Notes

Synthesis and Properties of Well-Defined Elastomeric Poly(alkylnorbornene)s and Their Hydrogenated Derivatives

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Introduction

Over the past two decades, the development of well-defined catalysts for ring-opening metathesis polymerization (ROMP) has opened the door to the synthesis of ROMP polymers of well-defined architecture, including block copolymers.[1−3] Of particular interest would be polymers which behave as thermoplastic elastomers (TPEs),[4] where the prototype architecture is an ABA triblock copolymer with glassy or semicrystalline A blocks, and an amorphous B block with a glass transition temperature (T_g) well below room temperature. Unfortunately, very few ROMP monomers yield low-T_g homopolymers; the most common ROMP monomers are derivatives of norbornene or other bicyclic olefins,[3] which typically yield polymers with T_g values above ambient. Monocyclic olefins[3] such as cyclopentene[5,6] and cyclooctene[6] can be polymerized by ROMP to yield elastomers with low T_g, but these suffer from two drawbacks. First, the low ring strain in such monomers (especially cyclopentene[5]) limits their equilibrium conversion, so ideal ABA triblocks cannot be obtained by sequential polymerization of the monomers, which relies on the essentially complete conversion of a monomer prior to the addition of subsequent monomer charges. Second, if such polymers are hydrogenated to remove the thermooxidatively unstable double bonds, they become highly crystalline materials (structurally identical to linear polyethylene[5,7,8]) and lose all elastomeric properties. The high ring strain of cyclobutene[7] makes alkyl-substituted[9−11] or disubstituted[10,12] cyclobutenes suitable choices, but such monomers are not commercially available and require multistep syntheses to obtain.

By contrast, alkyl-substituted norbornenes are readily obtained by Diels−Alder reaction of cyclopentadiene with the appropriate α-olefin. In 1970, Vergne et al.[13] reported the ROMP of several such 5-*n*-alkylnorbornenes and found that very low T_g values could be obtained (−51 °C for poly(decylnorbornene)). However, the synthesis of well-defined polymers from these monomers has not been demonstrated, nor have their hydrogenated derivatives been investigated. Here, we use "living" ROMP to prepare homopolymers of controlled and narrowly distibuted chain lengths and find that sufficiently long alkyl substituents yield polymers of low T_g both before and after hydrogenation.

Experimental Section

Polymerization. Four 5-*n*-alkylnorbornene monomers (methylnorbornene, butylnorbornene, hexylnorbornene, and decylnorbornene) were provided by Promerus Electronic Materials (Brecksville, OH). All had endo/exo ratios of 77/23 (±2%), as determined by ^{1}H NMR (Figure S1 of the Supporting Information). All monomers were purified by vacuum transfer from Na. The "Schrock-type" initiator 2,6-diisopropylphenylimidoneophylidenemolybdenum (VI) bis(*tert*-butoxide) was used as received (Strem Chemicals). Polymerizations were run at 4 wt % monomer in toluene, in stopper-sealed flasks inside a nitrogen-atmosphere glovebox (Innovative Technologies System One). The reactions were terminated with a 100-fold molar excess of propionaldehyde or benzaldehyde; for measuring reaction kinetics, aliquots were removed at various times and terminated similarly. Additional procedural details are provided in the Supporting Information.

Hydrogenation. Polymers were dissolved at 5 g/L in cyclohexane:THF (4:1 v/v), with butylated hydroxytoluene added (1 wt % of polymer) to prevent degradation prior to complete saturation. The hydrogenation catalyst (5 wt % Pd on $CaCO_3$, Strem) was typically added in a 1:1 mass ratio (including support) to polymer. Hydrogenations were done in a 2 L Parr reactor, at ∼500 psi of H_2 and 100 °C, for ≈48 h. The reaction was stopped when the trans double-bond infrared stretch at 966 cm^{-1} was no longer detectable (>99% hydrogenated).

Characterization. A gel permeation chromatography (GPC) system, comprising a Waters 515 HPLC pump, two 30 cm PLgel 5 μm Mixed-C columns, a Waters 410 differential refractive index (RI) detector operating at 950 nm, and a Precision Detectors PD2020 light scattering detector operating at 685 nm, all running at 35 °C, was used (1) to determine the fractional conversion of monomer during the polymerization, from the areas of the monomer and polymer peaks, after correcting for their relative specific refractive index increments (d*n*/d*c*), (2) to determine the molecular weight and polydispersity of each polymer, and (3) to confirm the absence of backbone rearrangements during hydrogenation. The mobile phase was toluene for (1) and tetrahydrofuran (THF) for (2) and (3). A Tecator Optilab 5902 differential refractomer was used to determine d*n*/d*c* at 633 nm and 35 °C for each polymer in THF (≈1 mg/mL solution). The T_g of each polymer was measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 calibrated with indium and mercury, at a scan rate of 10 °C/min. Densities at 23.0 ±0.1 °C were measured in thermostated methanol/ethylene glycol density gradient columns (Techne DC-4), calibrated with glass floats; 6−8 replicate specimens were run for each polymer, with a typical standard deviation of 0.0002 g/cm^3. Dynamic mechanical measurements were made using a Rheometrics RSA-II, with the shear sandwich fixture (1 mm gap) in frequency sweeps at 31 °C.

Results and Discussion

Figure 1 shows the time course for a polymerization of norbornene. The fraction of unconsumed monomer

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Table 1. Properties of Poly(5-*n*-alkylnorbornenes) and Hydrogenated Derivatives[a]

polymer	$(\mathrm{d}n/\mathrm{d}c)_u$ (mL/g)[b]	$(\mathrm{d}n/\mathrm{d}c)_h$ (mL/g)[b]	$M_{w,u}$ (kg/mol)	$(M_w/M_n)_u$	R_u	$M_{w,h}$ (kg/mol)	$(M_w/M_n)_h$	R_h	$T_{g,u}$ (°C)	$T_{g,h}$ (°C)	ρ_h (g/cm^3)[c]	$G_{0,h}$ (MPa)[d]	$M_{e,h}$ (g/mol)
polynorbornene	0.174		100	1.11	1.78				37	4			
poly(methylnorbornene)	0.142	0.116	117	1.04	1.68	117	1.05	1.46	45	43			
poly(butylnorbornene)	0.120	0.110	117	1.06	1.44	118	1.06	1.29	8	1	0.9185	0.54	4200
poly(hexylnorbornene)	0.114	0.106	108	1.09	1.32	107	1.09	1.19	−16	−22	0.9086	0.37	6000
poly(decylnorbornene)	0.106	0.097	104	1.07	1.17	105	1.07	1.03	−34	−40	0.8947	0.20	11000

[a] Subscript "u" indicates the measured value for the poly(alkylnorbornene) and subscript "h" for the hydrogenated derivative. [b] In THF at 35 °C and 685 nm, determined by interpolation between values measured at 633 and 950 nm according to the two-term Cauchy equation.[17] [c] At 23 °C. [d] At 31 °C.

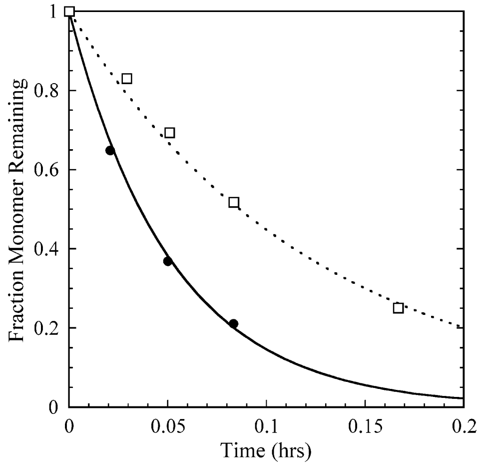

Figure 1. Course of polymerization for a 50 kg/mol polynorbornene at 26 °C, with no modifier (●) and with 5 equiv of PMe_3 relative to initiator (□). Initial concentrations: monomer, 0.367 M; initiator, 0.692 mM.

decays exponentially with a time constant $\tau = 0.052$ h. On the assumption of a simple bimolecular reaction, the propagation rate constant $k_p = (\tau[\mathrm{Mo}])^{-1} = 28\,000$ L/(mol h). We also conducted the polymerization in the presence of 5 equiv of trimethylphosphine (PMe_3) relative to Mo; in the polymerization of cyclobutene[7] and cyclopentene,[5] PMe_3 acts as a reversibly binding ligand to slow propagation relative to initiation and produce narrow-distribution polymers of predetermined molecular weight. In the polymerization of norbornene, PMe_3 has a much smaller effect, as shown in Figure 1; the rate is reduced by only about 2×, presumably because the larger cross section of the polynorbornene chain sterically hinders the binding of PMe_3 to the metal center, thereby limiting its influence. The rate is only weakly dependent on the length of the alkyl substituent, decreasing by <40% on going from norbornene to decylnorbornene (Table S1 in the Supporting Information). The cis/trans ratio for the unsubstituted polynorbornene was determined by ^{1}H NMR[14] to be 54/46, as previously reported.[15] For the poly(alkylnorbornenes), the presence of both endo/exo isomerism and a racemic mixture of enantiomers in the monomer, coupled with regioirregularity[16] in the polymer, greatly complicates the NMR spectrum, but the ratio of intensities for cis (near 741 cm^{-1}) and trans (966 cm^{-1}) bands in the infrared spectrum indicates a comparable cis/trans ratio in the poly(alkylnorbornene)s.

For property characterization, homopolymers of each monomer were synthesized at target molecular weights of 100 kg/mol, in the presence of PMe_3, and hydrogenated. GPC showed that all polymers possessed a narrow molecular weight distribution (PI ≤ 1.11, Table 1). The GPC traces for poly(butylnorbornene) before and after hydrogenation, shown in Figure 2, demonstrate that no discernible chain scission or branching occurs during hydrogenation, though the peak shifts to longer elution times due to a reduction in the polymer's hydrodynamic volume. Absolute weight-average molecular weights M_w were obtained from the GPC light scattering detector, in conjunction with the values of dn/dc at 685 nm listed in Table 1. Good agreement was found between the hydrogenated and unhydrogenated polymers. Also given in Table 1 are the ratios (R) of "polystyrene equivalent" molecular weight (obtained by referencing the elution time trace to narrow-distribution polystyrenes) to true molecular weight for each polymer.[18] In all cases, R decreases upon hydrogenation (smaller hydrodynamic volume in THF) and decreases with increasing length of the alkyl substituent (smaller coil volume per unit mass as more of the mass is in the side chain).

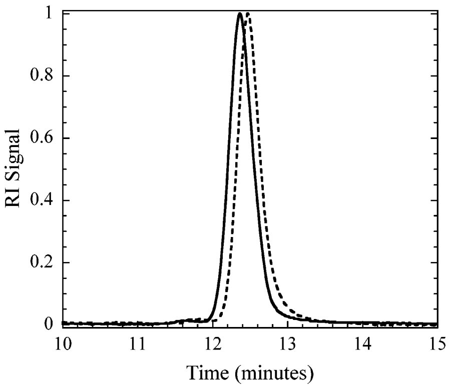

Figure 2. GPC traces of poly(butylnorbornene) before (—) and after (···) hydrogenation; THF mobile phase.

The T_g values for all polymers are given in Table 1. Though T_g increases on going from polynorbornene to poly(methylnorbornene), further increases in the alkyl chain length decrease T_g monotonically. These T_g values are generally in very good agreement with those reported previously by Vergne et al.[13] for polymers prepared by $RuCl_3$ catalysis, except for poly(decylnorbornene), for which they reported a melting peak at $T_m = -48$ °C which transformed to a glass transition at $T_g = -51$ °C in quenched specimens. None of our unhydrogenated polymers showed any evidence of a melting peak by DSC. Hydrogenation of the polymers produces a slight further lowering of the T_g, by an average of 5 °C for all of the alkyl-substituted norbornenes, all of which remain amorphous. By contrast, hydrogenation of unsubstituted polynorbornene yields a crystalline polymer[15] with an amorphous-phase $T_g =$ 4 °C; this assignment was confirmed by DMTA (1 Hz loss modulus maximum observed at 8 °C). Thus, the T_g reduction upon hydrogenation (by 33 °C) is much more pronounced for the unsubstituted polynorbornene.

The decrease in T_g with increasing alkyl chain length (beyond methyl) reflects the well-known phenomenon

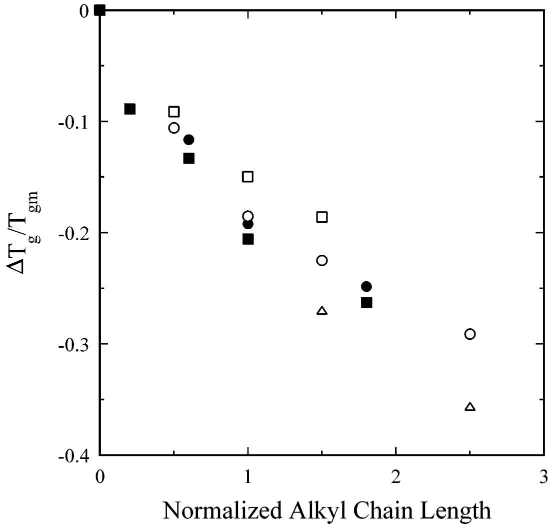

Figure 3. Magnitude of internal plasticization $\Delta T_g/T_{gm}$, where ΔT_g is defined relative to the methyl-substituted member of each class of materials (having T_{gm}). Abscissa (normalized alkyl chain length) is the number of carbons in the alkyl substituent (beyond methyl), normalized by the number of backbone carbons per repeat unit. Values are shown for poly(alkylnorbornene)s (●) and hydrogenated poly(alkylnorbornene)s (■); the latter includes the value for hydrogenated poly(ethylidenenorbornene),[5] which is analogous to hydrogenated poly(ethylnorbornene). For comparison, literature data are shown for amorphous poly(alkyl methacrylate)s (○),[20] polyolefins (□),[20,21] and poly(4-alkylstyrene)s (△).[20]

of "internal plasticization".[19] Figure 3 shows that the magnitude of this effect in our polymers is comparable to that in other well-known systems—amorphous polyolefins,[20,21] poly(alkyl methacrylates),[20] and poly(alkylstyrenes)[20]—when normalized by the number of backbone carbons per substituent (= 5 for the poly(alkylnorbornene)s and their hydrogenated derivatives, = 2 for the comparison systems).

Finally, another important consideration in the behavior of an elastomer is its rubbery plateau modulus, G_0. We determined this quantity for the three hydrogenated polymers which behave as elastomers at 31 °C (butyl, hexyl, decyl); G_0 was evaluated from frequency sweeps as the value of G' where G'' exhibited its minimum, which occurred ~2 decades higher in frequency than the G'' maximum[22] (Figures S2−S4 in the Supporting Information). Essentially identical values of G_0 were obtained from the empirical relation $G_0 = 3.56G''_{\max}$, valid for narrow-distribution polymers.[22] Entanglement molecular weights M_e may be obtained[23] from $M_e = \rho RT/G_0$, where ρ is the mass density; values of G_0, ρ, and M_e are listed in Table 1. In common with other systems such as polyolefins[24] and poly(alkyl methacrylate)s,[23] G_0 progressively decreases and M_e progressively increases with alkyl chain length. This plateau modulus range also encompasses the value of G_0 for the hydrogenated mixed-microstructure polybutadienes[24] which are the midblocks in commercial styrene−(ethylene-*co*-butene)−styrene TPEs.[25] Thus, these hydrogenated poly(alkylnorbornene)s are promising as the midblocks in TPEs with either glassy or crystalline end blocks, which we are currently exploring.

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Supporting Information Available: Additional details of the polymerizations, selected polymerization rate constants, ^{1}H NMR spectrum revealing monomer endo/exo ratio, and frequency sweeps for higher poly(alkylnorbornene)s. This material is available free of charge via the Internet at http://pubs.acs.org.

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