Macromolecules **2000,** *33,* 6722−6731

Free-Radical Ring-Opening Polymerization of Cyclic Allylic Sulfides. 2. Effect of Substituents on Seven- and Eight-Membered Ring Low Shrink Monomers

Richard A. Evans* and Ezio Rizzardo*

CSIRO Molecular Science, Bag 10, Clayton South, Victoria, Australia 3169

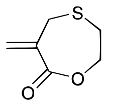
Received October 21, 1999; Revised Manuscript Received June 13, 2000

ABSTRACT: The effect of substituents on the free-radical ring-opening polymerization behavior and polymerization volume shrinkage of the cyclic allylic sulfides 6-methylene-1,4-dithiacycloheptane (**2a**) and 3-methylene-1,5-dithiacyclooctane (**2b**) has been investigated. The monomers were 2-(hydroxymethyl)-6-methylene-1,4-dithiacycloheptane (**3a**), 6-methylene-1,4-dithiacycloheptan-2-ylmethyl acetate (**3b**), 6-methylene-1,4-dithiacycloheptan-2-ylmethyl methacrylate (**3c**), 7-methylene-1,5-dithiacyclooctan-3-ol (**4a**), 7-methylene-1,5-dithiacyclooctan-3-yl acetate (**4b**), 7-methylene-1,5-dithiacyclooctan-3-yl benzoate (**4c**), and the bicyclic monomer bis(6-methylene-1,4-dithiacycloheptan-2-ylmethyl) diglycolate (**5**). The monomers were polymerized in bulk with thermal (AIBN, VAZO88) and photochemical initiators (Darocur 1173) with selected solution polymerizations also performed. The presence of a substituent on the monomers gave clear amorphous polymers unlike the crystalline polymers obtained from the unsubstituted parent monomers (**2**) previously reported. The substituted, monofunctional seven-membered ring monomers (**3a,b**) polymerize to moderate conversions (ca. 60%) and gave amorphous, soluble sticky gumlike polymers. The difunctional monomer **3c** in contrast gave an insoluble rigid material. Eight-membered ring monomers **4a, 4b,** and **4c** were made to undergo complete conversions. The dual cyclic monomer **5** was polymerized to give an insoluble material containing only traces of extractable monomer. Those liquid monomers **3c**, **4b**, and **5** that polymerized to complete conversion (**3c**, **4b**) or near complete (**5**) were further examined and gave polymerization shrinkages of 7.3, 2.0, and 2.1% (respectively) and glass transition points of 78, −0.2, and 28 °C, respectively.

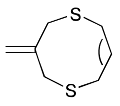
Introduction

Over the past 20 years, free radical ring-opening polymerization has been seen as a solution to the problem of polymerization volume shrinkage. Reports,[1−13] patents,[14−17] and reviews[18−20] in this field appear regularly in the literature, and a monograph has also been published. Whereas much work continues on ketene acetal and vinylcyclopropane derivatives, we have developed novel sulfur-containing monomers such as the activated monomer **1**[4,15,21] and the unactivated monomers **2**.[1,2,5,14] These monomers propagate via a sulfur-centered radical, which has a distinct advantage over the oxygen- or carbon-centered radicals produced from spiroortho carbonates or ketene acetals and vinylcyclopropanes, respectively. Thiyl radicals readily add to many monomers with less competition from the side reaction of hydrogen abstraction (i.e., degradative chain transfer) which occurs to varying degrees with oxygen- and carbon-centered radicals.[22−24]

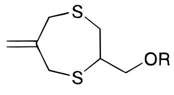
We reported earlier the facile polymerization of unsubstituted monomers **2** which produced high molecular weight crystalline polymers to very high conversion under mild conditions.[1] Although they had lower polymerization volume shrinkages than vinyl monomers of the same molecular weight, even lower shrinkages are desirable. The crystallinity in the polymers is a source of additional polymerization volume shrinkage, and its elimination should give lower shrinkages. Crystallinity may also have an effect on conversion.[25] We examined the use of substituents on seven- and eight-membered ring monomers as a means of preventing crystallinity in their respective polymers. We now report on the polymerization of these substituted monomers (**3** , **4**) together with a dual cyclic monomer (**5**).



1



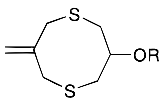
2a: n=0
2b: n=1



3a: R = H

3b: R = CH_3CO

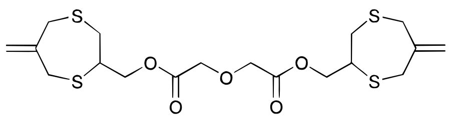
3c: R = $CH_3(C{=}CH_2)CO$



4a: R = H

4b: R = CH_3CO

4c: R = C_6H_5CO



5

Experimental Section

Measurements. ^1H and ^{13}C NMR spectra of monomers and polymers were recorded on either a Bruker 200 MHz or a Bruker 250 MHz spectrometer using various deuterated solvents at room temperature. FT-IR spectra were obtained with either a Biomem MB series or a Mattson Instruments spectrometer. FT-IR spectra of samples were obtained using

---

* E-mail: richard.evans@molsci.csiro.au; ezio.rizzardo@molsci.csiro.au.

10.1021/ma9917646 CCC: $19.00 Published 2000 by the American Chemical Society

thin films on salt plates directly or thin shavings via a Bach-Shear FT-IR microscope. Densities were determined in a gradient density column using sodium bromide solutions at 20 °C with a calibration curve correlation coefficient of greater than 0.998. Refractive indices were measured on a Carl Zeiss Abbe type refractometer. Gel permeation chromatography (GPC) was performed on a Waters Instrument connected to six μ-Styragel columns (10^6, 10^5, 10^4, 10^3, 500, and 100 Å pore size). Tetrahydrofuran was used as eluent at 20 °C and a flow of 1 mL/min. The system was calibrated using narrow distribution polystyrene standards (Waters). Sample concentration used for analysis was ca. 2 mg/mL. The glass transition temperatures of the samples were obtained from a Rheometric Mark IIIe DMTA by clamping a rectangular bar with dimensions ca. 6 mm × 0.92 mm in the single cantilever bending mode with a 5 mm free length frame. The strain was set at 0.5%, and the oscillating frequency used was 1 Hz as the temperature was scanned from −100 to 100 °C at a constant heating rate of 2 °C/min. The T_g's were taken as the maxima in the tan δ spectrum. UV irradiation were carried out in a purpose built apparatus at 365 nm at 0.8−1.0 mW/cm^2.

2,3-Dimercapto-1-propanol (**6**) (95%), 2-(chloromethyl)-3-chloro-1-propene (**7**) (99%), diglycolyl chloride (95%), benzoyl choride (99%), and acetyl choride (98%) were obtained from Aldrich Chemical Co. Methacryloyl chloride (97%) and *o*-ethylxanthic acid potassium salt (AR) were obtained from Fluka AG, and ethylenediamine (LR) was obtained from Ajax Chemicals. The initiators AIBN and DAROCUR 1173 were from TCI and Ciba, respectively. The acid chlorides were distilled prior to use and the other chemicals were used as received. Solvents were analytical grade obtained from BDH and used as received. As the unsubstituted eight-membered ring monomer **2b** had once previously polymerized on storage, most of the monomers were routinely stored in a freezer (−13 °C) as a precaution.

Synthesis of 2-(Hydroxymethyl)-6-methylene-1,4-dithiacycloheptane (3a). *Solution 1.* Sodium metal (0.77 g, 33 mmol) was dissolved in 35 mL of absolute ethanol at room temperature under nitrogen atmosphere. Then 2,3-dimercapto-1-propanol (**6**) (1.99 g, 1.60 mL, 16.0 mmol) was added dropwise. The solution was taken up in a syringe and diluted to 44 mL. *Solution 2.* 2-(Chloromethyl)-3-chloro-1-propene (**7**) (2.0 g, 16 mmol) was dissolved in 30 mL of absolute ethanol and diluted to a volume of 44 mL in a syringe. Solutions 1 and 2 were added simultaneously (via syringe pump using separate Teflon feed lines) to 40 mL of absolute ethanol at room temperature under nitrogen protection over a period of 1 h. After the addition was complete the reaction was refluxed for 1 h. The reaction was then worked up by evaporation of the solvent, dilution with water, and extraction with ether. The ether extracts were dried and evaporated to yield 2.6 g of oil. The oil was purified by column chromatography using silica gel and ether:hexane (1:3) as eluent to yield 1.6 g (57%) of clear oil. ^{1}H NMR ($CDCl_3$): δ 2.60−3.80 (m, 9H), 4.80 (s, 2H, $=C\mathbf{H}_2$). ^{13}C NMR ($CDCl_3$): δ 34.5 ($-S\mathbf{C}H_2CH(CH_2OH)S-$), 39.0 and 40.0 (both $=C-\mathbf{C}H_2S-$), 52.8 ($-SCH_2\mathbf{C}H(CH_2OH)S-$), 63.6 ($-\mathbf{C}H_2OH$), 111.8 ($=\mathbf{C}H_2$), 147.4 (q $=C$). IR (thin film): 3385 br vs, 3074 sh m, 2910 s, 1632 sh m, 1401 vs, 1291 m, 1241 s, 1179 m, 1082 s, 1015 s, 903 s, 868 w, 845 w, 719 m cm^{-1}. Mass spectrum (CI, CH_4): *m/z* 177 ($M^{\bullet+} + 1$, 43%), 159 (100), 143 (20), 125 (23), 113 (46), 97 (51), 87 (37), 75 (26), 61 (67). Mass spectrum (HR, CI): *m/z* 177.0401 ($C_7H_{12}OS_2 + H$ requires 177.0408). $n = 1.5941$; $d^{20} = 1.236$ g/cm^3.

Synthesis of 6-Methylene-1,4-dithiacycloheptan-2-ylmethyl Acetate (3b). 2-(Hydroxymethyl)-6-methylene-1,4-dithiacycloheptane (**3a**) (2.00 g, 11.4 mmol) was dissolved in 10 mL of dichloromethane, and triethylamine (2.40 mL, 1.73 g, 17.1 mmol) was added to it. The solution was cooled under nitrogen to −10 °C, and then a solution of acetyl chloride (1.20 mL, 1.34 g, 17.1 mmol) in dichloromethane was added dropwise such that the reaction temperature was kept at about −10 °C. After the addition was completed, the solution was stirred for ca. 10 min and then allowed to warm to room temperature. The reaction was worked up by evaporation of the solvent, addition of water, and extraction with ether. The ether extracts were dried and evaporated to yield 2.2 g of pale yellow oil. The oil was purified by column chromatography using silica gel to yield 2.0 g (80%) of clear oil. ^{1}H NMR ($CDCl_3$): δ 2.00 (s, 3H, $-C\mathbf{H}_3$), 2.80−3.80 (m, 7H), 4.1−4.3 (m, 2H, $-C\mathbf{H}_2O-$), 4.85 (d, 2H, $=C\mathbf{H}_2$).^{13}C NMR ($CDCl_3$): δ 20.9 ($-CH_3$), 35.1 ($-S\mathbf{C}H_2CH(CH_2O-)S-$), 39.0 and 40.3 (both $=C-\mathbf{C}H_2S-$), 48.2 ($-SCH_2\mathbf{C}H(CH_2O-)S-$), 65.3 ($-CH_2O-$), 111.7 ($=\mathbf{C}H_2$), 147.5 (q $=C$), 170.5 ($\mathbf{C}=O$). IR (thin film): 3075 w, 2948 m, 2900 m, 1741 vs, 1633 sh m, 1401 br s, 1233 br vs, 1037 s, 975 w, 905 m, 870 w, 839 w, 720 w cm^{-1}. Mass spectrum (CI, CH_4): *m/z* 219 ($M^+ + 1$, 5%), 205 (2), 159 (100), 147 (22), 113 (25), 97 (35), 87 (15), 75 (10) 61 (45). Mass spectrum (HR, CI): *m/z* 218.0399 ($C_9H_{14}O_2S_2$ requires 218.0435). $n = 1.5500$; $d^{20} = 1.223$ g/cm^3.

Synthesis of 6-Methylene-1,4-dithiacycloheptan-2-ylmethyl Methacrylate (3c). 6-Methylene-1,4-dithiacycloheptan-2-ylmethyl methacrylate (**3c**) was prepared in 58% yield in an analogous manner to 6-methylene-1,4-dithiacycloheptan-2-ylmethyl acetate (**3b**), using methacryloyl chloride in place of acetyl chloride. This monomer occasionally spontaneously polymerized, but this was presumed to be due to the methacrylate functionality and not the allylic sulfide functionality of the monomer. ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 3H, $-C\mathbf{H}_3$), 2.90−3.80 (m, 7H), 4.1−4.3 (m, 2H, $-C\mathbf{H}_2O-$), 4.85 (d, 2H, allylic $=C\mathbf{H}_2$), 5.60 (s, 1H, acrylic $=C\mathbf{H}H$), 6.1 (s, 1H, acrylic $=CH\mathbf{H}$). ^{13}C NMR ($CDCl_3$): δ 18.3 ($-CH_3$), 35.0 ($-S\mathbf{C}H_2CH(CH_2O-)S-$), 38.7 and 40.2 (both $=C-CH_2S-$), 48.3 ($-SCH_2\mathbf{C}H(CH_2O-)S-$), 65.4 ($-CH_2O-$), 111.6 (allylic $=\mathbf{C}H_2$), 126.0 (acrylic $=\mathbf{C}H_2$), 135. 8 (q acrylic) 147.5 (q vinylidene $=C$), 168.0 ($\mathbf{C}=O$). IR (thin film): 3077 w, 2953 m, 1722 vs, 1716 vs, 1635 m, 1454 m, 1404 m, 1320 s, 1294 s, 1243 m, 1160 vs, 1090 w, 1047 w, 1012 m, 980 w, 943 m, 904 m, 870 w, 813 m, 722 w cm^{-1}. Mass spectrum (EI): *m/z* 244 ($M^+ + 1$, 20%), 159 (50), 158 (63), 125 (52), 117 (100), 111 30), 69 (51). Mass spectrum (HR, ES): *m/z* 267.048 937 6 ($C_{11}H_{16}O_2S_2Na$ requires 218.0435). $n = 1.5541$; $d^{20} = 1.188$ g/cm^3.

Synthesis of 3-Mercapto-2-(mercaptomethyl)-1-propene (8). *Part A. Synthesis of Bis-xanthate* ***9***. 3-Chloro-2-(chloromethyl)-1-propene (**7**) (5.0 g, 40.0 mmol) was dissolved in 5 mL of absolute ethanol and was added dropwise to *O*-ethylxanthic acid potassium salt (13.5 g 84.0 mmol) in 150 mL of absolute ethanol under nitrogen protection at room temperature. The reaction was stirred overnight, and the resulting pale yellow solution was worked up by evaporation of the solvent and addition of water followed by extraction with ether. The ether extracts were dried and evaporated to give 11.5 g (97%) of bis-xanthate as a yellow oil. It was used without further purification.^{1}H NMR ($CDCl_3$): δ 1.40 (t, 6H, $J = 7.1$ Hz. $-C\mathbf{H}_3$), 3.87 (s, 4H, $-C\mathbf{H}_2-S$), 4.63 (q, 4H, $-C\mathbf{H}_2CH_3$), 5.22 (s, 2H, $=C\mathbf{H}_2$). ^{13}C NMR ($CDCl_3$): δ 13.8 ($-\mathbf{C}H_3$), 40.0 (allylic $\mathbf{C}H_2$), 70.3 ($-\mathbf{C}H_2CH_3$), 118.5 ($=\mathbf{C}H_2$), 137.7 (q), 213.5 ($-O\mathbf{C}(=S)S-$).

Part B. Liberation of 3-Mercapto-2-(mercaptomethyl)-1-propene ***(8)***. The bis-xanthate (**9**) (10.0 g, 33.8 mmol) prepared above was added dropwise to ethylenediamine (20 mL) under nitrogen protection. The rate of addition was such that the reaction temperature was kept at ca. 30 °C. After the addition was complete, the mixture was stirred at 30 °C for 3 h. The reaction was worked up by pouring it cautiously into a solution of concentrated H_2SO_4 (50 mL) and crushed ice (ca. 200 g). The milky white solution was extracted with ether until a clear aqueous layer was obtained. The yellowish organic layer was washed with dilute H_2SO_4 (2 M) and then saturated sodium chloride solution and dried before being evaporated to give 4.18 g of yellow oil. The oil was bulb-to-bulb distilled at ca. 50 °C/0.1 mm to yield 2.6 g (64%) of clear, profoundly foul smelling oil being 3-mercapto-2-(mercaptomethyl)-1-propene (**8**). ^{1}H NMR ($CDCl_3$): δ 1.48 (t, 2H, $J = 8.1$ Hz. $-S\mathbf{H}$), 3.25 (d, 4H, $J = 8.1$ Hz, $-C\mathbf{H}_2-S$), 5.00 (s, 2H, $=C\mathbf{H}_2$). ^{13}C NMR ($CDCl_3$): δ 28.2 ($-\mathbf{C}H_2-S$), 113.3 ($=\mathbf{C}H_2$), 147.4 (q).

Synthesis of 7-Methylene-1,5-dithiacyclooctan-3-ol (4a). 3-Mercapto-2-(mercaptomethyl)-1-propene (**8**) (6.30 g, 52.5 mmol) was dissolved in a solution of sodium (2.51 g, 109 mmol) in absolute ethanol (60 mL) under nitrogen protection at room temperature. A second solution of the same volume as the first was also prepared of 1,3-dibromo-2-propanol (**10**) (11.4 g, 52.5 mmol) in absolute ethanol. Both solutions were then added to a refluxing solution of absolute ethanol via separate feed lines over 4 h using syringes and a syringe pump. After addition was completed the reaction was further refluxed for 40 min. The solution was evaporated and the residue extracted with chloromethane. The extracts were dried and evaporated to give 9.5 g of crude material. The oil was purified by column chromatography using silica gel and ether:hexane (1:1) as eluent to yield 4.7 g (50%) of white powder. ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 1H, $-\mathrm{O}\mathbf{H}$), 2.90 (dd, 2H, $J_{gem} = 15$ Hz, $J = 6.7$ Hz, $-\mathrm{S}-\mathrm{C}\mathbf{H}_2-\mathrm{CHOH}-$ cis to OH), 3.05 (dd, 2H, $J_{gem} = 15$ Hz, $J = 3.3$ Hz, $-\mathrm{S}-\mathrm{C}\mathbf{H}_2-\mathrm{CHOH}-$ trans to OH), 3.19 (s, 2H, allylic CH2), 3.92 (apparent sept, 1H, $J = 3.3$ Hz, C**H**-OH), 5.21 (s, 2H, $=\mathrm{C}\mathbf{H}_2$). ^{13}C NMR ($CDCl_3$): δ 35.8 and 39.4 ($-\mathrm{CH}_2-$), 68.9 (**C**$-$OH), 120.4 ($=\mathbf{C}\mathrm{H}_2$), 144.1 (q). IR (KBr): 3248 br s, 2917 m, 1628 m, 1408 s, 1337 m, 1303 m,1237 m, 1188 m, 1084 m, 1013 vs, 924, 900 m, 833 w, 812 w, 741 w cm^{-1}. Mass spectrum (CI, CH_4): *m/z* 177 ($M^{\bullet+} + 1$, 53%), 159 (100), 125 (52), 113 (79), 99 (70), 97 (84), 87 (32), 75 (47), 61 (76). Mass spectrum (HR, CI): *m/z* 177.0403 ($C_7H_{12}OS_2$ + H requires 177.0408); mp 54$-$56 °C.

Synthesis of 7-Methylene-1,5-dithiacyclooctan-3-yl Acetate (4b). 7-Methylene-1,5-dithiacyclooctan-3-ol (**4a**) (3.20 g 18.2 mmol) and triethylamine (3.80 mL, 2.75 g, 27.3 mmol) was dissolved in dry ether and dichloromethane required for solubility at -10 °C under nitrogen protection. A solution of acetyl choride (2.06 mL, 2.14 g, 27.3 mmol) in ether was added dropwise to the cooled 8-methylene-1,6-dithiacyclooctan-3-ol (**4a**) solution. After the addition was complete, the solution was allowed to warm to room temperature and then refluxed for 1 h. The reaction was worked up by addition of water and extraction with ether. The evaporated dried ether extracts gave an oil. The oil was purified by column chromatography using silica gel and ether:hexane (1:1) as eluent to yield 2.0 g (51%) of clear oil. ^{1}H NMR ($CDCl_3$): δ 2.00 (s, 3H, $-\mathrm{C}\mathbf{H}_3$), 3.05 (apparent d, 4H, $J = 5.2$ Hz, $-\mathrm{SC}\mathbf{H}_2-\mathrm{CHO}-$), 3.21 (s, 4H, allylic $-\mathrm{C}\mathbf{H}_2-$), 4.95 (apparent pent, 1H, $J = 5.3$ Hz), 5.2 (s, 2H, $=\mathrm{C}\mathbf{H}_2$). ^{13}C NMR ($CDCl_3$): δ 21.0 ($-\mathrm{CH}_3$), 32.3 and 37.6 ($-\mathbf{C}\mathrm{H}_2-$), 72.3 ($-\mathbf{C}\mathrm{H}-\mathrm{O}-$), 120.3 ($=\mathbf{C}\mathrm{H}_2$), 144.7 (quat vinyl), 169.9 ($-\mathrm{O}\mathbf{C}(=\mathrm{O})-\mathrm{CH}_3$). IR (thin film): 3070 w, 2928 m, 1737 vs, 1632 w, 1411 m, 1370 m, 1236 vs, 1021 s, 991 m, 959 m, 909 m, 875 w, 737 w cm^{-1}. Mass spectrum (CI, CH_4): *m/z* 218 (M^+, 5%), 173 (5), 159 (100), 147 (10), 127 (10), 113 (6), 97 (10), 87 (5) 75 (5), 61 (24). Mass spectrum (HR, CI): *m/z* 218.0422 ($C_9H_{14}O_2S_2$ requires 218.0435). $n = 1.5613$; $d^{20} = 1.217$ g/mL.

Synthesis of 7-Methylene-1,5-dithiacyclooctan-3-yl Benzoate (4c). This compound was made in the same manner as 7-methylene-1,5-dithiacyclooctyl acetate except benzoyl choride was use in place of acetyl chloride.

From 7-methylene-1,5-dithiacyclooctan-3-ol (4.50 g, 25.6 mmol) was obtained 6.5 g of crude material which was chromatographed to give 3.8 g (53%) of product as a sticky oil. This oil slowly crystallized to a white solid. ^{1}H NMR ($CDCl_3$): δ 3.16 (d, 2H, $J = 1.7$ Hz, $-\mathrm{SC}\mathbf{H}\mathrm{HCO}-$), 3.18 (d, 2H, $J = 3.3$ Hz, $-\mathrm{SCH}\mathbf{H}\mathrm{CO}-$), 3.23 (s, 4H, allylic $-\mathrm{CH}_2-$), 5.2 (s, 2H, $=\mathrm{CH}_2$), 5.2 (m, 1H, $-\mathrm{C}\mathbf{H}\mathrm{O}-$), 7.3 (m, 3H, arom), 8.0 (m, 2H, arom). ^{13}C NMR ($CDCl_3$): δ 32.8, 38.0 (both $-\mathbf{C}\mathrm{H}_2-$), 73.1 ($\mathbf{C}\mathrm{H}-\mathrm{O}-$), 120.6 ($=\mathbf{C}\mathrm{H}_2$), 128.4, 129.8, 130.0, 133.2, (all aromatic),145.0 (quat vinyl), 166.0 ($\mathbf{C}=\mathrm{O}$). IR (CCl_4): 3071 m, 2929 m, 1717 s, 1632 m, 1601 m, 1584 m, 1491 w, 1450m, 1411 m, 1337 m, 1314 m, 1266 s, 1207 m, 1176 m, 1104 s, 1068 m, 1026 m, 978 m, 908 m cm^{-1}. Mass spectrum (CI, CH_4): *m/z* 280 (M^+, 10%), 159 (100), 147 (15), 113 (5), 97 (5), 61 (8). Mass spectrum (HR, CI): *m/z* 280.0559 ($C_{14}H_{16}O_2S_2$ requires 280.0581); mp 62$-$64 °C.

Synthesis of Bis(6-methylene-1,4-dithiacycloheptan-2-ylmethyl) Diglycolate (5). 2-(Hydroxymethyl)-6-methylene-1,4-dithiacycloheptane (**3a**) (3.00 g, 17.0 mmol) and triethylamine (2.60 mL, 1.89 g, 18.7 mmol) were dissolved in 25 mL of dry dichloromethane and cooled to ca. 0 °C under nitrogen protection. Then a solution of diglycolyl chloride (1.46 g, 8.52 mmol) in ca. 5 mL of dichloromethane was added dropwise. After the addition was complete, the reaction was warmed to room temperature and then refluxed for 2 h. The reaction was worked up by dilution with dichloromethane and washing the solution with water and saturated sodium chloride solution. The dichloromethane solution was dried and evaporated to give 3.6 g of clear oil. The oil was purified by column chromatography using silica gel and ether:hexane (1:4) as eluent to yield 1.7 g (44%) of clear oil.

^{1}H NMR ($CDCl_3$): δ 2.75$-$3.70 (m, 14H) 4.1$-$4.4 (m, 8H, $-\mathrm{C}\mathbf{H}_2\mathrm{O}-$), 4.83 ("d", 4H $=\mathrm{C}\mathbf{H}_2$). ^{13}C NMR ($CDCl_3$): δ 34.8 ($-\mathrm{S}\mathbf{C}\mathrm{H}_2\mathrm{CH}(\mathrm{CH}_2\mathrm{O}-)\mathrm{S}-$), 38.9 and 40.0 (both $=\mathrm{C}-\mathbf{C}\mathrm{H}_2\mathrm{S}-$), 47.7 ($-\mathrm{SCH}_2\mathbf{C}\mathrm{H}(\mathrm{CH}_2\mathrm{O}-)\mathrm{S}-$), 65.4 and 67.9 (both $-\mathrm{CH}_2\mathrm{O}-$), 111.8 ($=\mathbf{C}\mathrm{H}_2$), 147.3 (quat $=$C), 169.2 ($\mathbf{C}=\mathrm{O}$). IR (thin film): 3074 w, 2920 m, 1751 s, 1632 m, 1402 m, 1243 m, 1197 s, 1139 m, 1051 w, 995w, 906 m cm^{-1}. Mass spectrum (EI): *m/z* 450 ($M^+ + 1$, <1%), 292 (93), 232 (20), 176 (50), 118 (65), 117 (100), 86 (67) 84 (74). Mass spectrum (HR, ES): *m/z* 473.05607 ($C_{18}H_{26}O_5S_4Na$ requires 473.0518). $n = 1.5862$; $d^{20} = 1.295$ g/cm^3.

General Polymerization Techniques. Bulk thermal polymerizations were carried out on a 200$-$400 mg scale using AIBN as the initiator for 70 °C polymerizations and VAZO88 as the initiator for 90 °C polymerizations. The monomer and initiator were placed in a thick-walled tube (ca. 5 mm o.d. and ca. 3 mm i.d.) and flame-sealed after degassing the contents by three freeze$-$pump$-$thaw cycles to 10^{-3} mbar. Solution polymerizations were performed in a similar manner. Larger scale polymerizations were performed in purpose-specific bulbs with Teflon valves. Photopolymerizations were carried out in polypropylene 2.5 cm diameter molds with either 1 or 0.1 mm cavities. Monomer and initiator (Ciba DAROCUR 1173) were mixed together, sealed with the mold top, and photolyzed at 365 nm at 0.8$-$1.0 mW/cm^2 for the required time. No degassing was done on these samples. Polymerizations were analyzed in a variety of ways depending upon the nature of the polymer. Samples for GPC analysis were taken directly from the polymerization product. NMR spectroscopic analyses were performed on the crude polymerization products and also on polymers purified by dissolution in benzene or dichloromethane and precipitation into methanol.

Specific Examples of Polymerization Methods. *Photopolymerization of 2-(Hydroxymethyl)-6-methylene-1,4-dithiacycloheptane (**3a**).* 2-(Hydroxymethyl)-6-methylene-1,4-dithiacycloheptane (**3a**) (100 mg) and Darocur 1173 (0.38 mg) were mixed together in a polypropylene mold. No degassing or other preparation was performed. The mold was sealed, and the sample was photolyzed at 365 nm for 2 h (1 h for each side of the mold). After the reaction was completed, 10 mg of polymer/monomer was taken and diluted to 4 mL with THF and analyzed by GPC to give molecular weight and polydispersity given in run 2 of Table 1. The other samples of the polymer/monomer product were taken and analyzed by NMR and IR spectroscopy, and the spectra were as reported below.

*Thermal Polymerization of 7-Methylene-1,5-dithiacyclooctan-3-yl benzoate (**4c**).* 7-Methylene-1,5-dithiacyclooctan-3-yl benzoate (**4c**) (100 mg), AIBN (0.59 mg), and benzene (10 μL) were dissolved up to 0.5 mL in benzene-d_6 in a thick-walled 5 mm NMR tube. The solution was freeze$-$pump$-$thaw degassed three times, and the tube was flamed-sealed. The sample was heated at 70 °C with the polymerization being monitored periodically by NMR spectroscopy. The polymerization was stopped at 90% conversion as measured by the consumption of the monomer vinylidene peak at 4.9 ppm after 2.2 h. A sample of the solution was analyzed by GPC to give the molecular weight and polydispersity listed in run 15 of Table 1. The rest of the sample was purified by repeated dissolution in benzene and precipitation into methanol before finally dried under vacuum. The NMR and IR spectra were as reported below.

Poly(3a). Spectral data are of the sample taken directly of polymerization sample and contained monomer and polymer. ^{1}H NMR (200 MHz, DMSO-d_6 , 25 °C): δ 2.5$-$3.6 (m, all hydrogens except $=\mathrm{C}\mathbf{H}_2$ and $-\mathrm{C}\mathbf{H}_2\mathrm{OH}$) 4.8$-$5.2 (br s and m, $=\mathrm{C}\mathbf{H}_2$ and $-\mathrm{C}\mathbf{H}_2\mathrm{OH}$) ppm. ^{13}C NMR (50.3 MHz, DMSO-d_6, 25 °C): polymer signals δ 32.8, 34.2, 35.4 (all $-\mathrm{S}\mathbf{C}\mathrm{H}_2-$), 46.7 (**C**H), 62.5 ($-\mathrm{O}\mathbf{C}\mathrm{H}_2-$), 115.8 ($=\mathbf{C}\mathrm{H}_2$), 140.83, 141.31, 141.32, 141.75, 141.81 (all q vinylic $=\mathbf{C}$) ppm. Monomer signals δ 34.4,

Table 1. Characterization of Ring-Opened Polymers

run	monomer	temp (°C)	conditions, initiation[a]	time (h)	conversion (%)	M_w (M_w/M_n)
1	**3a**	70	neat thermal	19	57	35 000 (1.4)
2	**3a**	20	neat UV	2	77	31 200 (1.8)
3	**3b**	70	neat thermal	24	30	54 000 (2.4)
4	**3b**	70	neat thermal[f]	89	44	64 900 (1.9)
5	**3b**	90	neat thermal[f]	17	62	40 600 (2.6)
6	**3b**	20	neat UV	2	60	56 200 (2.2)
7	**3c**	70	neat thermal	17	100	xlinked
8	**3c**	20	neat UV	2	100	xlinked
9	**4a**	70	neat thermal	17	100	lightly xlinked[d]
10	**4b**	70	neat thermal	17	100	lightly xlinked[d]
11	**4b**	70	benzene thermal[c]	2.5	92	236 000 (1.9)
12	**4b**	70	benzene thermal[g]	2.2	90	79 500 (1.6)
13	**4b**	20	neat UV[b]	3	100	lightly xlinked[d]
14	**4c**	70	neat thermal	16	100	lightly xlinked[d]
15	**4c**	70	benzene thermal[g]	2.2	90	178 200 (2.0)
16	**5**	20	neat UV[b]	3	>90[e]	xlinked[e]

[a] Unless otherwise stated, UV initiator [Darocur 1173] = 1 wt %, UV cure 365 nm, thermal initiator [AIBN] = 1 mol %. [b] [Darocur 1173] = 2 wt % [c] [**4b**] = 2.0 M. [d] xlinked = cross-linked. Trace amounts of homopolymer were extractable with $CDCl_3$. [e] Some monomer extractable with $CDCl_3$. Conversion is estimated by comparison with extracted initiator and is therefore a lower limit. Actual conversion is likely to be higher. [f] [Vazo88] = 1 mol %. [g] [Monomer] = 0.71 M, [AIBN] = 0.0071 M.

37.9, 39.3, 52.0, 63.0, 111.0, 148.2 ppm. IR (thin film): 3369 br m, 3074 w, 2912 m, 1632 m, 1408 s, 1226 s, 1038 s, 906 vs 739 m cm^{-1}.

Poly(3b). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 2.10 (s, 3H, −C**H**$_3$), 2.65 (m, 2H, aliphatic C**H**$_2$), 2.90 (m, 1H, C**H**), 3.35 (m, 4H, allylic C**H**$_2$), 4.21 (m, 2H, −C**H**$_2$−OAc), 5.02 (apparent d, 2H, =C**H**$_2$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 20.9 (−**C**H$_3$), 33.31, 33.35, 33.39, 33.43, 35.10, 35.15, 36.20, 36.24, 36.29 (all −S**C**H$_2$−), 43.21, 43.36, 43.41 (**C**H), 65.1 (−O**C**H$_2$−), 116.00, 116.33, 116.61, 116.70 (all =**C**H$_2$), 140.70, 140.80, 140.84, 140.97 (all q vinylic =**C**), 170.5 (**C**=O) ppm. IR (thin film, CCl_4): 3077 w, 2933 m, 1740 vs, 1636 m, 1416 s, 1379 s, 1236 vs, 1036 s, 974 m, 911 s, 830 m cm^{-1}.

Poly(3c). IR (thin film): 3075 w, 2918 m, 1724 s, 1635 m, 1447 m, 1403, 1235 m 1142 s, 972m 905 m cm^{-1}.

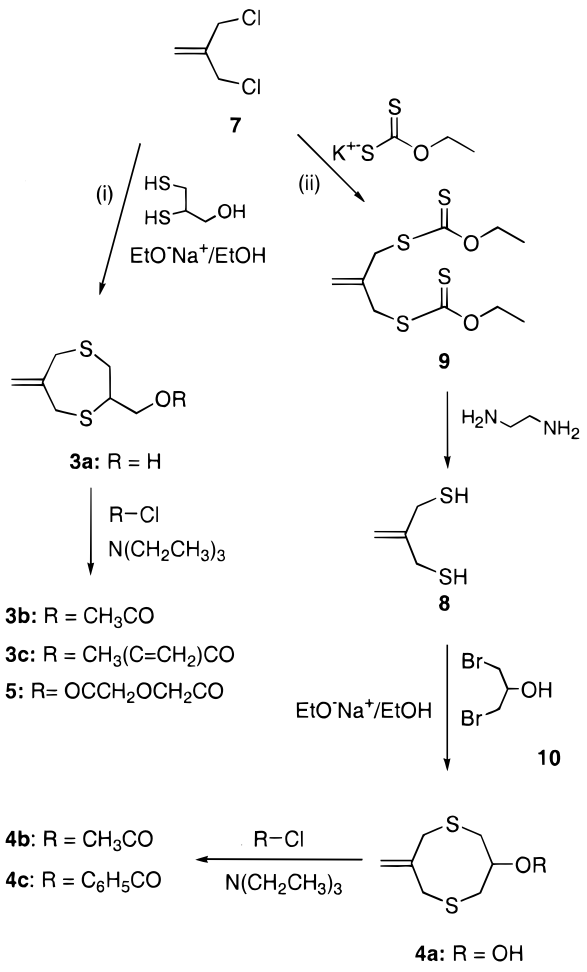
Poly(4a). ^{1}H NMR (250 MHz, THF-d_8, 25 °C): Signals are very broad due to polymer swelling. δ 2.5 (br m), 3.3 (br s), 3.6 (s), 4.3 (br s), 5.0 (s, =C**H**$_2$). ^{13}C NMR (62.9 MHz, THF-d_8, 25 °C): δ 39.5 (very low intensity), 36.5, 37.9 (both CH$_2$), 71.2 (**C**HOH), 116.2 (=**C**H$_2$), 142.6 (q vinylic =**C**) ppm. Addition of monomer **4a** gave additional peaks at 36.7, 38.2, 71.1, 119.3, and 147.5 ppm. IR (thin film): 3409 br s, 3076 w, 2913 s, 1639 m, 1412 s, 1294 m, 1226 s, 1030 s, 910 s cm^{-1}.

Poly(4b). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 2.10 (s, 3H, −C**H**$_3$), 2.64 (symmetrical m, 4H, aliphatic C**H**$_2$), 3.30 (s, 4H, allylic C**H**$_2$), 5.05 (s and m, 3H, =C**H**$_2$ and −C**H**O−) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ 21.1 (−**C**H$_3$), 33.5 and 35.6 (both −S**C**H$_2$−), 71.5 (−**C**HOAc), 117.0 (=**C**H$_2$), 140.0 (q vinylic =**C**), 170.2 (**C**=O) ppm. IR (thin film, CCl_4): 3078 m, 2934 m, 1742 s, 1637 m, 1397 m, 1233 s, 1011 m, 913 m cm^{-1}.

Poly(4c). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ 2.67 (s, 4H, aliphatic CH$_2$), 3.2 (s, 4H, allylic CH2), 4.95 (s, 2H, =CH2), 5.2 (m, 1H, −CH−O−), 7.4 (m, 3H, *m,p* aromatic), 7.9 (d, J = 8 Hz, 2H, *p*-aromatic) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ 33.6 and 35.7 (both −S**C**H$_2$−), 72.1 (−**C**HO−), 117.1 (=**C**H$_2$), 128.4, 129.7, 129.9, 133.1 (all aromatic), 139.1 (q vinylic =**C**), 155.7 (**C**=O) ppm. IR (thin film): 3068 vw, 2912 w, 1712 s, 1600 w, 1450 w, 1409 w, 1340 w, 1313 w, 1265 s, 1175 m, 1106 s, 1068 m, 1025 m, 980 m, 911 m cm^{-1}.

Poly(5). IR (thin film): 3075 w, 2913 m, 1754 s, 1633 m, 1407 m 1193 s, 1133 s, 1050 m, 997 m, 907m cm^{-1}.

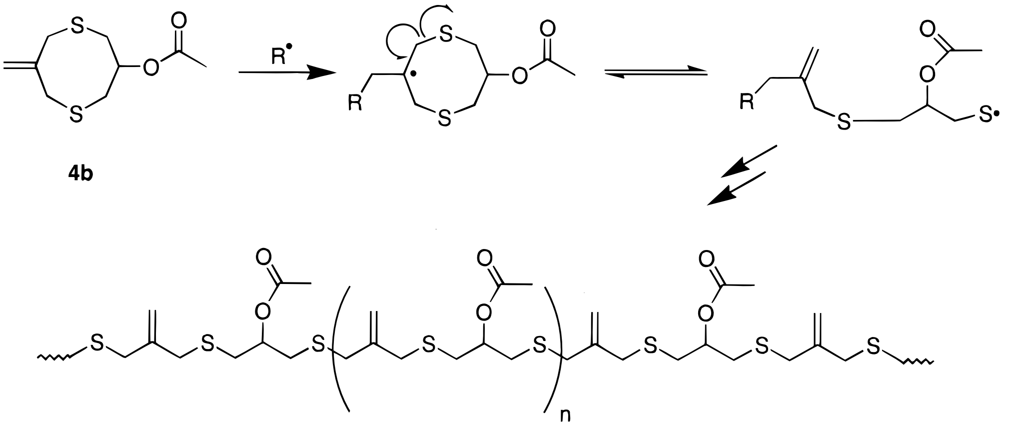
Scheme 1. Synthetic Pathways to Cyclic Allylic Sulfides 3−5



Results and Discussion

Monomers and Their Synthesis. We used two methods for synthesizing the functionalized cyclic allylic sulfides depending upon the availability of suitably functionalized dithiols. The substituted seven-membered ring monomers **3b, 3c**, and **5** were made from **3a** which was synthesized by reacting 3-chloro-2-(chloromethyl)-1-propene (**7**) with 2,3-dimercaptopropanol (Scheme 1(i)). However, the eight-membered ring monomers **4** were made from 3-mercapto-2-(mercaptomethyl)-1-propene (**8**) since 1,3-dimercapto-2-propanol is not commercially available. We could not reproduce the reported synthesis of 3-mercapto-2-(mercaptomethyl)-1-propene (**8**) and sought an alternative method.[26] 3-Mercapto-2-(mercaptomethyl)-1-propene (**8**) was successfully synthesized by converting the 3-chloro-2-(chloromethyl)-1-propene (**7**) to the bis-xanthate **9** followed by the liberation of the dithiol **8** with ethylenediamine

Scheme 2. Mechanism of Cyclic Allylic Sulfide Ring-Opening Polymerization



(Scheme 1b).[27] 3-Mercapto-2-(mercaptomethyl)-1-propene (**8**) was then reacted with 1,3-dibromo-1-propanol to give cyclic allylic sulfide **4a**.

The cyclic allylic sulfides were made under high dilution conditions using a syringe pump to control the slow addition of reagents to maximize the cyclicization reaction. The alcohols **3a** and **4a** were esterified to the various esters using the appropriate acid chloride and triethylamine (Scheme 1).

Ideally, monomers for low shrink applications should be liquids in order to polymerize in bulk. Monomers **3**, **4b**, and **5** were liquids with **5** being quite viscous. Monomers **4a** and **4c** were solids of moderate melting points (54−56 and 62−64 °C, respectively). The monomers (except for **3c**) were stable materials that withstood chromatography, acid/basic aqueous conditions, and storage without inhibitors at room temperature. Unlike the unsubstituted parent compounds **2**, all the monomers have very little or no odor.

Polymerization of Monomers. As described earlier, the unsubstituted parent monomers **2** are highly efficient ring-opening monomers.[1] Their polymers are crystalline and therefore have greater polymerization volume shrinkages than if the polymers were amorphous. The crystallinity arises from the highly ordered and symmetrical nature of the polymer backbone. Substituents on the monomers may interrupt this order and symmetry in the final polymers to give amorphous products with lower polymerization shrinkages. The mechanism of ring-opening polymerization is shown in Scheme 2. After radical addition has occurred to the monomer, the allylic carbon−sulfur bond fragments to give a new vinylidene group and a sulfur-centered radical which then adds to another monomer. The final polymer resembles the structure of the monomer as it too contains the allyl sulfide units and exo carbon−carbon double bonds. A primary concern in the field of low shrink polymerization is the ability of a monomer to polymerize in bulk under mild conditions to very high or preferably, complete conversion. Thus, we primarily examined our monomers under such conditions as summarized in Table 1.

Monomers **4b** and **3c** polymerized to complete conversion and **5** to high conversion at room temperature using Darocur 1173 as a UV photoinitiator. The polymers were colorless and transparent. In contrast to poly(**2a**) and poly(**2b**), poly(**4b**), poly(**3c**), and poly(**5**) were not crystalline. Monomers **3c** and **5** possess two polymerizable groups and are therefore formally cross-linking monomers. The polymers from **3c** and **5** are insoluble in solvents such as THF and chloroform presumably due to them being cross-linked. Monomer **4b** also gave an insoluble polymer, suggesting some cross-linking has occurred. Although **4b** is a monofunctional monomer, the polymer backbone possesses many vinylidene groups that have the potential to undergo further radical chemistry.

Poly(**3c**) did not swell in either THF or chloroform. Poly(**5**) swelled in THF and chloroform. Some residual monomer was extractable with $CDCl_3$. Poly(**4b**) greatly swelled in THF and chloroform, suggesting that cross-linking was not extensive. Trace amounts of soluble homopolymer could be extracted with $CDCl_3$. The other liquid monomers **3a** and **3b** photopolymerized to 77% and 60% conversion, respectively. This appears to be a limiting conversion due to the thermodynamics that effect ring-opening polymerizability of substituted seven-membered ring monomers. Generally the entropies and enthalpies of polymerization of seven-membered rings are small, making ΔG sensitive to the ring structure, substitutents, and reaction conditions with incomplete or no conversion often resulting.[25] Poly(**3a**) was soluble in THF and DMSO and poly(**3b**) in chloroform.

Thermal polymerizations of the monomers produced similar results. Monomers **4a**, **4b, 4c**, and **3c** produced insoluble polymers with complete conversion, whereas **3a** and **3b** did not achieve complete conversions (57% and 62%, respectively) and gave soluble polymers. Monomer **3b** was subsequently polymerized again at 70 °C for 89 h (VAZO88 initiator), and essentially the same conversion was obtained. This again appears due to the thermodynamics of seven-membered ring ring-opening polymerization and is consistent with observations for other types of ring-opening monomers both free radical and ionic.[25] The molecular weight of the soluble polymers ranged from ca. 25 000 to 60 000 polystyrene equivalents (Table 1). Poly(**4a**), poly(**4b**), and poly(**4c**) swelled greatly in THF again, suggesting that any cross-linking was not extensive. A trace amount of soluble homopolymer was extracted from poly(**4b**) with $CDCl_3$. Monomers **4b** and **4c** were polymerized in benzene at 70 °C and produced soluble polymers. The two monomer solutions were prepared at the same concentration and polymerized at the same rate to give 90% conversion after 2.2 h.

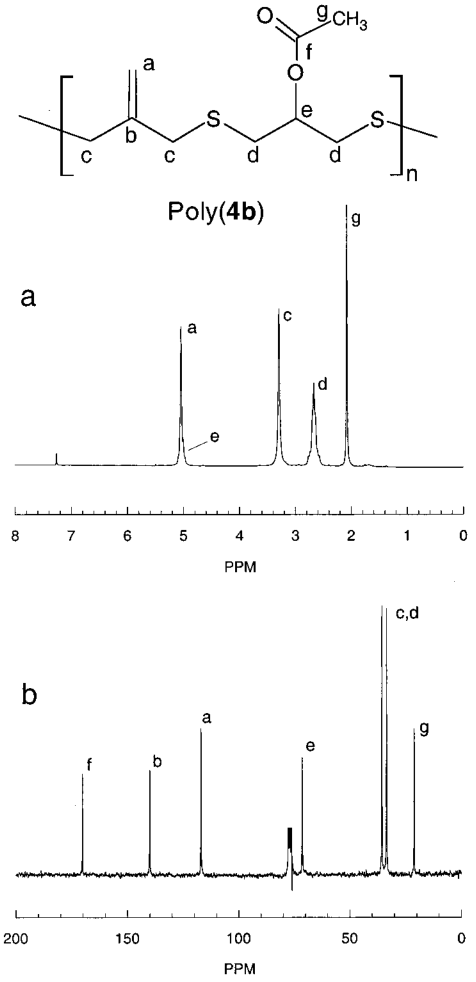


Figure 1. (a) ^{1}H and (b) ^{13}C spectra of poly(**4b**) in CDCl$_3$ at room temperature.

Spectroscopic Analyses. Monomer **4b** was also polymerized in benzene using AIBN as initiator at 70 °C. This produced a soluble polymer that could be easily analyzed by NMR spectroscopy. Figure 1a,b shows the ^{1}H and ^{13}C NMR spectra of poly(**4b**) in benzene-d_6. The polymerization was taken to 92% conversion as determined by NMR spectroscopy, and the spectrum shown is of polymer purified by precipitation in methanol to remove monomer. This was not a limiting conversion, but the reaction was stopped while the polymer was soluble to allow molecular weight analysis. The spectra clearly show all the structural components of the polymer. The simplicity of the spectra is due to the symmetry around each vinylidene group, which in turn is due to the symmetry present in the monomer itself. As Scheme 2 illustrates, it does not matter which carbon−sulfur bond breaks; the polymer will have a regular symmetrical structure. The ^{1}H NMR spectrum (Figure 1a) shows the expected peaks at with the key vinylidene peak appearing at 5.00 ppm, indicating that propagation by ring-opening with no 1,2 vinyl addition occurring. The ^{13}C NMR spectra (Figure 1b) similarly show the distinctive signals of the two vinylidene carbons at 116.5 and 140.4 ppm for carbons “a” and “b”, respectively.

Figure 2 shows the NMR spectra of poly(**3b**) obtained in bulk polymerization using AIBN and purified by precipitation into methanol to remove residual monomer. The spectra are more complex than those of poly(**4b**) as the monomer is unsymmetrically substituted. Since two different allylic carbon−sulfur bonds can break, the substituent is randomly distributed along the resultant polymer chain. The ^{1}H NMR spectrum (Figure 2a) shows the key vinylidene signal at 4.95 ppm together with the other peaks as assigned. Although the spectrum is more complex than poly(**4a**), there is no dyad sequence information discernible. The ^{13}C NMR spectrum similarly is consistent with the structure. The 125 MHz ^{13}C NMR spectrum shows apparent triplet signals at ca. 116 ppm (=**C**H$_2$) and 141 ppm (**C**=CH$_2$)-(Figure 2b insets) due to the four possible arrangements of substituent groups (*y,x x,x y,y x,y*) around a vinylidene group, two (*x,x y,y*) of which are degenerate (Scheme 3). Thus, the vinylidene carbons exhibit triplets. The triplet at 116 ppm has one of the peaks further split into a doublet due to resolution of cis and trans arrangements of the substituent in the *x,y* sequence. This triplet signal integrates into the expected 1:2:1 ratio. Similarly, the signal at 141 ppm showed a triplet with one of the peaks further split into a doublet due to the cis and trans arrangements. The peaks due to carbons c,c′,d,d′ are also partially resolved multiplets due to the various sequences of ring-opening, although none are as clearly assignable as those for the vinylic carbons.

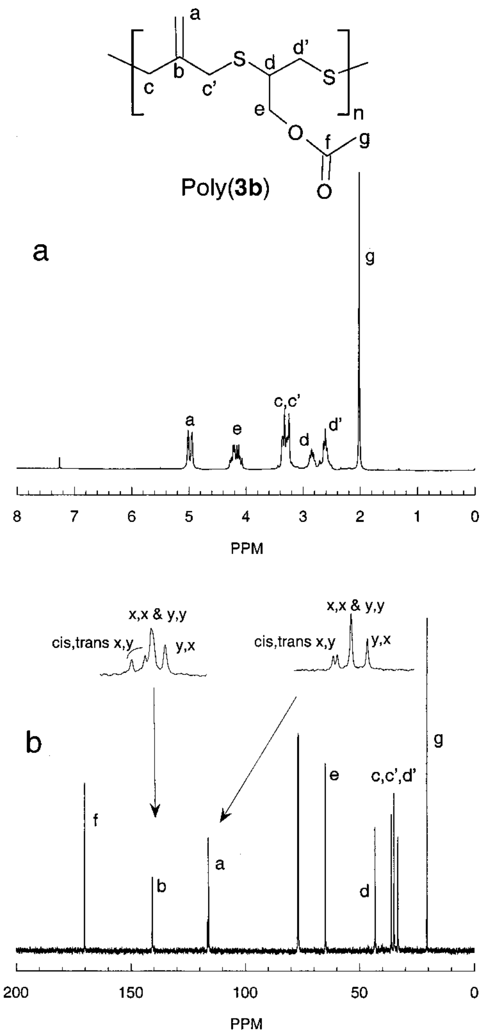
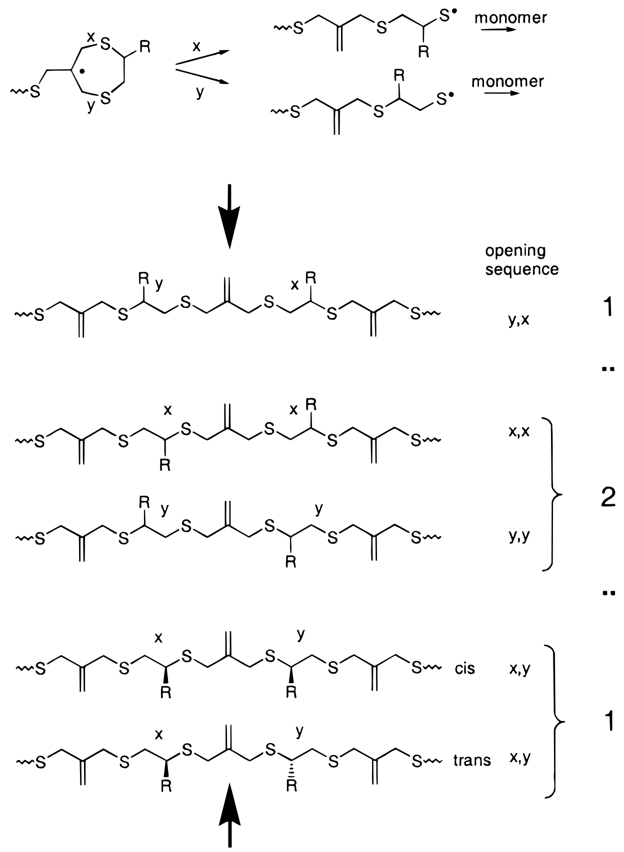


Figure 2. (a) ^{1}H and (b) ^{13}C spectra of poly(**3b**) in CDCl$_3$ at room temperature. Insets show expansions around 116 and 140 ppm. See text and Scheme 3 for details.

Figure 3 shows the ^{1}H and ^{13}C NMR spectra (DMSO-d_6) of a sample of material taken directly from the thermal polymerization of **3a** without purification. The

Scheme 3. Dyad Sequences in Poly(3a,b)



sample contains monomer and polymer. The ^{1}H NMR spectrum (Figure 3a) is complex with two groupings of signals, the $=CH_2$ and $-CH_2OH$ from monomer and polymer at 4.6–5.2 ppm and the other hydrogens from 2.4 to 3.6 ppm. Conversion cannot be determined from this spectrum because of the overlap of $=C\mathbf{H}_2$ and $-C\mathbf{H}_2OH$ monomer and polymer signals; however, in THF-d_8, the $-C\mathbf{H}_2OH$ (monomer and polymer) signal moves upfield clear of vinylidene region and allows conversion to be measured. In contrast to the proton spectrum, monomer and polymer signals can be clearly differentiated in the ^{13}C NMR spectrum (Figure 3b). As was observed in poly(**3b**) (Figure 2b), an apparent triplet signal for the quaternary vinylidene carbon ($\mathbf{C}=CH_2$) in poly(**3a**) was obtained (Figure 3b inset). This is due to the various arrangements of substituents around any vinylidene group in a polymer made from a substituted seven-membered cyclic allylic sulfide. The other peaks including the vinylidene carbon ($=\mathbf{C}H_2$) were simply broadened peaks with no multiplicity or other fine structure observed.

Figure 4 is a ^{13}C NMR spectrum of the insoluble poly(**4a**) swollen in THF-d_8. This spectrum is of a sample taken directly from the polymerization ampule with no precipitation or purification. The spectrum is similar to the spectra previously shown of non-cross-linked polymers. The symmetrically substituted monomer produces a very simple polymer spectrum as was observed for poly(**4b**) and poly(**4c**). As the sample was a gel, we verified that we were observing polymer signals and not simply extracted monomer by addition of genuine monomer **4a** (see Experimental Section). As the spectrum is so clean and the vinylidene carbon signals are quite prominent it seems that cross-linking is not extensive.

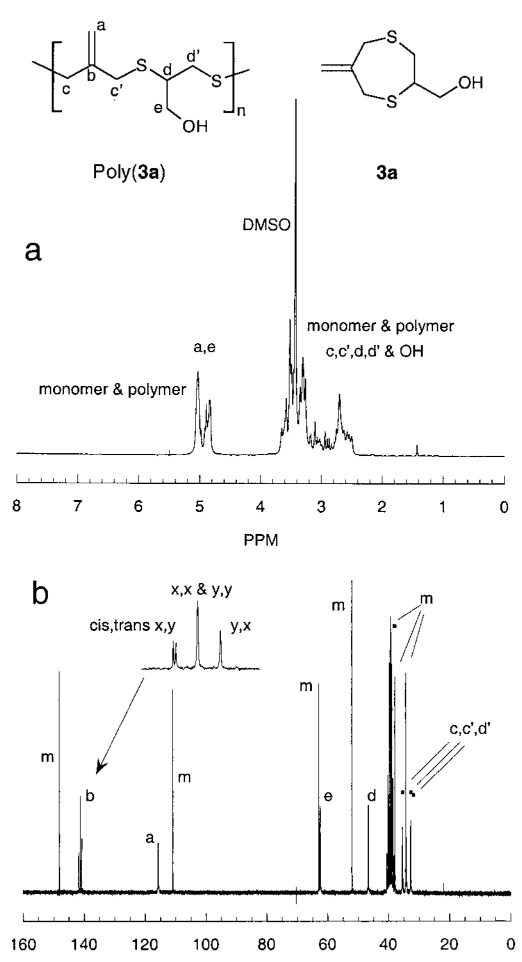


Figure 3. (a) ^{1}H and (b) ^{13}C spectra of poly(**3a**) in DMSO-d_6 at room temperature. Inset shows expansion around 140 ppm. See text and Scheme 3 for details. m = monomer.

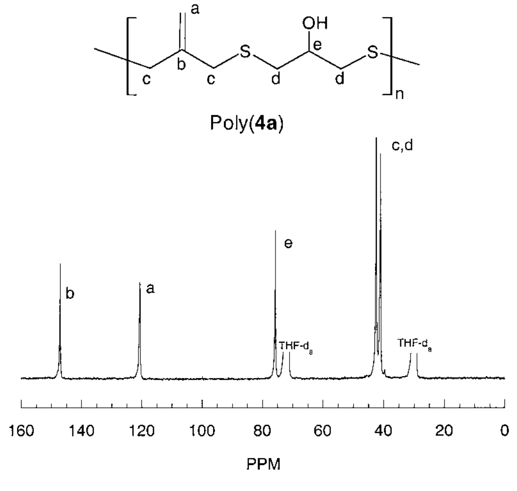


Figure 4. ^{13}C NMR spectrum of swollen gel of poly(**4a**) in THF-d_8 at room temperature.

The significant IR vibrations for vinylic C–H and C=C remain in all the polymer spectra as would be expected for the mechanism outlined (Scheme 2). The infrared spectra of monomer and its polymer appear very similar other than for minor changes in the fingerprint region. The greatest difference between monomer and polymer spectra was with monomer **3c** and poly(**3c**), but key structural elements remain in the

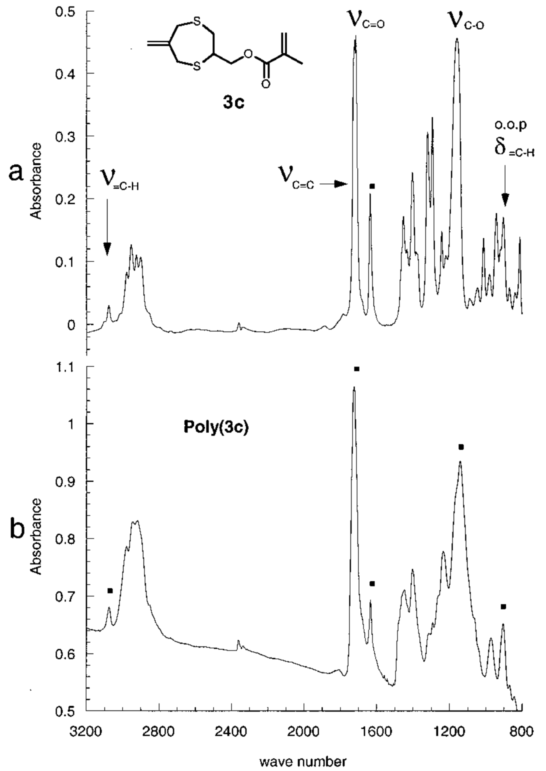


Figure 5. IR spectra of (a) **3c** and (b) poly(**3c**) as thin films.

polymer as evidenced by the $\nu_{=C-H}$, $\nu_{C=O}$, $\nu_{C=C}$, and oop $\delta_{=C-H}$ absorbances still present (Figure 5).

Our results have shown that substituents have a large effect not only on the polymerizability of the cyclic allylic sulfide type monomer but also on the final polymer itself. The seven-membered ring monomers **3a** and **3b** did not polymerize to complete conversion under our experimental conditions, and the polymers were sticky amorphous gums. This is in marked contrast to the behavior of the unsubstituted seven-membered ring monomer **2a** and its polymer.[1] The hybrid monomer **3c** did polymerize to complete conversion (no extractable monomer), but this would be largely due to the participation of the methacrylate group rather than the fact that the cyclic allylic sulfide was substituted. This is because the only point of difference between **3b** and **3c** is that **3c** possesses a polymerizable acrylic double bond. Crystallinity in a polymer that causes the polymer to precipitate, as happens in the polymerization of **2,** may provide an additional driving force to favor complete conversion as the polymerization is reversible.[25,28] Substitution in the seven-membered ring monomers did eliminate the crystallinity in the final polymers. The monomers did not polymerize to high conversion as they now showed behavior typical of a substituted seven-membered ring monomer—that behavior being a sensitivity to the nature of the substituent and reaction conditions, resulting in partial or no polymerizability.[25]

The substituted eight-membered monomers **4** gave polymers that appear highly symmetrical and could be crystalline (see Scheme 2, for example). However, the polymer will be a random tactic polymer due to the random placement of isotactic, syndiotactic, and heterotactic triads and thus be amorphous. The monomers **4a, 4b, 4c** were polymerizable to complete conversion with the final polymers being amorphous. In direct comparison to **3a** and **3b**, it appears ring strain in the eight-membered rings was sufficient to complete the polymerization.

The NMR spectra of the polymers also showed a number of interesting points. The polymers have great flexibility as evidenced by the sharpness of the spectral lines. This is illustrated in Figure 1 which shows the ^{1}H and ^{13}C NMR spectra of a polymer with a molecular weight of ca. 240 000 (polystyrene equivalents). In the case of the seven-membered ring monomers **3a** and **3b** the substituent had no effect on which allylic carbon—sulfur bond was broken. If, for example, the substituent enhanced the breaking of the ”y” bond (Scheme 3), then the statistical distribution of substituents around the vinylic carbons in the ^{13}C NMR spectrum (Figures 2b and 3b) would not have been observed.

The allylic sulfide type monomers polymerize only with ring-opening, and no 1,2 vinyl addition has yet been observed. Non-ring-opened fragments would be quite clear in the spectra as extraneous signals. Significant vinyl polymerization would also cause the integrals of the vinylidene hydrogens to be low relative to the other hydrogens as vinyl addition results in overall destruction of carbon—carbon double bonds whereas ring opening simply moves its position. No extraneous signals or reduction in relative integrations were observed at the limits of detection for the polymers for which we could analyze by NMR spectroscopy.

Bulk polymerization of monomers **4a** and **4b** to complete conversion gave polymers that were lightly cross-linked as suggested by their insolubility and swelling behavior. Two possible mechanisms of cross-linking are (i) radical addition and propagation through an in-chain carbon—carbon double bond and (ii) abstraction of an allylic hydrogen from the polymer backbone to give a radical that further reacts. A study of three other allylic sulfide monomers and model compounds of this type have shown that sulfur centered propagating radicals add to in-chain vinylidene bonds, but this is followed by fragmentation of the allylic carbon sulfur bond in the same manner that the monomers ring open.[28] This would not result in a cross-link. Although fragmentation is the predominant reaction after an addition, only a relatively small proportion of additions without subsequent fragmentation could create the observed gelations. Solution polymerization of monomer **4b** to high conversion gave soluble polymer as did bulk polymerizations of **3a, 3b**, and **4c.**

Polymerization Volume Shrinkage. Polymerization volume shrinkages were measured using densities of the monomers and polymers in the equation $[\rho_{\text{polymer}} - \rho_{\text{monomer}}]/\rho_{\text{polymer}}$. It calculates volume shrinkage relative to the initial volume of monomer and is also the one that has been used for the calculation of volume shrinkages for common monomers that appear in many tables.[29] The similar looking equation $[\rho_{\text{polymer}} - \rho_{\text{monomer}}]/\rho_{\text{monomer}}$, which was been occasionally used, calculates volume shrinkage relative to the final volume of the polymer. Thus, they calculate two different things, and care must be taken not to compare shrinkages calculated with one equation to those that have been calculated with the other. Although the difference in values each equation gives is small for very low polymerization shrinkages/expansions, it rapidly increases with increasing shrinkage/expansion. The density of a monomer should be measured in an amorphous state and not a crystalline one.[30] Polymerization volume shrinkages can appear to be very low or even appear as expansions

Table 2. Polymerization Volume Shrinkages

	density(g/cm^3)[a]			
monomer	monomer	polymer[b]	shrinkage (%)	T_g (°C)
3c	1.188	1.282	7.3	78
4b	1.217	1.234	1.4	−0.2
		1.244[c]	2.0	
5	1.295	1.323	2.1	28

[a] Measured in density gradient density tube at 20 °C. [b] UV initiated unless otherwise stated. [c] Run 10, Table 1, thermally initiated.

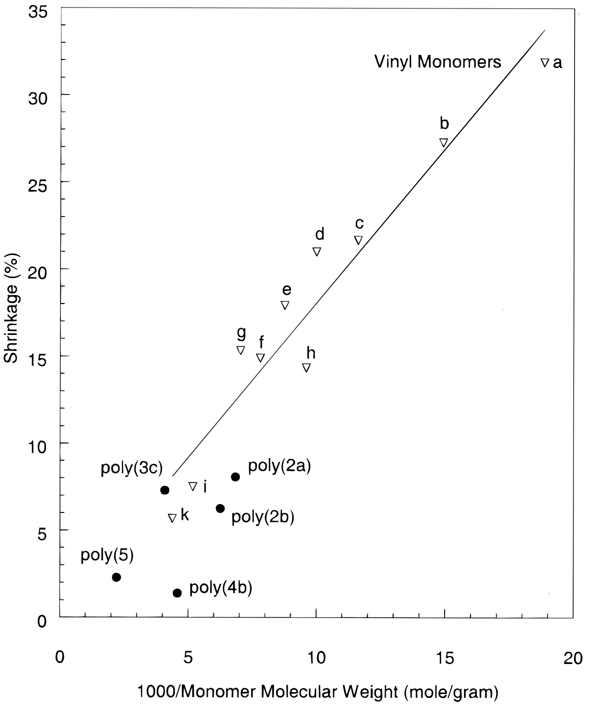


Figure 6. Variation of observed polymerization volume shrinkage with the molecular weight of monomer: (▽) vinyl monomers (a, acrylonitrile; b, methacrylonitrile; c, vinyl acetate; d, methyl methacrylate; e, ethyl methacrylate; f, *n*-propyl methacrylate; g, *n*-butyl methacrylate; h, styrene; i, *N*-vinylcarbazole; k, 1-vinylpyrene); (●) ring-opening monomers as labeled.

if crystalline monomer densities are used in their calculation. This is due to the volume expansion that occurs when a crystal melts to a liquid. Yet it is essentially in the amorphous (typically bulk liquid or solution) states that the polymerization (and hence polymerization shrinkage) occurs for practical applications. If the density of the liquid monomer is used, then higher shrinkage values are obtained.

Volume shrinkage measurements in this report were carried out on those liquid monomers that polymerized to complete or high conversion. Polymerization volume shrinkages for monomers **3c**, **4b**, and **5** are presented in Table 2. There is an approximately linear relationship between polymerization volume shrinkage and the inverse of the monomer's molecular weight (Figure 6).[31] Poly(**4b**) has not only low shrinkage in comparison to a conventional vinyl monomer but also low shrinkage in an absolute sense. Poly(**3c**) has higher shrinkage since it is a cross-linking difunctional monomer being compared to non-cross-linking monofunctional monomers. Poly(**5**) also shows low shrinkage. As it contains some residual monomer (estimated <10%) so its shrinkage for 100% conversion would be slightly higher. Figure 6 also displays the shrinkages previously reported for the crystalline poly(**2a**) and poly(**2b**)[1] and demonstrates that crystallinity in a polymer can significantly increase the volume shrinkage.

Glass transition temperatures for the three polymers poly(**3c**), poly(**4b**), and poly(**5**) are given in Table 2. Although the T_g's of the purely cyclic allylic sulfide polymers are higher than those reported for poly(**2**), the lack of crystallinity results in poly(**4b**) and poly(**5**) being rubbery or soft materials. This may be acceptable for some applications, but higher glass transition temperatures are always desirable for other important applications such as dental adhesives/composites and precision casting (optical lenses, etc.). The low T_g's arise from the flexibility of the polymer backbone of allylic sulfide polymers (Scheme 2). Thus, the new challenge with cyclic allylic sulfide polymerization is to develop methods that give stiffer the polymer backbones which does not also result in producing solid monomers or decreased polymerizability and ring-opening efficiency. The hybrid monomer **3c** has a significantly higher T_g of 78 °C due to the methacrylate derived groups in the polymer and a greater cross-link density. However, the price for the increased T_g is greater shrinkage as only one of the polymerizing groups is a ring-opening unit.

Conclusions and Outlook

Substituents on seven- and eight-membered cyclic allylic sulfide monomers (**3, 4**) can greatly modify the monomer's polymerizability and the nature of final polymers. The general effect is that the crystallinity that was present in the polymers of the unsubstituted monomers (**2**) is now eliminated in the polymers of the substituted monomers. Only 2% shrinkage was obtained for the liquid monomer **4b** polymerized at room temperature with an UV initiator to complete conversion**.** Ring size is also important with the substituted eight-membered rings generally polymerizing to higher conversions than the seven-membered ring monomers under similar conditions.

The cyclic allylic sulfide system continues to show great promise as a possible solution to polymerization volume shrinkage due to their general ease of handling and ability to polymerize under mild conditions. Examination of the effect of other substituents and ring size on this type of monomer is proceeding together with investigations of increasing the glass transition temperature of the polymers without otherwise compromising monomer polymerizability or low polymerization shrinkage behavior.

Acknowledgment. We thank Graeme Moad for valuable discussions and the following for their technical assistance in the course of this work: R. Ian Willing and Peter Pajalic (250 and 500 MHz NMR spectroscopy), Graeme Heath (microscope and ATR IR spectroscopy), Russell Varley and Julia Krstina (DMTA analyses), and Simon Harrisson (GPC analyses).

References and Notes

(1) Evans, R. A.; Rizzardo, E. *Macromolecules* **1996**, *29*, 6983−6989.

(2) Evans, R. A.; Rizzardo, E. *Low Shrink Polymerisation Using Ring-Opening Monomers*; World Polymer Congress, 37th International Symposium on Macromolecules, Gold Coast, Australia, 1998; p 159.

(3) Evans, R. A.; Rizzardo, E. *Free Radical Ring-Opening Polymerisation*; 21st Australian Polymer Symposium, Wollongong, Australia, 1996; pp 88−89.

(4) Evans, R. A.; Rizzardo, R.; Moad, G.; Thang, S. H. *Macromolecules* **1994**, *27*, 7935−7937.
(5) Rizzardo, E.; Chong, Y. K.; Evans, R. A.; Moad, G.; Thang, S. H. *Macromol. Symp.* **1996**, *111*, 1−11.
(6) Moszner, N.; Volkel, T.; Zeuner, F.; Rheinberger, V. *Synthesis and Radical Polymerization of 2-Vinylcyclopropanes*, World Polymer Congress, 37th International Symposium on *Macromolecules*, Gold Coast, Australia, 1998; p 952.
(7) Moszner, N.; Zeuner, F.; Rheinberger, V. *Macromol. Rapid Commun.* **1997**, *18*, 775−780.
(8) Moszner, N.; Völkel, T.; Rheinberger, V. *Macromol. Chem. Phys.* **1997**, *198*, 749−762.
(9) Schulze, T.; Klemm, E. *Angew. Makromol. Chem.* **1998**, *255*, 67−69.
(10) Schulze, T.; Letsch, J.; Klemm, E. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *24*, 81−87.
(11) Sugiyama, J.-i.; Kayamori, N.; Shimada, S.-i. *Macromolecules* **1996**, *29*, 1943−1950.
(12) Sugiyama, J.-i.; Ohashi, K.; Ueda, M. *Macromolecules* **1994**, *27*, 5543−5546.
(13) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1995**, *28*, 1346−1355.
(14) Evans, R. A.; Rizzardo, E.; Moad, G. Int. Pat. Appl. PCT/AU95/00859. US Patent 6,043,361, 2000.
(15) Rizzardo, E.; Evans, R. A.; Moad, G.; Thang, S. International Patent Application PCT/AU93/00667, WO 94/14792. US Patent 5,665,839, 1997.
(16) Stansbury, J. W. US Patent 5,463,008, 1995.
(17) Stansbury, J. US Patent 5,362,889, 1994.
(18) Klemm, E.; Schulze, T. *Acta Polym.* **1999**, *50*, 1−19.
(19) Evans, R. A. *Chem. Aust.* **1996**, 83−85.
(20) Endo, T.; Yokozawa, T. In *New Methods for Polymer Synthesis*; Mijs, W. J., Ed.; Plenum: New York, 1992; pp 155−77.
(21) Evans, R. A.; Moad, G.; Rizzardo, E.; Thang, S. H. *New Free-Radical Ring-Opening Monomers*, 20th Australian Polymer Symposium, Adelaide, Australia, 1995; pp 45−46.
(22) Meijs, G. F.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1988**, *21*, 3122−4.
(23) Meijs, G. F.; Morton, T. C.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1991**, *24*, 3689−95.
(24) Huang, R. L.; Goh, S. H.; Ong, S. H. *The Chemistry of Free Radicals*; Edward Arnold Ltd.: London, 1974.
(25) Ivin, K. J. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 1−14.
(26) Schulze, K.; Dietrich, E.-M.; Muhlstadt, M. *Z. Chem.* **1975**, *15*, 302−303.
(27) Mori, K.; Nakamura, Y. *J. Org. Chem.* **1969**, *34*, 4170−4172.
(28) Harrisson, S.; Evans, R. A.; Davis, T.; Rizzardo, E. Manuscript in preparation.
(29) Nichols, F. S.; Flowers, R. G. *Ind. Eng. Chem.* **1950**, *42*, 292−295.
(30) Bolln, C.; Frey, H.; Mulhaupt, R. *Macromolecules* **1996**, *29*, 3111−3116.
(31) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 3986−3991.

MA9917646