Ring-Opening Metathesis Polymerizations in D-Limonene: A Renewable Polymerization Solvent and Chain Transfer Agent for the Synthesis of Alkene Macromonomers

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Received July 26, 2006; Revised Manuscript Received October 10, 2006

ABSTRACT: D-Limonene has been utilized as a renewable solvent and chain transfer agent for the ring-opening metathesis polymerization (ROMP) of alkene macromonomers. The polymerization of various strained monomers, such as norbornene and 1,5-cyclooctadiene (COD), and low-strain monomers, such as cyclopentene, *trans,trans,-trans*-1,5,9-cyclododecatriene and cycloheptene, have been initiated with a ruthenium carbene complex. The metathesis reactions with D-limonene resulted in decreased weight-average (M_w) molecular weight values compared to ROMP in toluene and hydrogenated D-limonene. For the ROMP of COD in D-limonene, the amount of chain transfer and chain degradation increased with increasing time (1−20 h) and temperature (23−70 °C). The formation of the trisubstituted alkene during chain transfer, as evidenced by a model compound, was characterized by ^{1}H NMR (δ 5.14 ppm). Optimization of the reaction conditions for the ROMP of COD resulted in the synthesis of alkene macromonomers without the need for postpolymerization reactions.

Introduction

Ring-opening metathesis polymerizations (ROMP) have received widespread attention.[1−7] Many of these well-known ROMP systems tolerate a wide variety of functional groups. One prevalent strategy for incorporating chemical functionality at the polymer chain ends utilizes chain transfer agents (CTA).[4,8−11] Typically, these disubstituted *cis*- or *trans*-alkenes reduce the molecular weight and provide a variety of telechelic functional groups. In some cases, the functional groups allow self-assembly[12,13] or serve as initiators for the synthesis of diblock copolymers[14,15] and triblock copolymers.[16,17]

Advances in catalyst design have allowed metathesis reactions of vinylidene and trisubstituted alkenes.[18−20] Previously, examples of CTA focused on disubstituted alkenes due to the reactivity of the metal alkylidene catalysts.[4,8−11] Although ruthenium complexes with *N*-heterocyclic carbene ligands catalyze cross metathesis reactions with isobutylene,[18] metathesis reactions of vinylidene analogues, such as D-limonene, have not been reported. Monoterpenes, such as D-limonene, are a broad class of naturally occurring substances.[21] D-Limonene is produced as a byproduct (110−165 million lbs/year) of the citrus industry.[22] Because D-limonene is available in large quantities, requires no synthetic modification, and has negligible toxicity compared with certain chain transfer agents,[23] it has wide-ranging potential.

This report describes D-limonene as a renewable polymerization solvent and CTA for ROMP utilizing a ruthenium carbene complex. The characterization of the resulting alkene macromonomers is described. Examples of macromonomers for ROMP[24−28] or coordination polymerizations[29−31] often involve postpolymerization reactions. In our case, the polymerization conditions for the synthesis of alkene macromonomers have been optimized without the need for postpolymerization reactions. In the absence of CTA, the linear polymers that result from ROMP have an alkene at each end of the polymer chain. These α,ω-difunctional polymers are not ideal macromonomers due to the possibility of cross-linking reactions.[32] Choosing D-limonene as a polymerization solvent and CTA results in a terminal alkene at one end of the polymer chain and a monoterpene unit at the other end.

Experimental Section

Materials. D-Limonene (97%, Aldrich), 1,5-cyclooctadiene (COD) (97%, Aldrich), and cyclopentene (CP) (96%, Aldrich) were degassed, distilled from CaH_2, and stored in a glovebox. Cycloheptene (CH) (97%, Aldrich), *trans,trans,trans*-1,5,9-cyclododecatriene (*ttt*-CDT) (99%, Aldrich), *trans,trans,cis*-1,5,9-cyclododecatriene (*ttc*-CDT) (98+%, Acros), and norbornene (NB) (99%, Acros) were degassed and taken into a glovebox. The (1,3-dimesitylimidazolidine-2-ylidene)(tricyclohexylphosphine)-benzylidene ruthenium dichloride was purchased from Aldrich (Anal. Calcd: C, 65.08; N, 3.30. Found: C, 65.00; N, 3.29). Nitrogen (99.995%, high purity grade) and hydrogen (99.995%, high purity grade) were used as received.

Techniques. All polymerizations were setup in an MBraun glovebox. The molecular weights were measured by size exclusion chromatography (SEC). The SEC system was equipped with a three-angle Wyatt MiniDawn light scattering detector (λ = 690 nm, 30 mW Ga−As laser), a Wyatt ViscoStar viscometer, and a Waters 410 differential refractometer. The light scattering detector was calibrated with the known Rayleigh ratio for toluene. The three columns (MZ SDplus, 300 mm × 8 mm) contained 5 μm particles with pore sizes ranging from 50 to 10^6 Å. The columns were eluted with methylene chloride (1.0 mL/min) at 35 °C. The polymers were injected at a concentration of 10−15 mg/mL. The specific refractive increments (dn/dc) were calculated with a known polymer concentration using Wyatt Technology's Astra software (version 5.1.8.0), assuming that the area of the refractive index signal from the Waters 410 detector represented 100% mass recovery. For the

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10.1021/ma061699h CCC: $33.50

Table 1. Initial Monomer Screening for Ring-Opening Metathesis Polymerizations in D-Limonene^a

entry	monomer^b	solvent	yield (%)	M_w (g/mol)^c	M_w/M_n^{c}
1	NB	D-limonene	90	26 300	1.3
2	NB	toluene	88	80 300	1.7
3	COD	D-limonene	83	11 100	2.4
4	COD	toluene	68	57 900	2.6
5	*ttt*-CDT	D-limonene	29	2400	1.6
6	*ttt*-CDT	toluene	28^d		
7	*ttc*-CDT	D-limonene	16	8260	2.1
8	*ttc*-CDT	toluene	55^d		
9	CH	D-limonene	61	6320	2.0
10	CH	toluene	50	50 500	2.6
11	CP^e	D-limonene	38	5550	2.8

^{a} All polymerizations were run with monomer (4.0 mmol), ruthenium carbene complex (0.005 mmol), and solvent (3.0 mL) at ambient temperature for 1h. ^{b} NB = norbornene; COD = 1,5-cyclooctadiene; *ttt*-CDT = *trans, trans, trans*-1,5,9-cyclododecatriene; *ttc*-CDT = *trans, trans, cis*-1,5,9-cyclododecatriene; CP = cyclopentene; CH = cycloheptene. ^{c} Weight-average (M_w) molecular weight and polydispersity index (M_w/M_n) were measured by size exclusion chromatography. ^{d} Partially insoluble in CH_2Cl_2. ^{e} Reaction was run for 3 h with [CP] = 3 M; no polymer was recovered at 1.3 M.

polymers resulting from the polymerization of COD, *ttt*-CDT, and *ttc*-CDT (see Table 1, entries 3−8), the d*n*/d*c* value in methylene chloride was 0.110. For the polymers resulting from the polymerization of NB (see Table 1, entries 1 and 2) and CH (see Table 1, entries 9 and 10), the d*n*/d*c* value in methylene chloride was 0.115 and 0.089, respectively. The FTIR spectra were recorded with NaCl plates at a 4 cm^{-1} resolution on an ATI Mattson Genesis Series FTIR spectrometer. The ^1H NMR spectra were measured at 25 °C with a Bruker 300 or 500 MHz NMR spectrometer in deuterated chloroform ($CDCl_3$, 99.8% D, Cambridge Isotope Laboratories) or 1,1,2,2-tetrachloroethane-d_2 (Cl_4Et-d_2, Cambridge Isotope Laboratories). GC/MS samples were dissolved in methylene chloride and analyzed with a HP 5972 series gas chromatograph/mass spectrometer. The samples were analyzed on an Alltech AT-5 capillary column (30 m × 0.25 mm i.d. × 0.25 μm stationary phase thickness). Spectra were acquired via electron impact ionization at 70 eV.

Polymerization Procedure. The COD (0.43 g, 4.0 mmol) and D-limonene (2.0 mL, 18.5 mmol) were added to a small vial. Then initiator stock solution (1.0 mL, 5.0 mM, [COD]/[initiator] = 800 equiv) of the (1,3-dimesitylimidazolidine-2-ylidene)(tricyclohexylphosphine)benzylidene ruthenium dichloride in D-limonene was added. The vial was capped and shaken. After 60 min at ambient temperature, the polymerization was quenched with ethyl vinyl ether (0.3 mL, 3 mmol). The polymer solution was diluted with toluene (10 mL) and precipitated into methanol (200 mL) and stirred overnight. After decanting the methanol, the polymer was dried under vacuum overnight to yield 0.36 g (83%). SEC (CH_2Cl_2): M_w = 11 100 g/mol, M_w/M_n = 2.4. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.8 (m, 1H, vinyl CH), 5.4 (m, 21H, alkene CH), 5.14 (br, 1H), 4.95 (dd, 2H, vinyl CH_2), 2.0 (m, 42H, CH_2), 1.89 (br, 1H), 1.82 (br, 1H), 1.68 (s, 1H), 1.63 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), and 1.47 (m, 1H) ppm.

Synthesis of Model Compound 1. The D-limonene (3.0 mL, 18.5 mmol), 1-hexene (0.50 mL, 4.0 mmol), and (1,3-dimesitylimidazolidine-2-ylidene)(tricyclohexylphosphine)benzylidene ruthenium dichloride (68 mg, 0.08 mmol) were added to a 50 mL RB flask equipped with a Strauss adapter. The solution was periodically degassed while stirring at 55° C. After 40 h, the catalyst was quenched with ethyl vinyl ether (0.3 mL, 3 mmol). The product was dissolved in toluene (50 mL) and filtered through neutral alumina. The solvent was removed under vacuum to recover the product (0.30 g, 40% yield). IR (neat, NaCl) ν: 2958 (ν_{as} CH_3 st), 2925 (ν_{as} CH_2 st), 2871 (ν_s CH_3 st), 1678 (C=C st), 1450 (δ_{as} CH_3 bending), and 1377 (δ_s CH_3 bending). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.38 (br, 1H), 5.14 (m, 1H), 1.96 (br, 6H), 1.63 (s, 3H), 1.56 (s, 3H), 1.47 (m, 1H), 1.29 (m, 6H), and 0.87 (br, 3H) ppm. GC/MS *m*/*z* (abundance): 192 (91%), 208 (3%), 220 (6%).

Oligomerization of 1,5-Hexadiene (0.2 M) in D-Limonene. D-Limonene (15 mL, 92.5 mmol), 1,5-hexadiene (0.36 mL, 3.0 mmol), and (1,3-dimesitylimidazolidine-2-ylidene)(tricyclohexylphosphine)benzylidene ruthenium dichloride (25 mg, 0.03 mmol) were added to a 50 mL RB flask equipped with a Strauss adapter. The reaction was periodically vented with a nitrogen purge to remove ethylene. After heating to 45 °C for 24 h, the initiator was quenched with excess ethyl vinyl ether (0.5 mL, 5 mmol). The solution was filtered through neutral alumina. After washing the alumina with hexanes (15 mL), the solvent was removed under vacuum to recover the product (0.25 g, >95% yield). IR (neat, NaCl) ν: 3076 (vinyl CH st), 3008 (alkene CH st), 2964 (ν_{as} CH_3 st), 2920 (ν_{as} CH_2 st), 2854 (ν_s CH_2 st), 1678 (C=C st), 1643 (C=C st), 1377 (δ_s CH_3 bending), 991 (alkene CH bending), 968 (alkene CH bending), and 912 cm^{-1} (vinyl CH bending). GC/MS min (**component**, *m*/*z*, abundance): 6.1 (**CDT**, 162, 1.7%), 6.9 (**B$_3$**, 190, 5.2%), 7.6 (**A$_1$**, 190, 41.9%), 11.1 (**B$_4$**, 244, 3.4%), 11.7 (**A$_2$**, 244, 21.9%), 13.9 (**B$_5$**, 298, 2.0%), 14.5 (**A$_3$**, 298, 8.9%), 14.9 (**C$_1$**, 298, 8.6%), 16.1 (**B$_6$**, 352, 0.6%), 16.6 (**A$_4$**, 352, 2.6%), 17.1 (**C$_2$**, 352, 3.2%).

Hydrogenation of D-Limonene. Freshly distilled D-limonene (84 g, 0.62 mol) and 10% palladium on carbon (8.0 g) were added to a pressure reaction vessel (6 oz, Andrews Glass Co.) equipped with stainless steel Swagelok components. The reactor was purged with nitrogen before attaching the hydrogen. The solution was stirred for 3 days at 30 °C with 30 psi of hydrogen. The degree of hydrogenation was periodically monitored with FTIR spectroscopy by following the decrease in alkene absorbances at 3083, 1645, 914, and 887 cm^{-1}. After venting the reactor, the product was filtered to remove the catalyst. The product (82 g, 95% yield) was stirred over CaH_2 and distilled under reduced pressure. IR (neat, NaCl) ν: 2954 (ν_{as} CH_3 st), 2918 (ν_{as} CH_2 st), 2870 (ν_s CH_3 st), 2850 (ν_s CH_2 st), 1454 (δ_{as} CH_3 bending), 1448 (δ_{as} CH_3 bending), 1385 (δ_s CH_3 isopropyl), and 1367 cm^{-1} (δ_s CH_3 isopropyl). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.68 (br, 3H, CH), 1.39 (m, 2H, CH_2), 1.25 (d, 2H, CH_2), 0.98 (br, 2H, CH_2), 0.92 (d, 2H, CH_2), and 0.87 ppm (m, 9H, CH_3). GC/MS min (*m*/*z*, abundance): 3.4 (140, 69%), 3.5 (140, 25%), 3.7 (134, 6%).

Results and Discussion

Monomer Screening. An initial screening process was conducted to determine which monomers would undergo ROMP in D-limonene. D-Limonene was a suitable polymerization solvent for a variety of monomers as shown in Table 1. Both highly strained rings, such as norbornene, and low-strain monomers, such as cyclopentene and cycloheptene, were considered.[33] In the case of cyclopentene, a higher monomer concentration was necessary to recover polymer. Increasing the CP concentration in D-limonene to 3 M resulted in a 38% yield. Polymerization of 1,5-cyclooctadiene, *trans*,*trans*,*trans*-1,5,9-cyclododecatriene and *trans*,*trans*,*cis*-1,5,9-cyclododecatriene resulted in lower yields than the ROMP of NB.

After determining the feasibility of ROMP in D-limonene, the results were compared to polymerizations in toluene. The yields for polymerizations in D-limonene were comparable to polymerizations in toluene. Interestingly, the dielectric constants for toluene (ϵ = 2.379)[34] and D-limonene (ϵ = 2.3746)[35] are similar. As demonstrated in Figure 1, the SEC data for the ROMP in D-limonene were monomodal, but had lower molecular weight values than corresponding polymerizations in toluene. The molecular weight for the ROMP of COD in D-limonene decreased as a function of time and temperature, as shown in Figure 2. After evaluating the polymers by SEC, it was apparent that ring strain influenced the resulting weight-average (M_w) molecular weight values. For example, NB gave the largest M_w value, whereas CP and *ttt*-CDT gave lower M_w values.

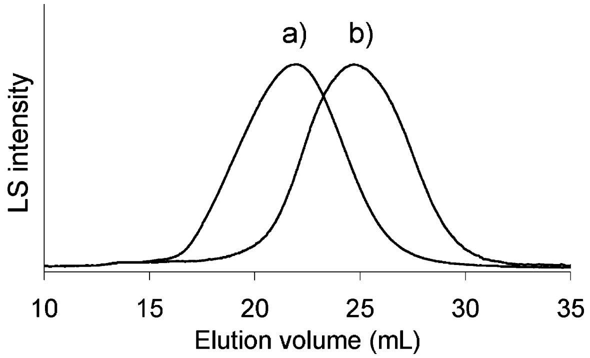


Figure 1. Size exclusion chromatography data (90° light scattering detector) for the ring-opening metathesis polymerization of 1,5-cyclooctadiene (1.3 M) after 1 h at 23 °C in (a) toluene and (b) D-limonene.

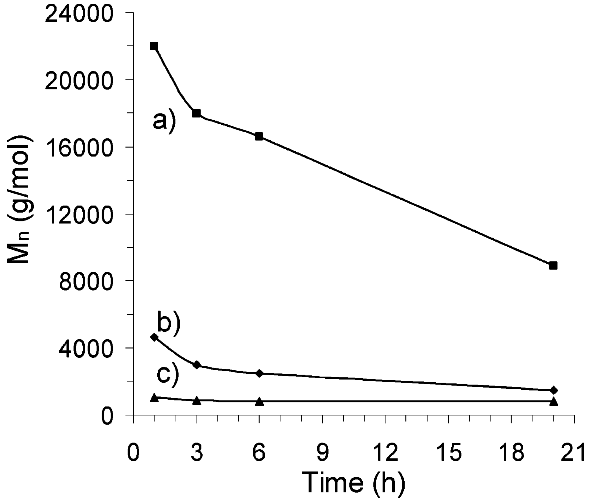


Figure 2. Effect of time and temperature on the ring-opening metathesis polymerization of 1,5-cyclooctadiene (1.3 M) in (a) toluene at 23 °C, (b) D-limonene at 23° C, and (c) D-limonene at 70 °C.

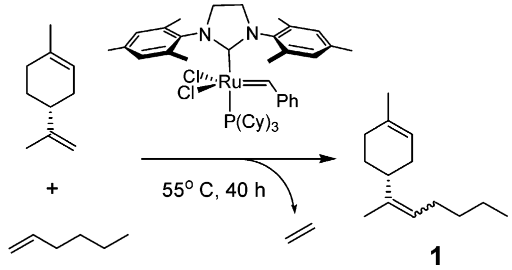
The ROMP of COD was also examined in hydrogenated D-limonene. The hydrogenation of D-limonene was monitored by the disappearance of the vinylidene alkene absorbance in the FTIR spectrum. The resulting products, *cis*-1-isopropyl-4-methyl cyclohexane and *trans*-1-isopropyl-4-methyl cyclohexane, were characterized by GC/MS (*m*/*z* 140). Although the hydrogenated D-limonene contained 6% *p*-cymene, the presence of small amounts of aromatic compounds were assumed insignificant. The ROMP of COD under ambient conditions for 1 h in hydrogenated D-limonene resulted in 66% yield with a higher M_w value (M_w = 56 100 g/mol; M_w/M_n = 2.0) than polymerizations in D-limonene (see Table 1, entry 3).

Model Reactions. We hypothesized that the M_w values for the ROMP in D-limonene were lower than polymerizations in toluene and hydrogenated D-limonene due to chain transfer. Because metathesis reactions involving D-limonene were not reported, two model reactions were investigated.

First, the cross metathesis of D-limonene and 1-hexene was catalyzed with a ruthenium carbene complex, as shown in Scheme 1. The product (**1**) was recovered in 40% yield and detected by GC/MS (*m*/*z* 192). FTIR spectroscopy of **1** detected the C=C absorbance at 1678 cm^{-1} for the trisubstituted cyclic alkene. The homodimerization of 1,1-disubstituted alkenes, such as D-limonene, is not expected.[19]

Second, the effect of monomer concentration was examined to investigate if chain transfer would compete with the rate of propagation during a polymerization. Because the acyclic diene metathesis (ADMET) of 1,5-hexadiene (HD) has a propensity toward the formation of oligomers,[36] a series of reactions in D-limonene were characterized by GC/MS. The oligomeric products shown in Scheme 2 represent the potential products for the ROMP of COD, *ttt*-CDT, or *ttc*-CDT in D-limonene.

Scheme 1. Cross Metathesis of D-Limonene and 1-Hexene Catalyzed with 2 mol % of a Ruthenium Carbene Complex



Scheme 2. Potential Product Distributions Resulting from the Acyclic Diene Metathesis Oligomerization of 1,5-Hexadiene in D-Limonene Initiated with a Ruthenium Carbene Complex

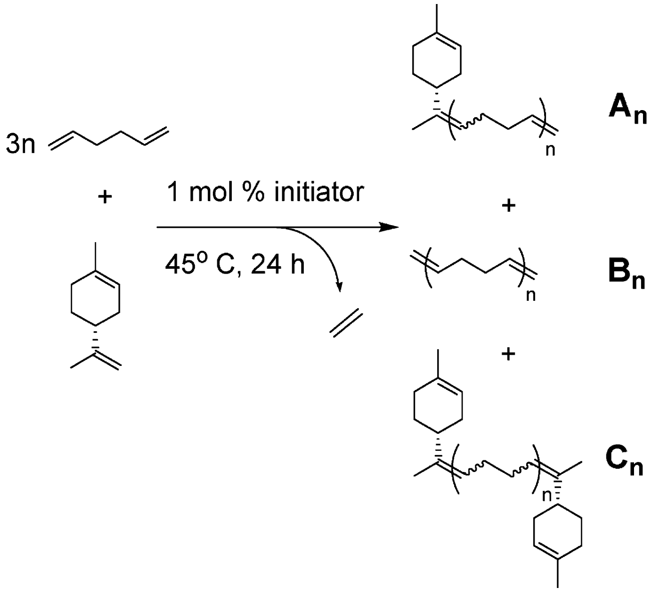


Table 2. Effect of 1,5-Hexadiene (HD) Concentration on Chain Transfer[a]

entry	[HD]	[D-limonene]/ [initiator][b]	A_n (%)[c]	B_n (%)[c]	C_n (%)[c]	CDT[d] (%)[c]
1	1.0	620	28	65	1	6
2	0.6	1030	55	37	4	4
3	0.3	2060	72	20	5	3
4	0.2	3080	75	11	12	2

[a] All reactions were run in D-limonene with HD (3.0 mmol) and 1 mol % initiator for 24 h. [b] Ratio of [D-limonene]/[ruthenium carbene complex]. [c] Determined by GC/MS; refer to Scheme 2 for definition of series $\mathbf{A_n}$, $\mathbf{B_n}$, and $\mathbf{C_n}$. [d] **CDT** = cyclododecatriene.

These model reactions determined the extent of the desired macromonomer (series $\mathbf{A_n}$) compared with homopolymer (series $\mathbf{B_n}$) and α,ω-difunctional polymer (series $\mathbf{C_n}$). Table 2 shows that series $\mathbf{A_n}$ increases as the monomer concentration decreases and the ratio of [D-limonene]/[initiator] increases. Series $\mathbf{A_n}$ was predominated by $\mathbf{A_1}$ with decreasing amounts of $\mathbf{A_2}$ to $\mathbf{A_5}$.[37] For comparison, the ROMP of COD at 0.2 M also resulted in series $\mathbf{A_n}$ (60%).

Series $\mathbf{C_n}$ was detected, but above a monomer concentration of 1.0 M, the amount of $\mathbf{C_{1-3}}$ appears negligible. Decreasing the reaction time for entry 4 (Table 2) from 24 to 3 h decreased $\mathbf{C_n}$ from 12% to 1.6%. Because the polymerizations in Table 1

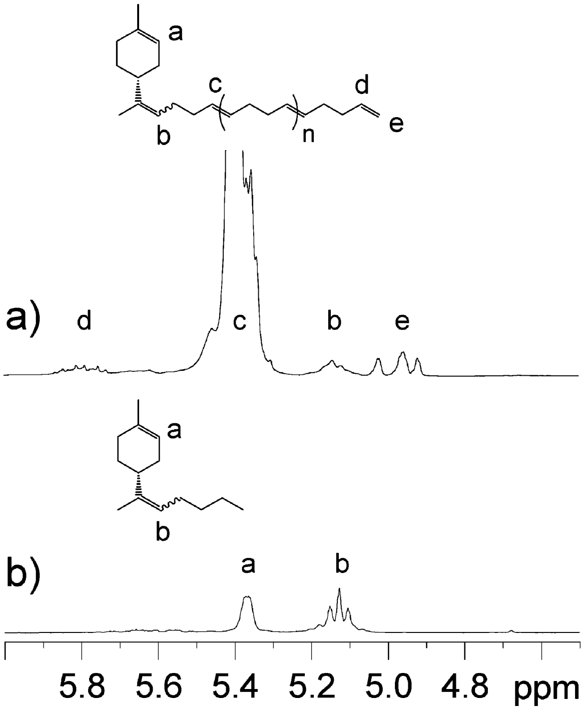


Figure 3. ^{1}H NMR (300 MHz, CDCl$_3$) spectra for (a) the product resulting from the ring-opening metathesis polymerization of 1,5-cyclooctadiene (1.3 M) in D-limonene after 20 h at 23 °C and (b) model compound **1**.

were run for 1 h with a monomer concentration of 1.3 M, we assume series $\mathbf{C_n}$ is not significant.

Cyclododecatriene was also detected for the oligomerization reactions. The formation of *ttt*-CDT is reported to be the predominant cyclic product during metathesis polymerizations.[38,39] Although $\mathbf{C_n}$ and *ttt*-CDT are expected to be effectively unreactive for coordination polymerizations, minimizing these components will allow a more accurate determination of $\mathbf{A_n}$.

Optimization of Macromonomer Synthesis. On the basis of the GC/MS results for the model reactions, metathesis reactions with D-limonene are competitive with propagation. To determine the amount of D-limonene attached to the polymers in Table 1, the ^{1}H NMR spectra of **1** and the polymers were compared. As shown in Figure 3, the trisubstituted alkene, which forms during the cross metathesis reaction with D-limonene, was detected at δ 5.14 ppm. This resonance for the terminal D-limonene unit is clearly distinguishable from the vinyl (δ 5.8 and 4.95 ppm) and disubstituted alkenes (δ 5.4 ppm) of the polymer. The percentage of $\mathbf{A_n}$ was based on the peak areas at δ 5.8 and 5.14 ppm.

To maximize $\mathbf{A_n}$, several design criteria were developed based on the model reactions. First, a monomer concentration greater than 1 M and a polymerization time of less than 24 h were used to minimize series $\mathbf{C_n}$. Second, a large ratio of [D-limonene]/[initiator] was employed to favor the formation of $\mathbf{A_n}$. For the polymerizations in Table 1, the [D-limonene]/[initiator] ratio was 3700. From this initial starting point, the amount of $\mathbf{A_n}$ for the ROMP of COD and CH in D-limonene (Table 1) was 36% and 25%, respectively.

Generally, increasing the polymerization time and temperature effected the M_n values (Figure 2) and the degree of $\mathbf{A_n}$, as estimated from the ^{1}H NMR peak area at δ 5.14 ppm. For instance, increasing the ROMP time at 23 °C from 1 to 20 h increased $\mathbf{A_n}$ to >96%.[40] Assuming each polymer chain had one vinyl group and one D-limonene unit, the M_n values from ^{1}H NMR (1300 g/mol) and SEC (1450 g/mol) compare reasonably well. Increasing the temperature from 23 to 70 °C for a 1 h polymerization time resulted in a slightly larger peak area at δ 5.14 ppm compared with δ 5.8 ppm. In this scenario, the additional area at δ 5.14 ppm is assumed to result from series $\mathbf{C_n}$. Consequently, the product was determined to contain 93% $\mathbf{A_n}$ and 7% $\mathbf{C_n}$. As a result of series $\mathbf{C_n}$, the M_n value from ^{1}H NMR (1360 g/mol) overestimated the M_n value from SEC (1070 g/mol).

Conclusion

D-Limonene is a suitable ROMP solvent for a variety of monomers. This report has described the vinylidene alkene on D-limonene as a chain transfer agent for ROMP. The resulting metathesis reactions with D-limonene decreased the molecular weight values compared to polymerizations in toluene and hydrogenated D-limonene. For the ROMP of COD in D-limonene, chain transfer and chain degradation increased with increasing time (1−20 h) and temperature (23−70 °C). Higher polymerization temperatures (70 °C) require shorter reaction times (≤1 h) to avoid the formation of series $\mathbf{C_n}$. Under the appropriate polymerization conditions, such as [D-limonene]/[initiator] ~ 3700 for 1 h at 70 °C, alkene macromonomers have been synthesized without the need for postpolymerization reactions.

Acknowledgment. This work was supported by the American Chemical Society Petroleum Research Fund (43244-GB1). K.C.M. is grateful to the ACS PRF for a summer research fellowship. We thank Jeffrey Baker for initial ROMP experiments with cyclopentene.

Supporting Information Available: GC/MS data, SEC data, and ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA061699H