*H bridgehead), 1.45 (s, C*Me*), 1.32 (br, C*H*H bridgehead), 1.23 (s, C*Me*), integration of resonances consistent with the proposed formulation; ^{13}C (CDCl$_3$) 133.0, 131.9, 113.4, 87.1, 86.0, 48.3, 44.3, 38.2, 27.7, 25.2. DSC: T_g = 102 °C; TGA polymer degradation begins at 300 °C. GPA data are found in Table I.

Typical Base Hydrolysis Procedure of Polyacetate Polymers. Conversion of Poly-6 to Poly(*exo-syn*-2,3-norbornenediol). Poly-6 (1.0 g) was dissolved in dry THF (150 mL) and added dropwise to a solution of dry THF (150 mL) and 20 mL of a 10% solution of sodium methoxide in methanol under vigorous stirring under reflux. The resulting solution was refluxed for 12 h, cooled, and neutralized with glacial acetic acid. The resulting fine suspension was filtered or centrifuged, washed with methanol, and placed under vacuum for 24 h to give the product as a light yellow powder (0.5 g, 83%), which was sparingly soluble in a variety of solvents: ^{1}H NMR δ (CF$_3$CO$_2$H:CDCl$_3$ 1:1) 5.6 (br, 2, C*H*=CH), 4.21 (br, 1, C*H*OH), 3.75 (br, 1, C*H*OH), 2.5–3 (br, 3, O*H* and allylic C*H*), 2.05 (br, 3, allylic C*H* and C*H*$_2$); IR 3350 (br, OH stretch), 1600 cm^{-1} (C=C stretch), no absorption observed in the carbonyl region.

Typical Acid Hydrolysis Procedure for Poly-8. Poly-8 (0.3 g) was dissolved in 10 mL of 80% aqueous trifluoroacetic acid and stirred for 3 h at room temperature. The resulting solution was cooled to 0 °C and slowly neutralized with aqueous KOH (5 M). During the neutralization procedure the color changes from light red to nearly colorless, at which time polymer began to precipitate. The resulting product was isolated by filtration or centrifugation, washed several times with water and methanol, and placed under vacuum for 24 h to yield the hydrolyzed polymer as a cream powder (0.2 g, 75%): ^{1}H NMR δ (MeOD) 5.6 (br m, 2, C*H*=CH), 3.55 (br, 2, CO*H* or C*H*OH), 2.9 (br, 2, CO*H* or C*H*OH), 2.5 (br, 2, allylic C*H*), 2.0 (br, 1, C*H*H), 1.1 (br, 1, C*H*H); IR 3350 (br, OH stretch), 1590 cm^{-1} (C=C stretch).

Thermal Reaction of Acetate Polymers. Thermal treatment of poly-6 and poly-7 was carried out by thermogravimetric analysis (TGA) and a temperature-programmable pyrolysis oven under a nitrogen atmosphere. Weight loss of the polymers in the powder state was monitored as a function of temperature at a fixed heating rate (10 °C/min) or isothermally as a function of time at a given temperature. Polymers in the film state were heated at the same rate and kept isothermally for 2 h at a given temperature resulting in insoluble black-red films.

Typical Polymerization of 5. A solution of **5** (122 mg, 1.02 mmol) in THF (1.0 mL) was added quickly to a solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 2.05 × 10^{-5} mol) in THF (1.0 mL) and stirred for 15 min. Termination was carried out by addition of 15 μL of *p*-(trimethylsilyl)benzaldehyde (8.4 × 10^{-5} mol). The polymer was purified by precipitation of the polymer from the reaction mixture into 250 mL of hexane. The final product is obtained as a white cream powder; yield 103 mg, 85%: ^{1}H NMR (CDCl$_3$) δ 5.70, 5.55, 5.37, 5.32, 5.20, 3.0, 2.73, 2.55, 2.30, 2.18, 2.03, 1.75, 1.43 (1.004, 0.981, 0.963, 0.956) (C(C*H*$_3$)$_3$), (0.232, 0.217) (Si(C*H*$_3$)$_3$) (the spectrum is too broad for integration within polymer peaks; however, integration of *tert*-butyl cap versus olefinic resonance is consistent with the assigned stoichiometry as well as 1:1 against the TMS cap); ^{13}C NMR (CDCl$_3$) δ 135.3, 134.6, 132.3, 131.7, 129.7, 129.2, (*C*N), 120.9 (*C*N), 58.5, 44.8, 41.8, 41.2, 39.8, 39.2, 37.0, 36.9, 36.2, 33.8, 29.6 (C(*C*H$_3$)$_3$), 1.3 (Si(*C*H$_3$)$_3$). T_g = 123 °C by DSC; M_n = 24 869 (vs polystyrene), PDI = 1.05 by GPC.

Preparation of Poly-1/5. A solution of norbornene (NBE; 193 mg, 2.05 mmol) in THF (2 mL) was added dropwise but quickly to a light yellow solution of Mo(CH-*t*-Bu) (10 mg, 2.05 × 10^{-5} mol) in THF (2 mL) under vigorous stirring. After stirring for 15 min a solution of **5** (244 mg, 2.05 mmol) in THF (2 μL) was added in the same fashion and allowed to stir for 25 min to yield a light yellow, slightly viscous solution. The polymerization was quenched by addition of benzaldehyde (15 μL) and stirred for an additional 30 min. The polymer was isolated by precipitation into a large excess of hexane and centrifugation. The resulting white powder was washed several times with hexane or methanol and placed under vacuum for 24 h to yield 381 mg (87%) of the product. The ^{1}H and ^{13}C NMR spectra were identical with the superposition of spectra for poly-NBE and poly-5. GPC: M_n = 55 780 (vs polystyrene), PDI = 1.05.

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