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Synthesis and Properties of (Alkylthio)methyl-Substituted Poly(oxyalkylene)s and (Alkylsulfonyl)methyl-Substituted Poly(oxyalkylene)s

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ABSTRACT: (Alkylsulfonyl)methyl-substituted poly(oxyalkylene)s were synthesized in two steps. (Alkylthio)methyl-substituted poly(oxyalkylene)s were made by the reaction of poly[oxy(chloromethyl)ethylene] (CE), poly[oxy(chloromethyl)ethylene-*co*-oxyethylene] (CEE), or poly[oxy-2,2-bis(chloromethyl)trimethylene] (BCT) with sodium alkanethiolates. Then they were oxidized to (alkylsulfonyl)methyl-substituted poly(oxyalkylene)s using *m*-chloroperbenzoic acid. Their structures were confirmed by NMR and IR. The polymer glass transition temperatures (T_g's) decreased as the number of carbon atoms in the alkyl side chains increased, except for the T_g of (*n*-pentylsulfonyl)methyl-substituted CE (the number of carbon atoms in the side chain is 5). Its T_g was about that of (butylsulfonyl)methyl-substituted CE. TGA studies showed that side-chain length did not affect the thermal decomposition behavior. However, polymers with different backbones had slightly different thermal decomposition behaviors. The solubility of the (alkylsulfonyl)methyl-substituted poly(oxyalkylene)s strongly depended on the side-chain length. (Methylsulfonyl)methyl-substituted poly(oxyalkylene)s were soluble only in polar solvents, such as DMAc, DMSO, and formic acid. (Alkylsulfonyl)methyl-substituted poly(oxyalkylene)s with long alkyl side chains were also soluble in less polar solvents, such as $CHCl_3$ and THF.

Introduction

A large number of vinyl polymers with functional side groups have been synthesized and used for widely varying applications. Poly(oxyethylene) derivatives with simple side chains, such as methyl, vinyl, phenyl, chloromethyl, and ether groups, have been synthesized by direct polymerization of the appropriate oxirane.[1−4] High molecular weight poly(oxyethyene)s with more complex and/or polar side groups, such as ester, cyano, nitro, and silyl, have not been synthesized.[4−10] Researchers have tried to make poly(oxyethylene)s with these functional side groups by direct polymerization. The synthesis of pure monomers proved difficult, and even when pure monomers were prepared, side reactions during polymerization resulted in low molecular weight polymer.

Sulfur-containing polymers have been drawing growing attention due to the desirable properties of sulfide (thioether), sulfoxide, and sulfone groups.[11,12] Sulfide groups can increase the polymer chain flexibility, whereas sulfone groups introduce stiffness and enhanced stability toward oxidation. Sulfoxide-containing polymers should have properties similar to those of DMSO.[13−17] Various polymers containing sulfur in the main chain have been synthesized.[11−17] However, synthesis of poly(oxyethylene)s with sulfur-containing side groups has not been reported.

The aim of this paper is to describe the syntheses and thermal properties of novel poly(oxyalkylene)s with sulfur-containing side groups. (Alkylthio)methyl-substituted poly(oxyalkylene)s were made from modification of poly[oxy(chloromethyl)ethylene], poly[oxy(chloromethyl)ethylene-*co*-oxyethylene], or poly[oxy-2,2-bis(chloromethyl)trimethylene] with sodium alkanethiolates. These were then oxidized using *m*-chloroperbenzoic acid to give the (alkylsulfonyl)methyl-substituted poly(oxyalkylene)s. Their physical and thermal properties were studied. These polymers have been synthesized in order to investigate their gas barrier properties; these will be discussed in subsequent papers.

Experimental Section

Materials. Poly[oxy(chloromethyl)ethylene] (CE) (Hydrin H, Zeon Chemical Inc., poly(epichlorohydrin)) and poly[oxy(chloromethyl)ethylene-*co*-oxyethylene] (CEE) (Hydrin C, mole ratio of oxy(chloromethyl)ethylene to oxyethylene is 1:1, Zeon Chemical Inc.) were purified by precipitating a 3 wt % chloroform solution into a 10-fold excess of methanol. Poly[oxy-2,2-bis(chloromethyl)trimethylene] (BCT) (PENTON, Hercules Inc.) was purified by precipitation of a 3 wt % cyclohexanone solution into a ten-fold excess of methanol. Sodium methanethiolate, sodium ethanethiolate, *n*-propanethiol, *i*-propanethiol, *n*-butanethiol, and *n*-pentanethiol (all from Fluka) were used as received. Tetrabutylphosphonium bromide (TBPBr) (Aldrich) was purified by recrystallization from ether/hexane solution. *m*-Chloroperbenzoic acid (*m*-CPBA) (Aldrich, 57−86 wt %) was purified according to the literature method.[18] All other reagents and solvents were used as received.

Techniques. Intrinsic viscosities of polymer solutions in DMAc, THF, or formic acid were measured at 30 °C using a Cannon-Ubbelohde viscometer.[19] ^{1}H-NMR and ^{13}C-NMR spectra were recorded using a 200 MHz Varian XL-200 spectrometer. The coupling constant, *J*, is given in hertz. FT-IR spectra were recorded using a Digi-lab FTS-60 spectrometer. The samples were cast from solution onto a KBr plate and dried under vacuum at 130 °C for at least 1 week. Differential scanning calorimetry (DSC) measurements of polymers (10−13 mg) were carried out under nitrogen using a DuPont 921 DSC. The glass transition temperatures of all samples and the melting temperatures of poly[oxy-2,2-bis((alkylthio)methyl)trimethylene]s (ATTs) (Scheme 1) were obtained from the second run at a heating rate of 20 °C/min. The melting temperatures of ASTs were obtained after annealing the sample just below its melting temperature for 12 h. The sample was quenched to below its T_g, and the thermogram was then obtained using a heating rate of 20 °C/min. TGA spectra were obtained using a DuPont 2000 analyzer with a 50 °C/min high-resolution heating rate in an atmosphere of nitrogen gas flowing at 50 mL/min (when there is no weight change, heating rate is 50 °C/min, but when there is any weight change, heating rate is as low as 0.1 °C/min).

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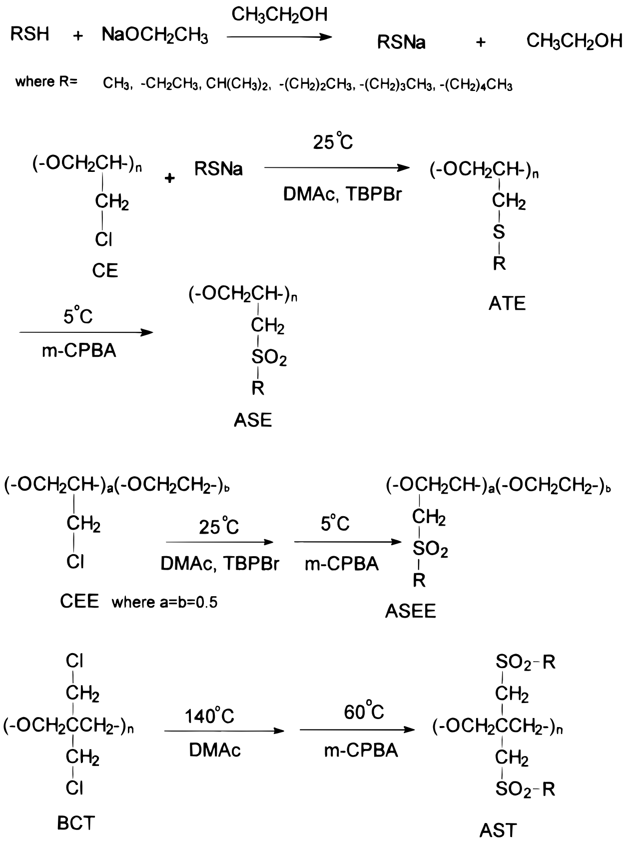
Scheme 1



Sodium Alkanethiolates. Sodium methanethiolate and sodium ethanethiolates were purchased from Fluka, but other sodium alkanethiolates were prepared by adding alkanethiols to a solution of sodium ethoxide in ethanol (Scheme 1); the solid residue obtained after evaporation of the solvent was washed with ether, filtered, and dried under vacuum.

Typical Procedure for Synthesis of (Alkylthio)methyl-Substituted Polymers. The following procedure was used to synthesize all the (alkylthio)methyl-substituted polymers. The synthesis is exemplified in the case of poly[oxy(methylthiomethyl)ethylene] (MTE). The abbreviations for the (alkylthio)methyl-substituted polymers and their NMR data are given in Tables 1 and 2, respectively. CE (1.70 g, 18 mmol) was dissolved in 100 mL of DMAc, and TBPBr (0.15 g, 0.4 mmol) and sodium methanethiolate (28.8 mmol) were added. The reaction mixture was magnetically stirred at room temperature for 2 h and poured into distilled water. The precipitate was purified by several precipitations from THF solution into distilled water and then dried under vacuum at 80 °C overnight. The yields were always above 90%. The reaction conditions of the other (alkylthio)methyl-substituted polymers are listed in Table 3.

Typical Procedure for Synthesis of (Alkylsulfonyl)methyl-Substituted Polymers. The following procedure was used to synthesize all the (alkylsulfonyl)methyl-substituted polymers. The synthesis is exemplified in the case of poly[oxy(methylsulfonylmethyl)ethylene] (MSE). The abbreviations for all the (alkylsulfonyl)methyl substituted polymers and the NMR data are given in Tables 4 and 5 respectively. MTE (1.00 g) was dissolved in DMAc (40 mL) at room temperature, and the polymer solution was cooled to 0 °C. An excess of *m*-CPBA (4.97 g) was added to the polymer solution. The reaction solution was stirred for 2 h and then poured into methanol. The precipitated polymer was purified by several reprecipitations from formic acid solution into methanol until all remaining *m*-CPBA and *m*-chlorobenzoic acid were removed. For ESE, MST, and MSEE, formic acid was used as the purification solvent. For the other (alkylsulfonyl)methyl-substituted polymers, chloroform was used. The polymer was dried under vacuum at 120 °C for 1 week. The yields were always above 90%. The reaction conditions for all the (alkylsulfonyl)methyl-substituted polymers are listed in Table 6. The ASTs were made using the same reaction scheme (Scheme 1), but higher temperatures were needed to dissolve the polymers.

Results and Discussion

(Alkylthio)methyl-substituted polymers such as poly[oxy((alkylthio)methyl)ethylene] (ATE), poly[oxy((alkylthio)methyl)ethylene-*co*-oxyethylene] (ATEE), and poly[oxy-2,2-bis((alkylthio)methyl)trimethylene] (ATT) were made by reacting CE, CEE, and BCT with sodium alkanethiolate, using DMAc as a solvent and TBPBr as a phase transfer catalyst (Scheme 1). The solvent effect on this reaction was described in the previous paper;[20] we found that DMAc was a suitable reaction solvent. Table 3 shows the reaction conditions and results. CE and CEE were reacted at 25 °C. The reaction temperature was 140 °C for BCT, because of its limited solubility in DMAc at low temperature. The reactions were followed by ^{1}H-NMR and/or ^{13}C-NMR and/or FT-IR.

Figure 1 shows the conversion of CE to *n*-PrTE (Figure 1A,B). By comparing the integral of the triplet in Figure 1B at 0.69 ppm (a, three protons) with the integral of the backbone peaks at 3.43−3.76 ppm (e, three protons), the degree of conversion could be calculated; it was 100% within experimental error. ^{13}C-NMR confirmed this. Figure 2 shows ^{13}C-NMR spectra of CE and MTE. The three peaks of CE (Figure 2A) transformed to new four peaks (Figure 2B); there was no trace of the chloromethyl peak in Figure 2B. Also, the FT-IR spectra of CE and MTE show that the reaction was complete. The C−Cl stretch of CE at 743 cm^{-1} (Figure 3A) has disappeared in the FT-IR spectrum of MTE (Figure 3B) while the C−O stretching adsorptions at 1108−1110 cm^{-1} are visible in both spectra. The substitution reaction did not cleave the polymer backbone; the intrinsic viscosity range of the (alkylthio)methyl-substituted polymers was 1.10−2.68 dL/g (Table 3).

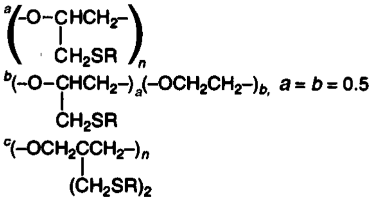
The thioether groups in the ATEs, ATEEs, and ATTs were oxidized to sulfone using *m*-CPBA, producing polymers such as poly[oxy((alkylsulfonyl)methyl)ethylene] (ASE), poly[oxy((alkylsulfonyl)methyl)ethylene-*co*-oxyethylene] (ASEE), and poly[oxy-2,2-bis((alkylsulfonyl)methyl)trimethylene] (AST) (Scheme 1). Reaction conditions and results are listed in Table 6. Figure 1C shows the ^{1}H-NMR spectrum of *n*-PrSE. Every proton peak is shifted downfield compared to those of *n*-PrTE. The triplet methyl peak (a) of *n*-PrSE, 1.08 ppm (Figure 1C), is shifted from the triplet (a) of *n*-PrTE, 0.96 ppm (Figure 1B). The peaks f (4.02−4.22 ppm, Figure 1C) β to the sulfone group shift downfield more than the peaks e (3.54−3.98 ppm); these are less affected, as they are γ to the sulfone group. Figure 2 shows the conversion from MTE to MSE very clearly. The sulfone group in MSE causes every peak in MTE to shift downfield. Figures 4 and 5 show the ^{13}C-NMR spectra of MSEE and MST, respectively; every peak is easily assigned.

Figure 3C shows the FT-IR spectrum of MSE. It displays the two distinctive sulfone group peaks, an asymmetric stretching peak at 1298 cm^{-1} and a symmetric stretching peak at 1130 cm^{-1}. There are no peaks at these wavenumbers in the spectra of CE and MTE (Figure 3A,B).

The intrinsic viscosities of the (alkylsulfonyl)methyl-substituted polymers remained high (Table 6), showing that there was little backbone cleavage. The polymer mechanical properties should still be reasonable.

Table 1. Abbreviations of the (Alkylthio)methyl-Substituted Polymers

full name	abbreviation	R
poly[oxy((methylthio)methyl)ethylene]	MTE[a]	CH_3
poly[oxy((ethylthio)methyl)ethylene]	ETE[a]	CH_2CH_3
poly[oxy((*n*-propylthio)methyl)ethylene]	*n*-PrTE[a]	$(CH_2)_2CH_3$
poly[oxy((isopropylthio)methyl)ethylene]	*i*-PrTE[a]	$CH(CH_3)_2$
poly[oxy((*n*-butylthio)methyl)ethylene]	BTE[a]	$(CH_2)_3CH_3$
poly[oxy((*n*-pentylthio)methyl)ethylene]	PeTE[a]	$(CH_2)_4CH_3$
poly[oxy((methylthio)methyl)ethylene-*co*-oxyethylene]	MTEE[b]	CH_3
poly[oxy((ethylthio)methyl)ethylene -*co*-oxyethylene]	ETEE[b]	CH_2CH_3
poly[oxy((isopropylthio)methyl)ethylene-*co*-oxyethylene]	*i*-PrTEE[b]	$(CH_2)_2CH_3$
poly[oxy((*n*-propylthio)methyl)ethylene-*co*-oxyethylene]	*n*-PrTEE[b]	$(CH)CH_3$
poly[oxy((*n*-butylthio)methyl)ethylene-*co*-oxyethylene]	BTEE[b]	$(CH_2)_3CH_3$
poly[oxy((*n*-pentylthio)methyl)ethylene-*co*-oxyethylene]	PeTEE[b]	$(CH_2)_4CH_3$
poly[oxy-2,2-bis((methylthio)methyl)trimethylene]	MTT[c]	CH_3
poly[oxy-2,2-bis((ethylthio)methyl)trimethylene]	ETT[c]	CH_2CH_3
poly[oxy-2,2-bis((isopropylthio)methyl)trimethylene]	*i*-PrTT[c]	$(CH_2)_2CH_3$
poly[oxy-2,2-bis((*n*-propylthio)methyl)trimethylene]	*n*-PrTT[c]	$(CH)CH_3$
poly[oxy-2,2-bis((*n*-butylthio)methyl)trimethylene]	BTT[c]	$(CH_2)_3CH_3$
poly[oxy-2,2-bis((*n*-pentylthio)methyl)trimethylene]	PeTT[c]	$(CH_2)_4CH_3$



$^a(\mathrm{-O-\underset{CH_2SR}{C}HCH_2-})_n$

$^b(\mathrm{-O-\underset{CH_2SR}{C}HCH_2-})_a(\mathrm{-OCH_2CH_2-})_b,\ a = b = 0.5$

$^c(\mathrm{-OCH_2\underset{(CH_2SR)_2}{C}CH_2-})_n$

Table 2. ^{13}C-NMR and ^{1}H-NMR spectral Data for (Alkylthio)methyl-Substituted Polymers

polymer	chemical shifts[a] (δ, ppm) and assignments
MTE	^{1}H-NMR: 2.20 (s, 3H, CH_3), 2.56−2.86 (m, 2H, $\mathrm{-}CH_2\mathrm{S-}$), 3.54−3.83 (m, 3H, $\mathrm{-O}CH_2CH\mathrm{-}$) ^{13}C-NMR: 16.7 (s, 1C, $\mathrm{-}C\mathrm{H_3}$), 35.9 (s, 1C, $\mathrm{-}C\mathrm{H_2S-}$), 70.3−71.5 (m, 1C, $\mathrm{-OCH_2}C\mathrm{H-}$), 79.2 (s, 1C, $\mathrm{-O}C\mathrm{H_2CH-}$)
ETE	^{1}H-NMR: 1.27 (t, 3H, $J = 7.2$, $\mathrm{-}CH_3$), 2.59 (quartet, 2H, $J = 7.3$, $\mathrm{-S}CH_2\mathrm{CH_3}$), 2.56−2.84 (m, 2H, $\mathrm{-CH}CH_2\mathrm{S}$), 3.48−3.72 (m, ^{1}H, $\mathrm{-OCH_2}CH\mathrm{-}$), 3.65−3.80 (m, 2H, $\mathrm{-O}CH_2\mathrm{CH-}$)
n-PrTE	^{1}H-NMR: 0.96 (t, 3H, $J = 9.2$, $\mathrm{-}CH_3$), 1.59 (sextet, 2H, $J = 8.6$, $\mathrm{-}CH_2\mathrm{CH_3}$), 2.50 (t, 2H, $J = 7.2$, $\mathrm{-S}CH_2\mathrm{CH_2-}$), 2.55−2.81 (m, 2H, $\mathrm{-CH}CH_2\mathrm{S-}$), 3.43−3.76 (m, 3H, $\mathrm{-}CHCH_2\mathrm{O-}$)
i-PrTE	^{1}H-NMR: 1.29 (d, 6H, $J = 6.2$, $\mathrm{-CH(}CH_3\mathrm{)_2}$), 2.59−2.91 (m, 2H, $\mathrm{-}CH_2\mathrm{S-}$), 2.91−3.10 (m, ^{1}H, $\mathrm{-}CH\mathrm{(CH_3)_2}$), 3.52−3.85 (m, 3H, $\mathrm{-O}CH_2CH\mathrm{-}$)
BTE	^{1}H-NMR: 0.95 (t, 3H, $J = 6.7$, $\mathrm{-}CH_3$), 1.43 (sextet, 2H, $J = 6.7$, $CH_2\mathrm{CH_3}$), 1.62 (quintet, 2H, $J = 7.2$, $\mathrm{-CH_2}CH_2\mathrm{CH_2-}$), 2.59 (t, 2H, $J = 7.1$, $\mathrm{-S}CH_2\mathrm{CH_2-}$), 2.62−2.85 (m, 2H, $\mathrm{-CH}CH_2\mathrm{S-}$), 3.51−3.82 (m, 3H, $\mathrm{-O}CH_2CH\mathrm{-}$)
PeTE	^{1}H-NMR: 0.91 (t, 3H, $J = 7.2$, $\mathrm{-}CH_3$), 1.22−1.48 (m, 4H, $\mathrm{-}CH_2CH_2\mathrm{CH_3}$), 1.57 (quintet, 2H, $J = 7.2$, $\mathrm{-SCH_2}CH_2\mathrm{-}$), 2.55 (t, 2H, $J = 7.2$, $\mathrm{-S}CH_2\mathrm{CH_2-}$), 2.61−2.81 (m, 2H, $\mathrm{-CH}CH_2\mathrm{S-}$), 3.49−3.78 (m, 3H, $\mathrm{-OCH_2}CH\mathrm{-}$)
MTEE	^{1}H-NMR: 2.16 (s, 3H, $\mathrm{-}CH_3$), 2.53−2.87 (m, 2H, $\mathrm{-}CH_2\mathrm{S-}$), 3.45−3.84 (m, 7H, $\mathrm{-O}CH_2CH_2\mathrm{O}CH_2CH\mathrm{-}$)
ETEE	^{1}H-NMR: 1.27 (t, 3H, $J = 7.2$, $\mathrm{-}CH_3$), 2.58 (quartet, 2H, $J = 7.8$, $\mathrm{-S}CH_2\mathrm{CH_3}$), 2.60−2.79 (m, 2H, $\mathrm{-CH}CH_2\mathrm{S-}$), 3.47−3.83 (m, 7H, $\mathrm{-O}CH_2CH_2\mathrm{O}CH_2CH\mathrm{-}$)
n-PrTEE	^{1}H-NMR: 0.97 (t, 3H, $J = 7.4$, $\mathrm{-}CH_3$), 1.59 (sextet, 2H, $J = 8.$, $\mathrm{-}CH_2\mathrm{CH_3}$), 2.48 (t, 2H, $J = 7.3$, $\mathrm{-S}CH_2\mathrm{CH_2-}$), 2.60−2.81 (m, 2H, $\mathrm{-CH}CH_2\mathrm{S-}$), 3.47−3.781 (m, 7H, $\mathrm{-O}CH_2CH_2\mathrm{O}CH_2CH\mathrm{-}$)
i-PrTEE	^{1}H-NMR: 1.30 (d, $J = 6.8$, $\mathrm{-CH(}CH_3\mathrm{)_2}$), 2.58−2.87 (m, 2H, $\mathrm{-}CH_2\mathrm{S-}$), 2.88−3.11 (m, ^{1}H, $\mathrm{-S}CH\mathrm{-}$), 3.52−3.82 (m, 7H, $\mathrm{-O}CH_2CH_2\mathrm{O}CH_2CH\mathrm{-}$)
BTEE	^{1}H-NMR: 0.96 (t, 3H, $J = 6.9$, $\mathrm{-}CH_3$), 1.45 (sextet, 2H, $J = 6.7$, $CH_2\mathrm{CH_3}$), 1.62 (quintet, 2H, $J = 7.3$, $\mathrm{-CH_2}CH_2\mathrm{CH_2-}$), 2.60 (t, 2H, $J = 7.1$, $\mathrm{-S}CH_2\mathrm{CH_2}$), 2.59−2.83 (m, 2H, $\mathrm{-CH}CH_2\mathrm{S-}$), 3.51−3.82 (m, 7H, $\mathrm{-O}CH_2CH_2\mathrm{O}CH_2CH\mathrm{-}$)
PeTEE	^{1}H-NMR: 0.90 (t, 3H, $J = 7.2$, $\mathrm{-}CH_3$), 1.21−1.48 (m, 4H, $\mathrm{-}CH_2CH_2\mathrm{CH_3}$), 1.58 (quintet, 2H, $J = 7.4$, $\mathrm{-SCH_2}CH_2$), 2.57 (t, 2H, $J = 7.3$, $\mathrm{-S}CH_2\mathrm{CH_2-}$), 2.59−2.80 (m, 2H, $\mathrm{-CH}CH_2\mathrm{S-}$), 3.50−3.80 (m, 7H, $\mathrm{-O}CH_2CH_2\mathrm{O}CH_2CH\mathrm{-}$)
MTT	^{1}N-NMR: 2.16 (s, 6H, $\mathrm{-}CH_3$), 2.67 (s, 4H, $\mathrm{-}CH_2\mathrm{S-}$), 3.37 (s, 4H, $\mathrm{-O}CH_2\mathrm{C}CH_2\mathrm{-}$)
ETT	^{1}H-NMR: 1.29 (t, 6H, $J = 7.4$, $\mathrm{-}CH_3$), 2.55 (quartet, 4H, $J = 7.5$, $\mathrm{-S}CH_2\mathrm{CH_3}$), 2.65 (s, 4H, $\mathrm{-C}CH_2\mathrm{S-}$), 3.31 (s, 4H, $\mathrm{-O}CH_2\mathrm{C}CH_2\mathrm{-}$)
i-PrTT	^{1}H-NMR: 1.28 (d, 6H, $J = 7.3$, $\mathrm{-}CH_3$), 2.70 (s, 4H, $\mathrm{-}CH_2\mathrm{S-}$), 2.86−3.07 (m, 2H, $\mathrm{-S}CH\mathrm{(CH_3)_2}$), 3.40 (s, 4H, $\mathrm{-O}CH_2\mathrm{C}CH_2\mathrm{-}$)
n-PrTT	^{1}H-NMR: 0.95 (t, 6H, $J = 7.5$, $\mathrm{-}CH_3$), 1.59 (sextet, 4H, $J = 8.3$, $\mathrm{-}CH_2\mathrm{CH_3}$), 2.51 (t, 4H, $J = 7.2$, $\mathrm{-S}CH_2\mathrm{CH_2-}$), 2.65 (s, 4H, $\mathrm{-C}CH_2\mathrm{S-}$), 3.35 (s, 4H, $\mathrm{-O}CH_2\mathrm{C}CH_2\mathrm{-}$)
BTT	^{1}H-NMR: 0.93 (t, 6H, $J = 6.7$, $\mathrm{-}CH_3$), 1.42 (sextet, 4H, $J = 6.7$, $\mathrm{-}CH_2\mathrm{CH_3}$), 1.59 (quintet, 4H, $J = 7.2$, $\mathrm{-CH_2}CH_2\mathrm{CH_2-}$), 2.60 (t, 4H, $J = 7.1$, $\mathrm{-S}CH_2\mathrm{CH_2}$), 2.68 (s, 4H, $\mathrm{-C}CH_2\mathrm{S-}$), 3.39 (s, 4H, $\mathrm{-O}CH_2\mathrm{C}CH_2\mathrm{-}$)
PeTT	^{1}H-NMR: 0.90 (t, 6H, $J = 7.2$, $\mathrm{-}CH_3$), 1.20−1.53 (m, 8H, $\mathrm{-}CH_2CH_2\mathrm{CH_3}$), 1.58 (quintet, 4H, $J = 7.2$, $\mathrm{-SCH_2}CH_2$), 2.53 (t, 2H, $J = 7.2$, $\mathrm{-S}CH_2\mathrm{CH_2-}$), 2.71 (s, 4H, $\mathrm{-C}CH_2\mathrm{S-}$), 3.36 (s, 4H, $\mathrm{-O}CH_2\mathrm{C}CH_2\mathrm{-}$)

[a] In $CDCl_3$. All J values are in hertz.

T_g's and melting points, when applicable, of (alkylthio)methyl-substituted polymers are listed in Table 3. The T_g's are lower than those of the corresponding starting polymers because the alkylthioether group is less polar than the chloromethyl group. Normally, polar polymers have higher T_g's than nonpolar polymers, other factors being equal. The T_g's of CE, CEE, and BCT are −17, −35, and 13 °C, respectively. As the number of carbon atoms in the thioether side chain increases, T_g decreases. For example, the T_g of MTE is −37 °C, while the T_g of ETE is −57 °C. For the longest side chain, the T_g dropped to −68 °C (PeTE) (Figure 6). It is known that, as the length of the side chain increases, neighboring chains are pushed apart, decreasing the hindrance to chain backbone motions, so T_g decreases.[21−23] When an isopropyl group is in the

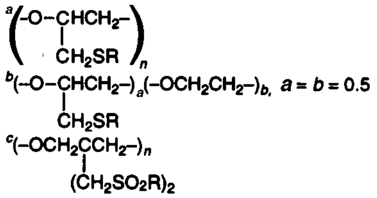
Table 3. Conditions of Substitution Reaction and Polymer Properties

starting polymer (18 mmol)	reagent (amount, mmol)	reaction time (h)	reaction temp (°C)	product	T_g (°C)	T_m (°C)	$[\eta]^a$ (dL/g)
CE	NaSCH$_3$ (28.8)	2	25	MTE	−37		1.82
CE	NaSCH$_2$CH$_3$ (28.8)	2	25	ETE	−57		1.99
CE	NaSCH(CH$_3$)$_2$ (28.8)	4	25	*i*-PrTE	−44		2.16
CE	NaS(CH$_2$)$_2$CH$_3$ (28.8)	3	25	*n*-PrTE	−61		2.03
CE	NaS(CH$_2$)$_3$CH$_3$ (28.8)	4	25	BTE	−65		2.38
CE	NaS(CH$_2$)$_4$CH$_3$ (28.8)	4	25	PeTE	−68		2.68
CEE	NaSCH$_3$ (18.0)	2	25	MTEE	−47		1.69
CEE	NaSCH$_2$CH$_3$ (18.0)	2	25	ETEE	−63		1.82
CEE	NaSCH(CH$_3$)$_2$ (18.0)	4	25	*i*-PrTEE	−51		1.28
CEE	NaS(CH$_2$)$_2$CH$_3$ (18.0)	4	25	*n*-PrTEE	−66		1.35
CEE	NaS(CH$_2$)$_3$CH$_3$ (18.0)	4	25	BTEE	−69		1.42
CEE	NaS(CH$_2$)$_4$CH$_3$ (18.0)	4	25	PeTEE	−71		1.43
BCT	NaSCH$_3$ (64.8)	0.5	140	MTT	−6	117	1.16
BCT	NaSCH$_2$CH$_3$ (64.8)	0.5	140	ETT	−32	82	1.10
BCT	NaSCH(CH$_3$)$_2$ (64.8)	0.5	140	*i*-PrTT	−9	89	1.44
BCT	NaS(CH$_2$)$_2$CH$_3$ (64.8)	0.5	140	*n*-PrTT		49	1.23
BCT	NaS(CH$_2$)$_3$CH$_3$ (64.8)	0.5	140	BTT		36	1.34
BCT	NaS(CH$_2$)$_4$CH$_3$ (64.8)	0.5	140	PeTT	−33	61	1.25

[a] In THF at 30 °C.

Table 4. Abbreviations of the (Alkylsulfonyl)methyl-Substituted Polymers

full name	abbreviation	R
poly[oxy((methylsulfonylmethyl)ethylene]	MSE[a]	CH$_3$
poly[oxy((ethylsulfonylmethyl)ethylene]	ESE[a]	CH$_2$CH$_3$
poly[oxy((*n*-propylsulfonylmethyl)ethylene]	*n*-PrSE[a]	(CH$_2$)$_2$CH$_3$
poly[oxy((isopropylsulfonylmethyl)ethylene]	*i*-PrSE[a]	CH(CH$_3$)$_2$
poly[oxy((*n*-butylsulfonylmethyl)ethylene]	BSE[a]	(CH$_2$)$_3$CH$_3$
poly[oxy((*n*-pentylsulfonylmethyl)ethylene]	PeSE[a]	(CH$_2$)$_4$CH$_3$
poly[oxy((methylsulfonylmethyl)ethylene-*co*-oxyethylene]	MSEE[b]	CH$_3$
poly[oxy((ethylsulfonylmethyl)ethylene-*co*-oxyethylene]	ESEE[b]	CH$_2$CH$_3$
poly[oxy((isopropylsulfonylmethyl)ethylene-*co*-oxyethylene]	*i*-PrSEE[b]	(CH$_2$)$_2$CH$_3$
poly[oxy((*n*-propylsulfonylmethyl)ethylene-*co*-oxyethylene]	*n*-PrSEE[b]	(CH)CH$_3$
poly[oxy((*n*-butylsulfonylmethyl)ethylene-*co*-oxyethylene]	BSEE[b]	(CH$_2$)$_3$CH$_3$
poly[oxy((*n*-pentylsulfonylmethyl)ethylene-*co*-oxyethylene]	PeSEE[b]	(CH$_2$)$_4$CH$_3$
poly[oxy-2,2-bis((methylsulfonylmethyl)trimethylene]	MST[c]	CH$_3$
poly[oxy-2,2-bis((ethylsulfonylmethyl)trimethylene]	EST[c]	CH$_2$CH$_3$
poly[oxy-2,2-bis((isopropylsulfonylmethyl)trimethylene]	*i*-PrST[c]	(CH$_2$)$_2$CH$_3$
poly[oxy-2,2-bis((*n*-propylsulfonylmethyl)trimethylene]	*n*-PrST[c]	(CH)CH$_3$
poly[oxy-2,2-bis((*n*-butylsulfonylmethyl)trimethylene]	BST[c]	(CH$_2$)$_3$CH$_3$
poly[oxy-2,2-bis((*n*-pentylsulfonylmethyl)trimethylene]	PeST[c]	(CH$_2$)$_4$CH$_3$



[a] $(\text{-O-}\underset{\text{CH}_2\text{SR}}{\text{CH}}\text{CH}_2\text{-})_n$

[b] $(\text{-O-}\underset{\text{CH}_2\text{SR}}{\text{CH}}\text{CH}_2\text{-})_a(\text{-OCH}_2\text{CH}_2\text{-})_b,\ a = b = 0.5$

[c] $(\text{-OCH}_2\underset{(\text{CH}_2\text{SO}_2\text{R})_2}{\text{C}}\text{CH}_2\text{-})_n$

side chain, hindrance to backbone motion increases due to its bulkiness, so T_g increases. For example, the T_g of *i*-PrTE (−44 °C) is higher than that of ETE (−57 °C).

Similar phenomena were observed for the ASEs (Scheme 1). Since the sulfone group is much more polar than the thioether group, the T_g's of ASEs were much higher than those of corresponding ATEs. For example, oxidation of MTE ($T_g = -37$ °C) to MSE raised the T_g to 85 °C. Figure 6 shows the side-chain effect on T_g for the ASE series. As the number of carbon atoms in the sulfone side chain increases from 1 to 4, T_g decreases. For PeSE (five carbons atoms in the *n*-alkyl side chain), the T_g is about the same as or slightly higher than that of BSE (four carbon atoms in the *n*-alkyl side chain). The increase in T_g with increase in side-chain length beyond a critical number (N_c) has been ascribed to the side-chain crystallization;[24] the crystallites act as fillers in the amorphous phase and raise the T_g.[25,26] The N_c values of poly(alkyl vinyl ether)s, poly(alkyl acrylate)s, poly(alkylstyrene)s, and poly(alkyl methacrylate)s are 8, 9, 10, and 12, respectively.[24] Compared to these polymers, the N_c value of the ASE series is very small, 4. The sulfone group in the side chain, which has the highest polarity of all the simple functional groups,[27] increases the interaction between the side chains and their tendency to form ordered phases such as liquid crystals, even with short side chains.

The organization of PeSE was studied using DSC and a polarizing optical microscope. Figure 7 shows the DSC thermograms of quenched ASEs. PeSE shows two endothermic peaks at 60 ($\Delta H_m = 0.38$ J/g) and 128 °C ($\Delta H_m = 0.69$ J/g), which could come from side-chain organization. To confirm these endotherms, a DSC thermogram of PeSE was run after different annealing conditions. PeSE was held at 200 °C for 5 min, quenched to 110 °C, and kept at this temperature for 12 h. Then the sample was quenched to below its T_g and heated at 20 °C/min. The annealed PeSE showed two peaks, at 58 ($\Delta H_m = 1.43$ J/g) and 130 °C ($\Delta H_m = 6.16$ J/g) (Figure 7). It should be noted that the 60 °C

Table 5. ^{13}C-NMR and ^{1}H-NMR Spectral Data for (Alkylsulfonyl)methyl-Substituted Polymers

polymer	chemical shifts^a (δ, ppm) and assignments
MSE	^{13}C-NMR (DMSO-d_6): 42.1−42.8 (m, 1C, -CH_3), 55.2−56.3 (m, 1C, -CH_2SO$_2$-), 67.9−70.4 (m, 1C, -OCH_2CH-), 73.6−74.8 (s, 1C, -OCH$_2CH$-)
ESE	^{1}H-NMR (CDCl$_3$): 1.34 (t, 3H, $J = 7.2$, -CH_3), 2.95−3.29 (m, 2H, -SO$_2CH_2$CH$_3$), 3.12−3.48 (m, 2H, -CHCH_2SO$_2$-), 3.50−4.02 (m, 2H, -OCH_2CH-), 4.02−4.30 (m, ^{1}H, -OCH$_2CH$-)
n-PrSE	^{1}H-NMR (CDCl$_3$): 1.08 (t, 3H, $J = 7.6$, -CH_3), 1.85 (sextet, 2H, $J = 7.3$, -CH_2CH$_3$), 2.93−3.13 (m, 2H, -SO$_2CH_2$CH$_2$-), .20−3.52 (m, 2H, -CHCH_2SO$_2$-), 3.54−3.98 (m, 2H, -OCH_2CH-), 4.02−4.22 (m, ^{1}H, -OCH$_2CH$-)
i-PrSE	^{1}H-NMR (CDCl$_3$): 1.38 (d, 6H, $J = 6.7$, -CH(CH_3)$_2$), 2.96−3.45 (m, 3H, -CH_2SO$_2CH$-), 3.47−3.97 (m, 2H, -OCH_2CH-), 3.98−4.19 (m, ^{1}H, -OCH$_2CH$-)
BSE	^{1}H-NMR (CDCl$_3$): 0.97 (t, 3H, $J = 7.6$, -CH_3), 1.48 (sextet, 2H, $J = 7.2$, -CH_2CH$_3$), 1.80 (quintet, 2H, $J = 7.5$, -CH$_2CH_2$CH$_2$-), 2.94−3.18 (m, 2H, -SO$_2CH_2$CH$_2$-), 3.19−3.47 (m, 2H, -CHCH_2SO$_2$-), 3.52−3.95 (m, 2H, -OCH_2CH-), 3.98−4.23 (m, ^{1}H, -OCH$_2CH$-)
PeSE	^{1}H-NMR (CDCl$_3$): 0.94 (t, 3H, $J = 7.4$, -CH_3), 1.28−1.61 (m, 4H, -CH_2CH_2CH$_3$), 1.76 (quintet, 2H, $J = 7.3$, -SO$_2$CH$_2CH_2$-), 2.91−3.14 (m, 2H, -SO$_2CH_2$CH$_2$-), 3.18−3.47 (m, 2H, -CHCH_2SO$_2$-), 3.47−3.95 (m, 2H, -OCH_2CH-), 3.97−4.21 (m, ^{1}H, -OCH$_2CH$-)
MSEE	^{13}C-NMR (DMSO-d_6): 41.9−42.7 (m, 1C, -CH_3), 54.8−56.3 (m, 1C, -CH_2SO$_2$-), 67.3−70.9 (m, 3C, -OCH_2CH_2OCHCH$_2$-), 73.5−74.1 (m, 1C, -OCHCH_2-)
ESEE	^{1}H-NMR (CDCl$_3$): 1.32 (t, 3H, $J = 7.3$, -CH_3), 2.92−3.27 (m, 2H, -SO$_2CH_2$CH$_3$), 3.12−3.47 (m, 2H, -CHCH_2SO$_2$-), 3.51−3.97 (m, 6H, -OCH_2CH_2OCH_2CH-), 3.96−4.22 (m, ^{1}H, -OCH$_2CH$-)
n-PrSEE	^{1}H-NMR (CDCl$_3$): 1.10 (t, 3H, $J = 7.6$, -CH_3), 1.86 (sextet, 2H, $J = 7.3$, -CH_2CH$_3$), 2.95−3.16 (m, 2H, -SO$_2$CH$_2CH_2$-), 3.17−3.49 (m, 2H, -CHCH_2SO$_2$-), 3.50−3.98 (m, 6H, -OCH_2CH_2OCH_2CH-), 4.00−4.24 (m, ^{1}H, -OCH$_2CH$-)
i-PrSEE	^{1}H-NMR (CDCl$_3$): 1.40 (d, 6H, $J = 6.8$, -CH_3), 2.94−3.46 (m, 3H, -CH_2SO$_2CH$-), 3.48−3.96 (m, 6H, -OCH_2CH_2OCH_2CH-), 3.97−4.24 (m, ^{1}H, -OCH$_2CH$-)
BSEE	^{1}H-NMR (CDCl$_3$): 0.96 (t, 3H, $J = 7.4$, -CH_3), 1.50 (sextet, 2H, $J = 7.2$, -CH_2CH$_3$), 1.81 (quintet, 2H, $J = 7.3$, -CH$_2CH_2$CH$_2$-), 2.93−3.16 (m, 2H, -SO$_2CH_2$CH$_2$-), 3.18−3.49 (m, 2H, -CHCH_2SO$_2$-), 3.48−3.96 (m, 6H, -OCH_2CH_2OCH_2CH-), 3.95−4.21 (m, ^{1}H, -OCH$_2CH$-)
PeSEE	^{1}H-NMR (CDCl$_3$): 0.93 (t, 3H, $J = 7.4$, -CH_3), 1.29−1.59 (m, 4H, -CH_2CH_2CH$_3$), 1.77 (quintet, 2H, $J = 7.3$, -SO$_2$CH$_2CH_2$-), 2.92−3.16 (m, 2H, -SO$_2CH_2$CH$_2$-), 3.13−3.46 (m, 2H, -CHCH_2SO$_2$-), 3.50−3.98(m, 6H, -OCH_2CH_2OCH_2CH-), 4.00−4.23 (m, ^{1}H, -OCH$_2CH$-)
MST	^{13}C-NMR (DMSO-d_6): 30.3 (s, 1C, -C-), 43.6 (s, 2C, -CH_3), 54.4 (s, 2C, -CH_2SO$_2$-), 71.2 (s, 2C, -CH_2CCH_2-)
EST	^{1}H-NMR (CDCl$_3$): 1.33 (t, 6H, $J = 7.2$, -CH_3), 2.92−3.30 (m, 4H, -SO$_2CH_2$CH$_3$), 3.43−4.21 (m, 8H, -OCH_2-, -CCH_2SO$_2$-)
i-PrST	^{1}H-NMR (CDCl$_3$): 1.35 (d, 12H, $J = 7.3$, -CH_3), 2.89−3.38 (m, 2H, -SO$_2CH$-), 3.40−4.07 (m, 8H, OCH_2, -CCH_2SO$_2$-)
n-PrST	^{1}H-NMR (CDCl$_3$): 1.05 (t, 6H, $J = 7.6$, -CH_3), 1.83 (sextet, 4H, $J = 7.2$, -CH_2CH$_3$), 2.91−3.12 (m, 4H, -SO$_2CH_2$CH$_2$-), 3.39−4.15 (m, 8H, -OCH_2-, -CCH_2SO$_2$-)
BST	^{1}H-NMR (CDCl$_3$): 0.96 (t, 6H, $J = 7.5$, -CH_3), 1.46 (sextet, 4H, $J = 7.3$, -CH_2CH$_3$), 1.79 (quintet, 4H, $J = 7.4$, -CH$_2CH_2$CH$_2$-), 2.93−3.16 (m, 4H, -SO$_2CH_2$CH$_2$-), 3.41−4.23 (m, 8H, -OCH_2-, -CCH_2SO$_2$-)
PeST	^{1}H-NMR (CDCl$_3$): 0.93 (t, 6H, $J = 7.4$, -CH_3), 1.26−1.62 (m, 8H, -CH_2CH_2CH$_3$), 1.75 (quintet, 4H, $J = 7.3$, -SO$_2$CH$_2CH_2$-), 2.90−3.14 (m, 4H, -SO$_2CH_2$CH$_2$-), 3.43−4.25 (m, 8H, -OCH_2-, -CCH_2SO$_2$-)

[a] All J values are in hertz.

Table 6. Conditions of Oxidation Reactions and Polymer Properties

starting polymer (1.00 g)	*m*-CPBA (g)	reaction time (h)	reaction temp (°C)	product (°C)	T_g (°C)	T_m (°C)	[η] (dL/g)
MTE^a	4.97	2	5	MSE	85		1.63^c
ETE^b	4.38	2	5	ESE	57		1.31^c
i-PrTE^b	3.91	2	5	*i*-PrSE	64		0.83^c
n-PrTE^b	3.91	2	5	*n*-PrSE	43		1.17^c
BTE^b	3.64	2	5	BSE	35		0.90^c
PeTE^b	3.23	2	5	PeSE	40	58, 130	1.02^d
MTEE^b	4.49	2	5	MSEE	52		1.68^c
ETEE^b	3.19	2	5	ESEE	27		1.77^c
i-PrTEE^b	2.94	2	5	*i*-PrSEE	34		0.61^c
n-PrTEE^b	2.94	2	5	*n*-PrSEE	24		1.44^c
BTEE^b	2.72	2	5	BSEE	19		1.22^d
PeTEE^b	2.53	2	5	PeSEE	12		1.28^d
MTT^a	4.92	0.5	80	MST	126	191	0.84^c
ETT^b	4.35	0.5	60	EST	84	183	1.08^c
i-PrTT^b	3.89	0.5	60	*i*-PrST	91		1.23^c
n-PrTT^b	3.89	0.5	60	*n*-PrST	71	166	1.43^c
BTT^b	3.51	0.5	60	BST	66	143	1.24^d
PeTT^b	3.21	0.5	60	PeST	56	138	1.55^d

[a] Reaction solvent was DMAc. [b] Reaction solvent was chloroform. [c] In formic acid at 30 °C. [d] In THF at 30 °C.

endotherm increased from 0.38 to 1.43 J/mol, even though the sample had been annealed at 110 °C. Thus, the two endotherms must be related in the crystal structure. The low-temperature endotherm is possibly a solid/solid or perhaps a liquid crystal/liquid crystal transition. The texture change of the sample was observed using a polarizing optical microscope equipped with a hot stage. The sample was melted between two glass plates at 200 °C and cooled at 5 °C/min. When the temperature reached 58 °C, birefringence and schlieren textures were observed at edge of the sample. The feature disappeared when the polymer was heated to 62 °C but reappeared on cooling, which indicates low supercooling from the 60 °C transition temperature observed in the heating DSC scan. These results indicate that PeSE has a poorly ordered liquid crystalline phase. Liquid crystalline phase formation due to strong interchain dipole−dipole interaction between sulfone groups was also reported by Zhang et al.[28] Recent results on the ((*n*-octylsulfonyl)methyl)oxyethylene polymer confirm the liquid crystal behavior in this series.[29]

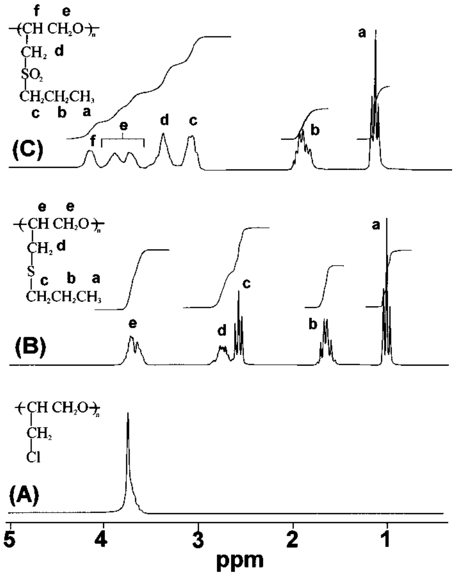


Figure 1. ^{1}H-NMR spectra of (A) CE, (B) *n*-PrTE, and (C) *n*-PrSE.

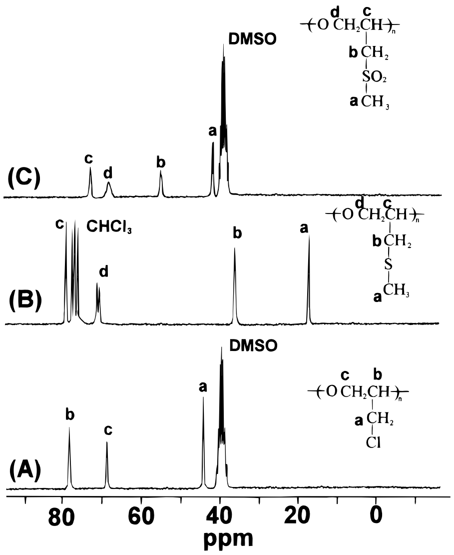


Figure 2. ^{13}C-NMR spectra of (A) CE, (B) MTE, and (C) MSE.

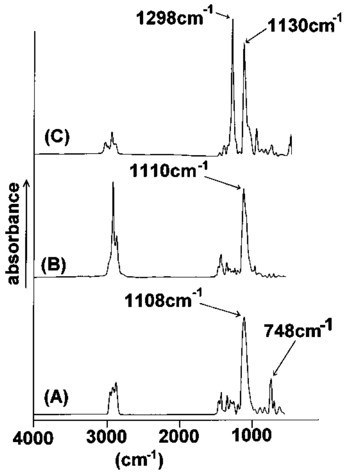


Figure 3. FT-IR spectra of (A) CE, (B) MTE, and (C) MSE.

A normal side-chain length effect on T_g for ATEE and ASEE was observed (Figure 8). As the chain length increased, T_g decreased in both cases. No melting peaks were observed in the DSC thermogram of PeSEE. This may be because PeSEE contains one sulfone side group per two oxyethylene units in its backbone, and there is not enough interaction to generate structure.

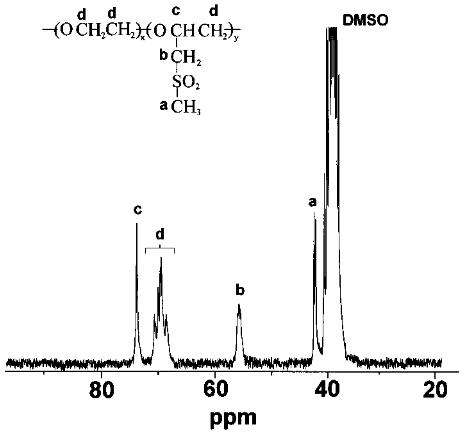


Figure 4. ^{13}C-NMR spectrum of MSEE.

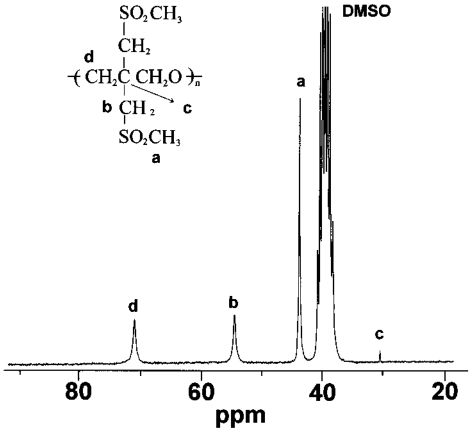


Figure 5. ^{13}C-NMR spectrum of MST.

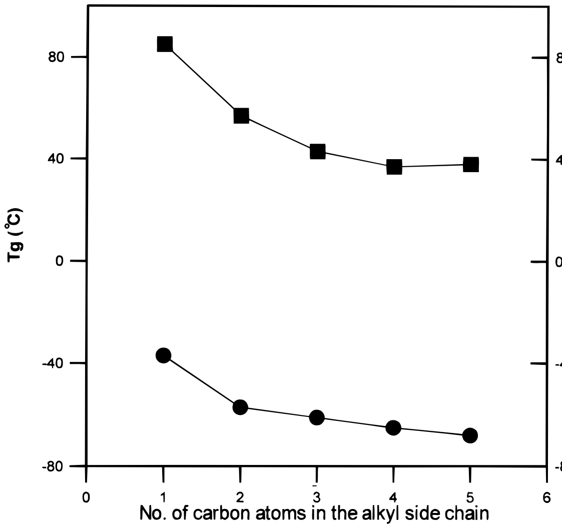


Figure 6. Effect of side chain length on T_g: (■) ASE and (●) ATE.

The structure/thermal property relationships of ATT and AST were investigated. BCT is a semicrystalline polymer. It shows a glass transition and crystallization and melting peaks (Figure 9). MTT showed the same behavior at lower temperature. In MST, without annealing, only a glass transition was observed. When MST was annealed at 170 °C for 12 h, a small melting peak appeared, but no crystallization exotherm could be observed. Because the (methylsulfonyl)methyl group is much more polar and bulkier than the (methylthio)-

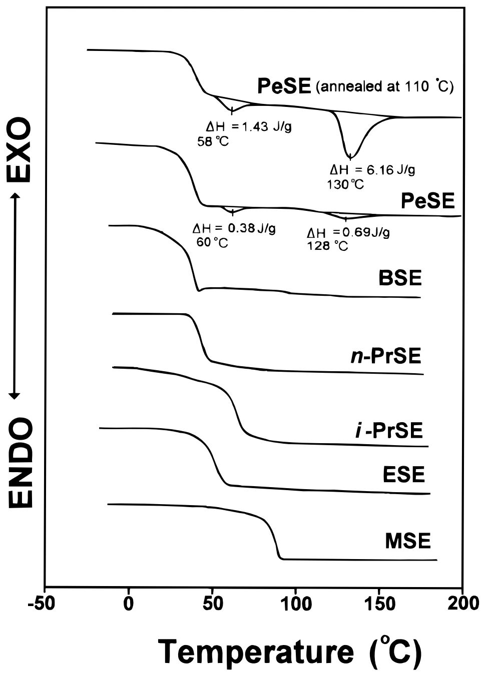


Figure 7. DSC curves of ASEs.

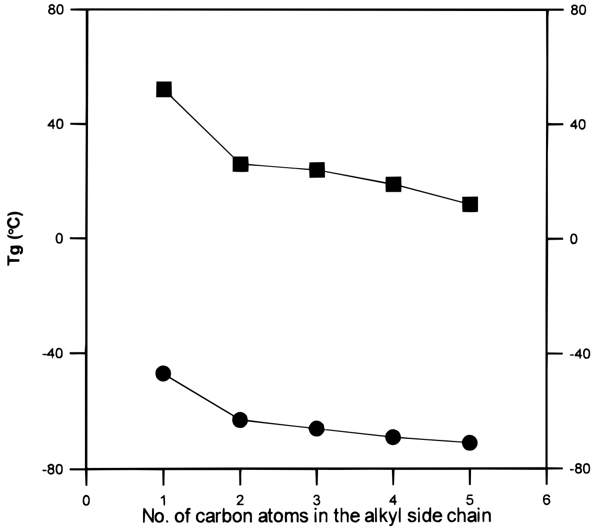


Figure 8. Effect of side-chain length on T_g: (■) ASEE and (●) ATEE.

methyl or the chloromethyl group, it decreased the flexibility of backbone chain but did not raise the melting point, so crystallization of MSE was retarded. As the number of side carbon atoms in the ATTs increases, T_m decreases up to butyl and then increases for the pentyl derivative (Figure 10). This is not seen in the T_g's (Figure 11). T_m's of these samples were measured after annealing just below their T_m for 12 h (Figure 12). The sulfone polymers did not recrystallize on quenching and reheating. No melting endotherms were observed in the second DSC run obtained after quenching the melted sample, probably because the T_g's and T_m's were close to each other. A melting endotherm was not observed for *i*-PrST even after annealing, possibly due to its side-chain bulkiness. For the same reason, the T_g of *i*-PrST (92 °C) was higher than those of *n*-PrST (71 °C) and EST (84 °C).

The thermal stability of the (alkylsulfonyl)methyl-substituted polymers was evaluated using dynamic thermogravic analysis (TGA) under N_2 (Table 7). All the (alkylsulfonyl)methyl-substituted polymers were stable until 300 °C. Figure 13 shows that all the ASEs have similar decomposition behavior; their initial decomposition and half-decomposition temperatures were very close. Table 7 shows that the side-chain length

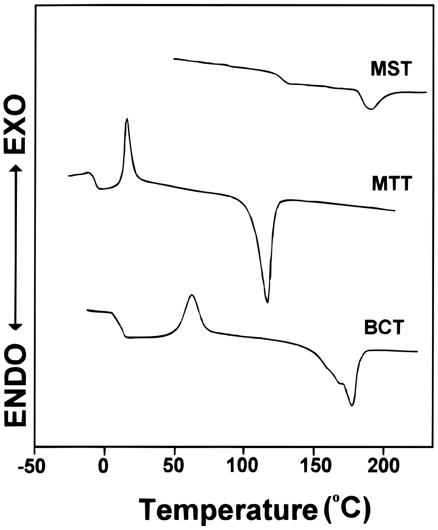


Figure 9. DSC curves of BCT, MTT, and MST.

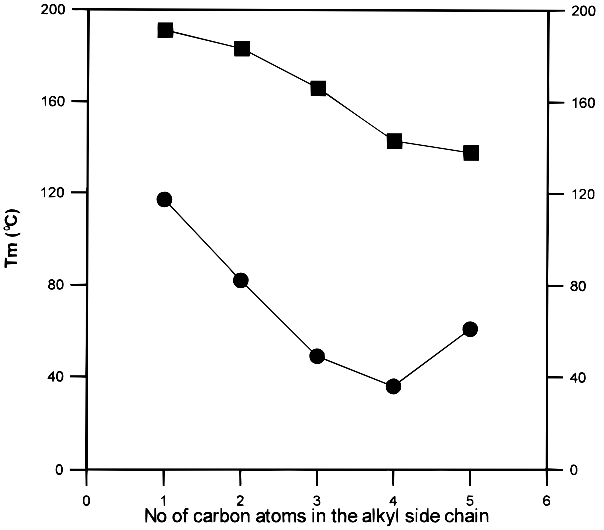


Figure 10. Effect of side-chain length on T_m: (■) AST and (●) ATT.

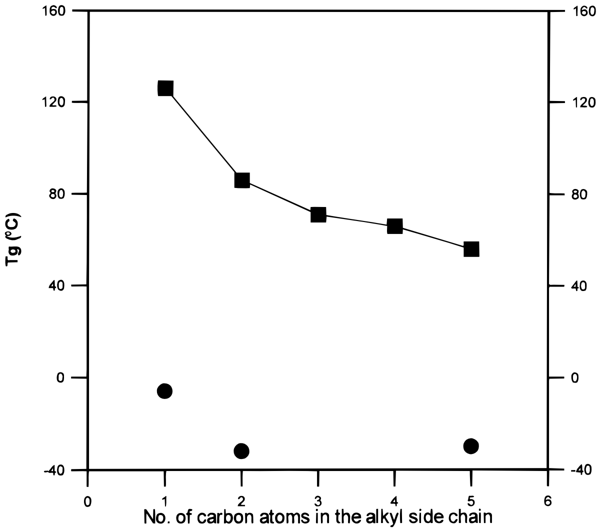


Figure 11. Effect of side-chain length on T_g: (■) AST and (●) ATT.

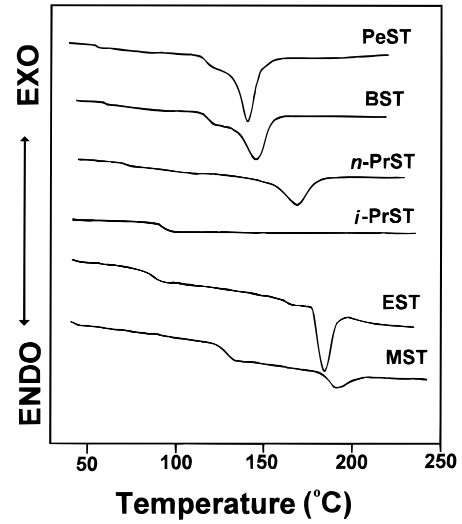


Figure 12. DSC curves of ASTs.

Table 7. Thermal Stability of Polymers by TGA

	$T_{d,0}$[a] (°C)	$T_{d,1/2}$[b] (°C)	Y^c (%)
MSE	308	333	5.4
ESE	309	330	2.9
i-PrSE	326	342	2.3
n-PrSE	305	331	1.7
BSE	310	337	2.4
PeSE	320	335	0.8
MSEE	330	360	14.7
MST	312	348	6.9

[a] Initial decompositiom temperature. [b] Half decomposition temperature. [c] Char yield at 600 °C.

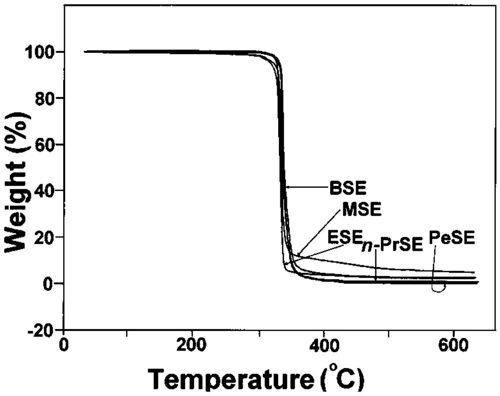


Figure 13. High-resolution TGA thermograms of ASEs under N_2.

does not affect the thermal decomposition behavior. Backbone structure does affect the decomposition behavior slightly. MST shows a two-step decomposition, and MSEE shows the highest thermal stability (Figure 14) of the three (methylsulfonyl)methyl-substituted polymers.

Finally, the solubility of the (alkylsulfonyl)methyl-substituted polymers in common organic solvents was studied (Table 8). The (alkylsulfonyl)methyl-substituted polymers showed different solubility behavior, depending on the side-chain length. The (methylsulfonyl)-methyl-substituted polymers, MSE, MST, and MSEE, were not soluble in medium-polarity solvents such as THF but were soluble in formic acid and in aprotic polar solvents such as DMAc and DMSO. However, the (alkylsulfonyl)methyl polymers where the alkyl group has more than two carbons were soluble in many solvents, including $CHCl_3$, THF, DMAc, DMSO, and formic acid. (Ethylsulfonyl)methyl-substituted polymers showed intermediate solubility behavior.

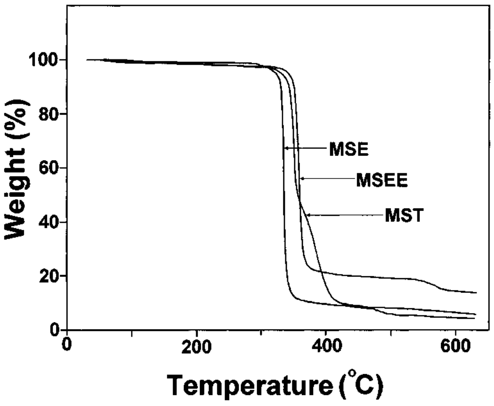


Figure 14. High-resolution TGA thermograms of MSE, MSEE, and MST under N_2.

Table 8. Solubility[a] of (Alkylsulfonyl)methyl-Substituted Polymers

	solvent					
polymer	THF	$CHCl_3$	DMAc	DMSO	formic acid	methanol
MSE	I	I	S	S	S	I
ESE	I	PS	S	S	S	I
i-PrSE	PS	S	S	S	S	I
n-PrSE	S	S	S	S	S	I
BSE	S	S	S	S	S	I
PeSE	S	S	S	S	PS	I
MSEE	I	PS	S	S	S	I
ESEE	I	S	S	S	S	I
i-PrSEE	S	S	S	S	S	I
MST	I	I	S	S	S	I
EST	I	PS	S	S	S	I
i-PrST	S	S	S	S	S	I

[a] S, soluble (>0.1%); PS, partly soluble (<0.1%); I, insoluble.

Conclusions

A series of (alkylthio)methyl substituted polymers were made by substituting the chloro side groups of CE, CEE, or BCT with alkylthioether groups using sodium alkanethiolates. This substitution reaction gave 100% conversion with little, if any, backbone cleavage. Highly polar poly(oxyalkylene)s containing alkylsulfonyl side groups were successfully synthesized by oxidizing the (alkylthio)methyl-substituted polymers under mild conditions, which also gave little, if any, backbone cleavage. The alkylthioether group, which is less polar than the chloromethyl group, lowers the T_g's compared to those of the corresponding starting polymers, while the alkylsulfonyl groups (sulfone is the most polar of all simple organic functional groups[27]) raised the T_g's of their substituted polymers above those of the corresponding chloromethyl-containing polymer. The nonpolar thioether groups seem to increase the chain backbone motions, which decrease the T_g's, while the very polar sulfone groups seem to increase the interactions between the polymer chains, which increase the T_g's.

The effectiveness and simplicity of these reactions make it possible to synthesize copolymers containing chloro and thioether or/and sulfone side groups; this gives us unlimited possibilities for making new polymers for various applications.

Glass transition behaviors of ASEs were different from those of other polymers with alkyl side chains. Normally, as the side-chain length increased, T_g decreased, while with ASEs, an increase in T_g with increase in chain length beyond a critical number of carbon atoms (N_c) in the side chains was observed. N_c for ASEs was 4, much smaller than those for poly(alkyl vinyl ether)s, poly(alkyl acrylate)s, poly(alkylstyrene)s, and poly(alkyl methacrylate)s (8, 9, 10, and 12, respectively).

Multiple endotherms, low supercooling, and birefringence were observed in poly[oxy((*n*-pentylsulfonyl)methyl)ethylene]. We propose that this polymer can organize to a liquid crystal structure, even with the very short five-carbon side chain because of the strong organizing character of the sulfone group.

All of the (alkylsulfonyl)methyl-substituted polymers were thermally stable until 300 °C, which is higher than the melting temperature of ASTs and at least 215 °C higher than the T_g's of the ASEs and ASEEs. These polymers should be melt processible.

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