Chain Transfer in the Sulfur-Centered Free Radical Ring-Opening Polymerization of 3-Methylene-6-methyl-1,5-dithiacyclooctane

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ABSTRACT: 3-Methylene-6-methyl-1,5-dithiacyclooctane (MDTO, **1**) was polymerized in both the presence and absence of a number of chain transfer agents, viz. 1-butanethiol (BuSH), dibutyl disulfide (BuSSBu), and dibutyl sulfide (BuSBu). Mark−Houwink−Sakurada (MHS) constants for poly(MDTO) were found to be $K = 23 \times 10^{-5}$ dL g^{-1} and $\alpha = 0.67$. Using these parameters, chain transfer constants were obtained at 60 °C and are reported as 0.13 (BuSH), 0.19 (BuSSBu), and 0.0025 (BuSBu). These values are compared to the corresponding chain transfer constants obtained for styrene (STY) and methyl methacrylate (MMA). Subsequently, the chain transfer activity was measured over a range of temperatures (40−80 °C), and Arrhenius parameters were determined. Significant differences in chain transfer activity between carbon- and sulfur-centered radicals were observed. In addition, the extent of transfer to monomer was determined across the range of temperatures 40−100 °C, yielding a value for C_M of 55×10^{-4} at 60 °C. The likely extent of transfer to polymer in MDTO polymerizations was estimated using a model compound, 3-butylthio-2-butylthiomethyl-1-propylene (BTMP, **2**), yielding an estimated value for C_P of 0.35 at 60 °C.

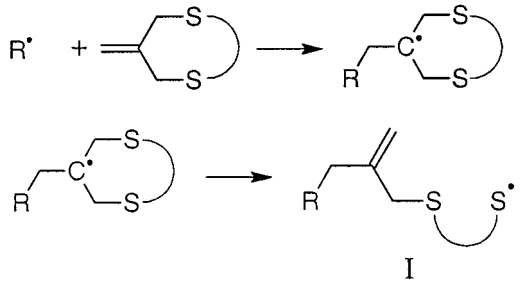
Introduction

The study of free-radical ring-opening polymerization has attracted considerable interest in recent years, as such systems may reduce the shrinkage that accompanies polymerization. A number of reviews have been published on this topic.[1−3] The cyclic allylic sulfide monomers[4−6] undergo complete ring opening under free-radical conditions, to produce high molecular weight polymers (Scheme 1). An unusual aspect of this polymerization is that the chain carrier is a sulfur-centered radical, **I**. This contrasts with most common free-radical polymerizations, which propagate via carbon-centered radicals. Thus, studies on the fundamental kinetics of the ring-opening polymerization of cyclic allylic sulfides provide a practical basis for investigating the reactivity of sulfur-centered radicals.

To date, no kinetic studies have been performed on these compounds, as initial experiments have concentrated on the synthetic aspects of polymerization. As a result, little data are available on the kinetics and thermodynamics of these reactions.

Sulfur radicals are strongly electrophilic and add rapidly (though reversibly in the case of aromatic thiyl radicals) to electron-rich double bonds.[7−15] Hydrogen abstraction reactions, however, are usually slow, due to the weakness of the S−H bond that is produced.[16] For this reason, in earlier work it has been surmised that cyclic allylic sulfide polymerizations should be relatively free from side reactions in competition with propagation.[5] This would be an advantage over other ring-opening systems such as orthocarbonates and ketene acetals, which propagate via oxygen- or carbon-centered radicals, and are prone to side reactions such as transfer to monomer[17] and backbiting.[18] Nevertheless, some examples of hydrogen abstraction by thiyl radicals have been documented in cases where the carbon−hydrogen bond is weak, for example in amino acids,[16] cycloalkenes,[19,20] and unsaturated cyclic ethers.[21] Furthermore, many transfer reactions involve transfer of a group other than hydrogen (e.g., transfer to disulfides[22]) or addition−fragmentation processes (e.g., allylic sulfides[23−25] and MMA oligomers[26]).

Scheme 1. Ring-Opening Polymerization of Cyclic Allylic Sulfides



In this work, the chain transfer behavior of a cyclic allylic sulfide has been investigated with a series of potential chain transfer agents, comprising a thiol, a disulfide, and a sulfide. Measurements of this nature provide a novel method of investigating the specificity of sulfur radicals, as each transfer reaction is measured against a standard reaction, viz. the propagation step of the polymerization. As it is possible to measure chain transfer constants over several orders of magnitude, the method permits the comparison of reactions that proceed at widely differing rates.

The reactivity of a particular chain transfer agent, S, with respect to a given monomer, may be quantified

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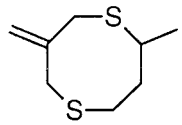
by measuring its chain transfer constant, C_S. This is defined as the ratio of the chain transfer and propagation rate constants, $k_{tr.S}/k_p$. In a similar manner, chain transfer to monomer, M, can be quantified by measuring the chain transfer to monomer constant, C_M. This is also defined as the ratio of chain transfer and propagation rate constants, $k_{tr.M}/k_p$, where $k_{tr.M}$ is the rate constant for transfer from the propagating radical to the monomer.

Thiols are well-known as efficient chain transfer agents for common monomers such as methyl methacrylate and styrene.[22] Butanethiol has chain transfer constants to these monomers of 0.65 and 22, respectively,[27] at 60 °C. Disulfides, such as dibutyl disulfides, are much less effective as chain transfer agents for MMA and STY but are useful in vinyl acetate polymerizations (dibutyl disulfide has a chain transfer constant of 1.0 in VAc at 60 °C[22]). Sulfides are comparatively poor chain transfer agents for all monomers (dibutyl sulfide has a chain transfer constant of 22×10^{-4} in STY at 60 °C[28]).

In the experiments described in this paper, the monomer was 3-methylene-6-methyl-1,5-dithiacyclooctane (MDTO, **1**). This compound is readily synthesized from commercially available precursors and undergoes polymerization with complete ring opening over a range of temperatures.[6] A model compound, 3-butylthiomethyl-2-butylthio-1-propene (BTMP, **2**), which has a similar structure to the polymer backbone, was synthesized in order to investigate transfer to polymer.



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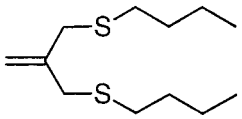

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Experimental Section

Materials. Butanethiol (99%), 1-bromobutane (99%), 3-chloro-2-chloromethylpropene (99%), and 1,3-dibromobutane (99%) were purchased from Aldrich. Thiourea (99%) was obtained from Merck. AIBN (1,1′-azobis(isobutyronitrile)) was purchased from TCI-E.P, VAZO88 (1,1′-azobis(cyclohexanenitrile)) from Dupont, and VR110 (2,2′-diazobis(2,4,4-trimethylpentane)) from Wako. AIBN was recrystallized from methanol before use. Other chemicals were used as received. Solvents were analytical grade obtained from BDH and used as received.

Characterization. ^{1}H and ^{13}C NMR were obtained using a Bruker 200 MHz NMR spectrometer using $CDCl_3$ (Cambridge Isotope Laboratory) as solvent at 25 °C. FT-IR spectra were obtained with a Biomem MB series spectrometer. Molecular weight data for chain transfer polymerizations were obtained by GPC (Waters Associates liquid chromatograph) equipped with differential refractometer and 10^6, 10^5, 10^4, 10^3, 500, and 100 Å Ultrastyragel columns. Tetrahydrofuran (THF, flow rate of 1.0 mL/min) was used as eluent. The columns were maintained at 31 °C. The GPC was calibrated with narrow polydispersity polystyrene standards. A third-order polynomial was used to fit the log *M* vs time calibration curve. Molecular weight data for Mark−Houwink−Sakurada constant determination were obtained by GPC using THF eluent (1.0 mL/min) and 10^6, 10^5, 10^4, and 10^3 Å columns (Polymer Laboratories). Two detectors were used: a PL differential refractive index detector and a Viscotek model 250 differential viscometer.

Synthesis of MDTO. MDTO (**1**) was prepared by the following series of reactions:

(a) Preparation of 1,3-Butanedithiol. Thiourea (74 g, 0.97 mol), 1,3-dibromobutane (100 g, 0.46 mol), and water (65 mL) were refluxed together until an homogeneous solution formed (ca. 1 h). The solution was cooled in an ice bath, and 70 mL of ethylenediamine (1.05 mol) was added dropwise. After the addition was complete, the mixture was heated at 100 °C for 1 h. Over this period, the mixture separated into two phases. The upper, yellow phase was separated and dried to give 43.2 g (77%) of 1,3-butanedithiol.

^{1}H NMR (200 MHz, $CDCl_3$, TMS, 25 °C): δ1.33 (CH_3-, *d*, 3 H, J = 6.3 Hz), 1.33 ($-CH_2S\mathbf{H}$, *t*, 1 H, J = 7.96 Hz), 1.43 ($\mathbf{H}SCH(CH_3)-$, *d*, 1 H, J = 6.8 Hz), 1.64−1.93 ($HSCH_2C\mathbf{H}_2$-$CH(CH_3)-$, *m*, 2 H), 2.54−2.61 ($HSC\mathbf{H}_2-$, *m*, 2 H, J_{SH} = 7.9 Hz), 2.95−3.15 ($HSC\mathbf{H}(CH_3)-$, *m*, 1 H, J_{SH} = 6.8 Hz). ^{13}C NMR: δ22.499 ($-CH_3$), 25.686 ($-CH_2SH$), 34.030 ($-\mathbf{C}H(CH_3)$-SH), 44.574 ($HSCH_2\mathbf{C}H_2-CH(CH_3)SH$).

(b) Preparation of 1 from 1,3-Butanedithiol and 3-Chloro-2-chloromethyl-1-propene. This compound was synthesized according to the method of Evans and Rizzardo.[6] Sodium metal (16.9 g, 0.74 mol) was dissolved in MeOH (1 L) in a 2 L, three-necked round-bottom flask under Ar. The dithiol (43.2 g, 0.35 mol) and the 3-chloro-2-chloromethyl-1-propene (44.4 g, 0.35 mol) were added simultaneously to the refluxing MeOH by syringe pump at a rate of 4 mL/h. The resulting mixture was concentrated under reduced pressure, 200 mL of H_2O was added, and the product was extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ and concentrated, before being distilled (bp 68−73 °C, 0.1 mmHg) to give 36.3 g (59%) of a slightly yellow liquid. This was redistilled (bp 80 °C, 0.1 mmHg) to produce 32.0 g (52%) of water-clear 3-methylene-6-methyl-1,5-dithiacyclooctane.

^{1}H NMR (200 MHz, $CDCl_3$, TMS, 25 °C): δ 1.2 (*d*, 3H, $-CH_3$) 1.4−1.9 (*m*, 2H, $-SCH_2C\mathbf{H}_2CH(CH_3)S-$), 2.7−3.4 (*m*, 7H, $-C\mathbf{H}_2SC\mathbf{H}_2CH_2C\mathbf{H}(CH_3)SC\mathbf{H}_2-$), 5.1 (*s*, 2H, $CH_2=$). ^{13}C NMR: δ 23.5 ($-CH_3$), 30.6 ($-SCH_2\mathbf{C}H_2CH(CH_3)S-$), 37.7, 37.8, 38.6, 39.7 (carbons α to S), 118.6 ($CH_2=$), 146.65 (quat. C).

Synthesis of Dibutyl Sulfide. Sodium metal (1.96 g, 85.2 mmol) was dissolved in a mixture of 1-butanethiol (6.60 g, 73.2 mmol) and MeOH (50 mL). To this was added dropwise 1-bromobutane (10.0 g, 73.0 mmol). The mixture was refluxed for 3 h with the formation of a white precipitate. The solution was filtered and concentrated, and 50 mL of H_2O was added. The resulting mixture was extracted with CH_2Cl_2, dried, and concentrated. The resulting oil was distilled at 62 °C, 7 mmHg (lit. 182 °C, 1 atm[29]), to give 5.6 g (53%) of dibutyl sulfide.

^{1}H NMR (200 MHz, $CDCl_3$, TMS, 25 °C): δ 0.9 (t, 6H, $S(C_3H_6C\mathbf{H}_3)_2$), 1.3−1.6 (m, 8H, $S(CH_2C\mathbf{H}_2C\mathbf{H}_2CH_3)_2$), 2.5 (t, 4H, $S(C\mathbf{H}_2C_3H_7)_2$).

Synthesis of Dibutyl Disulfide. Butane-1-thiol (10.0 g, 0.11 mol) was dissolved in a mixture of 90 mL of 50% aqueous MeOH. The solution was titrated with a solution of I_2 (16 g) in methanol (150 mL) until the color of iodine persisted (ca. 125 mL of solution was required). The mixture was concentrated and extracted with CH_2Cl_2. The extract was washed with $Na_2S_2O_3$ solution to remove any excess iodine. The clear extract was concentrated to produce a yellow oil, which was distilled at 79 °C, 3 mmHg (lit. 226 °C, 1 atm[29]), giving 5.5 g (56%) of dibutyl disulfide as a clear oil.

^{1}H NMR (200 MHz, $CDCl_3$, TMS, 25 °C): δ 0.9 (t, 6H, $(SC_3H_6C\mathbf{H}_3)_2$), 1.2−1.8 (m, 8H, $(SCH_2C_2\mathbf{H}_4CH_3)_2$), 2.6 (t, 4H, $(SC\mathbf{H}_2C_3H_7)_2$).

Synthesis of BTMP (2). Butane-1-thiol (10.7 mL, 100 mmol) was added to a solution of Na (2.56 g) in methanol (100 mL). To the refluxing solution, 3-chloro-2-chloromethyl-1-propene (3.125 g, 25 mmol) was added dropwise. A white precipitate of NaCl was formed. The mixture was refluxed for a further hour, before removal of the MeOH under reduced pressure, and the addition of 100 mL of H_2O. The product was extracted with Et_2O, dried over $MgSO_4$, and evaporated to give 6.67 g of clear colorless liquid. Subsequent distillation produced 4.9 g (84%) of clear colorless liquid; bp 91 °C (0.1 mmHg).

^{1}H NMR (200 MHz, $CDCl_3$, TMS, 25 °C): δ 0.8 (CH_3-, *t*, 6 H, J = 7 Hz), 1.2−1.7 ($-SCH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$, *m*, 8 H), 2.3 ($-SC\mathbf{H}_2CH_2CH_2CH_3$, *t*, 4 H, J = 7 Hz), 3.2 ($CH_2{=}C(C\mathbf{H}_2SBu)_2$,

s, 4 H), 4.9 (CH_2=C($CH_2SBu)_2$, *s*, 2 H). ^{13}C NMR: δ 13.7 ($-CH_3$), 22.0 ($-CH_2CH_3$), 30.8, 31.2 ($-SCH_2CH_2CH_2CH_3$), 35.4 (CH_2=C($CH_2SBu)_2$), 114.9 (CH_2=C), 141.2 (quat. C). IR (NaCl): 3074 w, 2956 s, 2871 m, 1636 m, 1463 s, 1416 s, 1378 m, 1293 m, 1275 m, 1221 s, 902 s, 747 m cm^{-1}. Mass spectrum (EI): *m*/*z* 232 ($M^{\bullet+}$, 20%), 175 (25), 143 (60), 99 (100), 85 (60), 57 (35), 55 (45).

Determination of Mark−Houwink−Sakurada (MHS) Constants. Ten solutions were prepared containing varying concentrations of AIBN in bulk MDTO. The mixtures were purged with N_2, sealed, and polymerized in a 60 °C oil bath to produce broad polymers covering a range of molecular weights. Samples from each mixture were analyzed by size exclusion chromatography using a PL differential refractive index detector and a Viscotek model 250 differential viscometer.

Chain Transfer Polymerizations: General Procedure. Polymerization mixtures were made up using appropriate volumes of stock solutions of monomer (MDTO), initiator, and chain transfer agent in benzene. The initiators used were AIBN (polymerizations at 40−60 °C), VAZO88 (80 °C), and VR110 (100 °C). Eight separate polymerizations were performed for each chain transfer agent at each temperature, including a replicate of the control (no added chain transfer agent) polymerization. The solutions were placed in glass ampules and flame-sealed after degassing the contents by three freeze−thaw cycles to 10^{-3} mbar. Polymerization was carried out by immersing the ampules in an oil bath at the desired temperature (controlled to ±0.1 °C) for the required amount of time (usually 80 min at 40 °C, 20 min at 50−80 °C), after which they were removed and rapidly cooled in an ice−water bath. The polymerization times were chosen such that conversion remained below 10%. Hydroquinone was then added to each sample to prevent further polymerization, and the solvent was removed under vacuum.

Polymer Analysis: General Procedure. The residues, consisting of monomer, polymer, excess initiator, and chain transfer agent, were dissolved in $CDCl_3$, and ^1H NMR spectra were obtained. The conversions were estimated from the relative intensities of the CH_2= resonance of the monomer (δ 5.15 ppm) and the vinylidene resonance of the repeat unit of the polymer (δ 4.95 ppm). The polymerization mixtures were then precipitated in MeOH, decanted, and dried under vacuum. The resulting polymers were dissolved in THF and analyzed by GPC.

Each sample's intensity vs elution volume data were converted to the absolute molecular weight distribution of the MDTO sample using the Mark−Houwink constants for styrene and MDTO, and the calibration curve was obtained using narrow polydispersity polystyrene standards. Number- and weight-average molecular weights and chain length distribution (CLD) plots were obtained from the absolute MWD using KaleidaGraph software. This software was also used to determine the slope of the CLD plot, using least-squares linear regression analysis. Chain transfer constants were obtained from plots of the resulting data vs [S]/[M] (e.g., Figure 2), again using least-squares linear regression analysis. Errors quoted are the standard errors in the gradients of the lines of best fit.

Transfer to BuSH, BuSSBu. Polymerization mixtures were made up using appropriate volumes of stock solutions of MDTO (2.5 M in benzene), initiator (0.25 M in benzene), and chain transfer agent (1 M in benzene) and then diluted with more benzene to a volume of 500 μL. The concentration of MDTO was maintained at 1 M, and the concentration of chain transfer agent was varied from 0 to 0.1 M in steps of 0.02 M. Initiator concentrations were 0.03 M (40, 50 °C), 0.006 M (60 °C), and 5×10^{-3} M (80 °C).

The polymerization and analysis of the samples are described above in the general procedure.

Transfer to BuSBu. Polymerization mixtures were made up using appropriate volumes of stock solutions of MDTO (2.5 M in benzene) and initiator (either AIBN or VAZO88, 0.25 M in benzene). Dibutyl sulfide was added, and the mixture was then diluted with more benzene to a volume of 1000 μL (40, 50 °C) or 500 μL (60, 80 °C). The concentration of MDTO was kept constant at 0.5 M (40, 50 °C) or 1 M (60, 80 °C), and the concentration range of BuSBu was 0−3.44 M (40 °C), 0−2.29 M (50 °C), and 0−1.03 M (60, 80 °C). Initiator concentrations were as follows: 15 mM (40, 50 °C), 6 mM (60 °C), or 5 mM (80 °C).

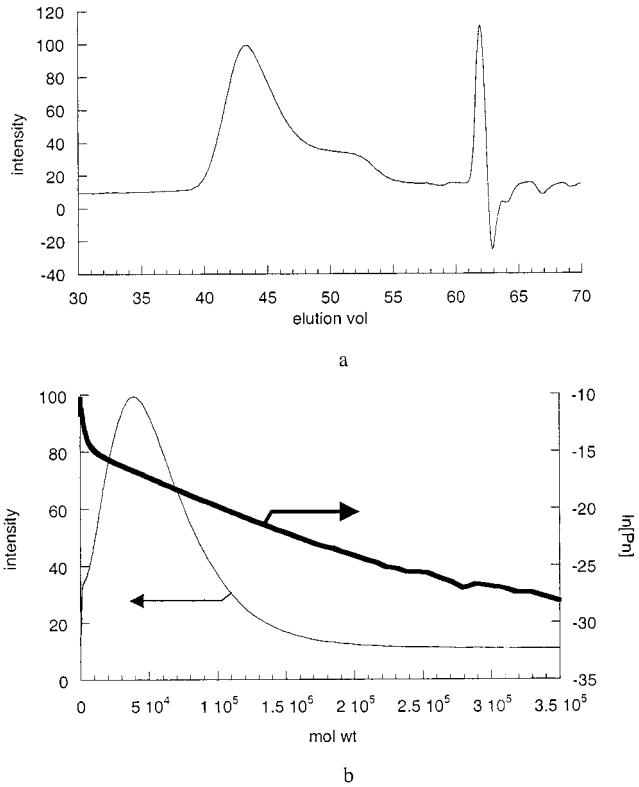


Figure 1. (a) A typical GPC trace showing characteristic bimodal distribution ($M_n = 5.8 \times 10^3$, $M_w = 30.7 \times 10^3$, PDI = 5.27). (b) The same sample plotted as ln[$P(M)$] vs mol wt and intensity vs mol wt showing a linear chain length distribution (CLD) plot.

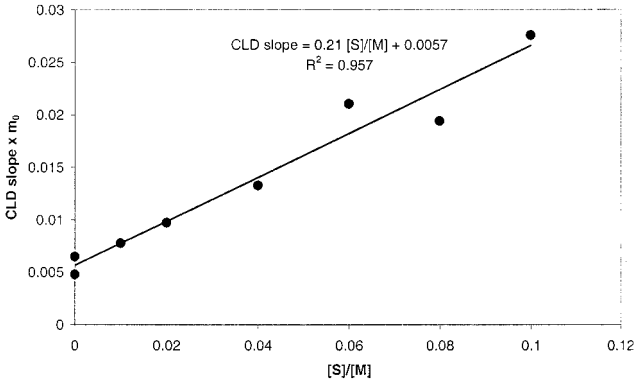


Figure 2. Chain length distribution (CLD) plot for transfer to BuSSBu (S) from MDTO (M) at 50 °C.

The polymerization and analysis of the samples are described in the general procedure.

Transfer to BTMP. Polymerization mixtures were made up using appropriate volumes of stock solutions of MDTO (2.5 M in benzene), AIBN (0.25 M in benzene), and BTMP (0.1 M in benzene) and then diluted with more benzene to a volume of 500 μL. The concentrations of MDTO and AIBN were maintained at 1 and 0.006 M, respectively, and the concentration range of BTMP was 0−0.01 M. All polymerizations were carried out at 60 °C.

The polymerization and analysis of the samples are described in the general procedure. Experimental details for these polymerizations are shown in Table 1.

Table 1. Experimental Data for Transfer to 3-Butylthio-2-butylthiomethyl-1-propylene (BTMP, 2)—a Model for Transfer to Polymer

[MDTO] (mol/L)	[BTMP] (mmol/L)	conv (%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	CLD slope $\times 10^3$
1.00	0	8	9.8	56.4	4.8
1.00	0	6	9.2	50.5	5.3
1.00	1.0	7	9.5	58.0	4.4
1.00	2.0	8	10.0	48.7	5.8
1.00	4.1	7	8.9	42.8	6.5
1.00	6.1	8	9.0	39.9	6.8
1.00	8.2	7	9.4	37.7	7.4
1.00	10.2	7	7.8	32.4	8.6

Transfer to Monomer. Polymerization mixtures were made up using appropriate volumes of stock solutions of MDTO (2.5 M in benzene) and initiator (0.25 M in benzene). The solutions were diluted with benzene to a volume of 500 μL.

The polymerization and analysis of the samples are described in the general procedure. Experimental details for these polymerizations are shown in Table 2.

Results

Determination of Mark–Houwink–Sakurada (MHS) Constants. The approach used to determine MHS parameters has been described in earlier publications by this group and will not be repeated here.[30] Ten different samples were analyzed, and the MHS plots obtained were linear, with good agreement between samples, yielding MHS parameters of $K = 23 \times 10^{-5}$ dL g^{-1} and $\alpha = 0.67$. As the samples tested were mixtures of linear polymer and cyclic oligomers (vide infra), there remains some uncertainty in the true MHS parameters of linear poly(MDTO).

The parameters determined above were used to convert the polystyrene-equivalent molecular weight distributions obtained by GPC analysis to absolute molecular weight distributions.

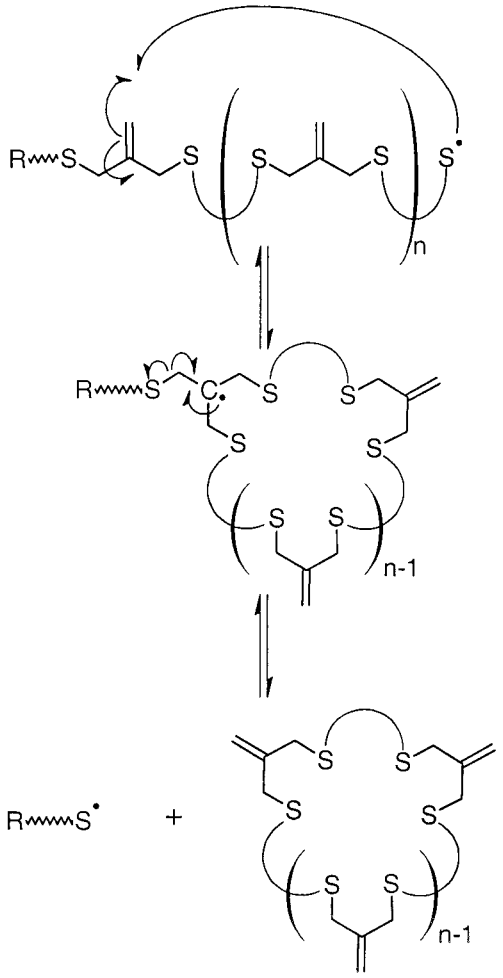
Molecular Weight Distributions. Typical molecular weight distributions were broad and bimodal (Figure 1). A credible explanation for this is the occurrence of reversible backbiting reactions. Similar backbiting reactions have been observed in many ionic ring-opening polymerizations involving monomers such as ϵ-caprolactone.[31] In the specific case of MDTO, backbiting would take place via addition of the sulfur radical to one of the double bonds on the polymer backbone, followed by β-scission as shown in Scheme 2. The occurrence of similar bimolecular addition–fragmentation reactions in allyl sulfides has been established,[32] and such compounds have been used as chain transfer agents for common monomers.[23–25] This hypothesis is corroborated by the occurrence of chain transfer to 3-butylthio-2-butylthiomethyl-1-propylene (BTMP, see below). Backbiting as described above is an intramolecular version of this chain transfer reaction.

Backbiting in MDTO would yield cyclic oligomers with a range of molecular weights. The distribution of these oligomers, superimposed on the distribution of linear polymer, would produce the observed bimodality.

The oligomers have a large influence on the average molecular weight, M_n, of the total bimodal distribution. The M_n is often used to evaluate the effect of chain transfer, in conjunction with the Mayo equation (eq 1):

$$\frac{1}{DP_n} - \frac{1}{DP_n^0} = C_S \frac{[S]}{[M]} \qquad (1)$$

Scheme 2. Backbiting in Growing MDTO Chains



where DP_n is the number-average degree of polymerization (given by M_n/m_0, where m_0 is the molecular weight of the repeat unit), DP_n^0 is the number-average degree of polymerization in the absence of added chain transfer agent, S and M represent the chain transfer agent and monomer, respectively, and C_S is the chain transfer coefficient, equal to k_p/k_{tr}, the ratio of the rate coefficients of propagation and transfer.

Application of eq 1 to the MDTO system produces erroneous chain transfer coefficients, as the occurrence of backbiting is independent of the presence of chain transfer agents in the solution, and hence the oligomer distribution remains constant, limiting the effect of addition of chain transfer agent on M_n. There are, however, several other ways of determining chain transfer coefficients from molecular weight distributions.

One alternative is to use the weight-average molecular weight moment, M_w. This value is less affected by the low molecular weight portions of the distribution, thus providing a better measure of the effect of chain transfer agent addition on the linear polymer chains. In molecular weight distributions where chain stopping is dominated by transfer, the polydispersity should equal 2. Consequently, the Mayo method can be used, substituting $2/DP_w$ for $1/DP_n$ in eq 1.[33]

Another method is to use the chain length distribution (CLD) method developed by Gilbert and co-workers.[34,35] This approach is founded on the principle that, at the high molecular weight end of the molecular weight

Table 2. Experimental Data for Chain Transfer to Monomer in MDTO Polymerizations

T (°C)	initiator	[I] (mmol/L)	[M] (mol/L)[a]	time (min)	conv (%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	CLD slope × 10^3
40	AIBN	30.43	1.00	80	7	8.5	46.4	3.7
40	AIBN	15.22	1.00	113	8	9.4	34.9	5.2
40	AIBN	7.61	1.00	160	7	8.8	35.0	5.0
40	AIBN	3.55	1.00	280	5	9.4	56.0	3.1
50	AIBN	30.43	1.00	20	8	6.0	41.7	3.8
50	AIBN	15.22	1.00	28.5	6	7.0	39.8	4.3
50	AIBN	7.61	1.00	40	5	6.7	41.7	4.1
50	AIBN	3.55	1.00	70	5	6.5	38.7	4.1
60	AIBN	6.09	1.00	20	7	9.0	54.5	3.2
60	AIBN	3.04	1.00	28.5	7	7.2	46.6	3.5
60	AIBN	1.52	1.00	40	4	8.8	41.3	3.8
60	AIBN	0.51	1.00	70	6	7.8	42.9	3.8
80	VAZO88	5.07	1.00	21.5	7	7.7	48.9	4.1
80	VAZO88	2.53	1.00	30	7	9.7	51.0	4.2
80	VAZO88	1.01	1.00	40	4	8.2	44.2	4.6
80	VAZO88	0.51	1.00	70	7	8.3	55.3	3.7
100	VR110	2.00	1.00	15	5	15.8	60.5	4.4
100	VR110	0.50	1.00	27.5	4	12.8	48.7	4.9
100	VR110	0.20	1.00	40	3	10.4	36.7	5.8
100	VR110	0.10	1.00	60	5	12.4	45.5	5.6

[a] All polymerizations were performed in solution in benzene.

distribution, the number distribution can be represented as the following function of the molecular weight, *M*:

$$\lim_{M\to\infty} P(M) = \text{constant} \times \exp\left(-\frac{\langle k_t\rangle[R^\bullet] + k_{tr.M}[M] + k_{tr.S}[S]}{k_p[M]}\frac{M}{m_0}\right) \quad (2)$$

where $P(M)$ is the number of chains of molecular weight M, m_0 is the molecular weight of the monomer, [M], [S], and [R•] are the concentrations of monomer, chain transfer agent, and radicals, respectively, k_p and $\langle k_t\rangle$ are the rate coefficients of propagation and termination, respectively, and $k_{tr.X}$ represents the rate coefficient for transfer to species X.

The slope of a plot of ln $P(M)$ vs M will thus be described by eq 3.

$$\frac{d(\ln P(M))}{dM} = \left(-\frac{\langle k_t\rangle[R^\bullet] + k_{tr.M}[M] + k_{tr.S}[S]}{k_p[M]}\frac{1}{m_0}\right) \quad (3)$$

If a series of experiments are carried out at different transfer agent concentrations, keeping all other variables constant, the values of the resulting ln $P(M)$ vs M slopes may be plotted against [S]/[M], to give a linear plot whose gradient is C_S/m_0.

One such plot, obtained for dibutyl disulfide at 50 °C, is shown in Figure 2.

Heuts et al.[33] have shown that the CLD and Mayo methods are completely equivalent. However, the CLD method has significant practical advantages when the molecular weight distribution suffers from contamination.

In this present work, good agreement was obtained between the CLD and M_w methods. Transfer values obtained using the number-average degree of polymerization were often divergent, as shown in Table 3 and Figure 3 for the BuSH−MDTO system.

Transfer Reactions Involving MDTO. The chain transfer constants obtained for MDTO are significantly different from those measured previously in polymerizations with standard acrylic and vinylic monomers such as styrene (STY), methyl methacrylate (MMA), and vinyl acetate (VAc). The chain transfer constants estimated in this work are compared with literature values[27] (where available) for chain transfer to STY, MMA, and VAc in Table 4.

Table 3. Experimental Chain Transfer Constants of Sulfur Compounds in the Polymerization of MDTO

T (°C)	CTA	by M_n[a]	by M_w[b]	by CLD[c]
40	BuSH	0.11	0.12	0.11 ± 0.0078
	BuSSBu	0.16	0.20	0.19 ± 0.011
	BuSBu	0.0004	0.0013	0.0009 ± 0.00008
50	BuSH	0.12	0.15	0.13 ± 0.018
	BuSSBu	0.16	0.20	0.21 ± 0.012
	BuSBu	0.0011	0.0015	0.0012 ± 0.0002
60	BuSH	0.13	0.14	0.13 ± 0.021
	BuSSBu	0.13	0.19	0.19 ± 0.012
	BuSBu	0.0043	0.0055	0.0025 ± 0.0006
80	BuSH	0.077	0.17	0.16 ± 0.014
	BuSSBu	0.15	0.30	0.30 ± 0.013
	BuSBu	0.0049	0.0032	0.0025 ± 0.0003

[a] Determined by Mayo method using number-average molecular moment. [b] Determined by Mayo method using weight-average molecular moment. [c] Determined by chain length distribution method. Errors given are standard deviations.

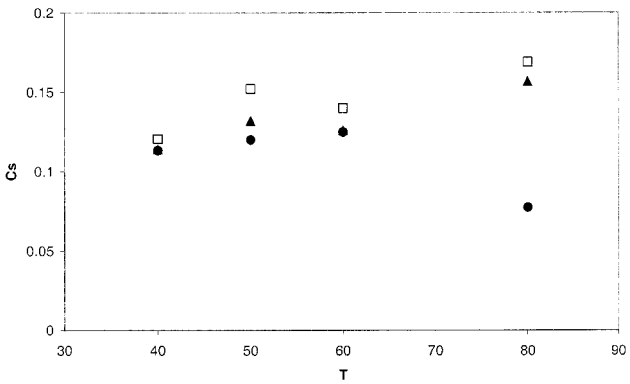


Figure 3. Calculated C_S values for BuSH, 40−80 °C. Solid circles calculated from M_n data, open boxes from M_w data, and solid triangles from chain length distribution (CLD) data.

Transfer to Butanethiol. Butanethiol is an effective chain transfer agent for vinylic and acrylic monomers, with chain transfer constants ranging from 0.67 for MMA to 48 for VAc at 60 °C.[27] In contrast, it is a relatively poor chain transfer agent for MDTO, with a C_S value of ∼0.1 across the range of temperatures

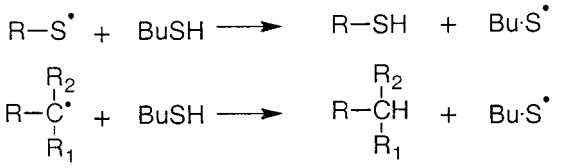
Table 4. Chain Transfer Constants[a] of Sulfur Compounds in the Polymerization of MDTO

monomer	*T* (°C)	BuSH	BuSSBu	BuSBu
MDTO	40	0.11	0.19	0.0009
MDTO	50	0.13	0.21	0.0012
MDTO	60	0.13	0.19	0.0025
MDTO	80	0.16	0.30	0.0025
MMA[b]	60	0.67	0.00013[c]	
STY[b]	60	22	0.0024	0.0022
VAc[b]	60	48	1.0	0.026

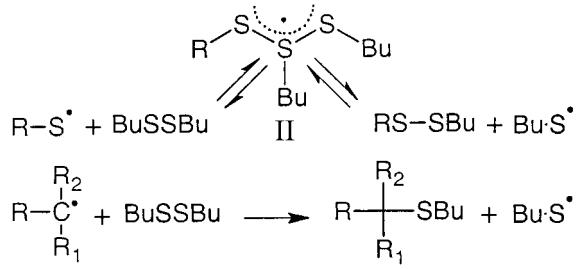
[a] Determined by chain length distribution method. [b] Numbers given for these monomers are representative values from the *Polymer Handbook*.[27] [c] Value given is for diethyl disulfide.

Scheme 3. Transfer Routes in Sulfur-Centered vs Carbon-Centered Radicals

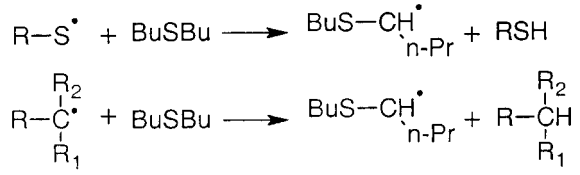
a) Transfer to butanethiol.



b) Transfer to dibutyl disulfide.



c) Transfer to dibutyl sulfide.



studied. This can be rationalized by considering the likely mechanism of transfer from a growing poly(MDTO) radical to a molecule of BuSH, which involves breaking the weak S−H bond on BuSH, and replacing it with an equally weak S−H bond on the polymer. Thus, there is little enthalpic driving force for the reaction. However, in a reaction between a carbon-centered radical and butanethiol, the weak S−H bond is replaced by a stronger C−H bond (Scheme 3a).

The chain transfer coefficient for the MDTO−BuSH reaction rises slightly with temperature, consistent with an activation energy difference, $E_p - E_{tr}$, of −7 kJ mol^{-1} (Figure 4). This value is similar to that reported for transfer to BuSH in MMA polymerizations[36] ($E_p - E_{tr} = -6.06 \pm 0.96$). Hence, the main difference between the two chain transfer constants is found in the preexponential factor, *A*, which equals 1.2 for MDTO and 7.6 for MMA. This difference may be due to a larger preexponential factor in the propagation reaction of MDTO, caused by reduced steric hindrance experienced by the primary sulfur propagating radical compared to the tertiary propagating radical in MMA polymerizations.

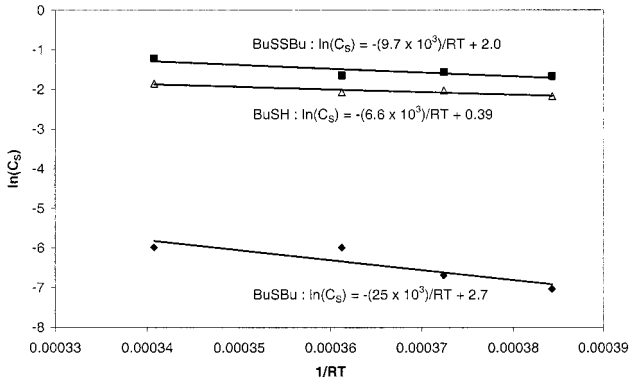


Figure 4. Arrhenius plot for chain transfer to BuSSBu (filled squares), BuSH (open triangles), and BuSBu (filled diamonds), with lines of best fit.

Transfer to Dibutyl Disulfide. For carbon-centered radicals, dibutyl disulfide is a much weaker chain transfer agent than butanethiol. While disulfides are useful chain transfer agents for vinyl acetate ($C_{BuSSBu} = 1.0$ at 60 °C), for less reactive monomers such as STY and MMA typical chain transfer constants at 60 °C range from 0.0024 (STY−BuSSBu) to 0.000 13 (MMA−diethyl disulfide).[27,28]

In MDTO polymerizations, however, dibutyl disulfide is an effective chain transfer agent; not only is it more active than BuSH in the same monomer, but its chain transfer constant is orders of magnitude greater in MDTO than in MMA or STY and approaches that of VAc. Clearly, chain transfer from sulfur-centered radicals to disulfides is a more favorable process than from carbon-centered radicals.

The explanation for this increase in chain transfer activity may be found in the mechanism of chain transfer to disulfides. In the case of carbon-centered radicals, transfer to disulfides takes place via an S_H2 homolytic substitution reaction, producing a sulfide and a thiyl radical (Scheme 3b). However, studies on the addition of sulfur radicals to disulfides[37,38] have shown evidence for a three-electron bonded resonance-stabilized intermediate in which the free electron is shared between the antibonding σ^* orbitals of the two sulfur−sulfur bonds. We hypothesize that a similar mechanism is occurring in the MDTO−BuSSBu system; formation of this intermediate radical decreases the activation energy required for transfer, thus increasing the rate. The chain transfer coefficient for dibutyl disulfide appears to increase slightly with temperature, consistent with an activation energy difference between propagation and transfer ($E_p - E_{tr}$) of approximately −10 kJ mol^{-1} (Figure 4).

Transfer to Dibutyl Sulfide. The final compound studied in this series of experiments, dibutyl sulfide (BuSBu), showed chain transfer activity in MDTO which was orders of magnitude lower than that observed for either butanethiol or dibutyl disulfide. The values observed are similar to those seen for STY and somewhat lower than those observed in VAc.[27] No data are available for MMA polymerizations. The chain transfer constant to dibutyl sulfide is slightly lower than the chain transfer to monomer constant (vide infra). This should not affect the accuracy of the values obtained, as the ratio of chain transfer to monomer vs propagation is constant, while that of chain transfer to BuSBu vs propagation is dependent on the BuSBu concentration (eq 2). The two factors are readily separated by varying [BuSBu].

Table 5. Average Values of Chain Transfer to Monomer Constant (C_M) in MDTO Polymerizations

T (°C)	$C_M \times 10^4$ by M_n[a]	by M_w[b]	by CLD[c]
40	193	81	63
50	266	86	61
60	212	75	55
80	206	70	51
100	136	73	52

[a] Determined by Mayo method using number-average molecular moment. [b] Determined by Mayo method using weight-average molecular moment. [c] Determined by chain length distribution method.

Table 6. Comparison of Values of Chain Transfer to Monomer Constant (C_M)[a]

monomer[b]	T (°C)	$C_M \times 10^4$	monomer[b]	T (°C)	$C_M \times 10^4$
MMA	60	0.1	MDTO	60	55
STY	60	0.6	AlAc	80	700
VAc	60	2	AlC	80	1600
VC	60	12			

[a] Numbers are taken from the *Polymer Handbook*[27] except for the value for MDTO which is from this work. [b] MMA, methyl methacrylate; STY, styrene; VAc, vinyl acetate; VC, vinyl chloride; MDTO, 2-methyl-6-methylene-1,5-dithiacyclooctane; AlAc, allyl acetate; AlC, allyl chloride.

The low chain transfer activity is expected, as chain transfer to dibutyl sulfide must involve either hydrogen abstraction (breaking a C−H bond, Scheme 3c) or homolytic substitution at sulfur (breaking a C−S bond). There is no possibility of forming a stabilized intermediate adduct, as may occur in disulfide transfer.

Once again, the chain transfer coefficient increases with temperature, although in this case the activation energy difference is much higher, with $E_p - E_{tr} \approx -25$ kJ mol^{-1} (Figure 4).

Transfer to MDTO Monomer. The chain transfer coefficient for transfer to monomer, C_M, can be determined by reducing the initiator concentration in polymerization until a limiting molecular weight is achieved. At this point, the radical concentration is low enough that bimolecular termination becomes negligible, and the molecular weight is controlled by transfer.[33] In this work, reducing the initiator concentration had no discernible effect on the molecular weight or the slope of the CLD plots at any of the temperatures studied. We conclude that in all the experiments termination is transfer-dominated. Transfer to monomer constants, C_M, were estimated at each temperature using CLD and Mayo methods. The results are shown in Table 5. As before, the CLD method is preferred as a means of determining the transfer coefficient.

The transfer to monomer constant for MDTO, C_M, is approximately $(55 \pm 5) \times 10^{-4}$ across the range of temperatures from 40 to 100 °C. This value is much larger than that of most vinyl and acrylic monomers, although comparable in magnitude to vinyl chloride. Allylic monomers, however, generally have C_M values that are substantially higher, as shown in Table 6. As MDTO is an allylic monomer, with four easily abstractable hydrogens α to both the double bond and the sulfide group, it should also undergo substantial transfer to monomer. Its relatively low C_M (compared to those of other allylic monomers) is due to the poor ability of the propagating sulfur radical to abstract hydrogen atoms relative to the carbon-centered radicals

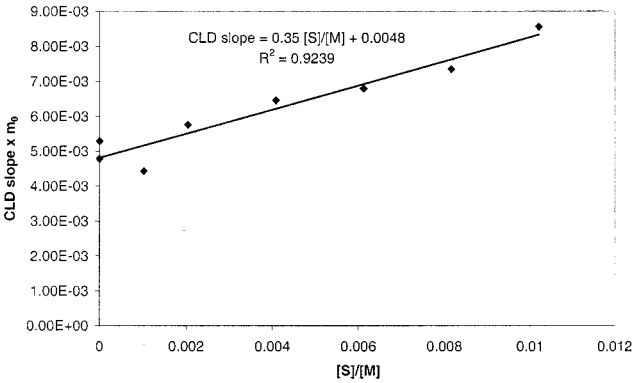
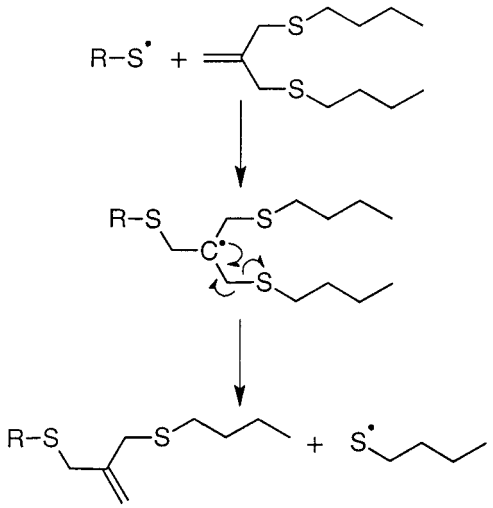


Figure 5. Chain length distribution (CLD) plot for transfer to 2-butylthiomethyl-3-butylthio-1-propene (BTMP, **2**) showing transfer constant of 0.35.

Scheme 4. Addition−Fragmentation Chain Transfer to BTMP



that are the chain carriers in the polymerizations listed in Table 6. The C_M value remains significantly lower than that of another ring-opening monomer, methylene dioxepane, which has a C_M value of 17×10^{-3} at 40 °C.[17]

There is a slight decrease in the value of C_M with increasing temperature. The data are subject to uncertainty in the results, however, and any temperature dependence of C_M is small.

Transfer to Polymer. A model compound (BTMP, **2**) was synthesized to mimic the structure of the polymer backbone. MDTO was polymerized in the presence of BTMP at 60 °C. A significant amount of transfer activity was observed, resulting in a decrease in molecular weight. A chain transfer constant of 0.35 was obtained (Table 1, Figure 5). BTMP has a structure that is virtually identical to that of the polymer backbone; this result suggests that transfer to polymer is likely to play a significant role in polymerizations carried to high conversions.

The mechanism of transfer is likely to involve addition−fragmentation steps similar to those reported in activated allylic sulfides[23−25,32] (Scheme 4). Unlike most documented cases of transfer to polymer, this mechanism will not introduce branching to the polymer chain. Instead, the effect will be to cause an equilibration of the chain length distribution, similar to the effect of transesterification reactions in polyesters.

Conclusions

Chain transfer reactions play a dominant role in the free-radical ring-opening polymerization of MDTO. In the absence of a chain transfer agent, transfer to monomer restricts the development of the molecular weight. Transfer to polymer via addition−fragmentation reactions may also occur to a large extent at high conversions. In this work, however, transfer to polymer is unlikely to be significant as the polymerizations were stopped at low conversions.

In the presence of added chain transfer agent the propagating sulfur-centered radical behaves quite differently to the carbon-centered radicals found in most radical polymerizations. In most transfer reactions, the sulfur-centered MDTO radical is less reactive than carbon-centered radicals. In transfer to a disulfide, however, the sulfur radical is generally more reactive. Furthermore, disulfides are more reactive than thiols as transfer agents in MDTO, suggesting that there is an additional driving force in the transfer reaction, such as the formation of a resonance-stabilized radical intermediate.

Arrhenius parameters have been established for the transfer reactions studied here, revealing low levels of temperature dependence (≈7 kJ mol^{-1} for BuSH, 10 kJ mol^{-1} for BuSSBu, 25 kJ mol^{-1} for BuSBu). No significant temperature effect was seen on transfer to monomer, which takes place to a greater extent than is usual for most acrylic or vinylic monomers, although it is comparable to the extent of transfer seen in methylene dioxepane[17] and lower than that found in several allylic monomers.

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