

Syntheses and Properties of Oxyalkylene Copolymers Containing Methylsulfonylmethyl and Chloromethyl Side Groups or Methylthiomethyl and Chloromethyl Side Groups

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ABSTRACT: Three series of oxyalkylene copolymers containing chloromethyl and methylthiomethyl side groups were synthesized by reacting the starting chloromethyl polymers with sodium methanethiolate. The methylthiomethyl groups were oxidized to sulfone groups using *m*-CPBA to produce oxyalkylene copolymers containing chloromethyl and methylsulfonylmethyl side groups. T_g versus composition for methylthiomethyl-substituted copolymers followed those calculated from the Fox equation, while 2 of the 3 series of methylsulfonylmethyl-substituted copolymers showed positive deviations from the Fox equation. T_g s of the copolymers calculated using the Johnston equation showed very good agreement with experimental values in all cases. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2261–2270, 1998

Key words: copolymer; glass transition temperature; melting temperature; thioether; sulfone

INTRODUCTION

Alkylsulfonylmethyl-substituted poly(oxyalkylene)s have been synthesized in our laboratory.¹ Methylsulfonylmethyl-substituted poly(oxyalkylene)s were found to be high gas barrier polymers.^{1,2} Some polymers were miscible, and volume shrinkage upon mixing was observed. These blends had better barrier properties than that of any single polymer.²

Furthermore, many pairs of alkylsulfonylmethyl-substituted poly(oxyalkylene)s were miscible, and their miscibility behavior has been studied.^{2,3} In some cases, 2 polymers were miscible even though their solubility parameter differences were as large as $1.4 \text{ (cal/cm}^3)^{1/2}$.³ Normally, polymers with this solubility parameter difference are miscible only if they have strong

specific interactions, such as H-bonding.^{4,5} However, as all the polymers we synthesized have alkylsulfonyl side groups and oxyalkylene backbones, no specific interaction between the polymers was expected. It is known that polymer blends with negative heats of mixing also have negative volume changes.^{6–12} Both volume contraction and negative heats of mixing have been described as the driving forces for polymer miscibility. In our miscible blend systems, volume contractions upon mixing were observed; we postulated that the volume contraction occurred when the two polymers had different unoccupied volumes and/or different backbone flexibilities. The unoccupied volume differences between the polymers were inferred by analyzing their chemical structures and permeabilities as a function of the volume shrinkage in blending.

However, the gas barrier properties and miscibility behavior of copolymers containing sulfonyl side groups have not been studied. For this reason, the synthesis of methylsulfonylmethyl-substituted copolymers side groups is very important. In this

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article, such syntheses are described. They were synthesized by oxidizing copolymers containing chloro and methylthiomethyl side groups, which were obtained by the modification of commercial polymers. The T_g -composition relationship of these copolymers is also discussed. The syntheses and nomenclature are given in Schemes 1 to 3.

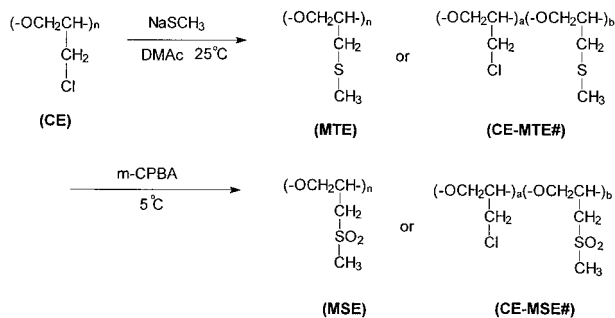
EXPERIMENTAL

Materials

Poly[oxy(chloromethyl)ethylene] (CE) (Hydrin H[®], Zeon Chemical Inc., Louisville, KY) and poly[oxy(chloromethyl)ethylene-*co*-oxyethylene] (CEE) (Hydrin C[®], in which the mole ratio of oxy(chloromethyl)ethylene and 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[®], an old sample originally obtained from Hercules Inc., Wilmington, DE) was purified by precipitation of a 3 wt % cyclohexanone solution into a 10-fold excess of methanol. Sodium methanethiolate was used as received. *m*-Chloroperbenzoic acid (*m*-CPBA) (Aldrich, Milwaukee, WI, 57–86 wt %) was purified by the method in the literature.¹³ All other reagents and solvents were used as received.

Techniques

Intrinsic viscosities of polymer solutions were measured at 30°C using a Cannon–Ubbelohde viscometer. DMAc, tetrahydrofuran (THF), or formic acid were the solvents.¹⁴ Molecular weights were obtained at 40°C with a Waters Model 590 gel permeation chromatography (GPC) using a differential refractometer as detector. THF was used as a solvent, and polystyrenes were used as standards. ¹H nuclear magnetic resonance (¹H-NMR) and ¹³C-NMR spectra were recorded using a 200-MHz Varian XL-200 spectrometer. The coupling constant, J , is given in hertz. Differential scanning calorimetry (DSC) measurements of polymers (10–13 mg) were carried out under nitrogen using a DuPont 921 DSC calorimeter. The samples were annealed at 200°C for 10 min, quenched to below their T_g s, and then heated to obtain the thermogram. The glass transition temperatures (T_g s), the melting temperatures (T_m s), and the crystallization temperatures (T_c s) of all samples were obtained from the 2nd run at a heating rate of 20°C/min.



Scheme 1

Syntheses of Poly[oxy(methylthiomethyl)ethylene] (MTE) and Its Chloromethyl Copolymers (CE-MTE)

Typically, CE (1.70 g, 18 mmol) was dissolved in 100 mL of DMAc, and a certain amount of sodium methanethiolate was added (Scheme 1). The amounts of sodium methanethiolate used are listed in Table I. The reaction mixture was magnetically stirred at room temperature for 2 h and then poured into distilled water. The precipitate was further purified by several precipitations from THF solution into distilled water, then dried under vacuum at 80°C overnight.

¹H-NMR (CDCl₃) chemical shifts: δ 2.20 (s, 3H, —CH₃), 2.56–2.86 (m, 2H, —CH₂—S—), 3.54–3.83 (m, 3H, —OCH₂—CH—). ¹³C-NMR (CDCl₃) chemical shifts: δ 16.7 (s, 1C, —CH₃), 35.9 (s, 1C, —CH₂—S—), 70.3–71.5 (m, 1C, O—CH₂—CH—), 79.2 (s, 1C, O—CH₂—CH—).

The degree of conversion was calculated by comparing the singlet at 2.20 ppm (3H) with the backbone peaks at 3.54–3.83 ppm (3H), which includes the contribution of residual poly[oxy(chloromethyl)ethylene]. MTE and CE-MTEs were obtained with yields above 90%.

Synthesis of Poly[oxy(methylthiomethyl)ethylene-*co*-oxyethylenes] (MTEE) and Its Chloromethyl Copolymers (CE-MTEE)

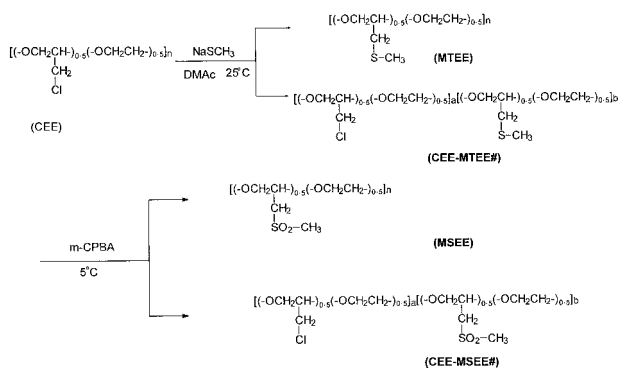
The procedure used for MTE and CE-MTE copolymers was followed, except that CEE (1.70 g, 12.4 mmol) was used in place of CE.

¹H-NMR (CDCl₃) chemical shifts: δ 2.16 (s, 3H, —CH₃), 2.53–2.87 (m, 2H, —CH₂—S—), 3.45–3.84 (m, 7H, —OCH₂CH₂—OCH₂CH—) (Scheme 2).

Table I Syntheses and Physical Properties of Copolymers Containing Chloromethyl and Methylthiomethyl Side Groups

Starting Polymer (g, mmol)	NaSCH ₃ (g, mmol)	Degree of Substitution (%)	Product	T _g (°C)	T _m , ΔH _m (°C, KJ/mol Per Unit)	T _c (°C)	[η] ^a (dL/g)	M _n /M _w ^b
CE (1.70, 18.4)	0.64, 9.2	0	CE	-17			2.76	2,130,000/2,730,000
	0.90, 12.9	23	CE-MTE23	-24			2.23	
	1.16, 16.6	42	CE-MTE42	-28			2.19	
	1.55, 22.1	54	CE-MTE54	-29			1.78	
	1.81, 25.8	66	CE-MTE66	-31			1.92	
	2.32, 33.1	82	CE-MTE82	-34			1.88	
		100	MTE	-38			1.82	639,000/1,490,000
		0	CEE	-35			2.65	1,390,000/2,610,000
	0.61, 8.7	20	CEE-MTEE20	-37			2.03	
	0.74, 10.6	39	CEE-MTEE39	-39			2.32	
CEE (1.70, 12.4)	0.87, 12.4	56	CEE-MTEE56	-39			1.74	
	1.04, 14.9	62	CEE-MTEE62	-40			1.92	
	1.22, 17.4	82	CEE-MTEE82	-43			1.79	
	1.56, 22.3	100	MTEE	-46			1.69	367,000/886,000
		0	BCT	13	172, 6.51	60		189,700/690,000
	0.77, 11.0	34	BCT-MTT34	6	125, 7.35	46	1.45	
	1.08, 15.4	46	BCT-MTT46	5	124, 7.76	48	1.34	
	1.39, 19.8	63	BCT-MTT63	2	116, 7.22	36	1.24	
	1.70, 24.2	72	BCT-MTT72	1	118, 7.79	30	1.17	
	2.00, 28.6	92	BCT-MTT92	-5	112, 8.03	28	1.24	
2.78, 39.6	100	MTT	-6	112, 8.62	15	1.16	251,000/891,000	

^a THF at 30°C.^b Obtained from GPC at 40°C using THF as solvent with polystyrenes as standards.



where # is the mole percent of sulfur containing monomeric unit

Scheme 2

The degree of conversion was calculated by comparing the singlet at 2.16 ppm (3H) with the backbone peaks at 3.54–3.83 ppm (3H), which included the contribution of residual poly[oxy(chloromethyl)ethylene-co-oxyethylene]. The yields were above 88%.

Syntheses of Poly[oxy-2,2-bis(methylthiomethyl)-trimethylene] (MTT) and Its Chloromethyl Copolymers (BCT-MTT)

BCT (1.70 g, 11.0 mmol) and a certain amount of sodium methanethiolate were dissolved in 80 mL of DMAc (Scheme 3). The amounts of sodium methanethiolate used are listed in Table I. The reaction mixture was magnetically stirred at 140°C for 0.5 h. After cooling to room temperature, it was poured into distilled water. The product was purified and dried using the same procedure as for MTE and CE-MET (yield 89%).

$^{13}\text{C-NMR}$ (CDCl_3) chemical shifts: δ 2.16 (s, 6H, $-\text{CH}_3$), 2.67 (s, 4H, $-\text{CH}_2-\text{S}-$), 3.37 (s, 4H, $\text{O}-\text{CH}_2-\text{C}-\text{CH}_2-$).

The degree of conversion was calculated by comparing the singlet at 2.16 ppm (3H) with the backbone peak at 3.37 ppm (4H), which included the contribution of residual poly[oxy(chloromethyl)ethylene-co-oxyethylene]. The yields of recovered polymers were above 88%.

Syntheses of Poly[oxy(methylsulfonylmethyl)-ethylene] (MSE) and Its Chloromethyl Copolymers (CE-MSE)

1.00 g of MTE or CE-MTE was dissolved in 40 mL of DMAc at room temperature. CE-MTE66,

CE-MTE54, CE-MTE42, or CE-MTE23 was dissolved in 40 mL of chloroform. The polymer solution was cooled to 0°C, and an excess of *m*-CPBA (Table II) was added. The reaction solution was stirred for 2 h and then poured into methanol. The precipitated polymer was purified by several reprecipitations from dimethylformamide (DMF) solution into methanol until all remaining *m*-CPBA and *m*-chlorobenzoic acid were removed. The polymer was dried under vacuum at 100°C for 1 week. MSE and its copolymers were obtained with yields above 90%.

$^{13}\text{C-NMR}$ for MSE ($\text{DMSO}-d_6$) chemical shifts: δ 42.1–42.8 (m, 1C, $-\text{CH}_3$), 55.2–56.3 (m, 1C, $-\text{CH}_2=\text{SO}_2-$), 67.9–70.4 (m, 1C, $\text{O}-\text{CH}_2-\text{CH}-$), 73.6–74.8 (s, 1C, $\text{O}-\text{CH}_2-\text{CH}-$).

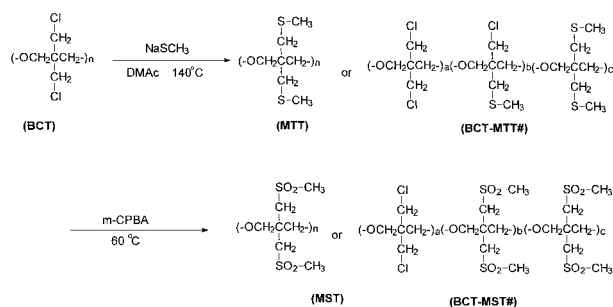
Syntheses of Poly[oxy(methylsulfonylmethyl)-ethylene-co-oxyethylenes] (MSEE) and Its Chloromethyl Copolymers (CE-MSEE)

The procedure for MSE and CE-MSE copolymers was used, except that MTEE or CE-MTEE82 (1.00 g) was dissolved in DMAc (35 mL). CE-MTEE62, CE-MTEE56, CE-MTEE39, or CE-MTEE20 was dissolved in chloroform (35 mL). The yields were above 90%.

$^{13}\text{C-NMR}$ ($\text{DMSO}-d_6$) chemical shifts: δ 41.9–42.7 (m, 1C, $-\text{CH}_3$), 54.8–56.3 (m, 1C, $-\text{CH}_2-\text{SO}_2-$), 67.3–70.9 (m, 3C, $-\text{OCH}_2\text{CH}_2-\text{OCHCH}_2-$), 73.5–74.1 (m, 1C, $-\text{OCHCH}_2-$).

Syntheses of Poly[oxy-2,2-bis(methylsulfonylmethyl)trimethylene] (MST) and Its Chloromethyl Copolymers (BCT-MST)

1.00 g of MTT or BCT-MTT92 was dissolved in DMAc (30 mL) at 80°C. 1.00 g of the other copolymers was dissolved in chloroform at 50°C. An ex-



where # is the mole percent of sulfur containing monomeric unit

Scheme 3

Table II Syntheses and Physical Properties of Copolymers Containing Chloromethyl and Methylsulfonylmethyl Side Groups

Starting Polymer (1.00 g)	<i>m</i> -CPBA (g, mmol)	Product	T_g (°C)	$[\eta]$ (dL/g)
CE-MTE23	1.24, 7.2	CE-MSE23	16	1.35 ^c
CE-MTE42	2.23, 12.9	CE-MSE42	41	1.45 ^c
CE-MTE54	2.80, 16.2	CE-MSE54	51	1.75 ^c
CE-MTE66	3.35, 19.4	CE-MSE66	59	1.53 ^c
CE-MTE82	4.18, 24.1	CE-MSE82	78	1.46 ^d
MTE	4.97, 28.8	MSE	85	1.63 ^d
CEE-MTEE20	0.74, 4.3	CEE-MSEE20	-10	1.67 ^c
CEE-MTEE39	1.43, 8.3	CEE-MSEE39	4	1.31 ^c
CEE-MTEE56	2.02, 11.7	CEE-MSEE56	21	1.46 ^c
CEE-MTEE62	2.23, 12.9	CEE-MSEE62	31	1.21 ^c
CEE-MTEE82	2.90, 16.8	CEE-MSEE82	48	1.72 ^c
MTEE	3.49, 20.2	MSEE	52	1.68 ^d
BCT-MTT34	2.02, 11.7	BCT-MST34	54 (141 ^a , 90 ^b)	1.03 ^c
BCT-MTT46	2.62, 15.0	BCT-MST46	67	1.13 ^c
BCT-MTT63	3.43, 19.9	BCT-MST63	90	0.93 ^c
BCT-MTT72	3.85, 22.3	BCT-MST72	104	0.89 ^c
BCT-MTT92	4.62, 26.8	BCT-MST92	112	0.79 ^d
MTT	4.92, 28.5	MST	127	0.84 ^d

^a T_m .^b T_c .^c DMAc at 30°C.^d Formic acid at 30°C.

cess of *m*-CPBA (Table II) was added to the reaction solution very slowly. The DMAc solution or chloroform solution was stirred at 80 or 60°C, respectively, for 30 min and then poured into methanol. The precipitated polymer was purified by several reprecipitations from formic acid solution into methanol until all *m*-CPBA and *m*-chlorobenzoic acid were removed. The product was dried under vacuum at 120°C for 3 days. The yields were above 86%.

¹³C-NMR (DMSO-*d*₆) chemical shifts: δ 30.3 (s, 1C, —C—), 43.6 (s, 2C, —CH₃), 54.4 (s, 2C, —CH₂—SO₂—), 71.2 (s, 2C, —CH₂—C—CH₂—).

RESULTS AND DISCUSSION

Methylthiomethyl-substituted homopolymers or copolymers were synthesized by reacting CE, CEE, or BCT with sodium methanethiolate using DMAc as solvent (Schemes 1–3). CE and CEE were reacted at 25°C. Due to the limited solubility of BCT at room temperature, it was reacted at 140°C. Table I shows the relationships between the amount of sodium methanethiolate used and the degree of conversion. As the amount of sodium

methanethiolate in the reaction was increased, the degree of conversion increased. When 1.8 equivalents of sodium methanethiolate were used, the degree of conversion was 100%. The degree of conversion was calculated from ¹H-NMR. Figure 1 shows the ¹H-NMR spectra of CE, CE-MTEs, and MTE. As the conversion increases, the intensity of the singlet at 2.20 ppm (3H) increases, while the intensity of the backbone peaks at 3.54–3.83 ppm decreases. When the degree of the conversion was 100%, the intensity of the singlet and that of the backbone peaks were equal.

From the conversion versus the amount of added sodium methanethiolate (Table I), we can see that 4 to 10 mmol of sodium methanethiolate did not react. When 1.8 equivalents of sodium methanethiolate were added, about 99% conversion was reached within 1 min. This means that the low conversion is due to impurities in the thiolate, solvent, and/or polymer. Such impurities could be acid that would neutralize some thiolate, or oxidizing agent that would generate disulfide groups. If we use carefully purified sodium methanethiolate, solvent, and polymer, we should be able to get 100% conversion with one equivalent of sodium methanethiolate.

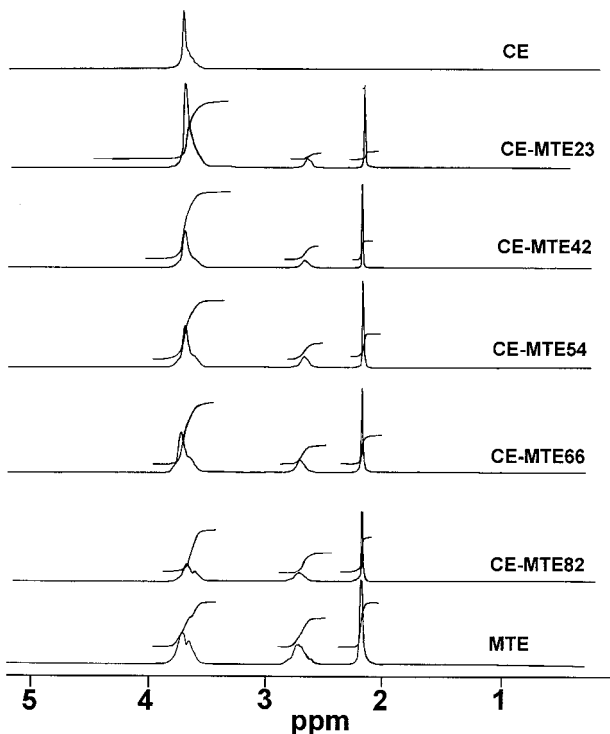


Figure 1 ^1H -NMR spectra of CE, CE-MTEs, and MTE.

Oxidation of methylthiomethyl-substituted polymers was performed using an excess of *m*-CPBA (Table II) as an oxidation agent and DMAc or chloroform as solvent, resulting in methylsulfonylmethyl-substituted polymers (Schemes 1–3). This reaction was confirmed by ^{13}C -NMR for all the polymers. Figure 2 shows the ^{13}C -NMR spectra of CE, CE-MSEs, and MSE. As the methylsulfonylmethyl content in copolymer increases, the intensity of the 4 signals (multiplet at 42.1–42.8 ppm, multiplet at 55.2–56.3 ppm, multiplet at 67.9–70.4 ppm, and multiplet at 73.6–74.8 ppm) attributed to the 4 carbons in the MSE structure increases, while the intensity of the 3 signals (singlet at 44.0 ppm, singlet at 68.2 ppm, and singlet at 78.1 ppm) attributed to the 3 carbons in the CE structure decreases. None of them shows any signals attributable to the MTE structure (Fig. 3).

The high molecular weight of the starting polymer was maintained after the substitution reaction. Molecular weights of methylthiomethyl-substituted homopolymers calculated using polystyrene standards were reasonably high; M_n s of MTE, MTEE, and MTT were 639,000, 367,000, and 251,000, respectively. The polymer viscosities also did not change much after the substitution reaction (Table I). Previously, when CE was modified, chain cleavage was a major problem. To in-

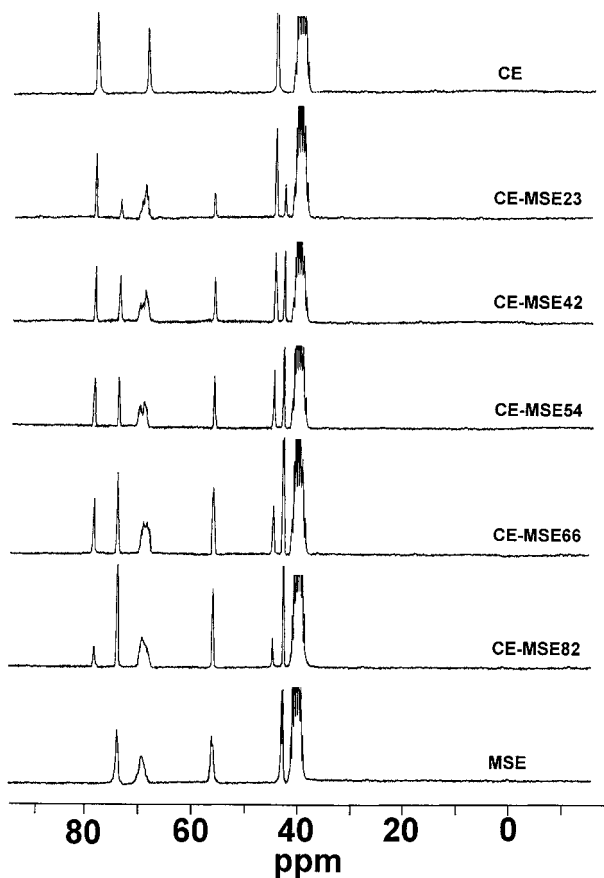


Figure 2 ^{13}C -NMR spectra of CE, CE-MSEs, and MSE.

crease the degree of substitution, researchers increased the reaction time or temperature, but this caused much polymer degradation. In our case, for CE and CEE, which could degrade at high temperatures or long reaction times, a short reaction time (2 h) and a mild reaction temperature (25°C) could be used since the thiolate group is a very strong nucleophile. When excess sodium methanethiolate (1.8 equivalent) was used, 100% conversion was obtained with very little, if any, polymer backbone cleavage. For BCT, which is

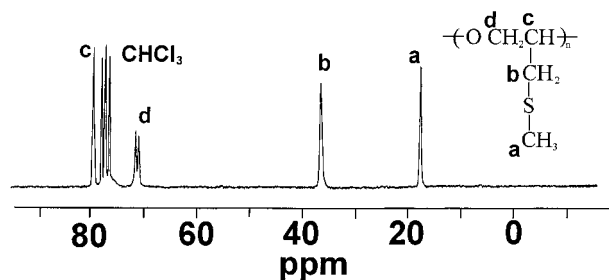


Figure 3 ^{13}C -NMR spectrum of MTE.

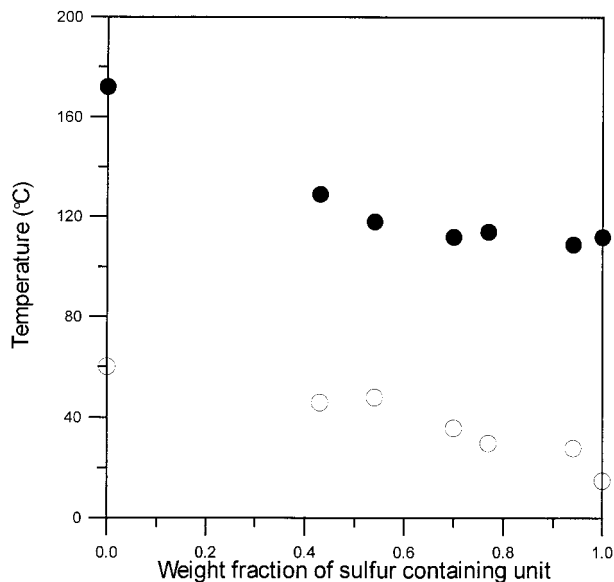


Figure 4 T_m (●) and T_c (○) of BCT-MTTs.

thermally and chemically stable,¹⁵ the reaction took 0.5 h at 140°C; still, the intrinsic viscosity of the products were high enough to retain good polymer physical properties.

Little backbone cleavage due to oxidation was observed (Table II). The methylsulfonylmethyl-substituted polymers still had quite high intrinsic viscosities; they ranged from 0.79 to 1.81 dL/g. Molecular weights of these polymers were not measured because they were insoluble in THF.

As the degree of methylthiomethyl group substitution increased, the glass transition temperature (T_g) decreased. The T_g decreased from -17°C for pure CE to -38°C at 100% conversion. For CEE, the initial T_g of -35°C dropped to -46°C , while that for BCT dropped from 13 to -6°C . Polymers with more polar side groups usually have higher T_g s than those with less polar side groups.^{16,17} In our case, the chloromethyl group is more polar than the thioether group (the dipole moments of chloromethyl and methylthio groups are 1.87 and 1.50 Debye, respectively¹⁸), so the polymers with chloro groups have higher T_g s than the corresponding polymers with thiomethyl side groups.

The melting (T_m) and crystallization (T_c) temperatures of the BCT-MTT copolymers decreased as the methylthiomethyl content of the BCT-MTT copolymers increased (Fig. 4). DSC thermograms in Figure 5 show the T_g s, T_m s, and T_c s of the BCT-MTTs. It is unusual for random copolymers to have crystallization and melting peaks over their entire composition range. Introduction of chemi-

cally different units into a polymer normally decreases the rate and degree of crystallization and also reduces the T_m .¹⁹ Random copolymers usually crystallize only when one component predominates in the chain repeat. For example, copolymers of vinylidene chloride (VDC) and vinyl chloride (VC) crystallize only when the VCD content is more than 70%.²⁰ However, when the 2 different monomeric units can cocrystallize, the copolymers can be crystalline over their entire composition range, and the T_m can change relatively linearly with composition (for example, styrene-*p*-fluoro styrene and hexamethylene sebacamide-hexamethylene sebacate copolymers).^{19,21} For the BCT-MTTs, T_m decreased as the MTT content increased, while ΔH_m remained almost constant or increased slightly (Table I). This indicates that the 3 possible monomeric units of BCT-MTT (Scheme 3) can cocrystallize.

As the methylsulfonylmethyl side group content in the copolymers increased, T_g increased. The sulfonyl group is the most polar of any single functional group (the dipole moment of methylsulfonylmethyl group is 4.49 Debye¹⁸). The polymers with 100% methylsulfonylmethyl content,

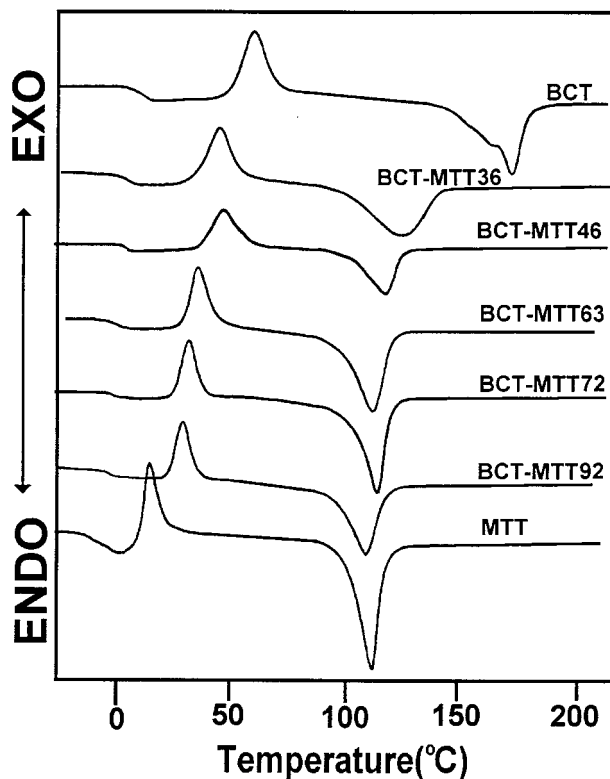


Figure 5 DSC thermograms of BCT, BCT-MTTs, and MTT.

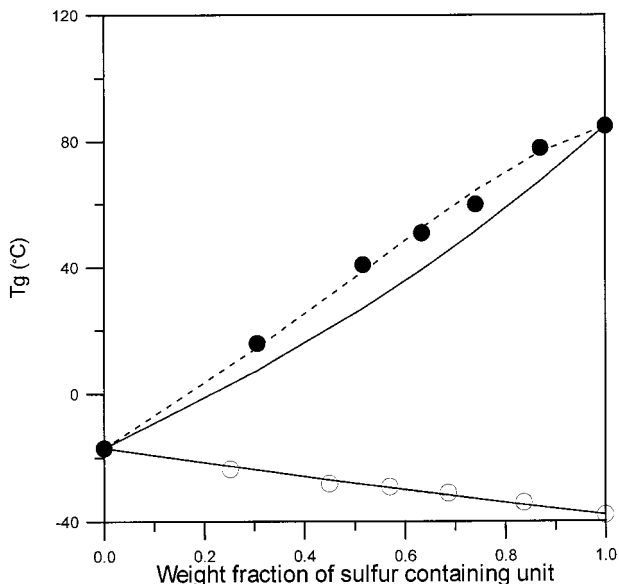


Figure 6 T_g s of CE-MTEs (○) and CE-MSEs (●): Fox equation (—) and Johnston equation (-----).

MSE, MSEE, and MST, have much higher T_g s than those of the polymers with chloromethyl or methylthiomethyl groups. T_g s of MSE, MSEE, and MST were 85, 52, and 125°C, respectively. For BCT-MST34, a very small and broad melting peak at 141°C ($\Delta H_m = 0.18$ KJ/mol per unit) and a crystallization peak at 90°C were observed; other BCT-MSTs showed no melting and crystallization. This is the usual behavior for random copolymers where one homopolymer is crystalline, while the other is amorphous.¹⁹

In Figures 6–8, the experimental T_g s of copolymers (circles) are compared to the T_g s calculated (solid lines) using the Fox equation, as follows:²²

$$1/T_{g,c} = W_A/T_{g,A} + W_B/T_{g,B} \quad (1)$$

where $T_{g,c}$ is glass transition temperature of copolymer containing weight fractions W_A and W_B of the monomer units A and B, whose homopolymers have glass transitions, $T_{g,A}$ and $T_{g,B}$, respectively. The Fox equation is based on the assumption that certain properties of a copolymer, for example, specific volume, molar cohesive energy, or chain stiffness, are linear combinations of the properties of the corresponding homopolymers. But this is not the case for many copolymers. Due to sequence distribution and (or) structural effects, T_g s of copolymers can show positive or negative deviations from the Fox equation.^{23–28}

The copolymers in this study are all random.

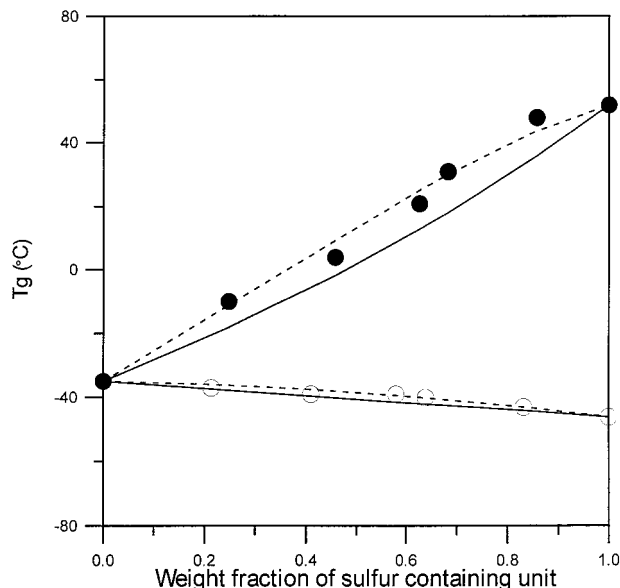


Figure 7 T_g s of CEE-MTEEs (○) and CEE-MSEEs (●): Fox equation (—) and Johnston equation (-----).

Since the reactions were run in homogeneous solution, the methanethiolate, a strong nucleophile, could attack any chloro group in CE randomly. The distribution of the thioether groups and corresponding sulfonyl groups in the substituted polymer should be random. If there are no specific interactions of the two comonomer units, only the chemical structure should affect the T_g .

T_g -composition data for the CE-MTEs and

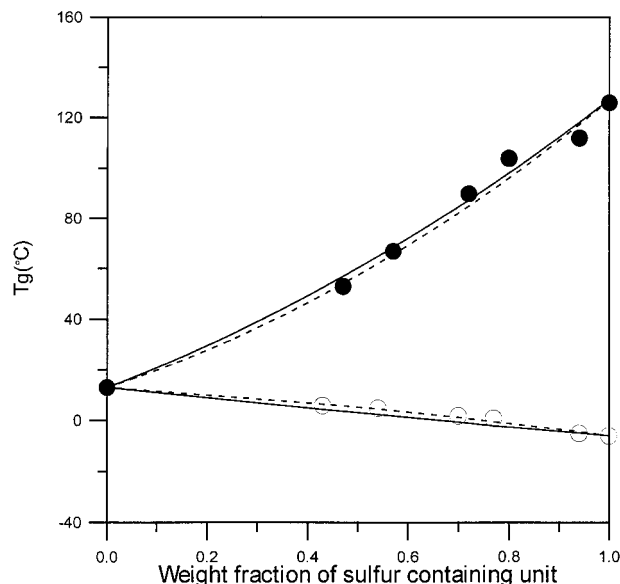


Figure 8 T_g s of BCT-MTTs (○) and BCT-MSTs (●): Fox equation (—) and Johnston equation (-----).

CEE-MTEEs show very good agreement with the Fox equation. However, those for CE-MSEs and CEE-MSEEs show strong positive deviations. Similar results for other copolymers in this series have been discussed.²⁹ T_g -composition data of *n*-alkylsulfonylmethyl-substituted poly(oxyethylene) copolymers showed positive deviation from the Fox equation. This was explained as being due to polar or H-bonding interactions between the side groups, which could reduce the free volume of the copolymers and raise the T_g . Polymer densities also increased above the expected values. T_g -composition data of poly(oxyethylene) copolymers with chloro and *n*-alkylthioether side groups followed the Fox equation because there was no steric and polar interaction between the side chains. Using the same rationale, the T_g behaviors of CE-MTEs, CEE-MTEEs, CE-MSEs, and CEE-MSEEs can be understood.

T_g -composition data for the BCT-MTTs followed the Fox equation within experimental error, which can be understood from the rationale used above. However, the BCT-MST T_g values also showed a relatively good fit with the Fox equation, although the polymers had the same side chains as the CE-MSEs and CEE-MSEEs. In BCT-MST, 2 side chains are attached to the same carbon in the backbone, and the methylsulfonyl group is relatively bulky; this can give rise to steric hindrance, and possible free volume decrease due to polar or H-bonding interactions in these poly(oxyalkylene) copolymers may not be possible. Another possible explanation is that since 2 side groups are attached to the same carbon, the major polar interactions occurring in the polymer can be between the side chains on the same repeat unit. This should not lead to positive deviation of the T_g s.

Johnston²⁵ rationalized the T_g of many copolymers by considering sequence distributions and the interaction effects between the two monomeric units. Copolymers containing A and B monomeric units can have AA, AB, BA, and BB dyads. The probabilities of these linkages (P_{AA} , P_{AB} , P_{BA} , and P_{BB}) can be calculated for a given monomer composition (N_A and N_B) because the copolymers are random.

$$P_{AB} = P_{BB} = N_B / (N_A + N_B) \quad (2)$$

$$P_{AA} = P_{BA} = N_A / (N_A + N_B) \quad (3)$$

Using these probabilities, the T_g s of the copolymers are calculated as follows.

$$\frac{1}{T_{g,c}} = \frac{W_A P_{AA}}{T_{g,A}} + \frac{W_A P_{AB} + W_B P_{BA}}{T_{g,AB}} + \frac{W_B P_{BB}}{T_{g,B}} \quad (4)$$

where $T_{g,AB}$ is the T_g of the AB dyad alternating copolymer, and the other parameters are same as in the Fox equation. $T_{g,AB}$ values have been determined by several techniques.^{25,30,31} In this study, $T_{g,AB}$ was calculated using eq. (4). As the data needed for eq. (4) are available from Tables I and II; $T_{g,AB}$ can be calculated for each copolymer. Average values were obtained for each series of copolymers, and they were -28.6 , -36.4 , 6.1 , 70.4 , 33.2 , and 67.6°C for CE-MTE, CEE-MTEE, BCT-MTT, CE-MSE, CEE-MSEE, and BCT-MST, respectively.

T_g -composition curves of the copolymers calculated from the Johnston equation [eq. (4)], using the best fit $T_{g,AB}$ values, are shown in Figures 6–8. They fit the T_g -composition data quite well.

The T_g -composition curves for CE-MTE, CEE-MTEE, BCT-MTT, and BCT-MST were almost identical for both the Fox and Johnston equations. However, $T_{g,AB}$ for the CEE-MSEE series deviated from the Fox equation value by 25°C (8°C versus 33°C), while that for CE-MSE system deviated by 36°C (34°C versus 70°C). This shows that some specific interaction (between the chloromethyl and sulfone groups) is occurring in these systems.

SUMMARY AND CONCLUSIONS

Methylthiomethyl-substituted copolymers, CE-MTEs, CEE-MTEEs, or BCT-MTTs, were synthesized by reacting CE, CEE, or BST with sodium methanethiolate. By varying the molar ratio of sodium methanethiolate to the starting polymer, copolymers with different compositions were made. As the methylthiomethyl content in the copolymers increased, the copolymer T_g decreased; the T_g -composition data followed that calculated using the Fox equation. For BCT-MTT, melting and crystallization peaks were observed. Their temperatures decreased as the methylthio content increased. It is unusual for random copolymers to have crystallization and melting transitions. It is probable that the double substitution forces an extended conformation in all the copolymers that allows them to pack. This conformation has been found in the BCT homopolymers.³²

Methylsulfonylmethyl-substituted copolymers, CE-MSEs, CEE-MSEEs, or BCT-MSTs, were synthesized by oxidation of the corresponding thio-

ether using *m*-CPBA. T_g s of copolymers increased as the methylsulfonyl content increased. T_g -composition data of CE-MSEs and CE-MSEEs showed positive deviation from those calculated using the Fox equation, while those of BCT-MSTs followed the Fox equation. Positive deviation of CE-MSEs and CE-MSEEs indicates some specific AB interaction between the side chains. Zero deviation of BCT-MSTs, although they have same side chains as CE-MSEs and CE-MSEEs, was attributed to a steric effect or possibly because the major interactions are between the side chains in the same repeat unit. The Johnston equation, which considers sequence distributions and interactions between the two different monomeric units, could fit T_g -composition data of all copolymers, including the methylthiomethyl-substituted copolymers.

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