

Controlled Polymerization of a Cyclic Diene Prepared from the Ring-Closing Metathesis of a Naturally Occurring Monoterpene

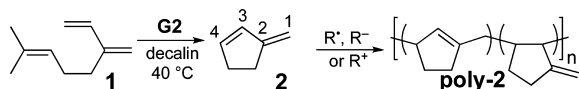
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The synthesis of polymers from renewable resources is driven by the desire to reduce our dependence on petroleum-based products and to develop sustainable materials technologies.¹ Much effort has focused on carbohydrate-derived hydroxy acid or vegetable oil based starting materials. Naturally occurring terpenes include unsaturated hydrocarbons and comprise another attractive class of biobased polymer precursors.² The importance of terpenes in the sustainable materials arena is underscored by the recent announcement of the planned commercial scale production of isoprene by fermentation.³ The monoterpene myrcene (**1**) can be readily obtained from plants⁴ or from the pyrolysis of pinene.⁵ We expected that the cyclic diene 3-methylenecyclopentene (**2**) could be prepared from **1** by ring-closing metathesis (RCM)⁶ and that **2** would be an attractive substrate for polymerization (Scheme 1). Furthermore,

Scheme 1



the byproduct of the metathesis cyclization of **2** is isobutene, the principal starting material for butyl rubber. Here, we report the synthesis of **2** using RCM and of poly-**2** using radical, anionic, and cationic polymerization. We demonstrate that the controlled cationic polymerization of **2** gives regioregular 1,4-poly-**2** and the hydrogenation of this polymer yields regioregular poly(cyclopentane-1,3-diylmethylene).⁷ We also show that 1,4-poly-**2** is semicrystalline by differential scanning calorimetry (DSC) with a melting temperature as high as 105 °C.

Compound **1** was converted to **2** in 45% yield (68% conversion) by RCM using 0.2 mol % of the Grubbs second generation initiator [G2, H₂IMes(Cl₂)(Cy₃P)Ru=CHPh] in decalin at 40 °C for 5 h. Complete conversion of **1** to **2** was achieved using 1.0 mol % G2. Due to its low concentration in the reaction mixture and lack of ring-strain, ring-opening metathesis polymerization of **2** is unfavorable. The RCM synthesis of **2** can be carried out on gram scale and represents a rare example of an ene-diene RCM reaction leading to an exocyclic conjugated double bond.⁸ The secondary product isobutene is also polymerizable and enhances the atom economy of our overall strategy. Previous reports describing the synthesis of **2** are not of preparative value.⁹

Radical,¹⁰ anionic,¹¹ and cationic¹² polymerizations of 2-methyl-1,3-pentadiene, an acyclic structural analogue of **2**, are known. In each case, the polymer obtained was of mixed regio- and stereochemistry. We studied the polymerization of **2** using the radical initiator AIBN. The conversion in benzene solution was low, but bulk polymerization afforded a polymeric product in 58% yield after 20 h at 80 °C. The *M_n* values of the resulting polymers were less than 1 kg mol⁻¹ by SEC versus PS standards. Anionic polymerization of 25 equiv of **2** in cyclohexane using *sec*-butyllithium (*s*-BuLi) as the initiator, on the other hand, afforded

polymeric products in near quantitative conversion after 96 h at 70 °C or after 5 h at 40 °C in the presence of tetramethylethylenediamine ([TMEDA]₀/[*s*-BuLi]₀ = 2).¹³ In both cases the poly-**2** product exhibited a narrow molecular weight distribution by SEC vs PS standards (PDI < 1.2). Without TMEDA the degree of polymerization calculated by ¹H NMR spectroscopy assuming one *s*-butyl initiating group per chain was 24, consistent with the predicted value of 25 (Table S1).

Cationic initiating systems were also effective for inducing polymerization of **2**. Upon addition of BF₃·OEt₂ (RT, 5 min) or Me₃O⁺BF₄⁻ (40 °C, 20 min) the polymerization media became highly viscous, and the conversion of **2** was quantitative in both cases (Table S1). The BF₃·OEt₂-initiated sample of poly-**2** exhibited quite low solubility, but the polymer obtained with Me₃O⁺BF₄⁻ possessed good solubility in common organic solvents. Both samples of poly-**2** exhibited low molecular weights (*M_n* < 4 kg mol⁻¹) and broad molecular weight distributions by SEC.

We also explored living cationic polymerizations with the known *i*-BuOCH(Cl)Me/Lewis acid initiator systems (Table 1).¹⁴ These

Table 1. Cationic Polymerization of **2** with *i*-BuOCH(Cl)Me/Lewis Acid/Et₂O in Toluene

entry	Lewis acid	time (min)	conv ^a (%)	<i>M_n</i> (kg mol ⁻¹)		PDI ^c	<i>T_g</i> (°C)	<i>T_m</i> (°C)
				calcd ^b	NMR ^a			
1 ^d	SnCl ₄	1	100	5.5	7.7	6.51	-4	68, 101
2 ^e	ZnCl ₂	1	68	3.8	3.8	1.25	-8	71-87 ^h
3 ^e	ZnCl ₂	2	85	4.7	4.7	1.15	-8	66, 87
4 ^f	ZnCl ₂	5	88	9.5	8.7	1.15	0	66, 101
5 ^g	ZnCl ₂	9	94	21	22	1.21	11	65, 105

^a ¹H NMR spectroscopy using the methyl group from the initiator (see Supporting Information). ^b *M_n*, calcd = (MW of monomer) × *M/I* × conversion + MW of initiator residue. ^c SEC in CHCl₃. ^d *2*/*i*-BuOCH(Cl)Me/SnCl₄/Et₂O = 68:1:1:20 in toluene (5.2 mL) at -78 °C. ^e *2*/*i*-BuOCH(Cl)Me/ZnCl₂ = 68:1:1, in Et₂O/toluene solution (0.8 mL/4.4 mL) -40 °C. ^f *2*/*i*-BuOCH(Cl)Me/ZnCl₂ = 136:1:1, in Et₂O/toluene solution (0.44 mL/6.3 mL) -40 °C. ^g *2*/*i*-BuOCH(Cl)Me/ZnCl₂ = 272:1:1, in Et₂O/toluene solution (0.3 mL/8.2 mL) -40 °C. ^h Multiple melting transitions were observed for this sample.

polymerizations were rapid at low temperature. While the poly-**2** obtained using *i*-BuOCH(Cl)Me/SnCl₄/Et₂O¹⁵ had a broad molecular weight distribution, the *i*-BuOCH(Cl)Me/ZnCl₂/Et₂O¹⁶ system afforded polymers with narrow molecular weight distributions. The *M_n* values for poly-**2** increased with the conversion of **2** and were in good agreement with the calculated values (Table 1, entries 2-5). Furthermore, the apparent *M_n* values could be tuned by changing the feed molar ratios of monomer to initiator. Thus, the cationic polymerization of **2** proceeded in a controlled fashion.

Figure 1 shows typical ¹H NMR spectral features of the vinylic protons in poly-**2** samples obtained by anionic and cationic

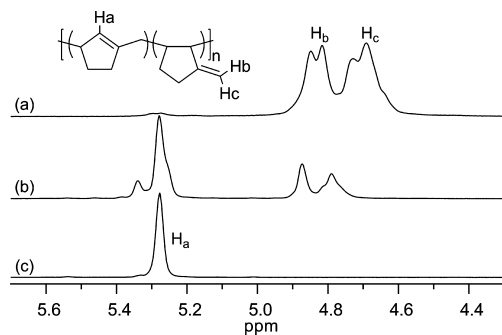


Figure 1. ^1H NMR spectra of poly-**2** prepared with (a) *s*-BuLi/TMEDA, (b) *s*-BuLi, and (c) *i*-BuOCH(Cl)Me/ZnCl₂/Et₂O.

polymerizations. For the former, two sets of signals at ~ 5.3 and 4.8 ppm were assigned to repeating units with 1,4- (H_a) and 4,3-regiochemistry (H_b/H_c), respectively. As with other anionic polymerizations of dienes, the use of TMEDA leads to a high content of 4,3-repeating units [96%, panel (a)]. Higher 1,4-content was observed without TMEDA [74%, panel (b)]. The ^1H NMR [panel (c)] and ^{13}C NMR (Figure 2) spectra of poly-**2** samples prepared

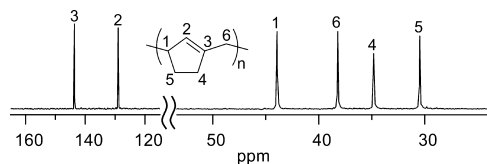


Figure 2. ^{13}C NMR spectrum of 1,4-poly-**2** prepared with *i*-BuOCH(Cl)Me/ZnCl₂/Et₂O (Assignments are based on analyses of COSY, HMQC, and DEPT NMR experiments).

by cationic polymerization were consistent with essentially regioregular structures. Cationic polymerization of the analogous 3-methylene cyclohexene also gives regioregular material.¹²

In samples of poly-**2** prepared using the *i*-BuOCH(Cl)Me/Lewis acid system, low intensity resonances in the ^1H NMR spectra (5.8–6.5 ppm) suggested the presence of a cyclopentadienyl group (cf. CPD in Table 1 graphic) at the chain end. Reaction of an oligomeric sample with maleic anhydride afforded Diels–Alder adducts (Figure S10a). We also showed that poly-**2**-*b*-polylactide block copolymers can be formed by the Diels–Alder coupling of a maleimide end-functionalized polylactide (Figure S10b). Thus the reactive CDP end group in poly-**2** can be exploited for a variety of end-functionalization reactions.

We could hydrogenate 1,4-poly-**2** and convert it into the saturated variant, poly(cyclopentane-1,3-diylmethylene), using *p*-toluenesulfonylhydrazide. SEC data for the hydrogenated product showed a narrow and unimodal peak at slightly lower elution volume consistent with the absence of significant side reactions (Figure S17). The ^{13}C NMR spectrum (Figure S14) of hydrogenated poly-**2** is consistent both with the spectrum of stereoirregular poly(cyclopentane-1,3-diylmethylene), synthesized by the cyclopolymerization of 1,5-hexadiene,⁷ and with our conclusion that poly-**2** formed by cationic polymerization is regioregular.

We analyzed the thermal properties of poly-**2** and hydrogenated poly-**2** by DSC. High 1,4-poly-**2** exhibited T_g values between -17 and 11 °C depending on molecular weight (Table 1). High 4,3-poly-**2** exhibited a particularly high T_g of 73 °C at relatively low molecular weight ($M_n = 3.6$ kg mol⁻¹). 1,4-Poly-**2** from the *i*-BuOCH(Cl)Me/Lewis acid/Et₂O systems exhibited multiple endo-

thermic peaks that we assign to melting and/or liquid crystalline transitions (Table 1).¹⁷ Regioregular poly-**2** from the BF₃•OEt₂ and Me₃O⁺BF₄⁻ systems did not show endothermic peaks (Figure S18). Such semicrystallinity suggests that regioregular poly-**2** obtained using *i*-BuOCH(Cl)Me/Lewis acid/Et₂O may have a more stereoregular structure. Hydrogenated 1,4-poly-**2** exhibited a T_g of -28 °C and a T_m of 106 °C, consistent with previously reported values for *trans*-rich or random poly(cyclopentane-1,3-diylmethylene).¹⁷ The regioregularity and narrow molecular weight distribution of hydrogenated 1,4-poly-**2** will facilitate systematic studies on the recently reported liquid crystalline behavior of this polyolefin.¹⁷

In conclusion, we demonstrated the RCM conversion of the natural monoterpene myrcene (**1**) to 3-methylenecyclopentene (**2**). Monomer **2** can be polymerized under radical, anionic, or cationic conditions. Cationic polymerization using the *i*-BuOCH(Cl)Me/ZnCl₂/Et₂O system afforded regioregular 1,4-poly-**2** with controlled molecular weight and narrow molecular weight distribution. Exploitable 1,3-diene end groups were identified in 1,4-poly-**2**. Finally, 1,4-poly-**2** exhibited melting transitions consistent with a stereoregular structure.

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Supporting Information Available: Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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