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Synthesis and Properties of Liquid Crystalline Polymers Containing an Oxyethylene Backbone and *n*-Octylsulfonylmethyl Side Groups

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ABSTRACT: Poly(oxyethylene)s containing *n*-octylthiomethyl side groups were synthesized by the reaction of poly[oxy(chloromethyl)ethylene] (CE) and sodium *n*-octanethiolate in DMAc. These were oxidized to poly(oxyethylene)s containing *n*-octylsulfonylmethyl side groups. When the mole percentage of sulfur containing monomeric units in the copolymers was about 60% or more, ordered phases formed. Structural analysis of the ordered phase of poly(oxyethylene)s containing *n*-octylthiomethyl side groups is in progress. The ordered phase of poly(oxyethylene)s containing *n*-octylsulfonylmethyl side groups was studied using differential scanning calorimetry, cross-polarizing optical microscopy, and X-ray diffraction. It was found to be a smectic A liquid crystalline phase.

Introduction

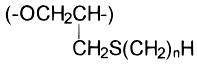
Polymers containing *n*-alkyl side chains can form mesophases as follows.

(1) Flexible alkyl side chains attached to the backbone of linearly rigid rod polymers, such as aromatic polyesters,[1−5] aromatic polyamides,[6−8] polypeptides,[9−11] polyisocyanates,[12,13] poly(ethylene sulfone),[14,15] etc., act like a solvent, diluting the steric and the attractive interactions between the rigid chains. Melting and liquid crystalline-isotropic transition temperatures can be adjusted by changing the length of the flexible side chains. Without the *n*-alkyl side chains, such polymers normally decompose below their melting temperature, so a thermotropic liquid crystalline (LC) phase cannot be obtained; however lyotropic LC phases can often be observed in concentrated solution. There is a certain range of side chain lengths that facilitate thermotropic transitions in the polymer. Very short side chains cannot work effectively as solvent while very long *n*-alkyl chains interact with themselves; the interactions can completely dominate the behavior of the whole ensemble. For example polyisocyanates[13] with side chain length of $4 \leq n < 13$ carbon atoms and poly(alkyl L-glutamate)s[10] with $10 \leq n \leq 18$ show thermotropic LC phases.

(2) Alkyl side chains attached to non rigid polymers backbones, such as poly(aliphatic ester)s[16−18] polyalkylenes,[19,20] and polyacrylates,[21] can form side chain crystalline structures. The outer parts of the long *n*-alkyl side chains can pack into ordered layers whereas in most cases the main chain, together with the inner portion of the side groups, remains in a disordered conformation. This type of ordering has been classified as mesomorphic. In many cases, side chain lengths are quite long. For example poly(aliphatic esters) with 18 carbon side chains showed a thermotropic LC phase.[18]

(3) Polysilylenes,[22−24] polysiloxanes,[25−27] and poly(silylenemethylenes)[28] that contain two *n*-alkyl side groups attached to the silicon atom in the backbone show thermotropic LC phases. The reasons for their mesomorphic behaviors are not fully understood; suggestions were made that the appearance of mesomorphic phase in the polysiloxanes is due to biphilicity resulting from the difference in interaction of inorganic main chains and organic side groups, and the full symmetry of the polymers.[27,29] The biphilicity and the symmetry of the polymers can increase their rigidity.

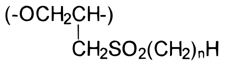
Poly[oxy(*n*-alkylthiomethyl)ethylene]s (ATEs) and poly[oxy(*n*-alkylsulfonyl methyl)ethylenes) (ASEs) have been made by the authors.[30]



$(\text{-OCH}_2\underset{\text{CH}_2\text{S(CH}_2)_n\text{H}}{\underset{|}{\text{CH}}}\text{-})$

$n = 1, 2, 3, 4, 5$

(ATEs)



$(\text{-OCH}_2\underset{\text{CH}_2\text{SO}_2\text{(CH}_2)_n\text{H}}{\underset{|}{\text{CH}}}\text{-})$

$n = 1, 2, 3, 4, 5$

(ASEs)

These polymers have flexible backbones (oxyethylenes) and *n*-alkyl side chains. The ATE series contains the weakly polar alkylthiomethyl side group, while the ASE series has alkylsulfonylmethyl side chains, containing the very polar sulfone group. For all polymers except ASE with $n = 5$, only glass transition temperatures were observed. These polymers were amorphous. ASE with $n = 5$ had a glass transition at 40 °C but also showed two small endotherms at 60 °C ($\Delta H_m = 0.38$ J/g) and 128 °C ($\Delta H_m = 0.69$ J/g); both increased after annealing at 110 °C. This implies that this polymer might be LC. From the ΔH_m values and polarizing optical microscopy observations, this polymer was found to be somewhat ordered.[30] Generally side chain liquid crystalline polymers have a flexible backbone with mesogenic side groups. However ASE with $n = 5$ did not contain any mesogenic side groups.

Since liquid crystal behavior in systems without mesogens was unusual, we felt that a more detailed study was warranted. We therefore decided to synthesize poly[oxy(octylthiomethyl)ethylene] (OTE), [oxy(chloromethyl)ethylene]/[oxy(octylthiomethyl)ethylene] copolymers (CE−OTEs), poly[oxy(octylsulfonylmethyl)ethylene] (OSE), and [oxy(chloromethyl)ethylene]/[oxy(octylsulfonylmethyl)ethylene] copolymers (CE−OSEs**)** (Scheme 1). The liquid crystalline properties of these polymers are discussed using the results of differential scanning calorimetry, polarizing optical microscopy, and X-ray diffractometer measurements.

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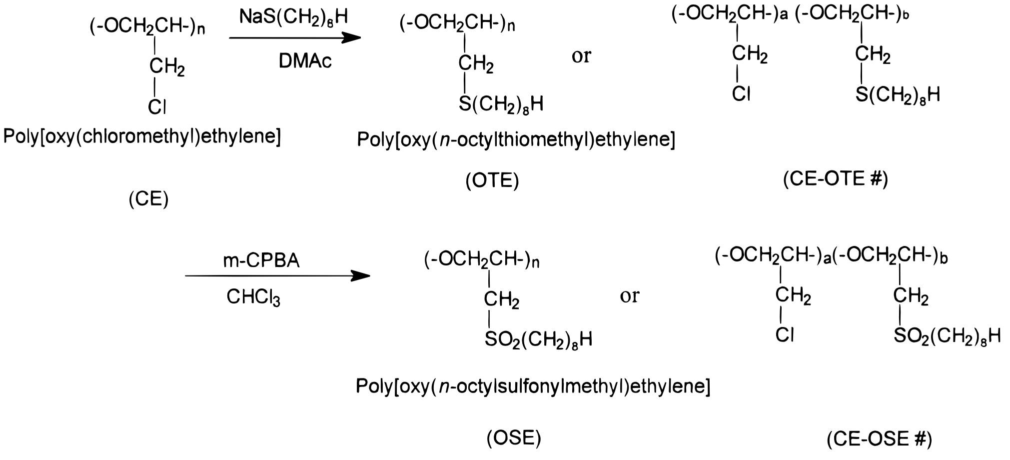
Scheme 1



where # is the mole percent of the sulfur containing monomer unit

Table 1. Reaction Conditions and Results in the Synthesis of OTE and CE−OTEs

polymer designation	solvent	sodium octanethiolate (mol %)	reaction temp (°C)	deg of substitution (%)	M_n[a]	M_w/M_n
CE					81 000	2.35
CE−OTE13	DMAc	30	25	13	53 000	2.64
CE−OTE34	DMAc	60	25	34	83 000	2.59
CE−OTE52	DMAc	90	25	52	77 000	2.56
CE−OTE68	DMAc	120	25	68	76 000	2.51
CE−OTE75	DMAc	180	35	75	67 000	2.63
CE−OTE82	DMAc	180	40	82	73 000	2.13
CE−OTE94	DMAc	180	60	94	71 000	2.73
OTE	DMAc	180	80	≅100	94 600	2.10
CE−OTE2	$CHCl_3$	120	25	2		
CE−OTE7	THF	120	25	7		
CE−OTE57	DMSO	120	25	57		
CE−OTE63	DMF	120	25	63		

[a] Obtained from GPC at 40 °C using THF as solvent with monodisperse polystyrenes as standards.

Experimental Section

Materials. Poly[oxy(chloromethyl)ethylene] (CE) (Hydrin H, Zeon Chemical Inc.) was purified by precipitating a 3 wt % chloroform solution into a 10-fold excess of methanol. After several washings with methanol, the precipitate was dried in a vacuum at 60 °C overnight. M_n and M_w of the purified CE were 81 000 and 191 000, respectively ($M_w/M_n = 2.35$). All solvents were reagent grade and were used as received. *n*-Octanethiol and sodium ethoxide (Aldrich) were used as received. *m*-Chloroperoxybenzoic acid (*m*-CPBA) (Aldrich, 57−86 wt %) was purified by the literature method.[31]

Sodium *n*-Octanethiolate. Sodium *n*-octanethiolate was prepared by adding *n*-octanethiol to a solution of sodium ethoxide in ethanol; the solid residue obtained after evaporation of the solvent was washed with ether, filtered, and dried under vacuum.

Preparation of Poly[oxy(octylthiomethyl)ethylene] (OTE) and Poly[oxy (chloromethyl)ethylene]/Poly[oxy(octylthiomethyl)ethylene] Copolymers (CE−OTEs). Typically CE (1.70 g, 18 mmol) was dissolved in 100 mL of solvent, and sodium *n*-octanethiolate was added. The reaction conditions and moles of sodium ethanethiolate used are listed in Table 1. The reaction mixture was magnetically stirred at a given temperature for 0.5 h and then poured into distilled water. The precipitate was further purified by several precipitations from THF solution into distilled water and then dried under vacuum at 80 °C overnight. OTE and CE−OTEs were obtained in above 90% yields. These were *n*-octanethiolate free, confirmed using GPC measurement. ^{1}H NMR chemical shifts: δ 0.86 (t, 3H, $J = 6.9$ Hz, $-CH_3$), 1.02−1.43 (m, 10H, $S-CH_2-CH_2-(CH_2)_5-CH_3$), 1.43−1.81 (m, 2H, $S-CH_2-CH_2-(CH_2)_5-CH_3$), 2.52 (t, 2H, $J = 7.3$ Hz, $S-CH_2-CH_2-(CH_2)_5-CH_3$), 2.58−2.83 (m, 2H, $CH_2-S-CH_2-CH_2-(CH_2)_5-CH_3$), 3.48−3.83 (m, 3H, $O-CH_2-CH-$) (Figure 1B).

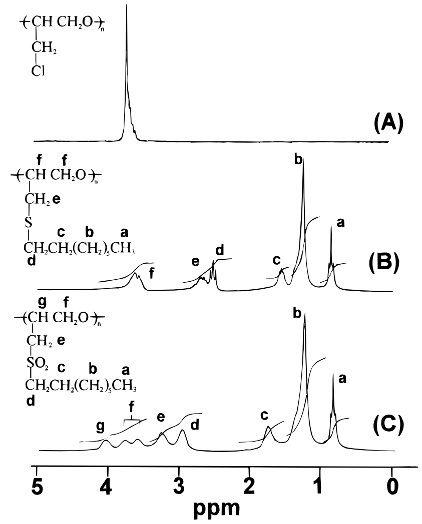


Figure 1. ^{1}H NMR spectra of (A) CE, (B) OTE, and (C) OSE.

The degree of conversion was calculated by comparing the triplet at 0.86 ppm (3H) with the backbone peak at 3.48−3.83 ppm (3H) which included the contribution of residual CE.

Oxidation of OTE and CE−OTE to Poly[oxy(octylsulfonylmethyl)ethylene] (OSE) and Poly[oxy(chloromethyl)ethylene]/Poly[oxy(octylsulfonylmethyl)ethylene] Copolymers (CE−OSEs). A 1.00 g sample of OTE (or CE−OTE) was dissolved in 35 mL of $CHCl_3$ at room temperature and the solution was cooled to 0 °C. A slight excess over two equivalents of *m*-CPBA was added to the reaction solution. Table 2 shows the reaction conditions. The reaction mixture

Table 2. Reaction Conditions and Results in the Synthesis of OSE and CE−OSEs

starting polymer (1.00 g)	*m*-CPBA (mmol)	M_n[a]	M_w/M_n	polymer designation
CE−OTE13	3.7	56 000	3.07	CE−OSE13
CE−OTE34	7.9	52 000	3.42	CE−OSE34
CE−OTE52	10.4	78 000	2.52	CE−OSE52
CE−OTE68	12.2	109 000	2.01	CE−OSE68
CE−OTE75	13.0	75 000	2.23	CE−OSE75
CE−OTE82	13.7	78 000	2.04	CE−OSE82
CE−OTE94	14.5	84 000	2.09	CE−OSE94
OTE	14.8	79 000	2.58	OSE

[a] Obtained from GPC at 40 °C using THF as solvent with monodisperse polystyrenes as standards.

was stirred for 1 h and then poured into methanol. The precipitated polymer was purified by several reprecipitations from chloroform solution into methanol until all *m*-CPBA and *m*-chlorobenzoic acid were removed. ^{1}H NMR chemical shifts: δ 0.86 (t, 3H, $J = 6.9$ Hz, $-CH_3$), 1.05−1.59 (m, 10H, $SO_2-CH_2-CH_2-(CH_2)_5-CH_3$), 1.61−1.96 (m, 2H, $SO_2-CH_2-CH_2-(CH_2)_5-CH_3$), 2.78−3.11 (m, 2H, $SO_2-CH_2-CH_2-(CH_2)_5-CH_3$), 3.12−3.42 (m, 2H, $CH_2-SO_2-CH_2-CH_2-(CH_2)_5-CH_3$), 3.50−3.92 (m, 2H, $O-CH_2-CH-$), 3.93−4.22 (m, 1H, $-O-CH_2-CH-$) (Figure 1C). OSE and CE−OSEs were obtained in yields above 90%.

Techniques. ^{1}H NMR spectra were obtained on a Varian 200 MHz spectrometer Model Gemini 200 using $CDCl_3$ as a solvent. Differential scanning calorimetry (DSC) was carried out on a TA Instruments 2910 Differential Scanning Calorimeter. The heating and cooling rates were 10 °C/min. The glass transition temperatures are taken as the inflection point in the change in heat capacity with temperature in the DSC thermogram. The other transition temperatures were given at the maxima or minima of the endothermic or exothermic peaks. All thermal transitions were read from reproducible second or later heating scans and first or later cooling scans. Pure indium was used to calibrate the instrument. Molecular weights were obtained at 40 °C with a Waters model 590 gel permeation chromatograph (GPC) using a differential refractometer as detector. THF was used as a solvent and monodisperse polystyrenes were used as standards. Cross-polarizing optical microscopy of thin samples, sandwiched between two glass slides, was performed using a Carl-Zeiss polarizing optical microscope equipped with a Mettler FP-82 hot-stage controlled by a Mettler FP-800 central processor. The photograph of OSE (125×) was taken at 142 °C after cooling the sample from the isotropic state (200 °C) at a cooling rate of 5 °C/min. Flat plate X-ray photographs were obtained at room temperature from oriented fibers using Ni-filtered copper Kα radiation ($\lambda = 1.5418$ Å) in a Searle toroidal focusing camera under vacuum with pinhole collimation. The *d* spacings were calibrated using calcium fluoride. The fibers were drawn with tweezers from homogeneous films of the samples on a microscope slide at 140, 138, 130, 66 and 48 °C for OSE, CE−OSE94, CE−OSE82, CE−OSE75, and CE−OSE68, respectively. The homogeneous films were obtained by cooling the samples from the isotropic state (200 °C) at cooling rate of 5 °C/min to the drawing temperatures.

Results and Discussion

OTE and CE−OTEs were made by the reaction of CE and sodium *n*-octanethiolate in DMAc (Scheme 1); the reaction conditions and results are listed in Table 1. Figure 1A,B shows the ^{1}H NMR spectra of CE and OTE. Previously, thiolated polymers with shorter side chains were synthesized. The 100% conversions were obtained using 180 mol % of sodium alkanethiolate at room temperature without any polymer precipitation, and 99% conversion was reached within 1 min.[30,32] The difference between the conversion and sodium thiolate/polymer ratio was ascribed to the side reactions of thiolate ions with impurities. This time, as the mole ratio of sodium *n*-octanethiolate was increased, conversion increased. However, at 25 °C, only 68% conversion of CE to OTE could be obtained. When 120 or 180 mol % of sodium *n*-octanethiolate to CE was used at 25 °C, the polymer precipitated within 5 min and the conversion was about 68% for both ratios. CE−OTE52 did not precipitate at room temperature. Therefore, at 25 °C, the reaction solvent (DMAc) can dissolve the thiolated polymers containing up to about 68 mol % of thioether monomeric units. At higher temperatures, higher conversions were obtained. 100% conversion was obtained by reacting at 80 °C, using 180 mol % of sodium *n*-octanethiolate; still polymer precipitation was observed within 10 min. On the basis of the results obtained at 25 °C, reaction stopped after the polymer precipitated. At higher temperature, the reaction solvent could dissolve thiolated polymers with higher thioether content, so conversion could be increased; at 80 °C, 100% conversion was reached.

Solvent effects were observed in the reaction when $CHCl_3$, THF, DMSO, and DMF were used (Table 1). The starting materials, CE and sodium octanethiolate, were soluble in these solvents. In lower polarity solvents such as $CHCl_3$ and THF, no precipitation was observed during the reaction, but conversions were very low. The low conversion observed when $CHCl_3$ was used as solvent might be due to reaction of the thiolate anion with the solvent. In the higher polarity solvents (DMSO and DMF), conversions were much higher than in the lower polarity solvents even though the polymers precipitated. This indicates that polar solvents facilitate the reaction.

OSE and CE−OSEs were obtained by oxidation of OTE and CE−OTEs using *m*-CPBA. Table 2 shows the amounts of reagents used and the molecular weights of the products. The structures of the products were confirmed by their ^{1}H NMR spectra; Figure 1 shows an ^{1}H NMR spectrum of OSE. In the previous paper,[30] oxidation of shorter side chain ATEs (poly[oxy(alkylthiomethyl)ethylene]s) was discussed in detail. Oxidation of the *n*-octylthio group occurred under the same conditions.

High molecular weight was maintained (Tables 1 and 2). Neither substitution nor oxidation cleaved the polymers backbone significantly. Therefore, the effect of molecular weight on the thermal properties of polymers can be ignored. However, since polystyrene standards were used, the calculated molecular weights and distributions are suspect, since we do not know the Mark−Houwink constant, α, for these systems. We would expect α to change with the copolymer composition and the linking group (S and SO_2) as well.

The thermal properties of OTE and CE−OTEs were studied using DSC. The transition temperatures and enthalpy changes are listed in Table 3. Figure 2 shows the DSC thermograms of OTE from the first cooling and second heating. Subsequent cooling and heating repeated the thermogram. Upon heating, two endotherms at −18 and 5 °C were observed, while upon cooling only one endotherm at −31 °C was observed. Similar thermograms were observed for CE−OTE94 and CE−OTE82, though their transition temperatures were lower. CE−OTE75 and CE−OTE68 showed only one transition. For CE−OTEs with less than 68 mol % of *n*-octylthio units, only a glass transition was observed.

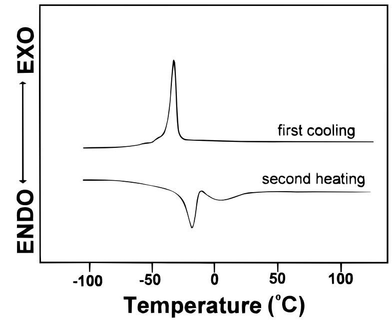


Figure 2. DSC first cooling and second heating curves of OTE.

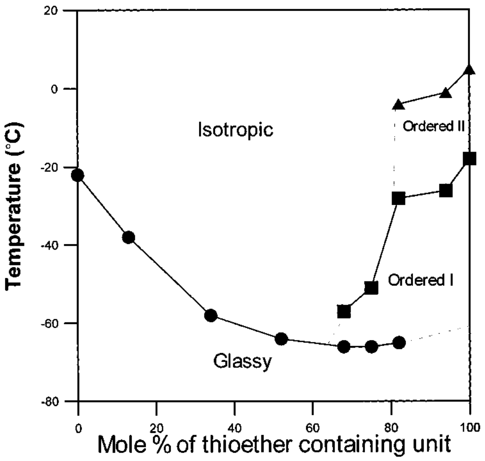


Figure 3. Phase diagram of CE−OTEs, second heating scan, 10 °C/min: (●) glass transition temperature; (■) first endotherm; (▲) second endotherm.

Table 3. Thermal Properties of CE, CE−OTEs, OTE, CE−OSEs, and OSE

		second heating	first cooling
polymer	T_g (°C)	endotherms (°C); ΔH (J/g)	exotherm (°C); ΔH (J/g)
CE	−22		
CE−OTE13	−38		
CE−OTE34	−58		
CE−OTE52	−64		
CE−OTE68	−66	−57; 3.5	−64; 3.8
CE−OTE75	−66	−51; 5.4	−61; 5.9
CE−OTE82	−65	−28; 25.1, and −4; 5.6	−43; 25.3
CE−OTE94		−26; 27.1, and −1; 10.1	−33; 28.9
OTE		−18; 21.1, and 5; 11.2	−31; 28.6
CE−OSE13	−28		
CE−OSE34	−8		
CE−OSE52	4		
CE−OSE68	28	55; 3.2	49; 3.1
CE−OSE75	34	74; 3.4	68; 2.5
CE−OTE82	54	139; 6.0	134; 7.2
CE−OSE94	59	148; 5.6	141; 6.7
OSE	60	150; 6.5	142; 7.4

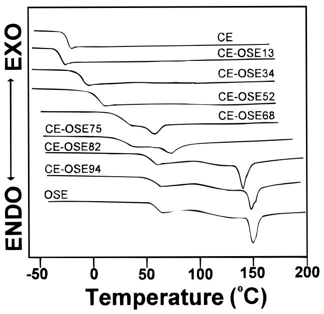


Figure 4. DSC second heating curves of CE, CE−OSEs, and OSE.

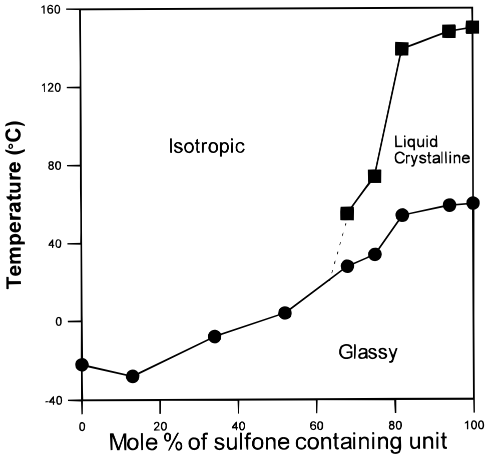


Figure 5. Phase diagram of CE−OSEs second heating scan, 10 °C/min: (●) glass transition temperature; (■) endotherm.

The DSC results show that about 60% substitution is necessary to form an ordered phase; CE−OTE68 showed peaks in the heating and cooling scans, while CE−OTE52 showed only a glass transition (Table 3).

A phase diagram of the CE−OTEs based on their compositions and transition temperatures, obtained from the second heating DSC curve data, is shown in Figure 3. The phase below the glass transition temperature (T_g) was assigned as glassy. The phase for copolymers with less than 60% n-octylthiomethyl group above T_g and above the highest endotherms for the other polymers is assigned as isotropic. Under these conditions, no birefringence was observed using cross-polarizing optical microscopy. The phases between the T_g's and the endotherms have not been analyzed; they were assigned as ordered I and ordered II phases, Figure 3. Analysis of their structures is in progress.

The T_g's of CE−OTE copolymers decrease as the mol % of n-octylthio groups increases. When it reaches about 60%, T_g no longer decreases but stabilizes at about −66 °C and may start to increase. This is the composition at which an ordered phase forms. When an ordered phase was present, it was very hard to detect the glass transition from the heating thermogram, and T_g's for CE−OTE92 and OTE could not be assigned. Only one ordered phase is observed for CE−OTEs containing between 60 and 79 mol % of an n-octylthio group (CE−OTE68 and CE−OTE75); two ordered phases were observed for CE−OTEs with more than 80 mol % of n-octylthio group. The n-octylthio side group in CE−OTE acts in two ways. It is a plasticizer; the T_g of CE−OTE decreased as the content of the nonpolar n-octylthio group increased, up to about 60 mol %. It is a mesogen when the content of the n-octylthio group in CE−OTE is more than 60 mol %. As the n-octylthio concentration in CE−OTE increases, the first-order transition temperatures increase, while the T_g's may increase slightly once the liquid crystal phase is formed.

DSC thermograms of CE−OSEs containing less than about 60 mol % of n-octylsulfonyl group showed only glass transitions. However those of the other CE−OSEs and OSE showed a glass transition and an exotherm upon first cooling and a glass transition and an endotherm upon second heating. The transition tempera-

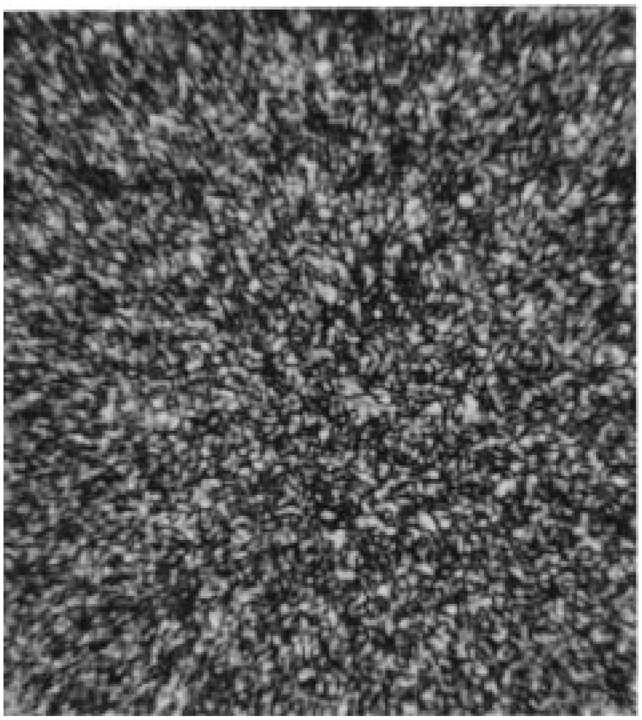


Figure 6. Granulated texture of OSE at 142 °C. Magnification: 125×.

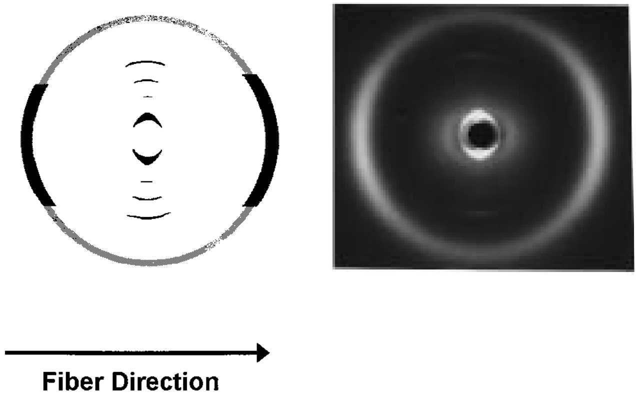


Figure 7. X-ray pattern of drawn fiber of OSE.

tures and enthalpy changes of sulfone homo- and copolymers, CE−OSEs and OSE, are listed in Table 3. Figure 4 shows the second heating thermograms of CE, CE−OSEs, and OSE. Double endothermic peaks for OSE, CE−OSE94, and CE−OSE82 at 139−150 °C indicate two very close phase transitions in this temperature range; however only a single phase change was observed using polarizing optical microscopy when heating or cooling through this range. A detailed discussion of the polarizing optical microscopy investigation will be given later in this paper

A phase diagram of CE−OSEs was made showing their transition temperatures as a function of composition, Figure 5. On the basis of this phase diagram, the functions of the *n*-octylsulfonyl side groups in CE−OSE can be rationalized as follows. It is well established that the T_g of a polymer can be lowered by attaching *n*-alkyl side chains, which act as plasticizers.[34] However, T_g can be increased by attaching polar side groups, where the polar side groups can undergo dipole−dipole interactions.[34] As the *n*-octylsulfonyl content in CE−OSE increases, the first T_g decreases slightly, then starts to increase and reaches a maximum (60 °C) when the *n*-octylsulfonyl content is 100 mol %. A small amount of the *n*-octylsulfonyl groups acts as a plasticizer. The T_g of CE−OSE13 is 6 °C lower than that of CE; this was confirmed by several DSC scans. This indicates that, when the *n*-octylsulfonyl content in CE−OSE is low, the dipole−dipole interactions between the sulfone groups are shielded and do not increase the T_g; the plasticizer effect of the *n*-octyl side group is dominant. However at 34 mol % of *n*-octylsulfonyl and above, dipole−dipole interactions increased the T_g. When the content of *n*-octylsulfonyl groups rose above 60 mol %, endotherms were observed in the DSC heating scan; *n*-octylsulfonyl groups start to organize. CE−OSEs with more than 60 mol % of *n*-octylsulfonyl group were liquid crystalline.

The liquid crystalline behaviors of the CE−OSEs are discussed below. The supercoolings for the first-order transitions were 8, 7, 5,6, and 6 °C for OSE, CE−OSE94, CE−OSE82, CE−OSE75, and CE−OSE68 respectively, and the enthalpy changes were low. The low supercooling and low enthalpy change are strong indications of

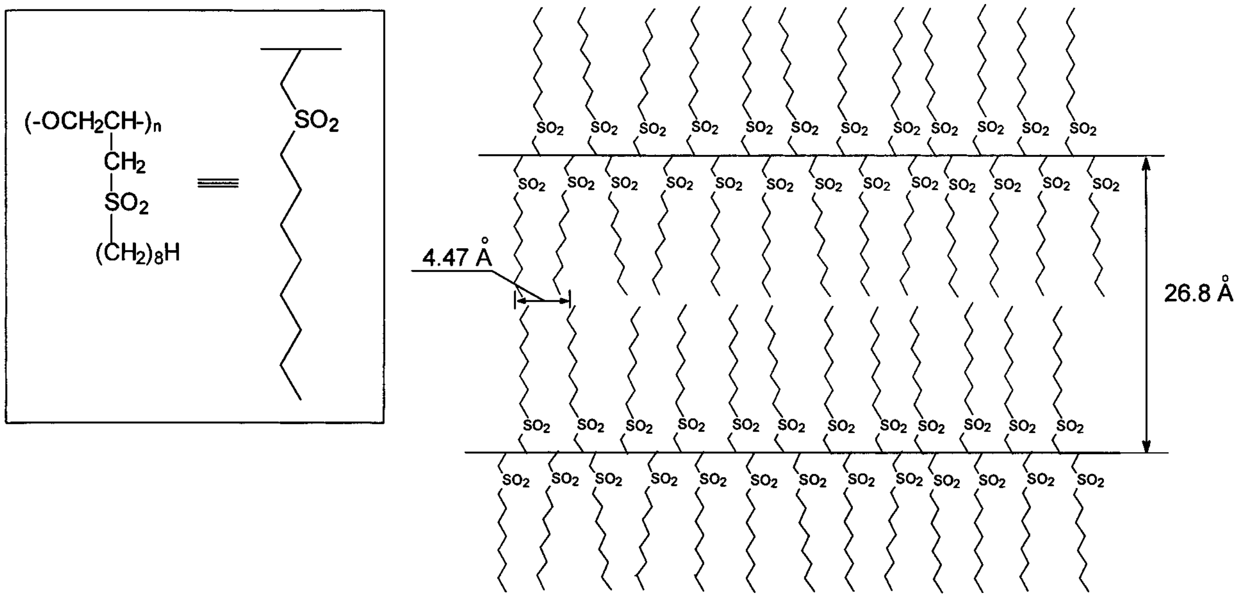


Figure 8. Schematic diagram of smectic A phase forming bilayer structures for OSE.

Table 4. X-ray Data for CE−OSEs and OSE

polymer	*d* spacings of equatorial reflections (Å)	*d* spacing of meridional reflection (Å)
OSE	26.8, 13.2, 8.89, 6.68	4.47
CE−OSE94	26.9, 13.6, 8.96, 6.78	4.49
CE−OSE82	26.8, 13.1, 8.82, 6.68	4.52
CE−OSE75	25.1, 12.5, 8.37, 6.34	4.50
CE−OSE68	24.7, 12.3, 8.19, 6.30	4.47

liquid crystallinity.[35] Liquid crystallinity was confirmed by a polarizing optical microscopy investigation. Figure 6 shows the granulated texture of OSE, obtained at 142 °C after it had been cooled from 200 °C at a cooling rate of 5 °C/min. The texture disappeared when the sample was heated to 150 °C but reappeared upon cooling. The sample was annealed at 142, 140 135, 130, 120, and 100 °C for 12, 24 or 48 h; no structural change was observed, but the texture became more birefringent. The liquid crystalline copolymers showed similar textures, but at lower temperatures, as expected from the endotherm peaks in the DSC's. It is well-known that the high viscosity of polymer melts can prevent the formation of normal LC texture.[36] This is especially true for smectic polymers; frequently, a granulated texture of birefringent domains is seen. On the basis of the optical microscopy and the size of ΔH, it is probable that the LC phases of OSE and CE−OSEs are smectic.

The above hypothesis was tested using X-ray analysis. Figure 7 shows a flat plate photographic X-ray pattern obtained from the drawn fiber of OSE. The draw direction is vertical. The *d* spacings corresponding to the reflections in the X-ray patterns of the polymer are listed in Table 4. The X-ray pattern of OSE shows four equatorial reflections and an outer ring. The equatorial reflection *d* spacings (26.8:13.2:8.89:6.68 Å) correspond to the 100, 200, 300, and 400 indices of periodic layer spacings. The 26.8 Å value is approximately double the size of the calculated extended length of the side chain. The intensity of the outer ring (4.47 Å, the intermolecular distance between the hydrocarbon chains) is higher in the meridional direction than in the equatorial direction, implying that this reflection could come from the packing of the *n*-octyl side chains in the layers. Since the backbones are parallel to the draw direction, the *n*-octyl side chains must be packed perpendicular to the main chains when they form the ordered phase. The liquid crystalline phase of OSE is probably smectic A, which forms a bilayer structure as shown in Figure 8. The X-ray patterns of the liquid crystalline copolymers were almost the same as that of OSE (Table 4). The outer ring *d* spacings of the copolymers were identical with those of the homopolymer within experimental error. However, the equatorial *d* spacings of the copolymers decreased as the content of *n*-octylsulfonyl side group decreased. This result indicates that liquid crystalline phases of the copolymers are the same as those of the homopolymer, but the periodic layer distances change according to the side chain concentration.

Summary and Conclusions

High molecular weight poly(oxyethylene) homo- and copolymers with *n*-octylthiomethyl side groups or *n*-octylsulfonylmethyl side groups have been successfully synthesized. CE−OTEs and OTE were synthesized by the reaction of the CE chloromethyl groups with sodium *n*-octanethiolate. CE−OSEs and OSE were synthesized by the oxidation of CE−OTEs and OTE using *m*-CPBA.

The flexible, nonpolar *n*-octylthiomethyl side groups lower the polymer T_g. When the *n*-octylthiomethyl side group content was more than 60 mol %, an ordered phase formed. This was probably a liquid crystal as shown by the very low degree of supercooling in the DSC heating and cooling scans.

The flexible but polar *n*-octylsulfonylmethyl side groups lowered the T_g of the copolymer at very low concentration (T_g's of CE and CE−OSE13 are −22 and −28 °C respectively), but increased the T_g at higher concentrations. When the *n*-octylsulfonylmethyl side group content was more than 60 mol, a liquid crystalline phase formed, Table 3 and Figure 4. Transitions to a birefringent phase with low degree of supercooling were observed by DSC and optical microscopy. The X-ray patterns were typical for smectic A. Sharp lamellar spacings were observed combined with a broad peak meridional for this system related to side-by-side chain packing, Table 4 and Figure 7.

The relatively long flexible side chains attached to the polymer help to form an ordered structure, if they are above a certain concentration. The minimum concentrations to form ordered structures for *n*-octylthio and *n*-octylsulfonyl side groups seem to be almost the same although their polarities are quite different; CE−OTE52 and CE−OSE52 were both amorphous while CE−OTE68 and CE−OSE68 were both ordered. The thioether group is not very polar (1.50 D), while the sulfonyl group is very polar (4.49 D). Probably the sulfone groups order themselves allowing the *n*-octylsulfonyl side groups to form an ordered phase at much higher temperatures than is possible for the *n*-octylthio side groups.

A new series of liquid crystalline polymers with alkyl side chains has been made and studied. As the starting polymer, CE, is amorphous, the ordered phase arises from side chain packing, analogous to case 2 for the liquid crystalline polymers discussed in the Introduction.

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