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Polymers Containing Ring-Strain Energy. 1. New Monomers and Polymers Based on Cyclopropane, Norbornadiene, and Quadricyclane

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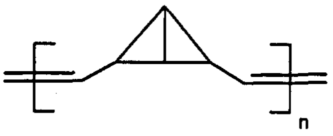
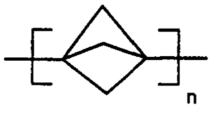
The synthesis and polymerization chemistry of 1,1-bis(XCH_2)cyclopropane {**1**, X = OH; **4**, X = I} was studied. Treatment of **1** with base in the presence of α,ω-dihalides did not produce a polyether. However, treatment of **4** with the bis(alkoxide) derived from hexanediol afforded a polyether of low molecular weight {M_n = 3000, PD = 3}. A general method for alkylating norbornadiene in the 2-position was developed. Treatment of norbornadiene with *tert*-BuOK, tetramethylethylenediamine (TMEDA), *n*-BuLi, and tributylchlorostannane (in that order) afforded 2-(tributylstannyl)norbornadiene in excellent yield. On the other hand, carbon electrophiles {*e.g.* bromobutane, 1,4-dibromobutane, and 2,3-dichloropropene} required the generation of the 2-(lithiocyanocuprate) in order to effect clean alkylation. Treatment of 2-[3-(2-chloropropenyl)]norbornadiene (**8a**) with RMgX {where R = vinyl and phenyl} in the presence of (dppp)$NiCl_2$ afforded the cross-coupling products 2-(XCH_2)-norbornadiene {**9**, X = 2-buta-1,3-dienyl; **10**, X = α-styryl; respectively} in high yield. Polymerization of **9** in THF initiated by *n*-BuLi resulted in an elastomeric polymer (**12**) [M_n = 18,000, PD = 1.5]. Photolysis of **12** in the presence of $(Ph_3P)_2CuBr$ converted the pendant norbornadiene to quadricyclane (**13**). Heating of the photoisomerized sample to 180 °C caused an exothermic (by DSC) reaction which corresponded to 59% of theory (using the value 26 kcal/mol: quadricyclane → norbornadiene).

Introduction

This is the first in a series of papers to be presented from our research group addressing the synthesis and characterization of polymers possessing ring-strain energy.[1] Of significant interest in such polymeric systems is their ability to store large amounts of energy. In an ideal situation it may be possible to reversibly induce and release the strain energy.[2] This latter type of system could then be a viable and efficient means of storing energy (*e.g.* solar) in chemical bonds.[3] Another point of interest is the development of energetic binders for solid rocket propellants having a low oxidative state (*i.e.* hydrocarbon polymers). Interestingly, only three examples of hydrocarbon polymers containing highly strained rings have been reported. Both polybenzvalene[4] and poly[1.1.1]propellane[5] have strained-rings as an integral part of the polymer backbone.



Polybenzvalene



Poly[1.1.1]propellane

Polymers containing norbornadiene {bicyclo[2.2.1]-hepta-2,5-diene} (NBD) and the photoinitiated valence isomer quadricyclane {quadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane} (Q) have been incorporated in several polymeric systems. In all examples that have been reported the norbornadiene was a pendant group, and a highly oxidized linkage (*e.g.* esters or amides) was used to attach the system to the polymer backbone.[2,3]

This paper describes the development of two dissimilar monomers based on cyclopropane[6] and quadricyclane. Synthetic methodology is reported for the functionalization of norbornadiene in the 2-position and its application in preparing new 2-norbornadienyl monomers. The polymerization and characterization of a new polyether and elastomeric polybutadiene containing cyclopropane and quadricyclane, respectively, is described along with the photo- and thermally-induced reactivity of the latter polymer.

Results and Discussion

Monomer Synthesis and Reactivity. Cyclopropane Monomers. Treatment of diethyl malonate with 1,2-

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[1] Some of this work was initially communicated: Wright, M. E.; Allred, G. D. *Polym. Prepr.* (*Am. Chem. Soc., Polym. Div.*) **1992**, *33* (1), 1123. For a compilation of ring-strain energies see: Aped, P.; Allinger, N. L. *J. Am. Chem. Soc.* **1992**, *114*, 1–16.

[2] Hirao, K.; Ando, A.; Hamada, T.; Yonemitsu, O. *J. Chem. Soc., Chem. Commun.* **1984**, 300–302. Hamada, T.; Ijima, H.; Yamamoto, T.; Numao, N.; Hirao, K.; Yonemitsu, O. *J. Chem. Soc., Chem. Commun.* **1980**, 696–97.

[3] For recent examples of where a norbornadiene–quadricyclane cycle has been developed for a polymeric material see: Izawa, T.; Mijikata, C.; Nishikubo, T. *Macromolecules* **1992**, *25*, 21–26 and ref cited therein. Kamogawa, H.; Yamada, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1501–1504. Maruyama, K.; Taniaki, M.; Kawabata, S. *J. Org. Chem.* **1985**, *50*, 4742–49.

[4] Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 4413–22. Swager, T. M.; Dougherty, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2973–74. For the polymerization of deltacyclene see: Lautens, M.; Abd-El-Aziz, A. S.; Reibel, J. *Macromolecules* **1989**, *22*, 4132.

[5] Schlüter, A.-D. *Macromolecules* **1988**, *21*, 1208. Schlüter, A.-D. *Polym. Commun.* **1989**, *30*, 34–5.

[6] We were unable to find examples of *saturated* polymeric materials which contain well-defined monocyclic cyclopropane units.

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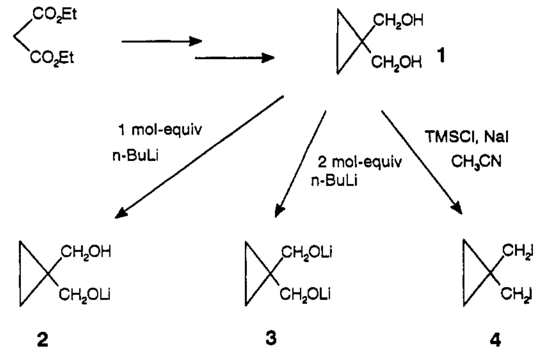
Scheme I



dibromoethane in the presence of lithium carbonate or potassium carbonate affords diethyl 1,1-cyclopropanedicarboxylate in good yield (Scheme I).[7] A particularly interesting point to the cyclization process is that stirring of the reaction mixture diminishes the desired cyclopropyl product and produces the product arising from *C*- and *O*-alkylation (i.e. six-membered ring).[8]

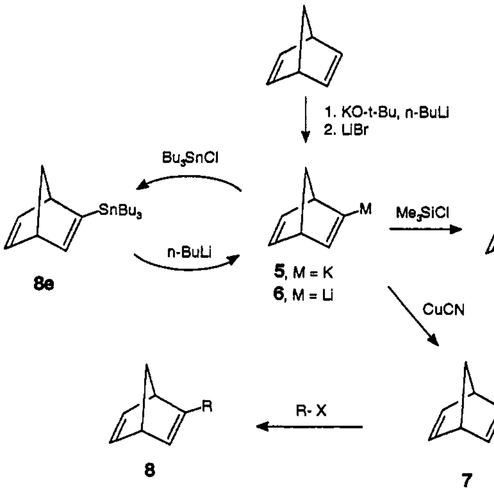
On treatment of 1 at −78 °C with 1 mol equiv of *n*-BuLi we observe nearly complete precipitation of the monoalkoxide (**2**) (Scheme I). Addition of 2 mol equiv of *n*-BuLi at −78 °C produces a *completely homogeneous solution of the bis(lithium alkoxide)* **3**. The increased solubility of **3** over **2** is attributed to formation of a THF-solvated lithium alkoxide aggregate.[9] Treatment of **2** or **3** with electrophiles (*e.g.* bromobutane) does not afford clean dialkylation. Conversion of **1** to the 1,1-bis(iodomethyl)cyclopropane (**4**)[10] is accomplished using the procedure of Olah and co-workers {TMSCl, NaI, CH_3CN, 25 °C, 16 h} (Scheme I).[11]

Norbornadiene Monomers. The reaction of excess norbornadiene (NBD) with *n*-BuLi, *t*-BuOK, and TMEDA (2:2:1) in THF at 0 °C presumably affords 2-norbornadienylpotassium (**5**).[12] Addition of LiBr to generate the lithium salt **6** appears critical in the stability and reactivity of the resulting cyanocuprate. The addition of CuCN to **5** effects the dimerization of norbornadiene via oxidative coupling.[13] Virtually no products from substitution are isolated. Treatment of 2-norbornadienyllithium (**6**) with 2,3-dichloropropene results in extensive tar formation and no **8a**. On the other hand, treatment of **6** with CuCN at 0 °C followed by addition of an electrophile, for example 2,3-dichloropropene, affords clean substitution (Table I, Scheme II). This appears to be the first general method available for the synthesis of 2-substituted norbornadiene derivatives starting from norbornadiene.[14]

Table I. Reagents and Yields for the Preparation of Compounds 8a–f

entry	M	RX	product	isolated yield (%)
1	Cu(CN)Li	$ClCH_2C(Cl){=}CH_2$	**8a**	80
2	Cu(CN)Li	1-bromobutane	**8b**	75
3	Cu(CN)Li	1,4-dibromobutane	**8c**	71
4	Cu(CN)Li	$ClCH_2CH{=}CH_2$	**8d**	70
5	Li or K	$ClSnBu_3$	**8e**	81
6	Li	$ClSiMe_3$	**8f**	95

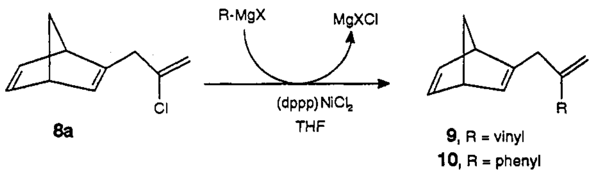
Scheme II



Only the most reactive and well-behaved electrophiles such as $ClSnBu_3$[14] and $ClSiMe_3$ can be used with **6**[15]. Treatment of **8e** with *n*-BuLi gives clean transmetalation[16] and 2-norbornadienyllithium (**6**) (Scheme II). Interestingly, compound **6** formed by this method is not stable at 0 °C. Compound **6**, generated by transmetalation of the tributylstannyl group, can be trapped by TMSCl to afford **8f** in 95% isolated yield.[17] Hence, 2-(tributylstannyl)norbornadiene (**8e**) is a new and very effective precursor for the preparation of 2-norbornadienyllithium.

We have initiated a study on cross-coupling reactions of **8e** and have yet to find a combination of reaction conditions and catalyst which will lead to successful cross-coupling chemistry.

Compound **8a** is reacted with vinylmagnesium bromide or phenylmagnesium chloride in the presence of a nickel catalyst[18] to afford monomers **9** and **10**, respectively, in excellent yield (eq 1, below).



(1)

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[7] For one of several examples describing the generation of cyclopropane rings from active methylene compounds see: Singh, R. K.; Danishefsky, S. *J. Org. Chem.* **1975**, *40*, 2969–70 and refs cited therein. This excellent phase-transfer alkylation procedure did work in the case of diethyl malonate.

[8] The true nature of this astonishing "stirring effect" is not understood. When using Li_2CO_3 we observe mostly cyclopropyl ring formation, albeit in much lower yield.

[9] For a general treatment of alkoxides see: Bradely, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978.

[10] In a related reaction, compound 1 was converted to 1,1-bis(bromomethyl)cyclopropane using PBr_3: Evans, D. A.; Mitch, C. H. *Tetrahedron Lett.* **1982**, 285.

[11] Olah, G. A.; Narany, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247–1251.

[12] Stahle, M.; Lehmann, R.; Kramar, J.; Schlösser, M. *Chimia* **1985**, *39*, 229.

[13] The 2,2′-bis(norbornadienyl) dimer was characterized by ^{1}H NMR spectroscopy: δ 6.78 (4H, H5 and H6), 6.44 (2H, H3), 3.58 (2H, H1 or H4), 3.51 (2H, H1 or H4), 1.96 (H7). The compound was very unstable and rapidly autopolymerized to yield a soluble polymer of unknown structure and a molecular weight (M_n) greater than 120000 (GPC, relative to polystyrene).

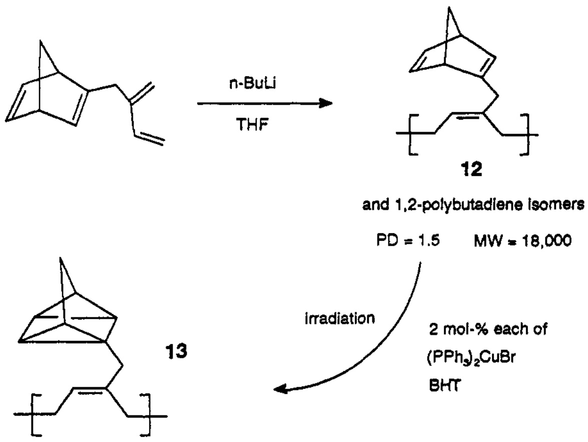
[14] The synthesis of 2-substituted norbornadienes has been accomplished by multistep processes centered around Diels–Alder chemistry. For example see: Duboudin, J. G.; Djeghaba, Z.; Jousseaume, M. R. *J. Organomet. Chem.* **1986**, *304*, 115–125.

[15] In certain cases, for example with 1,4-diiodobutane, compound **5** also gave clean alkylation. This is not the case for allylic or benzylic halides.

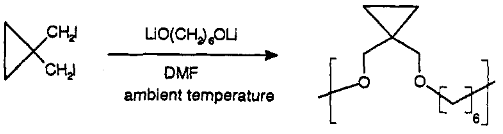
[16] Transmetalation reactions of tri-*n*-butylstannyl groups have been used extensively since the initial discovery by Seyferth and co-workers: Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 3538.

[17] Davis, A. P.; Whitman, G. H. *J. Chem. Soc., Chem. Commun.* **1980**, 639–640.

Scheme III



Polymerization Chemistry. Cyclopropane Polymers. We first attempted to copolymerize monomer 1 with α,ω-dihalides using a modification of the ether synthesis procedure developed by Johnstone and Rose.[19] Regardless of the temperature or solvent choice, the predominant products are dehydrohalogenation and monoalkylation of the cyclopropane monomer. Generation and isolation of 3 and other metal alkoxide salts (*e.g.* Na and K) followed by treatment with α,ω-dihalides produces similar results. By reacting the bis(sodium alkoxide) of 1,6-hexanediol with 4 we can successfully prepare polyether 11 (eq 2).[1] The polymer displays proton and carbon NMR spectra consistent with the proposed structure. We have also characterized the polyether by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and gel permeation chromatography (GPC). Spectroscopic and analytical data confirm the presence of residual water in the polymeric material.



4 11 (2)

The polymer shows no exothermic decomposition points below 200 °C and exhibits TGA stability characteristic of aliphatic hydrocarbon polymers with a break point (*i.e.* onset of continuous and rapid weight loss) of approximately 220 °C under a nitrogen atmosphere. Polyether 11 is obtained as a highly viscous liquid and as such may be a useful energetic plasticizer or linkage agent. The presence of alcohol termini as determined by NMR is advantageous for use in the preparation of block copolymers with isocyanates, a common technique in the preparation of elastomers for use as propellant binders.

Polymerization Chemistry. NBD Polymers. Compound 9 is readily polymerized anionically in THF (25 °C) using *n*-BuLi as the initiator (Scheme III). Initiation of polymerization is evidenced by formation of a bright yellow solution. Compound 9 also copolymerized with isoprene using anionic initiation. A 1:1 (mol/mol) mixture of 9 and isoprene results in the formation of a copolymer with identical composition. The anionic polymerization of monomer 10 produces only oligomeric products. Free-radical polymerization of 9 and 10 with AIBN results in highly cross-linked, intractable polymeric materials.

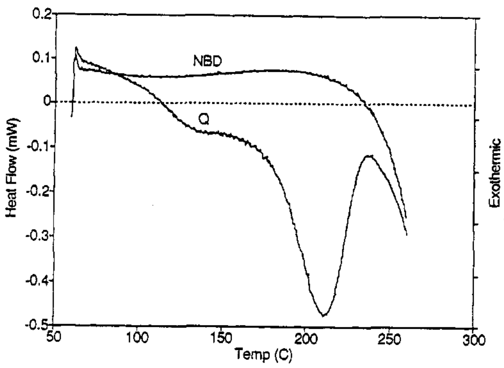


Figure 1. DSC scans (10 °C/min, nitrogen atmosphere) of the NBD polymer (12) and Q (13) polymer.

The polyisoprene derivative 12 exhibits good elastomeric properties as well as substantial adhesive characteristics, bonding well to glass. Polymer 12 shows TGA stability (*i.e.* no significant weight loss) up to 400 °C. However, DSC analysis shows an exothermic event beginning at ~250 °C which we believe corresponds to a cross-linking reaction/process. After heating, the DSC samples are strongly bonded to the aluminum sample pan and insoluble in organic solvents. Physical separation of the polymer from the pan results in an aluminum film bonded to the surface of the polymer.

NBD groups readily undergo photochemical isomerization to quadricyclane (13) in the presence of $(PPh_3)_2CuBr$ (serving as a catalyst[20]) and BHT (inhibits free-radical processes). The photo-converted polymer remains soluble in common organic solvents but is less elastomeric and more glassy in character. GPC of the photolyzed polymer showed no increase in molecular weight, indicating that cross-linking did not occur. The NMR spectra of the polymer displays very broad peaks between 2.5 and 1.0 ppm. DSC analysis of the converted polymers shows a large exotherm beginning at 180 °C corresponding to isomerization of Q to NBD {and possibly other products} (Figure 1). The calculated ΔH_{isom} from the DSC data is +15.3 kcal/mol per Q unit in the polymer which corresponds to a 59% conversion yield {using Q → NBD value of 26 kcal/mol[3]}. This agrees very closely to conversion yields reported previously for polymer-bound norbornadiene.[3]

Concluding Remarks

In this study we were successful in preparing a low molecular weight cyclopropane-containing polyether through the copolymerization of 1,1-bis(iodomethyl)-cyclopropane and a bis(alkoxide). Synthetic methodology has been developed to facilitate the high yield conversion of norbornadiene into functionalized 2-norbornadienyl derivatives. For instance, in two steps 2-[2-(1,3-butadienyl)methyl]norbornadiene (9) was prepared from norbornadiene, and then through anionic polymerization the first hydrocarbon polymer-containing norbornadiene was isolated. The latter material was photolyzed to generate a ring-strained energetic hydrocarbon polymer.

Experimental Section

Methods. All manipulations of compounds and solvents were carried out using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from

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(18) Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49* (7), 1958–1969.

(19) Johnstone, R. A. W.; Rose, M. E. *Tetrahedron* **1979**, *35*, 2169–73.

(20) Borsub, N.; Chang, S.; Kutal, C. *Inorg. Chem.* **1982**, *21*, 538–543.

standard drying agents. Spectroscopic measurements utilized the following instrumentation: ^{1}H NMR, Varian XL 300 (at 300 MHz), JEOL GSX 270 (at 270 MHz); ^{13}C NMR, Varian XL 300 (at 75.4 MHz). NMR chemical shifts are reported in δ versus Me_4Si in ^{1}H NMR and assigning the $CDCl_3$ resonance at 77.00 ppm in ^{13}C spectra. Diethyl malonate, dibromoethane, LAH, NaH, norbornadiene, 2,3-dichloropropene, vinylmagnesium bromide, and phenylmagnesium chloride were purchased from Aldrich Chemical Co. NBD was purified by distillation from CaH_2 and stored over K_2CO_3 (granular, AR grade, Mallinckrodt). Polymer analyses were performed using a Perkin Elmer TGA7 and DSC7 thermal analysis data station. GPC data was collected on a Varian 5000 HPLC employing a PL size-exclusion column (300 × 7.5 mm, 5μ particle size). Molecular weight data is referenced relative to polystyrene standards. Elemental analyses were performed at Atlantic Microlab Inc., Norcross, Georgia.

Synthesis of Diethyl 1,1-Cyclopropanedicarboxylate. A DMF (130 mL) solution of diethyl malonate (60 g, 0.38 mol) and potassium carbonate (150 g, 1.09 mol) was heated at 145 °C for 5–8 h. The mixture was cooled in an ice bath to 0 °C and then 1,2-dibromoethane (48 mL, 0.56 mol) was added over 30 min. The mixture was then heated again at 135 °C in an oil bath for 7–9 h *without stirring*. The mixture was diluted with H_2O (250 mL) and ether (250 mL) and the organic layer washed with H_2O (2 × 150 mL) and brine (150 mL) and then dried over K_2CO_3. The solvents were removed under reduced pressure, and the crude product was fractionally distilled (~8 mmHg). The fraction collected between 83–86 °C was pure diethyl 1,1-cyclopropanedicarboxylate (40 g, 57%).[21]

Preparation of 1,1-Cyclopropanedimethanol (1). A 200-mL flask equipped with an addition funnel was charged with a stir bar, LAH (10 g, 0.26 mol), and THF (150 mL). Diethyl 1,1-cyclopropanedicarboxylate (25 g, 0.13 mol) was added dropwise to the LAH–THF solution over a period of 1 h. After addition was complete, the mixture was heated at reflux for an additional 16 h. The mixture was cooled to 0 °C and quenched with H_2O (10 g), 10% aqueous NaOH (10 g), and H_2O (30 g), in that order. The solution was filtered and dried over K_2CO_3, and the solvents were removed under reduced pressure. The product was fractionally distilled to afford pure 1 as a colorless viscous oil (80%, bp 95–98 °C, 5 mmHg):[22] ^{1}H NMR ($CDCl_3$) δ 3.64 (d, 4 H, J = 4 Hz, $C\mathit{H}_2O$), 3.31 (d, 2 H, J = 4 Hz, $O\mathit{H}$), 0.48 (s, 4 H, cyclopropyl ring); ^{13}C NMR ($CDCl_3$) δ 67.8 ($\mathit{C}H_2OH$) 24.27 (*ipso*-cyclopropyl ring carbon), 8.71 (cyclopropyl-$\mathit{C}H_2$).

Generation of 1,1-Bis(hydroxymethyl)cyclopropane Monolithium Salt (2). A 100-mL Schlenk flask containing a THF (15 mL) solution of 1 (0.50 g, 0.49 mmol) was cooled to −78 °C and treated with *n*-BuLi (0.2 mL, 0.5 mmol). The mixture was allowed to react for an additional 30 min at −78 °C and the electrophile was added directly to the mixture.

Generation of 1,1-Bis(hydroxymethyl)cyclopropane (3). Compound 3 was prepared in a similar manner as above except employing 2 mol equiv of *n*-BuLi. The bis(lithium alkoxide) was isolated by removal of the solvent at reduced pressure while warming the mixture to ambient temperature. Compound 3 was isolated as a white powder in nearly quantitative yield.

Preparation of 1,1-Bis(iodomethyl)cyclopropane (4). A 100-mL Schlenk vessel was charged with acetonitrile (40 mL), 1 (2.00 g, 18.6 mmol), sodium iodide (9.0 g, 60 mmol), and chlorotrimethylsilane (7.6 mL, 60 mmol). The mixture was allowed to react at ambient temperature with stirring for 16 h. The resulting mixture was diluted with water (200 mL) and CH_2Cl_2 (150 mL). The organic layer was washed with 10% aqueous sodium thiosulfate and brine and dried over K_2CO_3, and the solvents were removed under reduced pressure. The crude product was purified by dilution with hexanes and filtration through a silica gel plug to yield pure 4, as a colorless oil (4.80 g, 80%). The product was stored under nitrogen and stabilized by copper metal: ^{1}H NMR ($CDCl_3$) δ 3.35 (s, 4 H, $C\mathit{H}_2I$), 1.03 (s, 4 H, cyclopropyl-CH_2); ^{13}C NMR ($CDCl_3$) δ 26.3 (*ipso*-cyclopropyl ring carbon), 23.0 ($\mathit{C}H_2I$), 19.5 (cyclopropyl-$\mathit{C}H_2$). Anal. Calcd for $C_5H_8I_2$: C, 18.65; H, 2.50; I, 78.84%. Found: C, 18.70; H, 2.56; I, 78.74%.

Preparation of 2-[3-(2-Chloropropenyl)]norbornadiene (8a). A 500-mL Schlenk flask was charged with a stir bar, THF (150 mL), NBD (15 g, 0.15 mol), *t*-BuOK (12 g, 0.10 mol), and TMEDA (12 g, 0.05 mol). The mixture was cooled to −78 °C and *n*-BuLi (40 mL, 2.5 M) was added slowly over 15-min period. The mixture was stirred at −78 °C for 30 min and then warmed to 0 °C and stirred for an additional 45 min resulting in a deep green solution. To this mixture was added 50 mL of a THF solution of LiBr (50 mL, 2 M) which resulted in a blue solution. CuCN (9 g, 0.10 mmol) was then added in small portions over 20 min and the mixture was stirred for an additional 30 min resulting in an olive-green solution. The mixture was cooled to −78 °C and 11 g (0.1 mol) 2,3-dichloropropene was added dropwise and allowed to stir 30 min. The mixture was warmed to 0 °C, stirred for 30 min, and then *carefully* quenched with water. The solution was diluted with ether (200 mL) and washed with water (2 × 500 mL) and brine (500 mL). The organic layer was dried over K_2CO_3, and the solvents were removed under reduced pressure. The crude mixture was purified by flash chromatography in hexanes and then fractional distillation. The fraction at 38–44 °C (0.25 mmHg) was collected to afford pure 7 as a colorless liquid (13 g, 80%): ^{1}H NMR ($CDCl_3$) δ 6.78 (d, J = 2.2 Hz, 1 H, H6 or H5 NBD), 6.74 (d, J = 2.9 Hz, 1 H, H6 or H5 NBD), 6.35 (s, 1 H, H3 NBD), 5.20 (s, 1 H, ${=}C\mathit{H}_2$), 5.11 (s, 1 H, $C{=}C\mathit{H}_2$), 3.54 (s, 1 H, H4 or H1 NBD), 3.32 (s, 1 H, H4 or H1 NBD), 3.21 (m, 2 H, $C\mathit{H}_2$), 2.04 (d, J = 1.7 Hz, 1 H, H7 NBD), 1.98 (d, J = 1.6 Hz, 1 H, H7 NBD); ^{13}C NMR ($CDCl_3$) δ 152.9 (C2 NBD), 142.9 (C5 or C6 NBD), 142.2 (C5 or C6 NBD), 140.0 ($CH_2{=}\mathit{C}$), 137.8 (C3 NBD), 112.9 ($\mathit{C}H_2{=}C$), 73.7 (C7 NBD), 52.8 (C1 or C4 NBD), 50.3 (C1 or C4 NBD), 41.1 (methylene). Anal. Calcd for $C_{10}H_{11}Cl$: C, 72.07; H, 6.65%. Found: C, 72.17; H, 6.71%.

2-Butylnorbornadiene (8b): ^{1}H NMR ($CDCl_3$) δ 6.75 (d, J = 1.7 Hz, 1 H, H6 or H5 NBD), 6.73 (d, J = 1.7 Hz, 1 H, H6 or H5 NBD), 6.10 (d, J = 2.3 Hz, 1 H, H3 NBD), 3.47 (s, 1 H, H1 or H4 NBD), 3.26 (s, 1 H, H1 or H4 NBD), 2.17 (m, 2 H, $C\mathit{H}_2CH_2CH_2CH_3$), 1.95 (d, J = 1.7 Hz, 1 H, H7 NBD), 1.93 (d, J = 1.8 Hz, 1 H, H7 NBD), 1.36 (m, 2 H, $CH_2C\mathit{H}_2CH_2CH_3$), 1.28 (m, 2 H, $CH_2CH_2C\mathit{H}_3$), 0.88 (t, J = 7.1 Hz, 3 H, methyl); ^{13}C NMR ($CDCl_3$) δ 158.7 (C2 NBD), 143.7 (C5 or C6), 142.2 (C5 or C6), 133.1 (C3), 73.3 (C7), 53.5 (C1 or C4), 50.0 (C1 or C4), 31.2 ($\mathit{C}H_2CH_2CH_2CH_3$), 29.4 ($CH_2\mathit{C}H_2CH_2CH_3$), 22.4 ($CH_2CH_2\mathit{C}H_2CH_3$), 13.9 (methyl).

1,4-Bis(2-norbornadienyl)butane (8c): ^{1}H NMR ($CDCl_3$) δ 6.74 (s, 2 H, H5 and H6 NBD), 6.09 (d, J = 1.5 Hz, 1 H, H3 NBD), 3.48 (s, 1 H, H1 or H4 NBD), 3.25 (s, 1 H, H1 or H4 NBD), 2.16 (t, J = 1.7 Hz, 4 H, $NBDC\mathit{H}_2$), 1.95 (d, J = 1.7 Hz, 1 H, H7 NBD), 1.93 (d, J = 1.7 Hz, 1 H, H7 NBD), 1.38 (m, 4 H, $C\mathit{H}_2CH_2NBD$); ^{13}C NMR ($CDCl_3$) δ 158.8 (C2 NBD), 143.8 (C5 or C6 NBD), 142.3 (C5 or C6 NBD), 133.2 (C3 NBD), 73.4 (C7 NBD), 53.4 (C1 or C4 NBD), 50.0 (C1 or C4 NBD), 31.3 ($NBD\mathit{C}H_2$), 26.9 ($\mathit{C}H_2CH_2NBD$).

2-Allylnorbornadiene (8d): ^{1}H NMR ($CDCl_3$) δ 6.76 (s, 1 H, H5 or H6 NBD), 6.75 (s, 1 H, H5 or H6 NBD), 6.17 (d, J = 1.3 Hz, 1 H, H3 NBD), 5.78 (dd, J = 11, 17 Hz, $C\mathit{H}{=}CH_2$), 5.07 (s, 1 H, $CH{=}C\mathit{H}_2$), 5.01 (d, J = 10 Hz, 1 H, $CH{=}C\mathit{H}_2$), 3.51 (s, 1 H, H1 or H4 NBD), 3.28 (s, H1 or H4 NBD), 2.94 (s, 2 H, $C\mathit{H}_2$), 1.99 (d, J = 2.0 Hz, 1 H, H7 NBD), 1.95 (d, J = 1.3 Hz, 1 H, H7 NBD); ^{13}C NMR ($CDCl_3$) δ 155.6 (C2 NBD), 143.7 (C5 or C6 NBD), 142.2 (C5 or C6 NBD), 135.4 ($\mathit{C}H{=}CH_2$), 134.5 (C3 NBD), 115.7 ($CH{=}\mathit{C}H_2$), 73.4 (C7 NBD), 53.3 (C1 or C4 NBD), 50.1 (C1 or C4 NBD), 36.0 (CH_2).

Preparation of 2-(Tributylstannyl)norbornadiene (8e). A 500-mL Schlenk flask was charged with a stir bar, THF (150 mL), NBD (15 g, 0.15 mol), *t*-BuOK (12 g, 0.10 mol), and TMEDA (12 g, 0.05 mol). The mixture was cooled to −78 °C and *n*-BuLi (40 mL, 2.5 M) was added slowly over a 15-min period. The mixture was stirred at −78 °C for 30 min and then warmed to 0 °C and stirred for an additional 45 min resulting in a deep green solution. The solution was then cooled to −78 °C and tributyltin chloride was added slowly until the green color faded. This mixture was stirred 20 min and then allowed to warm to room

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[21] This compound is available from Aldrich Chemical Co.

[22] To date, only the ^{1}H NMR spectrum of the diol has been reported and it did not show coupling to the hydroxy proton (as our sample did). The modified procedure presented appears to yield a diol in comparable yield and one which is free of water (since we do not observe broadening from exchange): Itoh, O.; Kohmura, Y.; Ichikawa, Y.; Umezu, M.; Okita, T.; Ichikawa, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 146.

temperature. The solution was diluted with ether (200 mL), and washed with water (2 × 500 mL) and brine (500 mL). The organic layer was dried over K_2CO_3, and the solvents were removed under reduced pressure. The crude mixture was purified by flash chromatography in hexanes and then fractionally distilled (0.25 mmHg, 120–122 °C). The fraction at 120–122 °C yielded pure **8e** as a colorless liquid (30 g, 81%): ^1H NMR ($CDCl_3$) δ 6.99 (d, J = 2.7 Hz, 1 H, H2 NBD), 6.67 (d, J = 3.1 Hz, 1 H, H5 or H6 NBD), 6.62 (d, J = 2.7 Hz, 1 H, H5 or H6 NBD), 3.74 (s, 1 H, H1 or H4 NBD), 3.61 (s, 1 H, H1 of H4 NBD), 1.88 (d, J = 1.5 Hz, 1 H, H7 NBD), 1.86 (d, J = 1.2 Hz, 1 H, H7 NBD), 1.46 (m, 6 H, $CH_2CH_2CH_3$), 1.25 (m, 6 H, CH_2CH_3), 0.88 (apparent t, J = 7.2 Hz, 6 H, $SnCH_2$), 0.87 (t, J = 7.2 Hz, 9 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 154.7 (C2 NBD), 154.3 (C3 NBD), 142.7 (C5 or C6 NBD), 142.6 (C5 or C6 NBD), 74.4 (C7 NBD), 56.2 (C1 NBD), 51.9 (C4 NBD), 29.3 ($SnCH_2CH_2CH_2CH_3$), 27.3 ($SnCH_2CH_2CH_2CH_3$), 13.7 (CH_3), 9.5 ($SnCH_2$). Anal. Calcd for $C_{19}H_{34}Sn$: C, 59.87; H, 8.99%. Found: C, 59.67; H, 9.05%.

Preparation of 2-(Trimethylsilyl)norbornadiene (8f). A Schlenk flask was charged with a stir bar, THF (50 mL), and **8e** (2.5 g, 6.7 mmol). The solution was cooled to −78 °C and n-BuLi (2.7 mL, 2.5 M) was added slowly and allowed to stir for 30 min. To this mixture TMSCl (0.9 g, 8 mmol) was added and stirred 20 min. The resultant mixture was diluted with hexanes and purified by flash chromatography, followed by Kugelrohr distillation to yield pure **8f** (1.0 g, 95%): ^1H NMR ($CDCl_3$) δ 7.01 (d, J = 2.9 Hz, 1 H, H3 NBD), 6.68 (s, 1 H, H5 or H6 NBD), 6.67 (s, 1 H, H5 or H6 NBD), 3.70 (s, 1 H, H1 or H4 NBD), 3.63 (s, 1 H, H1 or H5 NBD), 1.88 (d, J = 1.6 Hz, 1 H, H7 NBD), 1.85 (d, J = 1.6 Hz, 1 H, H7 NBD), 0.05 (s, 9 H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 155.6 (C2 NBD), 153.3 (C3 NBD), 143.1 (C5 or C6 NBD), 142.3 (C5 or C6 NBD), 74.1 (C7 NBD), 53.3 (C1 or C4 NBD), 51.9 (C1 or C4 NBD), −2.08 ($SiCH_3$).

Preparation of 2-[(2-Buta-1,3-dienyl)methyl]norbornadiene (9). A Schlenk flask was charged with a stir bar, THF (60 mL), **8a** (10 g, 60 mmol), (dppp)$NiCl_2$ (0.5 g, 1.2 mmol), and vinylmagnesium bromide (70 mL, 1.0 M, THF). The mixture was warmed to reflux and stirred for 16 h. The resultant solution was diluted with hexanes, washed with water and brine, and dried over K_2CO_3. The solvents were removed, and the product was purified by flash chromatography in hexanes followed by fractional distillation to yield pure **9** as a colorless liquid (6.7 g, 70%): ^1H NMR ($CDCl_3$) δ 6.75 (d, J = 2.2 Hz, 1 H, H6 or H5 NBD), 6.71 (d, J = 2.3 Hz, 1 H, H6 or H5 NBD), 6.36 (dd, J = 11, 17 Hz, 1 H $CH{=}CH_2$), 6.18 (s, 1 H, H3 NBD), 5.18 (d, J = 17 Hz, 1 H, $CH{=}CH_2$), 5.07 (s, 1 H, $C{=}CH_2$), 5.02 (d, J = 11 Hz, 1 H, $CH{=}CH_2$), 4.95 (s, 1 H, $C{=}CH_2$), 3.50 (s, 1 H, H1 or H4 NBD), 3.27 (s, 1 H, H1 or H4 NBD), 2.01 (d, J = 1.6 Hz, 1 H, H7 NBD), 1.94 (d, J = 1.6 Hz, 1 H, H7 NBD); ^{13}C NMR ($CDCl_3$) δ 155.5 (C2 NBD), 143.4 ($C{=}CH_2$), 142.9 (=CH NBD), 142.1 (=CH NBD), 138.4 (=CH), 135.3 (=CH), 117.0 ($CH{=}CH_2$), 113.7 ($C{=}CH_2$), 73.3 (C7 NBD), 53.1 (C1 or C4 NBD), 50.1 (C1 or C4 NBD), 33.9 (CH_2). Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92%. Found: C, 90.94; H, 9.05%.

Preparation of 2-[3-(2-Phenylpropenyl)]norbornadiene (10). A Schlenk flask was charged with a stir bar, THF (10 mL), **8a** (1.3 g, 7.8 mmol), (dppp)$NiCl_2$ (10 mg, 0.2 mmol), and phenylmagnesium chloride (4 mL, 2.0 M in THF). The mixture was heated at reflux with stirring for 16 h and then allowed to cool to ambient temperature. The mixture was diluted with hexanes (40 mL), washed with water (2 × 40 mL) and brine (40 mL) and then dried over K_2CO_3. The solvents were removed under reduced pressure, and the crude product was subjected to flash chromatography (alumina, hexanes) to afford pure **10** as a colorless oil (1.4 g, 90%): ^1H NMR ($CDCl_3$) δ 7.43 (d, J = 6.7 Hz, 2 H, Ar), 7.35 (d, J = 1.7 Hz, 1 H, Ar), 7.31 (d, J = 7.9 Hz, 2 H, Ar), 6.69 (d, J = 4.3 Hz, 1 H, H5 or H6 NBD), 6.68 (d, J = 4.3 Hz, 1 H, H5 or H6 NBD), 6.17 (s, 1 H, H3 NBD), 5.40 (d, J = 1.2 Hz, 1 H, $=CH_2$), 5.04 (d, J = 1.4 Hz, 1 H, $=CH_2$), 3.47 (s, 1 H, H1 or H4 NBD), 3.41 (d, J = 16.3 Hz, 1 H, methylene), 3.34 (d, J = 16.3 Hz, 1 H, methylene), 3.29 (s, 1 H, H1 or H4 NBD), 1.92 (m, 2 H, C7 NBD); ^{13}C NMR ($CDCl_3$) δ 155.9 (C2 NBD), 145.2 ($C{=}CH_2$), 143.0 (NBD CH), 142.2 (NBD CH), 140.9 (Ar C), 135.8 (NBD CH), 128.0 (Ar CH), 127.2 (Ar CH), 125.9 (Ar CH), 113 ($C{=}CH_2$), 73.4 (C7 NBD), 53.2 (C1 or C4 NBD), 50.2 (C1 or C4 NBD), 37.6 (methylene). Anal. Calcd for $C_{16}H_{16}$: C, 92.25; H, 7.74%. Found: C, 92.07; H, 7.88%.

Preparation of $[-(CH_2)_6OCH_2(C_3H_4)CH_2O-]_n$ (11). A 50-mL Schlenk vessel was charged with a stir bar, DMF (4 mL), 1,6-hexanediol (0.74 g, 6.2 mmol), NaH (0.30 g, 12.4 mmol), and 18-crown-6 ether (0.30 g, 1.1 mmol). The mixture was stirred and allowed to react at 40 °C for 18 h. The mixture was cooled to 0 °C and then comonomer **4** (2.0 g, 6.2 mmol) was added slowly. After the addition of **4** the mixture was stirred for 2 h at 0 °C and then warmed to 40 °C for 15 min. Additional diol and NaH was then added and stirred at 40 °C for 2 h to end-cap the polymer. The solution was diluted with ether (50 mL) and water (50 mL). The organic layer was washed with water (2 × 100 mL) and brine (100 mL) and dried over K_2CO_3, and the solvents were removed under reduced pressure. The crude polymer was redissolved in CH_2Cl_2 (1 mL) and precipitated into pentane (×2). The polymer was dried under reduced pressure at 65 °C for 24 h: ^1H NMR ($CDCl_3$) δ 3.40 (m, 4 H, cyclopropyl-CH_2OH), 3.32 (m, 4 H, OCH_2CH_2), 1.56 (m, 5 H, H_2O and OCH_2CH_2), 1.36 (m, 4 H, $OCH_2CH_2CH_2$), 0.45 (s, 4 H, cyclopropyl-CH_2); ^{13}C NMR ($CDCl_3$) δ 73.9 (OCH_2-cyclopropyl), 70.8 (OCH_2), 29.4 (s, OCH_2CH_2), 25.8 ($OCH_2CH_2CH_2$), 20.5 (*ipso*-cyclopropyl ring carbon), 8.4 (cyclopropyl-CH_2). Anal. Calcd for $[C_{11}H_{20}O_2{\cdot}0.5H_2O]_n$: C, 68.35; H, 10.95; I, 0.00%. Found: C, 68.40; H, 10.59; I, 0.00%.

General Procedure for Anionic Polymerizations. Polymerizations were performed under a purified nitrogen atmosphere. THF was initially purified by distillation from potassium. Monomers and THF were distilled from freshly crushed CaH_2 directly into the polymerization reaction vessel. The solution in the polymerization vessel was degassed (freeze-pump-thaw) and then the n-BuLi was injected through a rubber septum producing a brightly colored solution. The mixture was allowed to react with stirring for 16 h at ambient temperature. The polymer was isolated by diluting the solution with methanol and collecting the precipitated polymer. Further purification was carried out by dissolving the polymer in CH_2Cl_2 followed by precipitation with methanol.

$[-CH_2CH{=}C(CH_2C_7H_7)CH_2-]_n$ (12). ^1H NMR ($CDCl_3$) δ 6.69 (br s, 2 H, H5 and H6 NBD), 6.17 (br s, 1 H, H3 NBD), 5.4–4.6 (br s's, 2 H), 3.48 (br s, 2 H), 3.18 (br s, 1 H, H1 or H4 NBD), 2.77 (br s, 2 H, methylene), 2.03 (br s, 6 H, $CHCH_2$), 1.60–0.82 (m, 6 H). Strongest signals in the ^{13}C NMR ($CDCl_3$): δ 155.9 (C2 NBD), 143.1 (C5 or C6 NBD), 142.2 (C5 or C6 NBD), 136.5 ($CH{=}C$), 135.9 (C3 NBD), 111.3 ($CH{=}C$), 73.5 (C7 NBD), 53.3 (CH_2 backbone), 53.1 (CH_2 backbone), 50.2 (methylene).

Photolysis of Polymers. Polymers containing the NBD moiety were dissolved in benzene containing 2 mol % each of $(PPh_3)_2CuBr$ and BHT. The solution was degassed by three consecutive freeze-pump-thaw cycles. Photolysis of the polymer solution was carried out in a quartz reaction tube fitted with an internal cooling finger through which coolant was circulated at 5–10 °C. The solution containing **12** was irradiated with stirring in a rayonet reactor (medium pressure Hg lamps) for 5–8 h to afford polymer **13**.

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