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Mechanism and Kinetics of the Free Radical Ring-Opening Polymerization of Eight-Membered Cyclic Allylic Disulfide Monomers

Marisa Phelan,[†] Fawaz Aldabbagh,[*,†] Per B. Zetterlund,[*,‡,§] and Bunichiro Yamada[*,‡,⊥]

Department of Chemistry, National University of Ireland, Galway, Ireland;
Department of Applied and Bioapplied Chemistry, Graduate School of Engineering,
Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan;
and Graduate School of Science and Technology, Kobe University, Kobe 657-8501, Japan

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ABSTRACT: Remote methyl substituents were found to have a significant effect on the free radical ring-opening polymerization of cyclic allylic eight-membered disulfide monomers. High concentrations of initiator were required to achieve reasonable polymerization rates for the monomer with a greater number of methyl substituents, 2,2,4-trimethyl-7-methylene-1,5-dithiacyclooctane **(1b)**. Monomer **1b** polymerized significantly slower than the analogous monomer containing only one 2-methyl substituent, 2-methyl-7-methylene-1,5-dithiacyclooctane **(1a)**. Values of $k_p/k_t^{0.5}$ (k_p and k_t are the rate coefficients for propagation and termination, respectively) for both monomers were obtained at 30−120 °C. Examination of the Arrhenius parameters for propagation revealed that the fragmentation step appeared to exert a greater influence on the overall propagation rate for **1a**. Polymerization rates were influenced by depropagation at the relatively low temperatures of 50−60 °C (**1a**) and 70−85 °C (**1b**), and both monomers exhibited the same ceiling temperature of approximately 125 °C at $[M]_0 = 2$ M in benzene.

Introduction

Free radical ring-opening monomers have attracted consistent research attention owing to the smaller volume shrinkage that occurs upon polymerization in comparison to common vinyl monomer polymerizations. Additionally, such monomers allow the introduction of a variety of functional groups and heteroatoms into polymer backbones. These advantages are offered coupled with the advantages of free radical addition reactions such as compatibility toward a wide variety of functional groups and reaction media.[1−3]

Cyclic ring-opening monomers usually contain vinyl substituents and undergo polymerization via a two-step mechanism of radical addition onto the vinyl substituent followed by β-fragmentation. β-Fragmentation is favored owing to one or more of the following reasons: relief of ring strain, cleavage of a weak C−heteroatom bond, formation of a new stabilized radical center, and/or the accommodation of stereoelectronic requirements for β-fragmentation.[1,2] Starting in 1994, the Australian CSIRO group introduced a series of free radical ring-opening cyclic allylic sulfide monomers, which undergo polymerization under mild conditions via fragmentation of a weak C−S bond to generate propagating sulfanyl radicals.[4−6] The proposed advantage of propagating sulfur-centered radicals in comparison to more common carbon- and oxygen-centered radicals is the lack of a thermodynamic driving force for chain transfer via hydrogen abstraction because of the weak thiol (RS−H) bond. The monomer most extensively studied by the CSIRO with Harrisson and Davis was eight-membered methyl-substituted disulfide monomer 2-methyl-7-methylene-1,5-dithiacyclooctane, **1a** (which is also known as 3-methylene-6-methyl-1,5-dithiacyclooctane, MDTO) (Scheme 1).[6−10] Monomer **1a** was shown to undergo polymerization to complete conversion to provide high molecular weight polymer.[6] NMR analysis of the resultant homopolymer[6] and copolymer[7] backbones, copolymerization,[7,8] and chain-transfer mechanism and kinetics were presented.[9−11]

We now report the trimethyl-substituted analogue (2,2,4-trimethyl-7-methylene-1,5-dithiacyclooctane) **1b** and examine the influence of the additional dimethyl ring substituents located in a remote position from the carbon−carbon double bond on the polymerization process. The first step of propagation shown in Scheme 1 involves addition of the sulfanyl radical onto the monomer double bond to produce intermediate carbon-centered radicals **2a,b**, which do not propagate. The second step involves rapid fragmentation of adduct radicals **2a,b** via the allylic C−S bonds to generate new sulfanyl radicals **3** and **4** and polymer backbone double bonds. Both monomers produce propagating sulfanyl radicals containing an α-methyl substituent **3a,b**; however, monomers **1a** and **1b** also give α-unsubstituted (R = H) **4a** and α,α-dimethyl-substituted (R = Me) sulfanyl radicals **4b**, respectively. Values for the lumped parameter $k_p/k_t^{0.5}$ (where k_p and k_t are the rate coefficients for propagation and termination, respectively) were determined as a function of temperature and compared for the two monomers. Polymerizations were carried out at higher temperatures where depropagation kinetics exerted an influence on the polymerization rate, thus enabling us to estimate the ceiling temperatures. We believe that this is the first time that ceiling temperatures have been estimated for free radical ring-opening monomers, although the issue has been discussed in previous papers.[5,6] Further, the variation of $k_p/k_t^{0.5}$ with temperature in the region where depropagation does not exert an influence allowed us to deter-

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[†] National University of Ireland, Galway.
[‡] Osaka City University.
[§] Kobe University.
[⊥] Current address: National University of Ireland, Galway.
[*] Corresponding authors.

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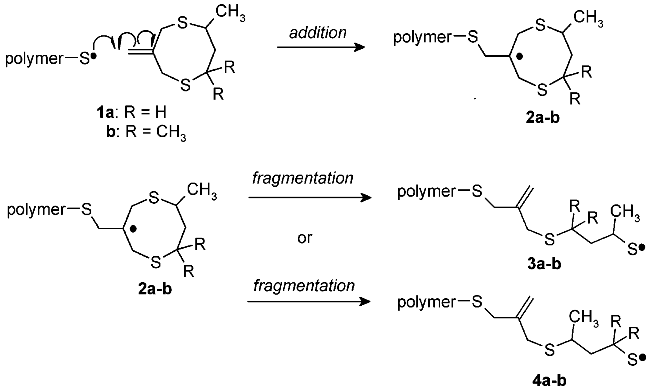
Scheme 1. Two-Step Ring-Opening Polymerization Mechanism for Monomers 1a,b



mine the effect of the additional remote dimethyl substituents on the propagation step.

Experimental Section

Materials. Commercial initiators (Wako Pure Chemicals) 2,2′-azobis(2,4-dimethylvaleronitrile) (AVN), 2,2′-azo(isobutyronitrile) (AIBN), and 1,1′-azobis(cyclohexane-1-carbonitrile) (ACN) were recrystallized using methanol before use, and the purity was assumed to be 100%. *tert*-Butyl peroxide (TBP, 99%) was used as purchased. Thin-layer chromatography and column chromatography were carried out with aluminum-backed plates coated with silica gel (Merck 60F$_{254}$) and Merck Isabel 60H silica, respectively. All other chemicals used were purchased from Aldrich.

Characterization. IR spectra were acquired using a Perkin-Elmer Spec 1 with ATR attached. All ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ at 400 and 100 MHz, respectively, using a JEOL GXFT 400 MHz instrument equipped with a DEC AXP 300 computer workstation. EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, carried out high-resolution mass spectrometry on the Finnigan MAT 900 XLT in the electron impact (EI) mode with EI source temperature of 200 °C and electron energy of 70 eV.

Preparation of Monomers. 2-Methyl-7-methylene-1,5-dithiacyclooctane (**1a)** was prepared according to a literature[9] procedure in 52% yield from 1,3-butanedithiol[6] and 3-chloro-2-chloromethyl-1-propene (99%). 2,2,4-Trimethyl-7-methylene-1,5-dithiacyclooctane (**1b)** was prepared by separate simultaneous syringe pump (4 mL/h) addition of 2-methyl-2,4-pentanedithiol[12] (2.79 g, 18.6 mmol) and 3-chloro-2-chloromethyl-1-propene (2.33 g, 18.6 mmol) to a refluxing solution of sodium methoxide (0.06 M) in methanol (600 mL). The resulting solution was refluxed for a further 6 h and evaporated to dryness. Water (150 mL) added, extracted with CH$_2$Cl$_2$ (3 × 50 mL), and dried (MgSO$_4$). Column chromatography using silica gel as absorbent and 3:1 hexane:CH$_2$Cl$_2$ as eluent gave monomer **1b** (2.19 g, 58%) as a colorless oil. IR (neat): 3074 w, 2955 s, 2921 m, 2863 w, 1634 m, 1448 s, 1402 m, 1383 w, 1364 w, 1239 m, 1145 s, 1057 w, 1019 w, 968 w cm^{-1}. δ_H 1.15 (s, 2-CH$_3$, 3 H), 1.26 (d, J = 7.8 Hz, 4-CH$_3$, 3 H), 1.35 (s, 2-CH$_3$, 3 H), 1.62 (dd, J^2 = 15.6 Hz, J^3 = 2.4 Hz, CHCH_2, 1 H), 2.52 (dd, J^2 = 15.6 Hz, J^3 = 4.8 Hz, CHCH_2, 1 H), 3.14 (d, J = 15.6 Hz, 6 or 8-CH$_2$S, 1 H), 3.22 (d, J = 14.7 Hz, 6 or 8-CH$_2$S, 1 H), 3.34 (m, CH, 1 H), 3.52 (d, J = 15.6 Hz, 6 or 8-CH$_2$S, 1 H), 3.86 (d, J = 14.7 Hz, 6 or 8-CH$_2$S, 1 H), 5.03 (d, J = 10.4 Hz, =CH$_2$, 2 H). δ_C 24.7 (CH$_3$), 27.8 (CH$_3$), 30.5 (CH$_3$), 34.6 (CH$_2$), 34.7 (CH$_2$), 38.4, (CH), 45.6 (2-C), 52.6 (CH$_2$), 114.1 (=CH$_2$), 146.5 (=C). HRMS calcd for C$_{10}$H$_{18}$S$_2$: 202.0844; found (M$^+$): 202.0842.

Polymerization Measurements. The conversions for the polymerization of monomers **1a** and **1b** were estimated from the decrease in the area of CH$_2$= (5.15 ppm) and CH$_2$S (3.86 ppm) peaks, respectively, after normalization with respect to the integration area of the entire ^{1}H NMR spectrum. Molecular weight measurements were carried out on crude polymerization mixtures with a Tosoh-800 series GPC System equipped with TSK-gel colomns G5000H$_{HR}$, GMultipoerH$_{XL}$-M, and GMH$_{HR}$-L (5 μm particle sizes; exclusion limits are 4 × 10^6, 2 × 10^6, and 4 × 10^6, respectively) connected in this order with a differential refractometer (RI-8082). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL min^{-1} at 40 °C. Poly(St) standards (M_n = 500−1090000) were used for calibration, since literature Mark−Houwink−Sakurada (MHS) constants are only available for poly(**1a**)[9] and not poly(**1b**).

Polymerization Procedure. All polymerizations were carried out in glass tubes, degassed by several freeze−thaw cycles, and sealed under vacuum. Polymerization solutions contained 2 M of **1a,b** with initiator in benzene. Polymerizations of **1a** at 30 and 40 °C used 0.4 and 0.2 M of AVN, respectively, at 45, 50, 60, and 70 °C used 0.6, 0.4, 0.1, and 0.018 M of AIBN, respectively, at 85 °C used 0.05 M of ACN, and at 100 and 120 °C used 0.2 and 0.04 M of TBP, respectively. Polymerization of **1b** at 40 °C used 0.5 M of AVN, at 50 and 60 °C used 0.4 M of AIBN, at 70 and 85 °C used 0.6 and 0.2 M of ACN, respectively, and at 100 and 120 °C used 0.4 and 0.02 M of TBP, respectively. The reactions were quenched on an ice bath and evaporated to dryness, and a sample was dissolved in CDCl$_3$ for conversion measurement by ^{1}H NMR.

Polymerization for NMR Characterization of Poly(1b). Polymerizations of **1b** containing [M]$_0$ = 2 M and [ACN]$_0$ = 0.6 M at 70 °C resulted in 80% conversion after 20 h; M_n = 9630, M_w/M_n = 1.89. The crude poly(**1b**) sample was dissolved in CH$_2$Cl$_2$ and precipitated from hexane for characterization by NMR. δ_H 1.31−1.36 (m, CH$_3$), 1.67−1.71 (m, CH_2CH), 1.80−1.92 (m, CH_2CH), 2.32−2.36 (m, possibly due to cyclic oligomers), 2.82−2.89 (m, CH), 3.17−3.19 (m, possibly due to cyclic oligomers), 3.22−3.38 (m, CH$_2$S), 4.86−4.95 (m, approximately 10% by NMR integration, possibly due to cyclic oligomers[9]), 4.99−5.16 (m, =CH$_2$). δ_C 23.7 (CH$_3$), 28.8 (CH$_3$), 29.6 (CH$_3$), 32.2 (CH$_2$CH), 32.8 (CH$_2$CH), 34.4, 34.7, 35.1, 35.5, 35.7 (all CH$_2$S), 37.1 (C(CH$_3$)$_2$), 46.4, 49.2, 50.0 (all CH$_2$S), 112.7−112.8 (d, possibly due to cyclic oligomers[9]), 115.1, 115.5, 115.9 (t, =CH$_2$), 141.4, 142.2, 142.7, 144.9 (all C=CH$_2$, possibly due to tacticity effects[6]). The ^{13}C NMR spectrum of poly(**1b**) is available in the Supporting Information.

Results and Discussion

NMR Analysis of Polymers. Polymerizations of monomer **1b** occurred with complete ring-opening and without significant loss of polymer backbone double bonds by analysis of the ^{1}H NMR spectra, as previously carried out on **1a**.[6] The vinylidene hydrogen integrals appeared in proportion with the number of hydrogens in the rest of the poly(**1a**) and poly(**1b**) spectra. Small peaks due to the formation of presumed cyclic oligomers (see Experimental Section) formed by backbiting reaction of propagating sulfanyl radicals[9] were observed in the ^{1}H NMR spectrum of poly(**1b**), but not poly(**1a**). A 1:2:1 triplet for vinylidene =CH$_2$ was observed in the ^{13}C NMR spectrum of both poly(**1a**) and poly(**1b**) (see Experimental Section and Supporting Information), as previously reported by Evans and Rizzardo for poly(**1a**),[6] thus providing evidence that fragmentation occurs at both allylic C−S bonds for each monomer.

Determination of $k_p/k_t^{0.5}$. Benzene solutions of monomers **1a,b** (2 M) were polymerized at 30−120 °C to various conversions. Monomer **1a** polymerized faster than **1b** at all temperatures, as illustrated by the polymerizations carried out at 50 °C, where under identical conditions monomer **1a** polymerized 19 times faster than **1b** (Figure 1). Relatively high initial initiator concentrations [I]$_0$ of 0.02−0.6 M were required in order to achieve reasonable polymerization rates for monomer **1b**. The lumped parameter $k_p/k_t^{0.5}$ is usually estimated

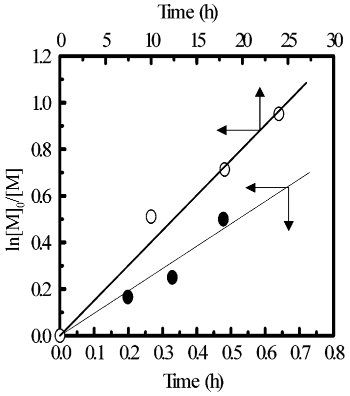


Figure 1. First-order plots for the polymerization of monomers **1a** (●) and **1b** (○) in benzene at 50 °C, where the initial monomer concentration $[M]_0 = 2$ M and initial 2,2′-azo(isobutyronitrile) concentration $[AIBN]_0 = 0.4$ M.

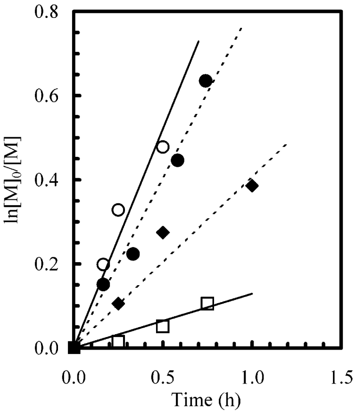


Figure 2. First-order plots for the polymerization of monomer **1a** in benzene at various temperatures, where initial monomer concentration $[M]_0 = 2$ M, and initial initiator concentrations are [AVN] = 0.4 and 0.2 M at 30 (□) and 40 °C (◆), respectively, and [AIBN] = 0.6 and 0.4 M at 45 (●) and 50 °C (○), respectively. Initiators defined under Table 2.

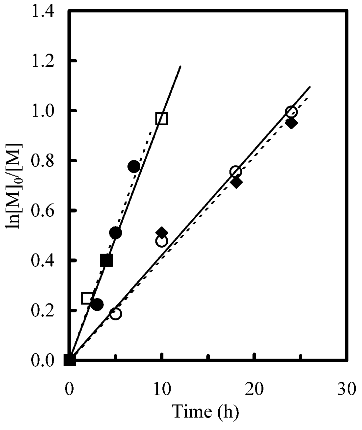


Figure 3. First-order plots for the polymerization of monomer **1b** in benzene at various temperatures, where initial monomer concentration $[M]_0 = 2$ M and initial initiator concentrations are [AVN] = 0.5 M at 40 °C (○), [AIBN] = 0.4 M at 50 °C (◆) and 60 °C (●), and [ACN] = 0.6 M at 70 °C (□). Initiators defined under Table 2.

as a function of temperature from the initial slopes of the first-order plots (Figures 1−3) according to eq 1.

$$\ln\frac{[M]_0}{[M]} = \left(\frac{k_p}{k_t^{0.5}}\right)(f k_d[I]_0)^{0.5}t \qquad (1)$$

Table 1. Estimated Arrhenius Parameters for the Polymerization of 2 M Solutions of Monomers 1a (30−50 °C) and 1b (40−70 °C) in Benzene

monomer	$E_p - 0.5E_t$ (kJ mol^{-1})	$A_p/A_t^{0.5}$ (L$^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$)
1a	72	1.7×10^{11}
1b	30	9.9×10^{2}

The quantity $2fk_d[I]_0$ is the rate of primary radical formation from the initiator (R_{pr}). However, under conditions of high concentrations of azo initiator, competition between addition of primary radicals (R$^\bullet$) to the double bond of **1a** or **1b** (rate = $k_i[R^\bullet][M]$), and bimolecular reaction of primary radicals (rate = $2k_{t1}[R^\bullet]^2$) cannot be neglected. To quantify this effect, [R$^\bullet$] was estimated by solving the quadratic equation describing the steady state with respect to R$^\bullet$: $2fk_d[I]_0 - k_i[R^\bullet][M] - 2k_{t1}[R^\bullet]^2 = 0$. The values of R_{pr} were calculated from the rate constants k_d as obtained from the literature:[13] AVN at 30 and 40 °C, 9.66×10^{-7} and 4.47×10^{-6} s^{-1}; AIBN at 45, 50, 60, and 70 °C, 1.10×10^{-6}, 2.09×10^{-6}, 8.45×10^{-6}, and 3.17×10^{-5} s^{-1}; ACN at 70 and 85 °C, 1.42×10^{-6} and 1.26×10^{-5} s^{-1}. The initiator efficiency (f) was assumed to be 0.5 for the azo initiators (due to the cage effect). The k_i values were approximated using the rate constants for addition of the 2-cyano-2-propyl radical to 1-butene (34 L/(mol s) at 315 K and activation energy of 35.2 kJ/mol).[14] This represents the addition of a resonance stabilized radical onto a nonconjugated carbon−carbon double bond and would be expected to be comparable to the k_i in the case of α-cyano-substituted carbon-centered radicals from AIBN, AVN, and ACN adding onto the vinyl substituent of **1a,b**. The value of k_{t1} was assumed to be 10^9 L/(mol s) in all cases. The values of R_i for the cyanoisopropyl radicals and **1b** were estimated to be less than R_{pr} by factors (F) of 0.59 (40 °C), 0.86 (50 °C), 0.79 (60 °C), 0.96 (70 °C), and 0.96 (85 °C) under the conditions in Table 1: $R_i = FR_{pr} = 2Ffk_d[I]_0$. Values of $k_p/k_t^{0.5}$, corrected for bimolecular reaction of primary radicals, were thus obtained via eq 1 by replacing $fk_d[I]_0$ with $Ffk_d[I]_0$. Similarly, the F values of 0.74 (40 °C), 0.86 (50 °C), 0.93 (60 °C), 0.97 (70 °C), and 0.99 (85 °C) were used to obtain R_i for **1a** polymerizations. The k_d values of TBP at 100 and 120 °C are 8.80×10^{-7} and 1.10×10^{-5} s^{-1},[13] and the f value was approximated to be 1.0 (no cage reaction). For the polymerization initiated by TBP, the value of F was approximated to be unity because of the higher reactivity of the *tert*-butoxy radical in comparison to the resonance stabilized primary radicals from the azo-initiators.

Ceiling Temperatures (T_c). The propagation step in free radical polymerization becomes increasingly reversible with increasing temperature. T_c is defined as the temperature at which polymer formation no longer occurs; at T_c, $\Delta G = \Delta H - T\Delta S = 0$. The ceiling temperatures were estimated on the basis of the approach previously suggested by Yamada,[15] which involves plotting $\ln(k_p'/k_t^{0.5})$ vs $1/T$, where $k_p'/k_t^{0.5}$ is obtained from the initial slope of the pseudo-first-order plots. Here k_p' denotes an apparent propagation rate coefficient which contains a contribution from depropagation. The value of T_c is subsequently obtained from eq 2:

$$\lim_{T\to T_c} \mathrm{d}(\ln k_p'/k_t^{0.5})/\mathrm{d}(1/T) = \infty \qquad (2)$$

It is apparent by the downward deviation from linearity in Figure 4 at approximately 50−60 and 70−

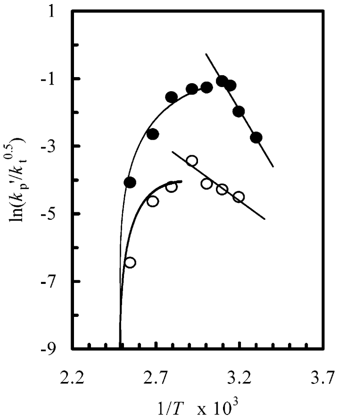


Figure 4. Plot of $\ln(k_p'/k_t^{0.5})$ vs $1/T$ for the polymerizations of monomers **1a** (●) and **1b** (○) in benzene using the initiators given in Table 2 and the Experimental Section, where the initial monomer concentration $[M]_0 = 2$ M.

85 °C for monomers **1a** and **1b**, respectively, that depropagation exerted an influence at much lower temperatures than for typical vinyl monomer polymerizations. The high positive values of the slopes of the curves above 100 °C indicate suppression of polymer formation as T_c is approached. Depropagation can be attributed to the reversibility at higher temperatures of the addition step. Support for the reversibility of the addition step is provided by the known reversible addition of sulfanyl radicals onto double bonds at relatively low temperatures in comparison to the addition of carbon-centered radicals.[16] This was first demonstrated many years ago by the reversible addition of methylsulfanyl radicals to *cis*-2-butene at 60 °C, which led to isomerization to *trans*-2-butene.[17] Further, the reversible addition of sulfanyl radicals onto styrene and methyl methacrylate has been attributed to be the cause of significant changes in copolymer composition in copolymerizations of **1a** with the latter monomers.[7] However, it cannot be excluded that reversibility of the ring-opening step may also be a contributing route to depropagation. According to the graphical treatment in Figure 4, it appears that for both monomers $T_c \approx 125$ °C at a monomer concentration of 2 M. Thus, the extra dimethyl substituents of monomer **1b** have no effect on T_c, despite significantly slowing down the polymerization of monomer **1b** relative to **1a**.

Estimation of Arrhenius Parameters. Using the temperature ranges where depropagation does not exert an influence on the polymerization rate (i.e., no downward curvature in Figure 4), we obtained information about the frequency factor (A_p) and activation energy (E_p) for the propagation of monomers **1a,b** (Table 1) from the temperature dependence of $k_p/k_t^{0.5}$ using the Arrhenius equation (3).

$$\ln \frac{k_p}{{k_t}^{0.5}} = \ln \frac{A_p}{{A_t}^{0.5}} - \frac{0.5E_t - E_p}{RT} \qquad (3)$$

The magnitude of the activation energy ($E_p - 0.5E_t$) for monomer **1a** of 72 kJ mol^{-1} (30–50 °C) and the lower value for monomer **1b** of 30 kJ mol^{-1} (40–70 °C) suggest that unimolecular and bimolecular reactions, respectively, are important in determining the propagation rate.[18] It follows that the lower activation energy of monomer **1b** may be interpreted in terms of the fragmentation step exerting less influence on the overall propagation rate in comparison to monomer **1a**. The value of A_t is typically of the order 10^9 L/(mol s),[19] resulting in $A_p = 5.4 \times 10^{15}$ and 3.1×10^7 L/(mol s) for monomers **1a** and **1b,** respectively. The magnitudes of the values of A_p also suggest that k_p for monomer **1a** is more significantly affected by a first-order reaction (i.e., the fragmentation step) than monomer **1b**.[18] This may be related to the fragmentation step for monomer **1b** forming sulfanyl radicals with different α-substituents to **1a**, as a more stable α,α-dimethyl-substituted **4b** as opposed to α-unsubstituted radical **4a** is formed. This is supported by the literature ring-opening of substituted cyclopropylmethyl radicals, where acceleration occurs with substituents that increase the stability of the rearranged or fragmented adduct radical.[20] However, the propagating sulfanyl radical **4a** would also be expected to undergo faster rates of addition than **4b** for steric reasons. Both of these effects (slower fragmentation and faster addition for monomer **1a**) would contribute to an increase in the observed values of $E_p - 0.5E_t$ and $A_p/A_t^{0.5}$. In support of our findings concerning monomer **1a**, Harrisson previously reported that polymerization of monomer **1a** proceeded with an order of reaction less than unity with respect to monomer concentration at temperatures of 40 and 50 °C and explained this in terms of the fragmentation rate affecting the overall propagation rate.[21]

$R_p/(R_i)^{0.5}$ and Molecular Weights. Table 2 shows the initial rates of polymerization (R_p) for monomers **1a,b**, which have been normalized with respect to the rates of initiation (R_i) according to classical kinetics (i.e., R_p is proportional to $R_i^{0.5}$) to enable direct comparison at each temperature. Monomer **1a** polymerizes much faster than monomer **1b**; the differences are greatest between 40 and 60 °C, where monomer **1a** polymerizes 13–19 times faster than **1b**. The differences in $R_p/(R_i)^{0.5}$ markedly decrease with increasing temperature (i.e., with increasing depropagation) up to 120 °C with monomer **1a** polymerizing 5–8.5 times faster, except at 85 °C, where the difference is a factor of 14. The main factor responsible for the lower polymerization rates of monomer **1b** is presumably the lower rates of addition of radical **4b**, as compared to the less congested radical **4a**. This is a more likely reason than steric effects by the extra 2,2-dimethyl substituents in **1b**, which are too remote to hinder the addition step. In contrast, the methyl substituent at the allylic position of a seven-membered acrylate-based sulfide monomer was reported to lower this monomer's reactivity in copolymerizations as compared to the unsubstituted analogue monomer for steric reasons.[4]

Table 2 also shows that molecular weights of the order of 10^4 were obtained for the polymerization of monomer **1a**, as compared to 10^3 for **1b**. The ratios between the M_n values of the two monomers are very similar to the ratios in $R_p/(R_i)^{0.5}$ at each temperature, except at 85 °C where the degree of polymerization obtained for **1a** was significantly greater than predicted by differences in $R_p/(R_i)^{0.5}$. In the case of **1a**, it has been shown that chain transfer to monomer is significantly higher than for common vinyl monomers.[9,11] Although the current study provides no direct information on the extent of chain transfer to monomer in the case of **1b**, it can be speculated that since the ratios between the M_n values of the two monomers are very similar to the ratios in $R_p/(R_i)^{0.5}$, the levels of chain transfer to monomer may be similar for the two monomers (because chain transfer

Table 2. Polymerizations of 2 M Benzene Solutions of Monomers 1a and 1b at 40−120 °C[a]

monomer	temp (°C)	initiator (M)	$R_i \times 10^{7\,b}$ (M s^{-1})	$R_p \times 10^5$ (M s^{-1})	$R_p/(R_i)^{0.5}$ (M$^{0.5}$ s$^{-0.5}$)	$M_n \times 10^3$ (M_w/M_n)^c
1a	40	AVN (0.2)	6.62	22.67	0.279	85.50 (1.66)
1b	40	AVN (0.5)	13.20	2.54	0.022	5.40 (1.62)
1a	50	AIBN (0.4)	7.19	44.68	0.527	36.80 (1.74)
1b	50	AIBN (0.4)	7.19	5.73	0.028	3.00 (1.62)
1a	60	AIBN (0.1)	7.86	50.17	0.567	35.10 (1.89)
1b	60	AIBN (0.4)	26.70	5.73	0.035	2.50 (2.20)
1a	70	AIBN (0.018)	5.53	40.31	0.542	22.80 (1.83)
1b	70	ACN (0.6)	8.18	5.83	0.064	2.20 (1.37)
1a	85	ACN (0.05)	6.24	33.53	0.425	77.40 (1.86)
1b	85	ACN (0.2)	24.20	4.63	0.030	2.10 (1.44)
1a	100	TBP (0.2)	3.48	5.93	0.101	36.30 (1.98)
1b	100	TBP (0.4)	6.96	1.16	0.014	6.10 (1.64)
1a	120	TBP (0.04)	8.80	2.30	0.026	47.40 (1.59)
1b	120	TBP (0.02)	4.40	0.31	0.005	6.00 (1.34)

[a] Abbreviations: AVN, AIBN, ACN, and TBP are 2,2′-azobis(2,4-dimethylvaleronitrile), 2,2′-azo(isobutyronitrile), 1,1′-azobis(cyclohexane-1-carbonitrile), and *tert*-butyl peroxide, respectively, and M_n, M_w, and M_w/M_n are number-average and weight-average molecular weights and polydispersity index, respectively. [b] $R_i = FR_{pr}$ for azo-initiated polymerizations (see text). [c] Conversions are 5−24% in all cases.

to monomer affects M_n, but not $R_p/(R_i)^{0.5}$, assuming negligible effects of chain length dependent termination and propagation). Chain transfer to polymer would be expected to be less significant for the polymerizations shown in Table 2 due to the relatively low conversions (5−24%). However, it has been shown for **1a** that at higher polymer concentrations chain transfer to polymer is very significant.[11] GPC traces are monomodal for all polymerizations shown in Table 2, except for low molecular weight shoulders for **1a** at 70 and 100 °C, which are likely due to cyclic oligomer formation as previously reported by Harrisson et al.[9] Despite observing possible cyclic oligomer peaks (approximately 10%) in the ^{1}H NMR of poly(**1b**), no low molecular weight shoulders were observed in the GPC traces presumably because of the lower degrees of polymerization for this monomer compared to **1a**. It would be anticipated that M_n (having accounted for the differences in R_i) for both monomers would decrease at higher temperatures as T_c is approached; however, this was not the case. It cannot be excluded that M_n at the lower temperatures was somewhat reduced because of primary radical termination as a result of the high primary radical concentrations. The polymerizations at higher temperature were carried out using TBP, and the high reactivity toward radical addition of the *tert*-butoxy radical may lead to minimization of primary radical termination and therefore higher M_n.

Conclusions

A new eight-membered cyclic allylic disulfide, 2,2,4-trimethyl-7-methylene-1,5-dithiacyclooctane (**1b**), containing three remote methyl substituents, required high initiator concentrations for polymerization to proceed at reasonable rates. Monomer **1b** polymerizes significantly slower than analogue 2-methyl-7-methylene-1,5-dithiacyclooctane (**1a**) containing only one remote 2-methyl ring substituent. Upon examination of the Arrhenius parameters for propagation, it was found that the fragmentation step appears to exert less influence on the overall propagation rate for monomer **1b** than for monomer **1a**. The polymerization rates of both monomers were influenced by depropagation at the relatively low temperatures of 50−60 and 70−85 °C for **1a** and **1b,** respectively, i.e., at much lower temperatures than for typical vinyl monomers. Although the extra dimethyl ring substituents of **1b** have a significant influence on the rate of polymerization and the nature of the propagation step in comparison to **1a**, both monomers exhibited the same ceiling temperature of approximately 125 °C at $[M]_0 = 2$ M in benzene. Polymerization rate and molecular weight data indicate that the levels of chain transfer to monomer are similar for monomers **1a** and **1b**.

Supporting Information Available: ^{13}C NMR spectrum of poly(**1b**). This material is available free of charge via the Internet at http://pubs.acs.org.

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