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Free-Radical Ring-Opening Polymerization of Cyclic Allylic Sulfides

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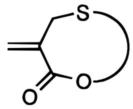
ABSTRACT: A new type of ring-opening monomer has been investigated and found to undergo facile and efficient free-radical polymerization. The monomers are cyclic allylic sulfides with 6-methylene-1,4-dithiepane (**3**) and 3-methylene-1,5-dithiacyclooctane (**4**) synthesized and investigated as two examples. 6-Methylene-1,4-dithiepane (**3**) is a clear oil and 3-methylene-1,5-dithiacyclooctane (**4**) has a low, near ambient temperature melting point, and in contrast to many ring-opening monomers, they readily survive exposure to moisture and aqueous acids and bases. These compounds were polymerized in bulk with complete ring opening to give highly insoluble crystalline homopolymers of high molecular weight (M_w ca. 500 000−700 000) with glass transition temperatures of ca. −30 to −50 °C and melting points of ca. 100−130 °C. The homopolymers and their 1:1 copolymer were characterized by FT-IR and high-temperature ^{1}H and ^{13}C NMR spectroscopies, high-temperature GPC, and DSC. They displayed volume shrinkages in the range expected of ring-opening monomers (4.5−8.5%) of their molecular weights in spite of the crystallinity present in the final polymers.

Introduction

There has been sustained interest in the study of free-radical ring-opening polymerization. This is due to the potential of ring-opening monomers to minimize the volume shrinkage that generally occurs during the polymerization process. Reports,[1−9] patents,[10−13] and reviews[14−16] in this field appear regularly in the literature and a monograph[17] has been published recently. We have previously reported a class of cyclic acrylate-based monomers (**1**) which readily polymerized with complete ring-opening.[1,2,10] From these results it is apparent that the key structural unit responsible for the facile ring opening is the allylic sulfide fragment in which the carbon−sulfur bond is readily cleaved. The cleavage of the carbon−sulfur bond produces a thiyl radical as the propagating radical species. Propagation by a sulfur-centered radical has a distinct advantage over propagation via oxygen- or carbon-centered radicals. Thiyl radicals readily add to many monomers[18,19] without significant competition from the side reaction of hydrogen abstraction (i.e. degradative chain transfer) which occurs to varying degrees with oxygen- and carbon-centered radicals.[20]

Thus, compounds of the generalized structure **2** may also be efficient ring-opening monomers. The compounds 6-methylene-1,4-dithiepane (**3**) and 3-methylene-1,5-dithiacyclooctane (**4**) were considered to be good specific examples of structure **2** suitable for further investigation. Cyclic allylic sulfides of the type **3** and **4** have appeared rarely in the literature,[21−25] and to the best of our knowledge there are no reports on their free-radical polymerizations. Monomers **5a**,**b** are the structurally closest monomers to **3** and **4** that have been previously reported. However, monomer **5a** polymerizes with only 15% ring opening while **5b** does not ring open at all.[14,26] We now report the use of cyclic allylic sulfides (**3**) and (**4**) as free-radical ring-opening monomers and their polymerization behavior.



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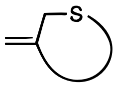

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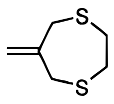

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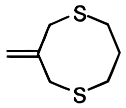

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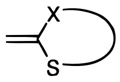

5 a X=O
b X=S

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra of monomers and polymers were recorded on either a Bruker 200 MHz or Bruker 250 MHz spectrometer using tetramethylsilane or hexamethyldisilane as internal standard in various deuterated solvents at the stated temperatures. FT-IR spectra were obtained with either a Biomem MB series or Mattson Instruments spectrometer. FT-IR spectra of samples were obtained using 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 ≥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). 1,2,4-Trichlorobenzene was used as eluent at 135 °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. Differential scanning calorimetry analyses were performed on a Metler TA3000 in conjunction with the GraphWare TA72.2/.5 software package. Heating rate was 10 °C/min.

Synthesis of 6-Methylene-1,4-dithiepane (3). A solution of 3-chloro-2-(chloromethyl)-1-propene (10 g, 80 mmol, Aldrich) and 1,2-ethanedithiol (7.5 g, 80 mmol, Fluka) was prepared

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in 80 mL of DMF. This solution was then added via a syringe pump over 20 h to a stirred solution of cesium carbonate (60 g, 180 mmol) in DMF (250 mL) at 60−70 °C under the protection of a calcium chloride drying tube. After the addition was complete, the reaction was stirred for an additional 24 h. The reaction was worked up by removing the DMF with a rotovapor (ca. 50 °C). The residue was triturated with ether a number of times, and the ether extracts were dried and evaporated to give 6.6 g of pale yellow oil. The oil was chromatographed on silica gel using hexane:dichloromethane (ca. 9:1) to give 3.5 g (30%) clear, foul-smelling oil.

^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, TMS, 25 °C): δ 3.00 (s, 4H, $\mathrm{SC\mathbf{H}_2C\mathbf{H}_2S}$), 3.65 (t, 4H, $J = 1.1$ Hz, $\mathrm{{=}CC\mathbf{H}_2S}$), 4.84 (pent, 2H, $J = 1.1$ Hz, $\mathrm{{=}C\mathbf{H}_2}$). ^{1}H NMR (250 MHz, pyridine-d_5, 90 °C, in the presence of its polymer): δ 2.90 (s, 4H, $\mathrm{SC\mathbf{H}_2C\mathbf{H}_2S}$), 3.65 (m, 4H, $\mathrm{{=}CC\mathbf{H}_2S}$), 4.84 (m, 2H, $\mathrm{{=}C\mathbf{H}_2}$). ^{13}C NMR (50.3 MHz, $\mathrm{CDCl_3}$, TMS, 25 °C): δ 38.8 and 38.9 (both $\mathrm{\mathbf{C}H_2S}$), 111.0 ($\mathrm{{=}\mathbf{C}H_2}$), 148.2 (quat =C). IR (thin film): 3073 w, 2946 m, 2899 s, 1810 br w, 1632 m, 1405 s, 1292 m, 1242 s, 1273 w, 1179 m, 1156 w, 904 s, 857 w, 815 m, 740 m, 677 w cm^{-1}. Mass spectrum (CI, $\mathrm{CH_4}$): m/z 147 ($\mathrm{M^{\bullet+}} + 1$, 100%), 101 (20), 87 (30). Mass spectrum (HR, CI): m/z 147.0298 ($\mathrm{C_6H_{10}S_2} + \mathrm{H}$ requires 147.0302). $n_\mathrm{D}^{20} = 1.5932$, $d^{20} = 1.162 \pm 0.004$ g/cm^3.

Synthesis of 3-Methylene-1,4-dithiacyclooctane (4). 3-Chloro-2-(chloromethyl)-1-propene (5 g, 40 mmol) was diluted to a volume of 58 mL with absolute ethanol and transferred to a 100 mL gastight syringe. Sodium metal (1.84 g, 80 mmol) was dissolved in absolute ethanol (40 mL) at ca. 10 °C under a nitrogen atmosphere protection. To the cold sodium ethoxide solution was added propane-1,3-dithiol (4.00 mL, 4.32 g, 40 mmol) and the solution was stirred for 30 min at room temperature. This solution was transferred to another 100 mL gastight syringe and diluted with absolute ethanol to a volume of 58 mL. The two solutions of 3-chloro-2-(chloromethyl)-1-propene and disodium propane-1,3-dithiolate were then added simultaneously with a syringe pump via separate Teflon feed lines to absolute ethanol (60 mL) at room temperature under nitrogen protection. The addition was performed over 2 h, during which a white precipitate of sodium chloride formed. After the addition was completed, the solution was refluxed for 1 h. The solvent was evaporated, water added, and the residue extracted with dichloromethane and ether. The solvents were dried and evaporated to give ca. 5.8 g of residue. The residue was triturated with ether and filtered through silica gel to remove the white solid. The ether extracts were evaporated to give 4.8 g of oil. The oil was chromatographed on silica gel (90% petroleum ether (60−80 °C), 10% ether) to give 3.0 g (47%) of a clear, foul-smelling oil. The oil slowly solidified when refrigerated and became a liquid/solid slurry at room temperature. Gentle heating easily melted the material into a clear mobile liquid that remained liquid at room temperature for a number of hours.

^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, TMS, 25 °C): δ 1.79 (m, 2H, $\mathrm{SCH_2C\mathbf{H}_2CH_2S}$), 2.88 (m, 4H, $\mathrm{SC\mathbf{H}_2CH_2C\mathbf{H}_2S}$), 3.25 (s, 4H, $\mathrm{{=}CC\mathbf{H}_2S}$), 5.20 (s, 2H, $\mathrm{{=}C\mathbf{H}_2}$). ^{1}H NMR (250 MHz, pyridine-d_5, 90 °C, in the presence of its polymer): δ 1.75 (m, 2H, $\mathrm{SCH_2C\mathbf{H}_2CH_2S}$), 2.88 (m, 4H, $\mathrm{SC\mathbf{H}_2CH_2C\mathbf{H}_2S}$), 3.25 (s, 4H, $\mathrm{{=}CC\mathbf{H}_2S}$), 5.15 (s, 2H, $\mathrm{{=}C\mathbf{H}_2}$). ^{13}C NMR (50.3 MHz, $\mathrm{CDCl_3}$, TMS, 25 °C): δ 29.4 ($\mathrm{S\mathbf{C}H_2CH_2\mathbf{C}H_2S}$), 30.0 ($\mathrm{SCH_2\mathbf{C}H_2CH_2S}$), 38.0 ($\mathrm{{=}C\mathbf{C}H_2S}$), 119.3 ($\mathrm{{=}\mathbf{C}H_2}$), 145.9 (quat =C). IR (thin film): 3074 w, 2949 s, 2837 m, 1811 br w, 1630 m, 1412 s, 1345 w, 1306 m, 1261 m, 1238 s, 1172 w, 903 s, 869 m, 739 s cm^{-1}. Mass spectrum (CI, $\mathrm{CH_4}$): m/z 161 ($\mathrm{M^{\bullet+}} + 1$, 100%), 160 (20), 101 (25) 61 (27). Mass spectrum (HR, CI); m/z 161.0479 ($\mathrm{C_7H_{12}S_2} + \mathrm{H}$ requires 161.0458). $n_\mathrm{D}^{20} = 1.5842$, $d^{20} = 1.141 \pm 0.004$ g/cm^3.

Polymerization of Cyclic Allylic Sulfides. General Procedure. Bulk polymerizations were carried out on a 200−400 mg scale using AIBN as an initiator. The monomer and initiator were placed in a thick-walled tube (ca. 5 mm external diameter and ca. 3 mm internal diameter) and flame sealed after degassing the contents by three freeze−pump−thaw cycles to 10^{-3} mbar.

Polymerization of 6-Methylene-1,4-dithiepane (3). 6-Methylene-1,4-dithiepane (**3**) (462 mg, 3.16 mmol) with AIBN (8.8 mg, 0.05 mmol, 1.6 mol %) was polymerized at 70 °C for 24 h in bulk as described above. A hard rigid white rod was formed. By NMR spectroscopy conversion was complete. ^{1}H NMR (250 MHz, DMSO-d_6, 90 °C): δ 2.65 (s, 4H, $\mathrm{SC\mathbf{H}_2C\mathbf{H}_2S}$), 3.30 (s, 4H, $\mathrm{{=}CC\mathbf{H}_2S}$), 5.08 (s, 2H, $\mathrm{{=}C\mathbf{H}_2}$). ^{1}H NMR (250 MHz, pyridine-d_5, 90 °C): δ 2.85 (s, 4H, $\mathrm{SC\mathbf{H}_2C\mathbf{H}_2S}$), 3.55 (s, 4H, $\mathrm{{=}CC\mathbf{H}_2S}$), 5.20 (s, 2H, $\mathrm{{=}C\mathbf{H}_2}$). ^{13}C NMR (62.9 MHz, DMSO-d_6, 90 °C): δ 30.7 and 34.9 (both $\mathrm{\mathbf{C}H_2S}$), 114.7 ($\mathrm{{=}\mathbf{C}H_2}$), 141.1 (quat =C). IR (neat): 3070 s, 2916 m, 1803 w, 1633 s, 1421 s, 1273 w, 1239 m, 1197 m, 1166 w, 1121 m, 901 s, 869 w, 742 m, 712 w, 700 w cm^{-1}. $d^{20}{}_{(\mathrm{av})} = 1.271 \pm 0.002$ g/cm^3.

Polymerization of 3-Methylene-1,5-dithiacyclooctane (4). 3-Methylene-1,5-dithiacyclooctane (**4**) (400 mg, 2.5 mmol) with AIBN (4.1 mg, 0.025 mmol, 1.0 mol %) was polymerized at 70 °C for 60 h in bulk as described above. The final polymer was a white, opaque, rigid rod. By NMR spectroscopy, conversion was complete. ^{1}H NMR (250 MHz, pyridine-d_5, 90 °C) δ 2.00 (pent, 2H, $J = 7.1$ Hz, $\mathrm{SCH_2C\mathbf{H}_2CH_2S}$), 2.70 (t, 4H $J = 7.1$ Hz, $\mathrm{SC\mathbf{H}_2CH_2C\mathbf{H}_2S}$), 3.48 (s, 4H, $\mathrm{{=}CC\mathbf{H}_2S}$), 5.2 (s, 2H, $\mathrm{{=}C\mathbf{H}_2}$). ^{13}C NMR (62.9 MHz, pyridine-d_5, 90 °C): δ 29.9 ($\mathrm{SCH_2\mathbf{C}H_2CH_2S}$), 31.3 ($\mathrm{S\mathbf{C}H_2CH_2\mathbf{C}H_2S}$), 36.7 ($\mathrm{{=}C\mathbf{C}H_2S}$), 115.3 ($\mathrm{C{=}\mathbf{C}H_2}$), 142.8 (quat). IR (neat): 3071 w, 2946 s, 2918 vs, 1842 w, 1633 m, 1404 s, 1340 m, 1292 m, 1266 m, 1227 s, 1173 w, 1128 w, 915 s, 867 m, 830 m, 759 m, 737 m cm^{-1}. $d^{20} = 1.223 \pm 0.004$ g/cm^3.

Copolymerization of 3 and 4. 6-Methylene-1,4-dithiepane (**3**) (192.2 mg, 1.30 mmol) and 3-methylene-1,5-dithiacyclooctane (**4**) (207.8 mg, 1.30 mmol) with AIBN (3.6 mg, 0.022 mmol, 1.6 mol %) was polymerized at 70 °C for 60 h in bulk as described above. The recovered polymer was a white, bendable solid that necked when pulled. ^{1}H NMR (250 MHz, pyridine-d_6, 90 °C): δ 1.98 (pent, $J = 7.0$ Hz, $\mathrm{SCH_2C}\boldsymbol{H}_2\mathrm{CH_2S}$), 2.68 (t, $J = 7.0$ Hz, $\mathrm{SC\mathbf{H}_2CH_2C\mathbf{H}_2S}$), 2.87 (s, $\mathrm{SC\mathbf{H}_2C\mathbf{H}_2S}$), 3.45 and 3.51 (both s, $\mathrm{{=}CC\mathbf{H}_2S}$), 5.20 (s, $\mathrm{{=}C\mathbf{H}_2}$). ^{13}C NMR (50.3 MHz, $\mathrm{CDCl_3}$, 25 °C): δ 28.5 ($\mathrm{SCH_2\mathbf{C}H_2CH_2S}$), 30.0 and 30.8 ($\mathrm{S\mathbf{C}H_2CH_2}$), 35.4 ($\mathrm{{=}C\mathbf{C}H_2S}$), 115.6, 115.8 and 116.0 (all $\mathrm{C{=}\mathbf{C}H_2}$), 140 (quat). IR (neat) 3072 w, 2913 s, 1813 br w, 1633 m, 1416 s, 1293 m, 1230 s, 1198 s, 1120 m, 1023 br m, 905 s, 742 m cm$^{-1.}$ $d^{20}{}_{(\mathrm{initial})} = 1.202$ g/cm^3, $d^{20}{}_{(1\ \mathrm{year})} = 1.223 \pm 0.004$ g/cm^3.

Depolymerization of Polymers. An initial test of thermal stability was performed on poly(**3**), poly(**4**) and poly(**3**-*co*-**4**). A sample of each polymer (1−2mg) was added to DMSO-d_6 (1 mL) in an NMR tube, heated at 130 °C for 1−2 h, and then examined by ^{1}H NMR spectroscopy. Poly(**4**) and poly(**3**-*co*-**4**) showed some minor decomposition/depolymerization to their constituent monomers and other unidentifiable products. In contrast, poly(**3**) cleanly produced the monomer **3**. This was further investigated. A sample of poly(**3**) (2.3 mg), *tert*-butylbenzene (1.0 mg) as reference, and DMSO-d_6 were added to an NMR tube, and the solution was degassed under vacuum and flame sealed. The sample was then heated at 130 °C. Through the use of *tert*-butylbenzene as the internal calibration standard, it was possible to determine the approximate extent of depolymerization. The extent of depolymerization was found to be ca. 10% after 1 h, ca. 40% after 3 h and remained at ca. 40% after 20 h.

Results and Discussion

Monomers and Their Synthesis. There have been few reports of compounds of type **3** and **4** in the literature. The reports that have appeared have been concerned with the syntheses of the compounds[22−25] and/or their subsequent functionalization.[21] Their synthesis has been achieved in two ways. The first is the reaction between the commercially unavailable but highly desirable 2-(mercaptomethyl)-3-mercapto-1-propene[27] and a dihaloalkane[24] and the second is the reaction between commercially available 2-(chloromethyl)-3-chloro-1-propene and a dithiol.[21] For this study, the reaction of 2-(chloromethyl)-3-chloro-1-propene and 1,2-ethanedithiol or 1,3-propanedithiol was used (Scheme 1).

Initially, the reaction was performed under high-dilution conditions in DMF using cesium carbonate (Scheme 1, path a). Although successful, it was desir-

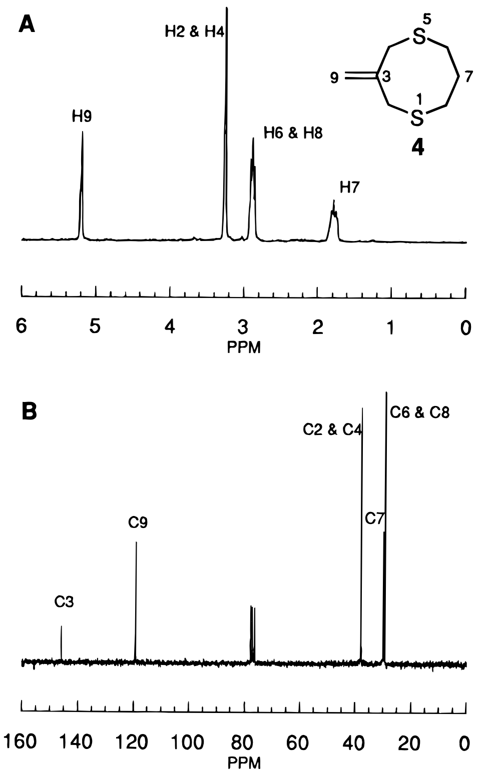
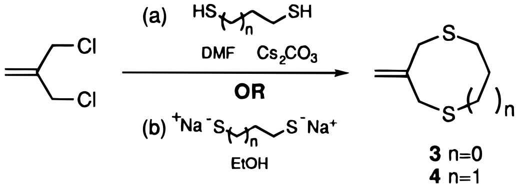


Figure 1. (A) ^{1}H and (B) ^{13}C NMR spectra of 3-methylene-1,5-dithiacyclooctane (**4**) in $CDCl_3$ at room temperature.

Scheme 1



able to avoid the difficulties and expense of using DMF and cesium carbonate, and an alternative method was sought. It was found that simultaneous addition of separate ethanolic solutions of (i) 2-(chloromethyl)-3-chloro-1-propene and (ii) the disodium salt of the dithiol to ethanol at room temperature gave slightly better yields with cleaner workup (Scheme 1, path b). 6-Methylene-1,4-dithiepane (**3**) was a clear oil and 3-methylene-1,5-dithiacyclooctane (**4**) had a low, near ambient melting point. Both compounds had penetrating unpleasant smells. They readily survived acidic or basic workup conditions and were quite stable, easily handled compounds. 6-Methylene-1,4-dithiepane (**3**) could be stored at room temperature for months with no apparent decomposition/polymerization; however, 3-methylene-1,5-dithiacyclooctane (**4**) polymerized after a few weeks. Both compounds could be stored indefinitely when refrigerated at -13 °C. The ^{1}H and ^{13}C NMR spectra of 3-methylene-1,5-dithiacyclooctane (**4**) are shown in parts A and B of Figure 1, respectively.

Radical Homopolymerizations of 3 and 4. Based on the observed polymerization behavior of cyclic allylic sulfide acrylates **1**,[1,2] compounds **3** and **4** would be expected to polymerize with ring opening via intermediates **6** and **7** as shown in Scheme 2 to give polymers with repeat units **8** and **9**. Note that the repeat unit also contains an allylic sulfide group. This has the potential for further reaction by either undergoing fragmentation itself after radical addition or acting as a point of cross-linking if fragmentation does not occur.

Scheme 2

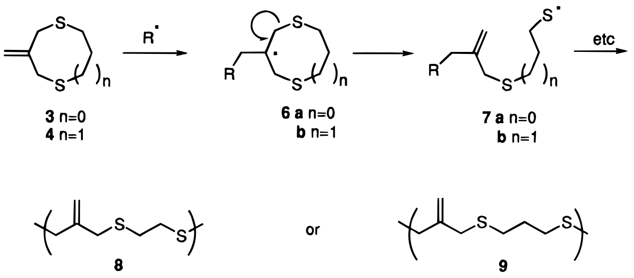


Table 1. Characterization of Poly(3), Poly(4), and Poly(3-*co*-4)

monomer(s)	conditions[a] (time)	conv (%)	M_w[c]	dispersity
3	bulk (24 h)[b]	ca. 100	687 000	3.8
4	bulk (60 h)[b]	ca. 100	486 000[d]	2.4
3:**4** (1:1)	bulk (60 h)	86:100	*e*	*e*

[a] Polymerization temperature 70 °C using 1 mol % AIBN. [b] The monomers polymerized into a solid white block in about 20−30 min but to ensure a complete as polymerization as possible, they were heated for at least 24 h. [c] Polystyrene equivalents. [d] Soluble fraction as sample did not completely dissolve. [e] No reliable results.

It was hoped to follow the homopolymerizations in benzene at 70 °C by ^{1}H NMR spectroscopy to high conversions. However, in the homopolymerization of **3**, a white precipitate of poly(**3**) formed within minutes of heating the sample in the NMR tube. The polymerization was followed (with increasing amounts of precipitate being formed) to 42% conversion after only 100 min at 70 °C and thereafter ^{1}H NMR spectroscopy was not possible. Although the insolubility was unexpected, the apparent speed of polymerization was encouraging. The homopolymerizations were then performed in bulk at 70 °C with AIBN as initiator. White precipitates of poly(**3**) or poly(**4**) were again formed within 15 min, and heating was continued for 24−60 h to ensure completion. When the polymers were recovered, they were solid white rods. Poly(**3**) was quite hard and brittle, and poly(**4**), while still hard, could be cut or shaved by a scalpel. The polymers were insoluble and showed no swelling in a range of solvents (chloroform, tetrahydrofuran, pyridine, benzene, dimethylformamide, chlorobenzene, 1,2,4-trichlorobenzene and 2% hexafluoro-2-propanol in chloroform) at room temperature with the sole exception of poly(**4**), which was swollen by a mixture of 2% hexafluoro-2-propanol in chloroform.

Characterization data of the polymers appear in Table 1. Figure 2A shows the ^{1}H NMR spectrum of poly(**3**) in pyridine-d_5 at 90 °C, with the expected peaks at 5.2 (vinylic), 3.5 ($C{=}CCH_2S$), and 2.8 ppm (SCH_2CH_2S) in the ratio of 1:2:2. Note the simplicity of the spectrum due to the highly symmetrical structure of the polymer. There was no unreacted monomer present in the polymer, and this was confirmed by the addition of genuine **3** to the solution and rerecording the spectrum. (Figure 2B). Figures 2A and 2B show clearly that efficient ring opening had occurred with no unopened units present in the polymer due to conventional vinyl polymerization. Although poly(**3**) was quite an insoluble polymer, it was not cross-linked (possibly via the backbone vinyl groups) as it dissolved in hot pyridine and precipitated on cooling (ca. 1 mg/mL). Interestingly, when another sample of poly(**3**) was heated in DMSO-d_6 at 120 °C for ca. 20 min; the ^{1}H NMR spectrum recorded at 90 °C showed the presence of monomer **3** (the spectrum looked very similar to Figure 2B). Since

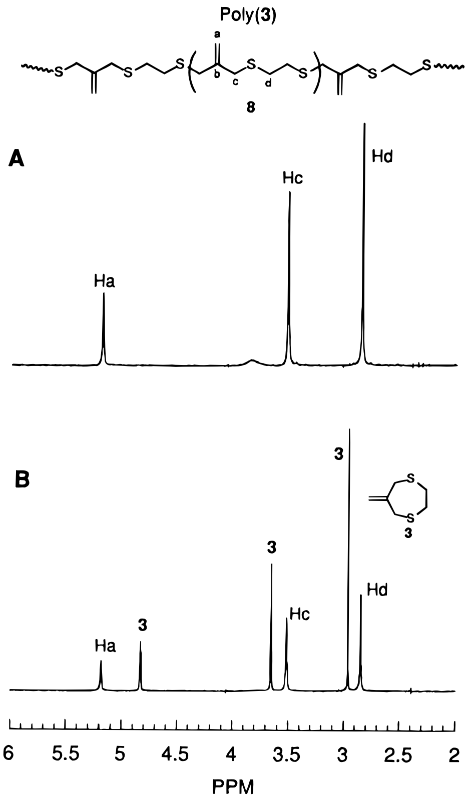


Figure 2. ^{1}H NMR spectra of (A) poly(**3**) consisting of repeat unit **8** and (B) poly(**3**) with monomer **3** added to the solution. Both in pyridine-d_5 at 90 °C.

no monomer was present in the sample of poly(**3**) initially (Figure 2A), we concluded some depolymerization of the polymer had occurred. A further experiment showed that the poly(**3**) cleanly underwent ca. 40% depolymerization to monomer **3** in DMSO-d_6 (1.2 mg/mL) at 130 °C in 2 h. Further heating did not increase the extent of depolymerization. This depolymerization was greatly suppressed when trichlorobenzene was used as a solvent. When poly(**4**) and poly(**3**-*co*-**4**) were heated in DMSO-d_6 at 130 °C, neither of them showed this facility for rapid and clean depolymerization. The difference in the behavior between these two polymers (poly(**4**) and poly(**3**-*co*-**4**)) and poly(**3**) is likely to be largely due to the thermodynamics of ring-opening polymerization; seven-membered ring monomers may be regenerated by depolymerization under suitable conditions. However, the greater ring strain present in eight-membered ring monomers makes their regeneration from their polymers far more unfavorable.[28]

Similarly, the spectra of poly(**4**) in pyridine-d_5 at 90 °C show the polymer to consist of ring-opened repeat unit **9** (Figure 3). The ^{1}H NMR spectrum shows the required signals at 5.2 (vinylic), 3.5 ($C{=}CC\mathbf{H_2}S$), 2.7 ($SC\mathbf{H_2}CH_2C\mathbf{H_2}S$), and 2.0 ppm ($SCH_2C\mathbf{H_2}CH_2S$) in the ratio 1:2:2:1 (Figure 3A). Addition of monomer **4** to the solution confirmed that the above signals were due to the polymer and not residual monomer. The ^{13}C NMR spectrum shows the distinctive signals of the two vinyl carbons "a" and "b" at 114.8 and 142.3 ppm, respectively (Figure 3A). As in the case of poly(**3**), note the simplicity of the spectra as a result of the symmetrical structure of the polymer. The majority of poly(**4**) greatly swelled in hot pyridine with a minor amount dissolving (as evidenced by its precipitation on cooling). This observation together with the narrow line widths seen in the NMR spectra indicates that some light cross-linking has occurred in some of the sample. Poly(**3**) and poly(**4**) observed insolubility, opacity, and physical properties suggest that they are semicrystalline polymers. This will be discussed further below.

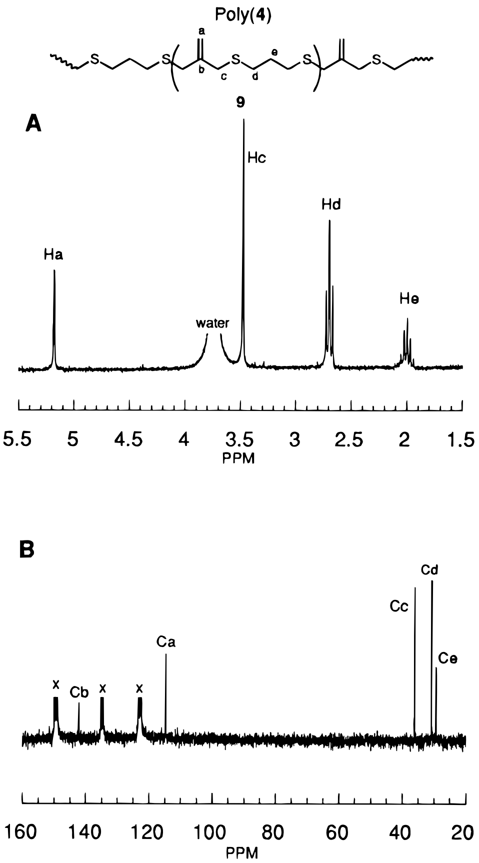


Figure 3. ^{1}H and ^{13}C NMR spectra of poly(**4**) consisting of repeat unit **9** in pyridine-d_5 at 90 °C. × = pyridine-d_5.

Radical Copolymerization of 3 and 4. Monomers **3** and **4** were copolymerized together in a 1:1 mole ratio. In contrast to the homopolymers of **3** and **4**, the resulting pale white copolymer could be easily bent and necked when pulled. Although it still did not dissolve at room temperature, the copolymer became clear and swelled in many solvents (chloroform, tetrahydrofuran, pyridine, benzene, chlorobenzene, trichlorobenzene, and 2% hexafluoro-2-propanol in chloroform) but not in dimethylformamide. Figures 4A and 4B show the ^{1}H and ^{13}C NMR spectra of poly(**3**-*co*-**4**), respectively.

The ^{1}H NMR spectrum of poly(**3**-*co*-**4**) in pyridine-d_5 at 90 °C shows the repeat units **8** and **9** and a trace of residual monomer **3** (Figure 4A). The conversions of **3** and **4**, as determined by integration, were 87 and 100%, respectively, indicating that **4** is slightly more reactive than **3**. This may be due to the greater ring strain present in an eight-membered ring versus a seven-membered ring.[29] As might be expected with two very similar repeat units, there is no evidence of sequence distribution in the spectrum. The similarity of their respective regions in the ^{1}H NMR spectrum (Figure 4A) show that each repeat unit is in essentially the same environment as it was in its corresponding homopolymer. Any given hydrogen in the backbone is at least seven bonds away from the first point of difference with respect to its homopolymer environment.

The ^{13}C NMR spectrum of poly(**3**-*co*-**4**) in $CDCl_3$ is consistent with the copolymer being a random copolymer made of repeat units **8** and **9** (Figure 4B). The expansion of the carbon signal due to carbon "a" ($C{=}\mathbf{C}H_2$) of the vinyl group at ca. 115 ppm reveals a triplet with peak heights of ca. 1:2:1 (inset of Figure 4B) due to the expected sequence distribution in the 1:1

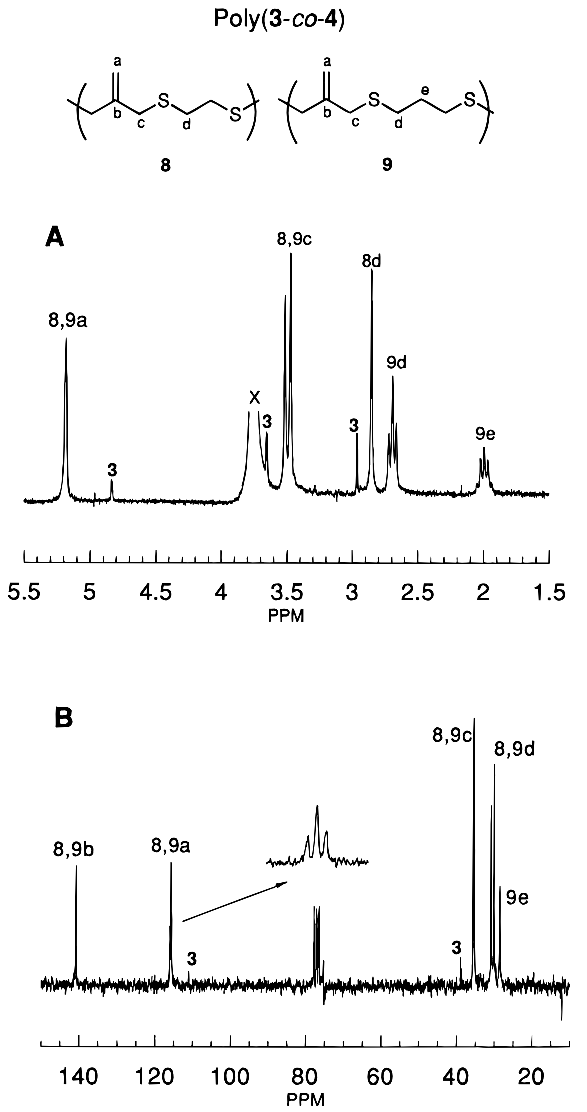


Figure 4. (A) ^{1}H NMR spectra of poly(**3**-*co*-**4**) consisting of repeat units **8** and **9** in pyridine-d_5 at 90 °C. Residual monomer **3** present. × = water (B) ^{13}C NMR spectra of poly(**3**-*co*-**4**) in CDCl$_3$ at room temperature. Inset shows expansion around signal at 115.7 ppm, illustrating evidence of sequence distribution. The spike at ca. 76 ppm is a spectrometer-generated artifact.

copolymer assuming near-equal reactivity of the comonomers. Scheme 3 illustrates the possible sequences centered around a given vinyl group in the copolymer and the origin of the observed triplet. It can be seen that there are three different types of vinyl groups, (i) one with ethylene units on both sides (Scheme 3 A), (ii) two equivalent combinations having an ethylene on one side and a propylene on the other (Scheme 3 B and 3C), and (iii) one with propylene units on both sides (Scheme 3D). Although a triplet was observed for carbon "a", no multiplicity was observed for the other vinylic carbon "b" (**C**=CH$_2$) at 140.8 ppm. Similarly for the allylic carbons "c", there are essentially two types, those that are next to (i) ethylene groups and (ii) propylene groups. Inspection of the carbon signal due to allylic carbons "c" at ca. 35 ppm revealed a partially resolved doublet. The copolymer dissolved completely in hot pyridine and was not cross-linked. The above results show that **3** and **4** readily copolymerize with propagation occurring exclusively via ring opening as was observed in the homopolymerizations of the individual monomers.

Scheme 3

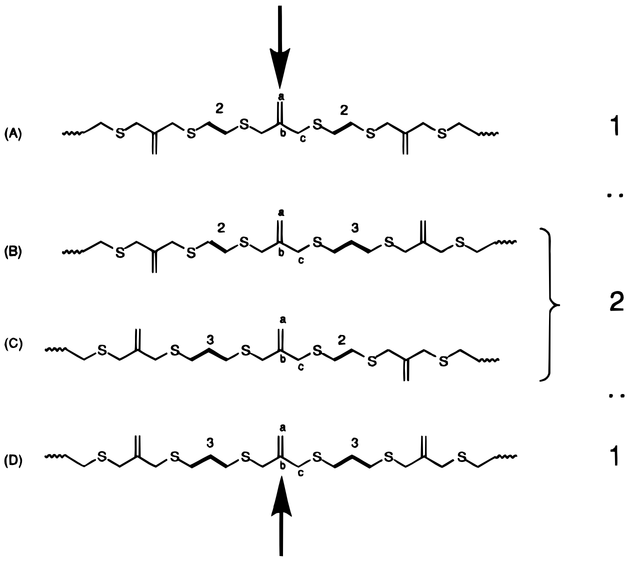


Table 2. Characteristic Infrared Absorptions of Poly(3), Poly(4), and Poly(3-*co*-4)

		infrared vibrational modes (cm^{-1})				
monomer		$\nu_{=\mathrm{C-H}}$	$\nu_{\mathrm{C=C}}$	δ_{CH}	o.o.p. $\delta_{\mathrm{C-H}}$	o.o.p. $\delta_{\mathrm{C-H}}$ overtone
3	monomer[a]	3074 sh w	1633 m	1404 s	904 s	1810 br w
	polymer[b]	3070 sh s	1633 s	1421 s	901 s	1803 w
4	monomer[a]	3075 sh w	1631 m	1412 s	903 s	1810 br w
	polymer[b]	3071 sh w	1633 m	1404 s	915 s	1842 w
3:**4** (1:1)	copolymer[b]	3072 sh w	1633 m	1416 s	905 s	1812 w

[a] Thin film. [b] Neat sample. sh, sharp; s, strong; m, medium; w, weak; o.o.p., out-of-plane.

Infrared Spectroscopic Analysis. Infrared spectroscopy provided further evidence that the backbone of the polymers consisted of the appropriate ring-opened unit(s) (**8** and/or **9**). The key infrared bands are tabulated in Table 2. The most characteristic bands occur at ca. 3070, ca. 1800–1840, and 1633 cm^{-1}, which correspond to the vinylic $\nu_{\mathrm{C-H}}$, the out-of-plane vinylic $\delta_{=\mathrm{C-H}}$ overtone and the vinylic $\nu_{\mathrm{C=C}}$ stretch, respectively.[30] Other major bands were of the aliphatic $\nu_{\mathrm{C-H}}$, aliphatic δ_{CH}, and out-of-plane $\delta_{=\mathrm{C-H}}$ vibrational modes. The infrared spectra of monomers **3** and **4**, poly(**3**), poly(**4**), and poly(**3**-*co*-**4**) all appear essentially the same, with only minimal differences occurring in the fingerprint regions of the spectra.

Molecular Weight Determination. The co- and homopolymers of **3** and **4** were insoluble in solvents at room temperature and so conventional GPC analysis of the polymers was not possible. However, poly(**3**) and poly(**3**-*co*-**4**) could be dissolved (at least 2 mg/mL) in trichlorobenzene at 135 °C. Poly(**4**) only partially dissolved, indicating it was a partially and lightly cross-linked polymer. Thus, high-temperature GPC analysis of the polymers could be attempted with the provison that molecular weights observed may be lower and/or distributions wider than actual due to partial depolymerization (poly(**3**)) or selective extraction of a soluble fraction (poly(**4**)) of the samples. Table 1 shows the molecular weight (polystyrene equivalents) of the two homopolymers poly(**3**) and poly(**4**) obtained by high-temperature GPC. A reliable result for the copolymer could not be obtained as its refractive index appears to be near that of trichlorobenzene and confounded accurate analysis. The molecular weights of the polymers are high in both cases and between 1 and 2 orders of magnitude higher than molecular weights generally observed from other free-radical ring-opening polymerizations[1,7,31,32] with the exception of recent results reported by Sugiyama et al.[6]

Thermal Analysis. The observed insolubility, color, physical properties and structural symmetry of the polymers and copolymer of **3** and **4** were consistent with the polymers being semicrystalline. This warranted an investigation of their thermal behavior. A small sample of the poly(**3**) was placed in a melting point capillary and heated in a melting point apparatus. Poly(**3**) was a white opaque solid at room temperature but on reaching ca. 120 °C, it became transparent without apparent deformation. At 160 °C deformation had occurred and decomposition accompanied by decoloration occurred above 220 °C. This behavior was consistent with poly(**3**) being a semicrystalline polymer. Poly(**4**) showed similar behavior with decoloration and decomposition occurring above 200 °C. Its transition from opaque to transparent (ca. 100 °C) was not as easily observed as thin shavings of poly(**4**) were already partially transparent. These polymers showed the same behaviour on repeated heating/cooling cycles. Thus, poly(**3**) and poly(**4**) had melting point transitions at ca. 120 and 100 °C, respectively.

The glass transition and melting points of the polymers were determined by differential scanning calorimetry (DSC). The melting points recorded match the visual observations above. The DSC heating traces of poly(**3**) and poly(**4**) are characterized by narrow, symmetrical melting point transitions at 129 and 100 °C, respectively, and glass transition temperatures of −30 and −51 °C, respectively (Figure 5A,B). The narrowness of the melting points is consistent with highly linear polymers. Poly(**3**-*co*-**4**) shows none of the stiffness or brittleness of the homopolymers and is presumably less crystalline. It has a DSC trace showing an asymmetric melting point at 53 °C and a glass transition at −47 °C, with some crystallization occurring slightly above that temperature (Figure 5C). As these are all new polymers, it is not possible to quantify the degree of crystallinity present in them from DSC experiments. The best that can be presently said is that the homopolymers appear to be highly crystalline and the copolymer much less so. The formation of a crystalline polymer is an additional driving force in favor of propagation.[28] Therefore, the high crystallinity of the homopolymers is likely to have been a contributing factor toward the high molecular weights observed.

Volume Shrinkage. The shrinkage that accompanies polymerization generally decreases with increasing molecular weight (size) of the monomer.[33] Furthermore, for a given molecular weight, a ring-opening monomer will shrink less than a vinyl monomer. This observation has been illustrated by plotting shrinkage versus the inverse of the molecular weight (Figure 6).[6] For this report, all shrinkages were calculated relative to the initial volume of monomer(s) using the formula $[(\rho_{\text{polymer}} - \rho_{\text{monomer(s)}})/\rho_{\text{polymer}}] \times 100\%$. The densities of the monomers **3** and **4**, their homopolymers, and copolymer were measured in a density gradient tube at 20 °C, and the results appear in Table 3. The poly(**3**) and poly(**4**) showed shrinkages of ca. 8.6 and 6.7%, respectively. The copolymer poly(**3**-*co*-**4**) showed an increase in density over time, with a new sample having a density of 1.202 g/cm^3 and one year later it had become 1.228 g/cm^3. This is likely to be due to slow crystallization of the sample and results in the polymerization shrinkage changing from an initial 4.5% to a final 6.3%. Although the polymers possess a significant degree of crystallinity, which causes extra contraction,[15] the shrinkages of these monomers fall well below the expected shrinkages of vinyl monomers into the range of values expected of ring-opening monomers (Figure 6 and Table 3). Thus, suitable derivatives of **3** or **4** that break the symmetry present in poly(**3**) and poly(**4**) are likely to give less crystalline or more amorphous polymers with lower shrinkages.

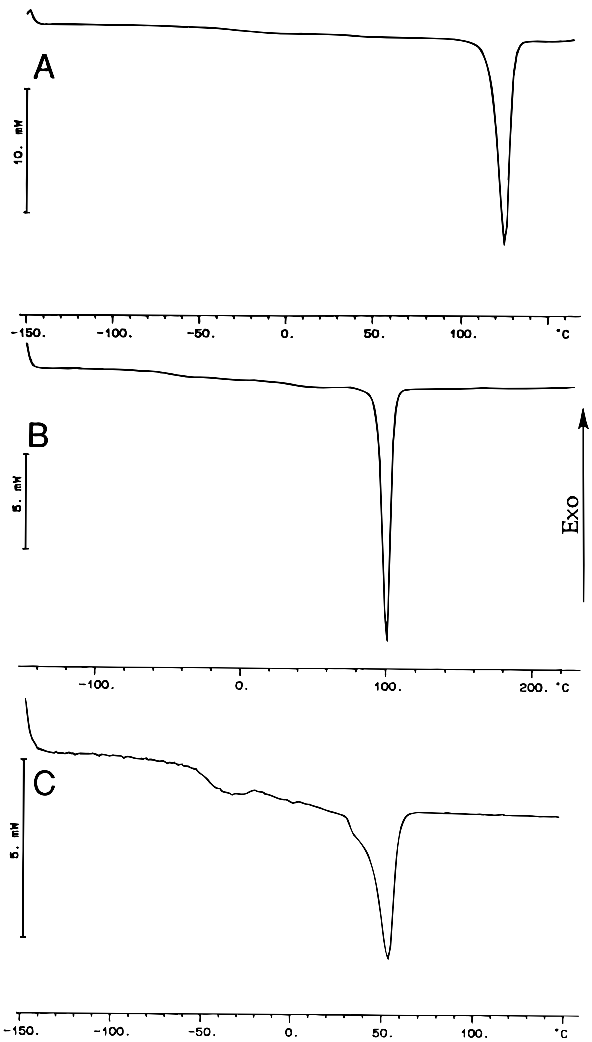


Figure 5. DSC heating traces of (A) poly(**3**), (B) poly(**4**), and (C) poly(**3**-*co*-**4**) (d^{20} = 1.202 g/cm^3). Scan rate 10 °C/min.

Conclusions and Outlook

Monomers **3** and **4** are allylic monomers that possess no substituents to enhance radical addition to the carbon−carbon double bond and yet they polymerize far more readily than conventional allylic monomers such as allyl acetate, propylene, or isobutylene.[34] This can be ascribed to the rapid ring opening of the monomers which "converts" the initially formed and highly reactive carbon-centered radical (**6**) into a less reactive, more selective sulfur-centered radical (**7**). Thus, the degradative chain transfer reaction that occurs with conventional allylic monomers via hydrogen abstraction is largely avoided. From these results and those previously described,[1,2,10] it is now apparent that compounds which include an allylic sulfide functionality (as illustrated in the generalized structure **2**) have potential to be good ring-opening monomers.[35]

To conclude, we have established that 6-methylene-1,4-dithiepane (**3**) and 3-methylene-1,5-dithiacyclooctane (**4**) are highly efficient free-radical ring-opening monomers that homopolymerize in bulk to complete conversion. The resulting high molecular weight ho-

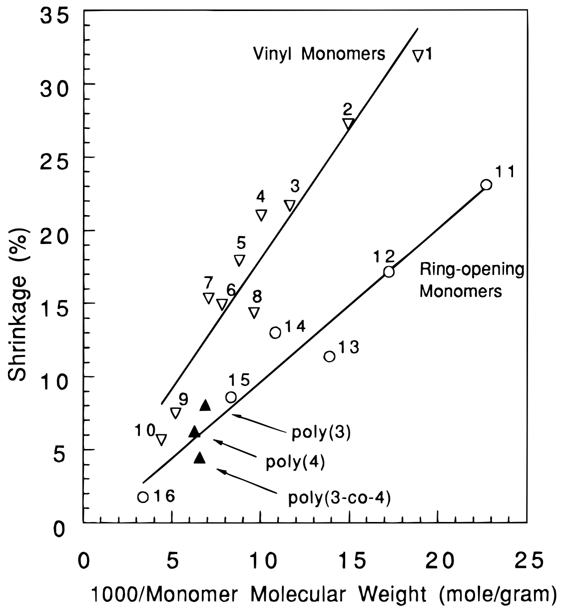


Figure 6. Variation of observed volume shrinkages with the molecular weight of the monomer. (▽) vinyl monomers, (○) ring-opening monomers (1, acrylonitrile; 2, methacrylonitrile; 3, vinyl acetate; 4, methyl methacrylate; 5, ethyl methacrylate; 6, *n*-propyl methacrylate; 7, *n*-butyl methacrylate; 8, styrene; 9, *N*-vinylcarbazole; 10, 1-vinylpyrene; 11, ethylene oxide; 12, propylene oxide; 13, tetrahydrofuran; 14, epichlorohydrin; 15, styrene oxide; 16, octamethylcyclotetrasiloxane).

Table 3. Shrinkage on Polymerization of 3 and 4

	density[a]		shrinkage (%)	
monomer(s)	monomer(s)	polymer	observed[b]	expected[c]
3	1.162 ± 0.004	1.271 ± 0.004	8.58 ± 0.04	ca. 12.5
4	1.141 ± 0.004	1.223 ± 0.004	6.70 ± 0.05	ca. 11.5
3 + **4** (1:1)	1.151 ± 0.008	1.202–1.228	4.5–6.3	ca. 12.0

[a] Measured in density gradient tube at 20 °C. [b] Shrinkage calculated with respect to initial volume of monomer(s) using the formula {[density(polymer) − density(monomer(s))]/density(polymer)} × 100. [c] This is the estimated shrinkage for the polymerization of a conventional vinyl monomer of the same molecular weight as the ring-opening monomer in question (see Figure 6).

mopolymers were white, opaque, rigid polymers that resisted most solvents at room temperature. The polymers possess high crystallinity with sharply defined melting points due to the symmetry in their structures. The 1:1 copolymer, which is not as crystalline as the homopolymers, is a softer material and necks when pulled. Despite the crystallinity present in the polymers, shrinkage during polymerization was low and within the shrinkage expected of a ring-opening monomer of similar molecular weight.

Monomers **3** and **4** possess a rarely found combination of qualities. They are stable in storage, are insensitive to aqueous acids and bases, and are clear mobile liquids at or slightly above room temperature, which enables them to be readily polymerized in bulk. Further investigation of these compounds and related mono- and bicyclic derivatives is proceeding.[35]

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