ADMET Depolymerization. Synthesis of Perfectly Difunctional ($f = 2.0$) Telechelic Polybutadiene Oligomers

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ABSTRACT: Diester, disilyl ether, and diimide telechelic 1,4-polybutadiene oligomers have been synthesized via acyclic diene metathesis (ADMET) depolymerization. Mass spectrometry, in combination with NMR spectroscopy and gel permeation chromatography, show that these telechelics are perfectly difunctional ($f = 2.0$). The mechanism yielding these telechelics is described, which illustrates that the chemistry first proceeds through intramolecular cyclization of 1,4-polybutadiene. These macrocyclic butadienes then cross metathesize with a functionalized monoene to form linear difunctional telechelic oligomers.

Introduction

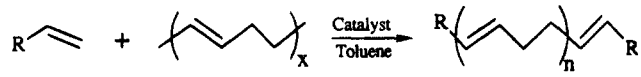
Preparing telechelics with perfect difunctionality ($f = 2.0$) has been a challenge for years. Many methods have been investigated, including step growth,[1-4] anionic,[5-10] cationic,[11-15] and free radical procedures,[16-19] and significant progress has been made in this field. In most cases, however, the average functionality of the oligomers is a value other than 2.

Recently, the metathesis polymerization of cyclooctadiene with a chain transfer agent has been described as producing telechelic polybutadiene where the functionality was close to 2.0.[20,21] There have also been attempts to produce perfectly difunctional telechelics by metathesis degradation.[21-26] These reactions employ classical catalyst systems such as those based on a WCl_6/Lewis acid cocatalyst, and it is evident that these classical systems cause side reactions which decrease the average functionality of the telechelic oligomers.

Earlier we reported the depolymerization of 1,4-polybutadiene to yield perfectly difunctional ($f = 2.0$) telechelic polybutadiene oligomers using α,ω-allylsilanes in an ADMET depolymerization scheme (Figure 1).[27] These 2.0 telechelics were synthesized with the well-defined Schrock catalyst, $M(NAr)(CHC(CH_3)_2Ph)(OCCH_3(CF_3)_2)_2$ where M = W[28] or Mo,[29] and the results prompted us to explore this opportunity more broadly. This chemistry is the subject of the present study. We now report the employment of various functionalized monoenes to generate 2.0 telechelics possessing diester, disilyl ether, and diimide end groups.

Experimental Section

^1H NMR 200 MHz and ^{13}C NMR 50 MHz spectra were obtained with a Varian XL-Series NMR Superconducting Spectrometer system. Chloroform-*d* ($CDCl_3$) or benzene-d_6 was used as solvent, and all chemical shifts reported are internally referenced to tetramethylsilane (TMS), $CDCl_3$, or benzene. Infrared analyses were performed between NaCl plates for neat liquids or KBr pellets for solids. Gas chromatography/mass spectral (GC/MS) data, using the chemical ionization technique were obtained with a Finnigan 4500 gas chromatograph/mass spectrometer. Elemental analyses were performed by Atlantic Microlab, Norcoss, GA. Gel permeation chromatography (GPC) data were collected using a Waters Associates liquid chromatograph apparatus equipped with a Perkin-Elmer LC-25 refractometer. Two Phenomex 7.8 mm × 30 cm Phenogel 5 consecutive linear cross-linked polystyrene gel columns were used; a 500 Å followed by a 1000 Å. 1,4-Polybutadiene **2** used in the synthesis of **7**, **9**, and **12** was purchased from Aldrich. The microstructure was 98% 1,4 cis and $M_w = 2 \times 10^6$. 1,4-Polybutadiene **3** used in the synthesis of **5** and **10** was provided by the DeSimone group at the University of North Carolina at Chapel Hill. The microstructure was 94% 1,4 and $M_n = 87\,000$. Catalyst **1**, $[(CF_3)_2CH_3CO]_2(NAR)Mo{=}CHC(CH_3)_2Ph$, was prepared by published methods.[29]



R	Catalyst	n
$-CH_2Si(CH_3)_3$	W	2, 3, 4
$-CH_2Si(CH_3)_3$	Mo	1, 2
$-CH_2Si(CH_3)_2Cl$	Mo	1

Figure 1. Depolymerization of 1,4-polybutadiene with allylsilanes.

Diethyl 4-octene-1,8-dioate (**4**), bis(*tert*-butyldimethylsilyl) 3-hexene-1,6-diol diether (**6**), bis(*tert*-butyldimethylsilyl 2-butene-1,4-diol diether (**8**), 2-butene-1,4-diylbis(phthalimide) (**11**), and *N*-(*tert*-butoxycarbonyl)allylamine (**13**) were synthesized by known organic transformations. Synthetic details and characterization can be obtained in an addendum to this manuscript.

Depolymerization of 1,4-Polybutadiene with Diethyl 4-Octene-1,8-dioate (5). Degassed polybutadiene **3** (0.55 g, 10 mmol) was added to catalyst **1** (5 mg, 6.03×10^{-3} mmol). Diethyl 4-octene-1,8-dioate (5.0 g, 42 mmol) was vacuum transferred into the reaction flask. Toluene (25 mL) was dried over sodium potassium alloy and added. The reaction was allowed to stir for 12 h. Volatiles were removed in vacuo and oligomers were purified by an alumina column (2.87 g) (100%). ^1H NMR ($CDCl_3$); δ 1.27 (t, 3H), 2.05 (m, 4H), 2.35 (t, 2H), 2.37 (m, 2H), 4.13 (q, 2H), 5.40 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 14.17, 27.85, 34.55, 60.22, 128.95 (cis), 129.36 (trans), 172.94. GC/MS: $M^+ = 283$, 337 M (100) = 237, 337. GPC (THF): $M_n = 295$, PDI = 1.07. IR spectrum: ν 1725 (C=O), 1640 (C=C), 1240 (C-O).

Depolymerization of 1,4-Polybutadiene with Bis(*tert*-butyldimethylsilyl)-3-hexene-1,6-diol Diether (7). Degassed polybutadiene **2** (0.50 g, 9 mmol) was added to catalyst **1** (5 mg, 6.03×10^{-3} mmol) and bis(*tert*-butyldimethylsilyl) 3-hexene-1,6-diol diether (5.0 g, 29.5 mmol). The reaction proceeded analogous to the synthesis of **5** (3.68 g) (100%). ^1H NMR ($CDCl_3$): δ 0.05 (s, 12H), 0.90 (s, 18H), 2.05 (m, 4H), 2.25 (m, 4H), 3.60 (t, 4H), 5.45 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 20.10,

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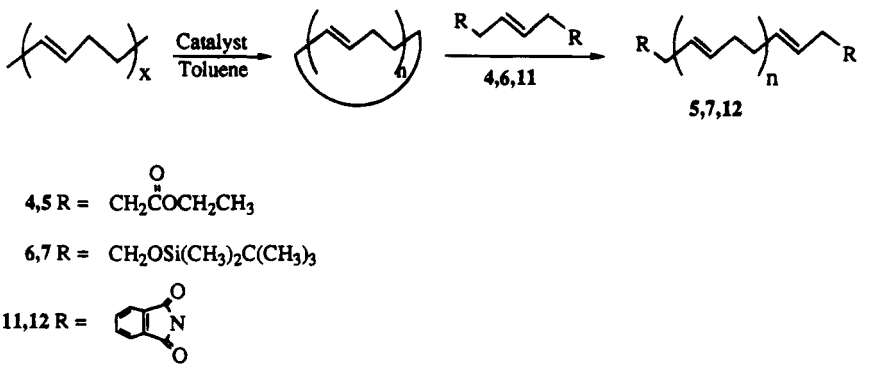

Figure 2. Depolymerization of 1,4-polybutadiene with diethyl 4-octene-1,8-dioate (**4**), bis(*tert*-butyldimethylsilyl)-3-hexene-1,6-diol diether (**6**), and 2-butene-1,4-diylbis(phthalimide) (**11**).

27.75, 34.18, 38.00, 63.85, 129.54, 130.27, 132.10, 134.05. GPC (THF): M_n = 362, PDI = 1.23. GC/MS: M^+ 399, 453 M (100) = 135, 189.

Depolymerization of 1,4-Polybutadiene with Bis(*tert*-butyldimethylsilyl)-2-butene-1,4-diol Diether (9). Degassed polybutadiene **2** (0.50 g, 9 mmol) was added to catalyst **1** (5 mg, 6.03 × 10^{-3} mmol) and bis(*tert*-butyldimethylsilyl) 2-butene-1,4-diol diether (5.0 g, 12.5 mmol). The reaction proceeded analogous to the synthesis of **5** (3.00 g) (88%). ^{1}H NMR ($CDCl_3$): δ 0.05 (s, 12H), 0.90 (s, 18H), 2.05 (m, 4H), 4.05 (d, 4H, trans), 4.07 (d, 4H, cis), 5.72 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 19.10, 26.75, 32.18, 32.56, 63.85, 64.04, 129.64, 130.17. GPC (THF): M_n = 397, PDI = 1.05. GC/MS: M^+ = 371, 425 M (100) = 107, 161.

Synthesis of Cyclic Butadienes (10). Degassed polybutadiene **3** (0.65 g, 12 mmol) and catalyst **1** (5 mg, 6.03 × 10^{-3} mmol) were placed in a reaction flask and proceeded analogous to the reaction of **5** (100%). ^{1}H NMR ($CDCl_3$): δ 2.05 (m, 4H), 5.35 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 26.84, 33.47, 129.84, 130.05. GPC (THF): M_n = 185; PDI = 1.03. GC/MS: M^+ = 163, 217 M (100) = 121. Anal. Calc (found): C, 88.83 (88.79); H, 11.17 (11.16).

Depolymerization of 1,4-Polybutadiene with 2-Butene-1,4-diylbis(phthalimide) (12). Degassed polybutadiene **2** (0.50 g, 9.0 mmol) was added to catalyst **1** (5 mg, 6.0 × 10^{-3} mmol) and 2-butene-1,4-diylbis(phthalimide) (5.0 g, 25 mmol). Methylene chloride (25 mL) was vacuum transfered from P_2O_5 and the reaction was stirred for 24 h. The volatiles were removed in vacuo, and the oligomers were purified through an alumina column (3.70 g) (100%). ^{1}H NMR ($CDCl_3$): δ 2.05 (m), 4.25 (d, 4H, trans), 4.55 (d, 4H, cis), 5.70 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 28.85, 39.35, 123.45, 127.78, 132.20, 134.05, 135.57, 168.13. GC/MS: M^+ = 401, 455, M (100) = 242, 160. GPC (THF): M_n = 345, PDI = 1.05.

Synthesis of Bis(*N*-(*tert*-butoxycarbonyl)amino)-2-butene (14). Bis(*N*-(*tert*-butoxycarbonyl)amino)-2-butene (10 mg, 6.0 × 10^{-2} mmol) and catalyst **1** (25 mg, 3.01 × 10^{-2} mmol) were reacted in a NMR tube in deuterated toluene over an 8 h period (60%). ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 18H), 3.65 (m, 4H), 4.70 (s, 2H), 5.60 (m, 2H).

Attempted Depolymerization of 1,4-Polybutadiene with *N*-(*tert*-butoxycarbonyl)allylamine (15). Degassed polybutadiene **2** (0.50 g, 9.0 mmol) was added to catalyst **1** (50 mg, 6.0 × 10^{-2} mmol) and bis(*N*-(*tert*-butoxycarbonyl)-amino)-2-butene (5.0 g, 25 mmol). Toluene (25 mL) was added, and the reaction was stirred for 24 h. The reaction yielded starting material.

Results and Discussion

It is now clear that the research reported earlier[27] can be exploited to broaden the scope of ADMET depolymerization. Perfectly difunctional α,ω-diester, disilyl ether, and dimide telechelic polybutadiene oligomers can be synthesized with a well-defined Lewis acid free catalyst (Figure 2). That perfect difunctionality exists is unequivocally shown via mass spectrometry.

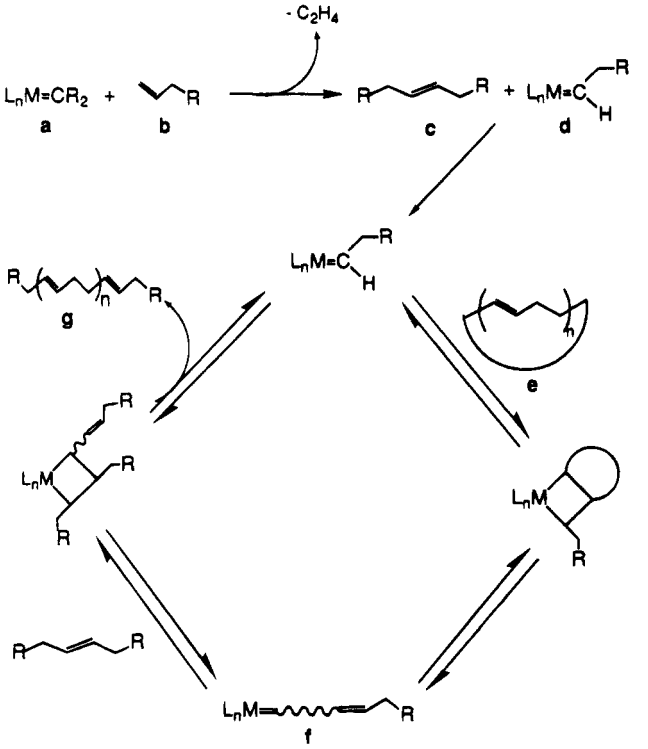

Figure 3. Proposed ADMET depolymerization mechanism.

The mechanism in which ADMET depolymerization proceeds is illustrated in Figure 3. Initially, the precatalyst (**a**) metathesizes with a functionalized monoene (**b**) to generate the symmetrical olefin (**c**) and a new alkylidene (**d**). Concurrently, intramolecular metathesis of polybutadiene is producing macrocyclic butadiene (**e**); the new alkylidene (**d**) and the macrocyclic (**e**) form a trisubstituted metallocyclobutane which can productively cleave, affording a ring-opened butadiene oligomer (**f**) with the catalyst at the α-position and the functionalized monoene at the ω-position. The catalyst exchanges with the symmetrical olefin (**c**) to produce a difunctional telechelic (**g**). This mechanism is substantiated by the data presented herein and precedented by Hummel's degradation chemistry.[30]

Synthesis of Diester-Terminated Telechelics. The synthesis of perfectly difunctionalized telechelics was achieved using diethyl 4-octene-1,8-dioate (**4**) in the depolymerization of 1,4-polybutadiene **3** to generate diester telechelics (Figure 2). Diethyl 4-octene-1,8-dioate was chosen because two methylene spacers separate the olefin from the carbonyl, and unless two or more methylenes are present, the negative neighboring group phenomenon inhibits productive metathesis.[31]

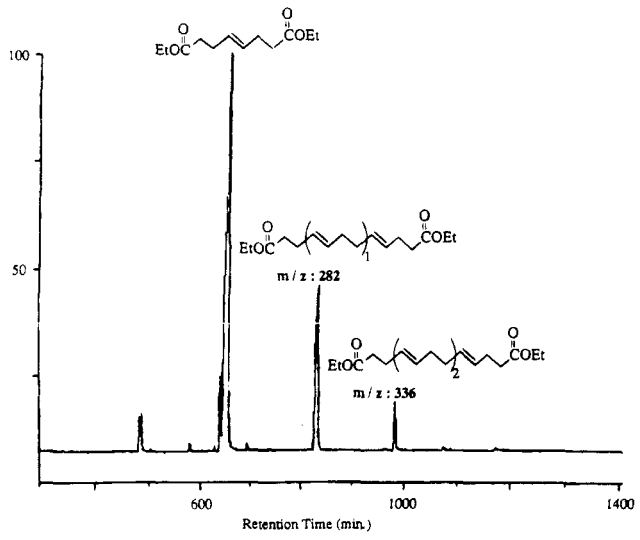

Figure 4. Gas chromatograph with mass labels obtained from mass spectrum of telechelic esters **5**.

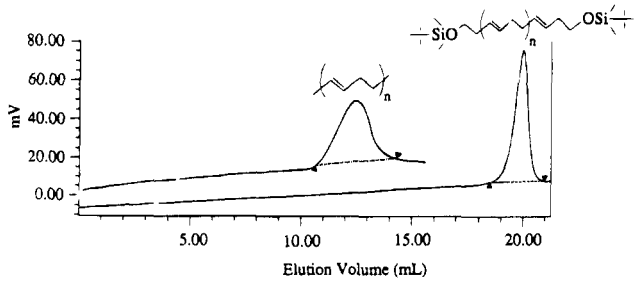

Figure 5. Gel permeation chromatograph of 1,4-polybutadiene **2** and resulting telechelics **7** where $n = 1$ and 2.

There are two possible explanations for this phenomenon. First, the electron-withdrawing ester may polarize the olefin such that the formation or decomposition of the metallocycles in the catalytic cycle are hindered.[31] Second, the carbonyl may coordinate with the metal center, forming ring structures, as shown in a similar system.[32] This process competes with productive metathesis, either decreasing the rate of reaction or completely inhibiting the reaction.

Keeping this effect in focus, depolymerization with **4** generates perfectly difunctional telechelic esters (**5**) with masses of 282 and 336 according to GC/MS techniques (Figure 4). These masses correspond to $n = 1$ and 2 butadiene repeat units. The ratio of $n = 1$ to 2 is 78:22.

Synthesis of Silyl Ether Terminated Telechelics. Diol-functionalized telechelics have been sought for their macromononer applications in the synthesis of polyurethanes.[33] However, ADMET depolymerization reactions utilizing alcohol monoenes in the synthesis of α,ω-(dihydroxy)-1,4-polybutadiene failed initially, most likely because the alcohol functionality decomposes the active catalytic species. Consequently, the alcohol must be protected, as shown in Figure 2. Bis(*tert*-butyldimethylsiloxy)-3-hexene-1,6-diol diether (**6**) was reacted with 1,4-polybutadiene **3** and the molybdenum catalyst (**1**), producing 2.0 telechelics (**7**), where $n = 1$ and 2 with a 81:19 ratio. Further addition of catalyst and monoene does not alter the product ratio. Nonetheless, gel permeation chromatography (GPC) data (Figure 5) demonstrate the complete conversion of high molecular weight 1,4-polybutadiene to telechelic oligomers of polybutadiene. No cyclics were observed in this case.

On the other hand, the chemistry illustrated in Figure 6 shows the depolymerization of 1,4-polybutadiene **3** with bis(*tert*-butyldimethylsilyl)-2-butene-1,4-diol diether (**8**) yields telechelic oligomers ($n = 1$ and 2) *and* macrocyclic polybutadiene ($z = 4$ and 5). The ratio of telechelic to macrocyclic was 88:12. The mass spectral data are shown in Figure 7. The formation of macrocyclics can be attributed to the negative neighboring group effect where the oxygen β to the alkylidene causes a competitive decomposition of the alkylidene before all macrocyclics can be quantitatively converted to the telechelic. Decomposition of the catalyst, caused by the β oxygen, has also been shown in the polymerization of telechelic polybutadiene.[20]

Earlier work with a classical catalyst system has shown that intramolecular cyclization can preclude the formation of linear telechelics. For example, Calderon *et al.* found that intramolecular metathesis degradation of polybutadiene yielded macrocyclics of three to eight repeat units.[34] This process is accelerated if the initial concentration of the polybutadiene is below the equilibrium concentration ("equilibrium concentration" is defined as the maximum concentration of polymer at which there is quantitative conversion of linear polymer to macrocyclics). If the concentration of polybutadiene is higher than the equilibrium concentration, then the polymer undergoes partial degradation, yielding macrocyclic oligomers and residual high molecular weight linear polymer. Although the equilibrium concentration has not been determined for toluene, the polybutadiene equilibrium concentration is 0.65 M in chlorobenzene at 30 °C.[35]

To prove that cyclization occurs under our conditions, a reaction analogous to Calderon's was attempted, except the molybdenum alkylidene was used instead of a classical catalyst system. Figure 8 illustrates generation of macrocyclics (**10**) when a 0.48 M polybutadiene (**2**) solution in toluene was exposed to the molybdenum catalyst. As shown in ^{1}H NMR (Figure 8), the macrocyclics have a vinylic proton resonance at 5.40 ppm, a shift from the vinylic protons of polybutadiene (5.75 ppm). The GC trace has nine peaks which represent macrocyclic trimer and tetramer regioisomers, and these data suggest that the depolymerization mechanism proceeds first through a competitive intramolecular formation of macrocyclics, followed by cross metathesis with the monoene to form telechelics.

Synthesis of Imide-Terminated Telechelics. As illustrated in Figure 2, polybutadiene **3** was depolymerized with 2-butene-1,4-diylbis(phthalimide) (**11**) and catalyst **1**, affording imide-functionalized telechelics (**12**), where $n = 1$ and 2 with a 79:21 ratio by GC/MS techniques (Figure 9). Depolymerization occurred quantitatively to the telechelics, even though one methylene spacer separated the nitrogen from the olefin. We believe coordination of the nitrogen was minimized by using an imide functionality, which sterically encumbers the nitrogen lone pair and resonance delocalizes the electron charge density, thereby obviating the negative neighboring group effect.

In order to study this "β nitrogen" phenomenon further, a secondary acyclic amine, *N*-(*tert*-butoxycarbonyl)allylamine (**13**), was reacted with the molybdenum catalyst in a NMR scale reaction (Figure 10). Productive metathesis was observed. Initially, the ^{1}H NMR spectrum displayed a molybdenum alkylidene at 12.4 ppm, a compound which results from the exchange of molybdenum neophylidene with **13** to produce an

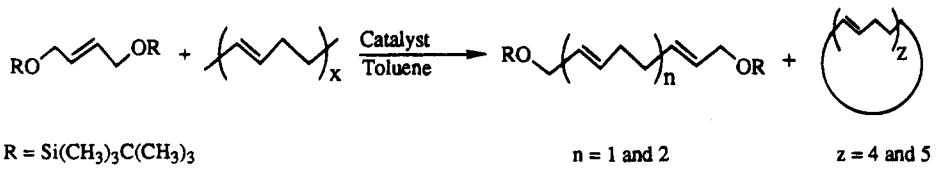

Figure 6. Depolymerization of 1,4-polybutadiene **2** with bis(*tert*-butyldimethylsilyl)-2-butene-1,4-diol ether (**8**).

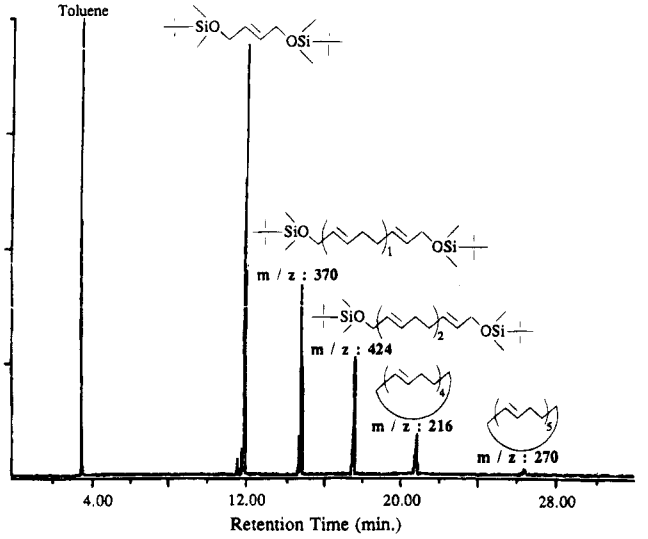

Figure 7. Gas chromatograph with mass labels obtained from mass spectra of the resulting α,ω-bis(*tert*-butyldimethylsiloxy)-1,4-polybutadiene (**9**) where n = 1 and 2 and macrocyclic butadiene where n = 4 and 5.

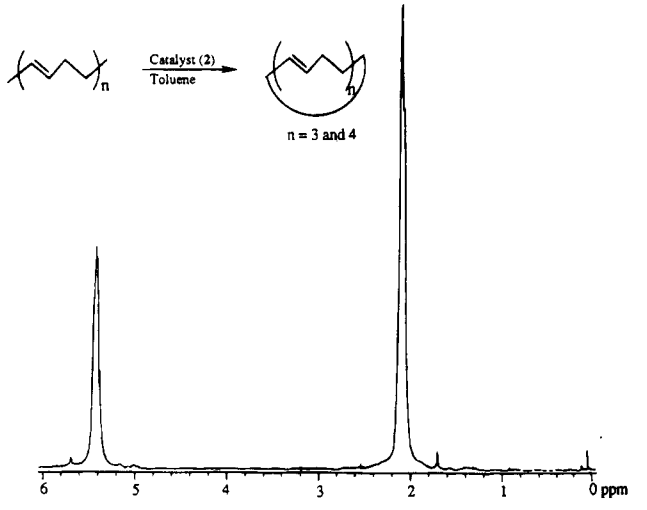

Figure 8. ^{1}H NMR of the resulting macrocyclic butadiene **10**.

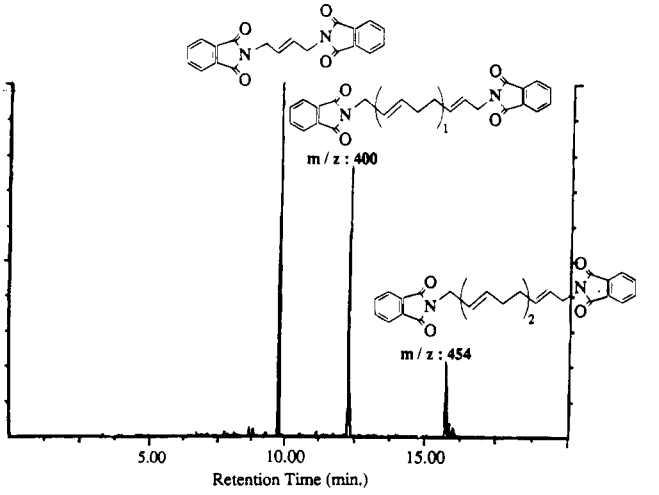

Figure 9. Gas chromatograph with mass labels obtained from mass spectra of the resulting α,ω-bis(phthalimido)-1,4-polybutadiene (**11**) where n = 1 and 2.

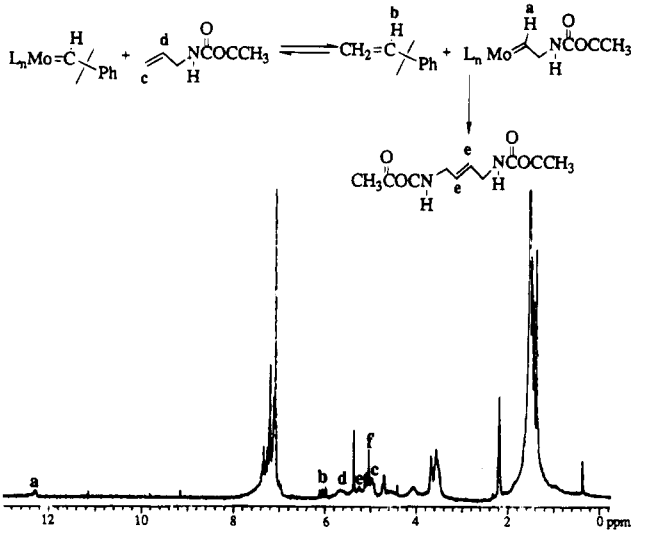

Figure 10. ^{1}H NMR of the reaction mixture in the dimerization of *N*-(*tert*-butoxycarbonyl)allylamine (**14**) after 1.5 h.

amide alkylidene (**a**) (s, 12.4 ppm) and 3-methyl-3-phenylbutene (**b**) (dd, 6.1 ppm). After 1.5 h, there was no change in the size of the alkylidene peak and an internal olefin peak appeared at 5.4 ppm corresponding to a 20% conversion to bis(*N*-(*tert*-butoxycarbonyl)-amino)-2-butene (**14**). An ethylene peak (**f**) was also present at 5.20 ppm, further suggesting that dimerization occurred. After 8 h, the alkylidene peak completely disappeared, resulting in only a 60% conversion to dimer. Unlike the imide reaction, these observations suggest that coordination competes with dimerization.

N-(*tert*-butoxycarbonyl)allylamine (**13**) was employed in the attempted depolymerization of polybutadiene, but no productive depolymerization occurred. From this result, we hypothesize that coordination of the nitrogen or carbonyl with the metal center is competing with productive depolymerization of 1,4-polybutadiene. The competing coordination slows the reaction and, ultimately, as in the case of the NMR reaction, decomposes the alkylidene.

Conclusions

ADMET depolymerization chemistry is a viable route in the synthesis of perfectly difunctional (f = 2.0) telechelic 1,4-polybutadiene oligomers. Telechelic diester or disilyl ethers can be synthesized if two methylene spacers separate the olefin from the carbonyl or ether functionalities, respectively.

The depolymerization mechanism has been elucidated whereby the reaction initially proceeds through macrocyclic butadienes which then ring open to form telechelic oligomers.

2-Butene-1,4-diylbis(phthalimide) can be used as a monoene even though a nitrogen is β to the olefin.

Apparently, coordination of the imide nitrogen is minimized, thereby allowing quantitative conversion of polybutadiene to the telechelics. By comparison, the less sterically hindered and more localized charge density of *N*-(*tert*-butoxycarbonyl)allylamine causes an increase in coordination which results in a much slower rate of metathesis and, ultimately, alkylidene decomposition.

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Supplementary Material Available: Techniques describing the syntheses of diethyl 4-octene-1,8-dioate, bis(*tert*-butyldimethylsilyl)-3-hexene-1,6-diol diether, bis(*tert*-butyldimethylsilyl)-2-butene-1,4-diol diether, 2-butene-1,4-diylbis(phthalimide), and *N*-(*tert*-butoxycarbonyl)allylamine are included (3 pages). Ordering information is given on any current masthead page.

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