Miscibility Behaviors of (Alkylsulfonyl)methyl-Substituted Poly(oxyalkylene) Blends

Jong-Chan Lee,[†] Morton H. Litt,* and Charles E. Rogers

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106

Received December 12, 1997; Revised Manuscript Received March 10, 1998

ABSTRACT: Miscibility behaviors of poly[oxy(alkylsulfonylmethyl)ethylene]s, poly[oxy(alkylsulfonylmethyl)ethylene-*co*-oxyethylene]s, and poly[oxy-2,2-bis(alkylsulfonylmethyl)trimethylene]s were studied. A group contribution parameter for the aliphatic sulfone group was developed and used to calculate solubility parameters for both oxyethylene series. Though there is no specific interaction between these polymers, they have similar backbones and the same side chains, and many pairs were found to be miscible. The poly(oxytrimethylene)s were miscible with certain oxyethylene homo- and copolymers even when their solubility parameters were very different ($\Delta\delta \leq 1.5$ (cal/cm^3)$^{1/2}$). However, no polymer was miscible with another containing the same backbone even when their solubility parameters were very close. The miscibility range was used to determine solubility parameters for two members of the oxytrimethylene series and a group contribution parameter for the *gem*-disubstituted disulfone group. When the unoccupied volumes of two miscible polymers are very different, volume contraction and negative heat of mixing can be expected; this decreases the free energy of mixing and promotes the miscibility of polymers with relatively large solubility parameter differences. The permeability coefficient and the chemical structure of poly[oxy-2,2-bis(methylsulfonylmethyl)trimethylene] imply that its unoccupied volume (probably excluded volume due to poor packing of the bulky substituent) is larger than those of the other backbone polymers. Miscible blends of oxytrimethylene polymers with oxyethylene homo- or copolymers showed volume contraction upon mixing. This implies that the monosubstituted oxyethylene polymers can pack into the excluded volume of the 3,3-disubstituted oxytrimethylene polymers.

Introduction

Efforts to identify new miscible polymer systems have been pursued for more than 40 years in order to develop new polymer blend materials with desirable properties. To form a miscible blend, the free energy of mixing (ΔG_m) of polymers (eq 1) should be negative. For high

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

molecular weight polymers, the entropy of mixing (ΔS_m) is negligibly small and the sign of ΔG_m is usually determined almost completely by the enthalpy of mixing (ΔH_m).[1,2] A negative ΔH_m is expected in polymer mixtures where specific interactions occur between the two polymers. Miscible polymer pairs can be found[1−4] when hydrogen bonding, ion−dipole forces, acid−base interaction, or transition metal complexation causes a negative heat of mixing.

Coleman and cowokers[3] rationalized the phase behavior and other thermodynamic properties of binary mixtures of polymers by expressing the free energy of mixing as

$$\Delta G_m/RT = (\phi_1/N_1)\ln\phi_1 + (\phi_2/N_2)\ln\phi_2 + \phi_1\phi_2\chi + (\Delta G_H/RT) \quad (2)$$

where ϕ_1 and ϕ_2 and N_1 and N_2 are respectively the volume fractions and degrees of polymerization of polymers 1 and 2; χ is the segmental interaction parameter representing physical forces only, while the ΔG_H term reflects free energy changes corresponding to specific interactions.[3] χ can be related to the Hildebrand solubility parameters of the polymers

$$\chi = \frac{V_r}{RT}[\delta_1 - \delta_2]^2 \quad (3)$$

where V_r is a reference molar volume and δ_1 and δ_2 are the solubility parameters of polymers 1 and 2. In eq 2, the $\phi_1\phi_2\chi$ term is zero or positive, the $\Delta G_H/RT$ term is negative when there is specific interaction, and the entropic term ($(\phi_1/N_1)\ln\phi_1 + (\phi_2/N_2)\ln\phi_2$) is negligible. Miscibility can be determined from the strength of the specific interactions and the solubility parameter difference between the two polymers. Coleman and coworkers discussed critical solubility parameter differences ($\Delta\delta_{crit} = |\delta_1 - \delta_2|$), the maximum solubility parameter differences between two miscible polymers, as a function of the different kinds of interactions. Table 1 shows their values.[3]

It has been known that miscible polymer blend systems with specific interactions, such as hydrogen bonding, have negative heats of mixing and also negative volumes of mixing.[5−9] However, some miscible polymer blends without any specific interactions show negative heats of mixing and negative volumes of mixing, for example poly(phenylene oxide)/polystyrene (PPO/PS)[7,10,11] and tetramethylbisphenol A polycarbonate/polystyrene (TMPC/PS).[12,13] Though there have been many studies on these blends,[14−18] no clear explanation for their miscibilities has emerged. Recently the free volumes and miscibility relationships of PS, polycarbonate (PC), and TMPC were investigated by Jean et al.[19,20] using positron annihilation lifetime spectroscopy. They mentioned that in the PS-TMPC systems, the larger mean free volume radius (R_f) in TMPC (PS, $R_f = 2.94 \pm 0.09$; PC, $R_f = 2.98 \pm 0.08$; TMPC, $R_f =$

---

* To whom all correspondence should be addressed.

[†] Permanent address: Department of Chemical Technology, Seoul National University, Seoul, Korea 151-742.

S0024-9297(97)01813-5 CCC: $15.00

Table 1. Summary of the Upper Limit of the Critical Values of Solubility Parameter Differences ($\Delta\delta_{\mathrm{Crit}}$)[a]

specific interactions involved	polymer blend examples	$\Delta\delta_{\mathrm{crit}}$ (cal. cm^{-3})$^{1/2}$
dispersive forces only	polyisoprene–poly(vinyl ethylene)	<0.1
dipole–dipole interactions	poly(methyl methacrylate)–poly(ethylene oxide)	0.1–0.5
weak hydrogen bonds	poly(vinyl chloride)–polycaprolactone	0.5–1.0
moderate hydrogen bonds	poly(vinyl phenol)–poly(vinyl acetate)	1.0–2.5
strong hydrogen bonds	poly(vinyl phenol)–poly(vinyl methyl ether)	2.5–3.0

[a] Taken from ref 3.

3.20 ± 0.08 Å) could accommodate the PS polymer chains in the space available; this generated favorable interactions between PS and TMPC. On the other hand, PC does not have sufficient free volume to enable PS to pack efficiently to form a miscible blend.[19] Therefore, a large free volume difference between the polymer pairs (PS and TMPC) gave densification upon mixing and stronger interaction (negative ΔH_{m}). We think that the effect is better understood if the large free volume is considered as excluded volume. The polymer with bulky groups packs very inefficiently, leaving large holes unoccupied. A polymer with a smaller cross section can then fill this volume.

Patterson[21–24] and Sanchez/Lancombe[25–28] have discussed mixing of polymers with solvents of similar composition (hydrocarbons with hydrocarbons). In these systems, there was a negative volume of mixing because of greater interaction between the components. This occurs even when the combinatorial ΔH_{m} is positive, leading to an overall negative ΔH_{m}.[24]

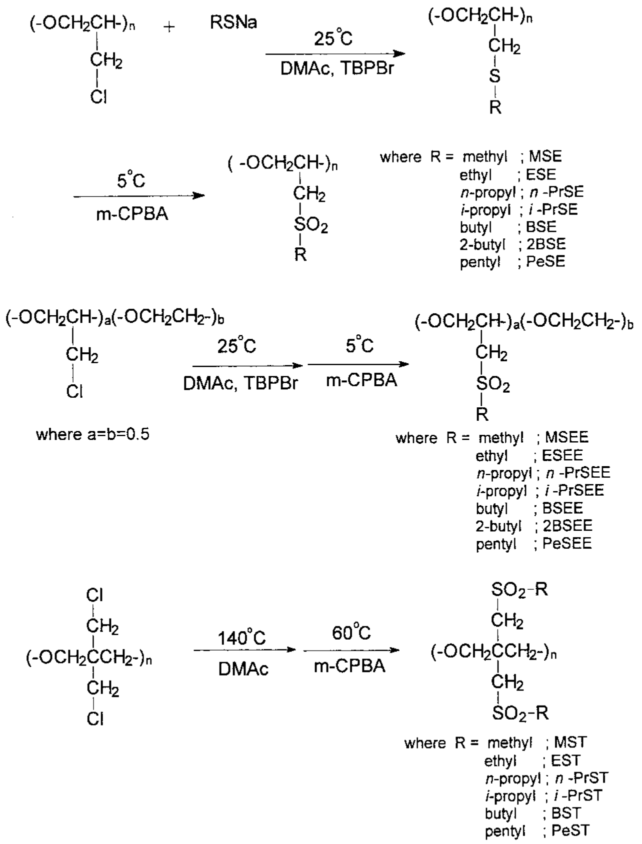
Sanchez and Lancombe state[27] that "addition of a small amount of polymer to solvent causes a density contraction", meaning volume loss. However, these authors were discussing polymer/solvent interactions where the solvent has a large free volume. When polymer blends are considered, the entropy of mixing of polymers is usually very small and is neglected. The major driving force is a negative ΔH_{m}. Polymer blends with donor/acceptor interactions can be miscible over a relatively wide range of $\delta_1 - \delta_2$. However, this does not apply to the systems quoted above where miscibility has been ascribed to the increased interactions generated by the better intermolecular packing possible for the polymers when one may have a large excluded volume.

Recently, our group synthesized a series of (alkylsulfonylmethyl)-substituted poly(oxyalkylene)s.[29] Here there was no possibility of specific interactions since all polymers had ether backbones and sulfonyl groups in the side chains. Members of one series of polymers were found to be miscible with appropriate members of the other two series, despite calculated large differences (in some cases) in solubility parameters. Miscibility was accompanied by a loss in volume on mixing. The only possible driving force for miscibility in these systems seemed to be volume contraction on mixing, which internal evidence showed was probably because one series seemed to have a large excluded, or free, volume that could be filled by the other polymer. We felt that the unusually large miscibility window, considering the lack of any possible donor/acceptor interactions, warranted a complete study of the system.

Experimental Section

Scheme 1 shows the synthetic routes and designations of (alkylsulfonyl)methyl-substituted poly(oxyalkylene)s; poly[oxy-(***a***lkyl***s***ulfonylmethyl)***e***thylene] (ASE) (MSE, ESE, *i*-PrSE, *n*-PrSE, BSE, PeSE), poly[oxy(***a***lkyl***s***ulfonylmethyl)***e***thylene-*co*-oxy***e***thylene) (ASEE) (MSEE, ESEE, *i*-PrSEE, *n*-PrSEE, BSEE, PeSEE), and poly[oxy-2,2-bis(***a***lkyl***s***ulfonylmethyl)-***t***rimethylene] (AST) (MST, EST, *i*-PrST, *n*-PrST, BST, PeST). Detailed synthetic methods were described in the previous paper.[29] Table 2 shows the properties of the polymers used in this study. Intrinsic viscosities of polymer solutions were measured at 30 °C using a Cannon-Ubbelohde viscometer.[30] THF and formic acid were used as solvents. Oxygen permeability measurements were conducted using the ASTM D1434 volumetric method. The densities were measured by a neutral buoyancy method using a pycnometer.[31] The standard deviation was about 0.5%. The detailed experimental procedures and film preparation methods for these measurements were described in the previous paper.[31]

Scheme 1



Polymer blends were prepared by precipitating a 3 wt % solution containing a certain weight percent of each component into methanol. Polymer blends containing MSE, MSEE, MST, ESE, ESEE, and EST were prepared from formic acid solutions; the others were prepared from chloroform solutions. The miscibility of a blend was determined by observing its glass transition temperature behavior using differential scanning calorimetry (Du Pont 912 DSC). The samples were annealed at 200 °C for 10 min in the DSC apparatus and then quenched to a temperature below that of the T_{g} of lower component. The T_{g}'s of blends and polymers were obtained from the maximum in the plot of $\mathrm{d}C_p/\mathrm{d}t$ vs temperature obtained at a heating rate of 20 °C/min, where C_p is the heat capacity. The criterion of miscibility was taken as the appearance of a single distinct T_{g} for the blend. Blends with two distinct T_{g}'s were classified as immiscible. There were several blends which showed

Table 2. Physical Properties and Calculated Solubility Parameter (δ) of (Alkylsulfonyl)methyl-Substituted Poly(oxyalkylene)s Used in This Study

polymer	T_g (°C)	$[\eta]$ (dL/g)	density (g/cm^3)	permeability coefficient^c × 10^{13} (cm^3(STP)·cm/cm^2·s·Pa)	δ^d [(cal/cm^3)$^{1/2}$]
MSE	85	1.63^a	1.442	0.0014	15.0^e
ESE	57	1.31^a	1.361	0.0088	13.9^e
i-PrSE	64	0.83^a	1.292	0.12	12.7^e
n-PrSE	43	1.17^a	1.291	0.22	13.1^e
BSE	37	0.90^a	1.265	0.40	12.7^e
2-BSE	51	1.24^a	1.269		12.6^e
PeSE	38	1.02^b	1.249	0.42	12.5^e
MSEE	52	1.68^a	1.340	0.0036	13.2^e
ESEE	27	1.77^a	1.325		13.0^e
i-PrSEE	34	0.61^a	1.310		12.6^e
n-PrSEE	24	1.44^a	1.312		12.8^e
BSEE	19	1.22^b	1.293		12.6^e
2-BSEE	25	1.44^b	1.302		12.5^e
PeSEE	13	1.28^b	1.270		12.4^e
MST	126	0.84^a	1.480	0.013	
EST	84	1.08^a	1.391		
i-PrST	91	1.23^a	1.314		
n-PrST	71	1.43^a	1.305		
BST	66	1.24^b	1.281		
PeST	56	1.55^b	1.260		

[a] Formic acid at 30 °C. [b] THF at 30 °C. [c] Permeability coefficient of oxygen at 30 °C.[27] [d] Solubility parameter. [e] Calculated by group contribution method using molar attraction factors provided by Hoy.

ambiguous T_g's. For example, the DSC thermogram of *i*-PrST/PeSEE blend showed a T_g at 14 °C and a very broad transition from 24 to 101 °C. Similar results were found for *n*-PrST/ESEE and *i*-PrST/PeSEE blends. These cases were classified as partially miscible. For a blend of polymers with close T_g values ($\Delta T_g < 15$ °C), the physical aging technique was used to determine the miscibility.[32] The samples were kept at 200 °C for 10 min in the DSC and then cooled by quenching, followed by annealing at a temperature $T < T_g$ overnight. Subsequently, a DSC scan was taken from below T_g to 200 °C. A single enthalpy relaxation peak was indicative of a miscible blend, while double enthalpy relaxation peaks indicated an immiscible blend.

Solubility parameters of the polymers were calculated by the group contribution method,[33] using group contributions to molar attraction factors, *F*, provided by Hoy,[34] eq 4. The molar

$$\delta = \sum F/V \tag{4}$$

volumes, *V*, of the monomeric units of the polymers were calculated from the measured densities and the monomeric molecular weights. The molar attraction factors of all the groups except sulfone are available from Hoy's tables.[34] That for the sulfone group was calculated from the densities and solubility parameters of sulfolane and methyl sulfolane,[35−37] the only organic aliphatic liquids containing a sulfone group whose densities and solubility parameters were available. The calculated *F*'s were 776 and 800 (cal·cm^3)$^{1/2}$·mol^{-1}, respectively. The solubility parameters of the polymers were calculated using the average value of F, 788 (cal·cm^3)$^{1/2}$·mol^{-1}. They are listed in Table 2. However, solubility parameters of the ASTs could not be calculated directly. Since two bulky, polar sulfone groups are attached to the same carbon in the backbone, *F* is different from that for the monosubstituted sulfone group. Normally *F* values for disubstituted polar groups are 5−20% smaller than the sum of *F* values for two similar monosubstituted polar groups.[34] Solubility parameters of ASTs were obtained using an indirect method that is explained in the Results and Discussion section. Other researchers,[33] such as Small, Van Krevelen, and Fedors also gave molar attraction factors or cohesive energy factors for the solubility parameter calculation. Solubility parameters of the (alkylsulfonyl)methyl-substituted poly(oxyalkylene)s and $\Delta\delta_{crit}$'s of their blends were also calculated using the Small, Van Krevelen, and Fedors parameters. Although these methods gave somewhat different solubility parameters and $\Delta\delta_{crit}$'s from the values obtained using Hoy's parameters, their trends were identical with the results in this paper. The reason we picked Hoy's method is that it gave the best correlation for all three series of polymers. The solubility parameter approach for predicting polymer miscibility has been controversial because the solubility parameter of a polymer obtained by calculation or measurements could differ widely.[3] In this study we use it just for the comparison. Therefore, while the absolute values could differ from those found by our calculations, the trends should be correct.

Table 3. T_g's, Densities, and Permeability Coefficients of Blends

blend (weight ratio)	density (g/cm^3)	permeability coefficient × 10^{13} [cm^3(STP)·cm/cm^2·s·Pa]	T_g (°C)
MSE/MST=1/9	1.482		120
MSE/MST = 3/7	1.480	0.0015	113
MSE/MST = 5/5	1.473	0.0007	103
MSE/MST = 7/3	1.458	0.0009	96
MSE/MST = 9/1	1.446		90
MSEE/MST = 1/9	1.479		117
MSEE/MST = 3/7	1.473	0.0013	105
MSEE/MST = 5/5	1.458	0.0008	92
MSEE/MST = 7/3	1.426	0.0009	70
MSEE/MST = 9/1	1.375		57
MSE/MSEE = 1/9			52, 86
MSE/MSEE = 3/7			52, 89
MSE/MSEE = 5/5			53, 88
MSE/MSEE = 7/3			52, 89
MSE/MSEE = 9/1			54, 89

Results and Discussion

In the previous paper,[31] the barrier properties of MSE/MST and MSEE/MST blends were studied. In this paper, the miscibility behavior of ASE, ASEE, and AST is studied and correlated with solubility parameters, densities, permeabilities, and free volumes. The miscibilities of MSE/MST, MSEE/MST, and MSE/MSEE blends will be discussed first.

Table 3 shows T_g's, densities, and permeability coefficients of MSE, MST, and MSEE and their blends. MSE/MST and MSEE/MST blends show single T_g's over the whole composition range, which indicates that these blends are miscible. Figures 1 and 2, the DSC curves of MSE/MST and MSEE/MST blends, show typical DSC thermograms for miscible blends. However two T_g's for the MSE/MSEE blends were found, Figure 3, which indicates that these blends are immiscible.

As the solubility parameter of MST could not be calculated, the solubility parameter differences between MSE and MST and between MSEE and MST cannot be obtained directly. However critical solubility parameter differences ($\Delta\delta_{crit}$, maximum solubility parameter difference between the two miscible polymers in blends)[3] of these blends can be estimated. The minimum $\Delta\delta_{crit}$ occurs if the solubility parameter of MST is midway between those of MSE and MSEE. So the $\Delta\delta_{crit}$ values for these blends are larger than 0.85 (cal/cm^3)$^{1/2}$. According to Coleman et al. (Table 1),[3] such values correspond to strongly interacting blends. However, since the backbone and side chains of each polymer contain the same structures, they cannot show donor−acceptor behavior.

The permeability and density data for these miscible blends were also unusual. As shown in Figures 4 and 5, the permeability coefficient vs blend composition

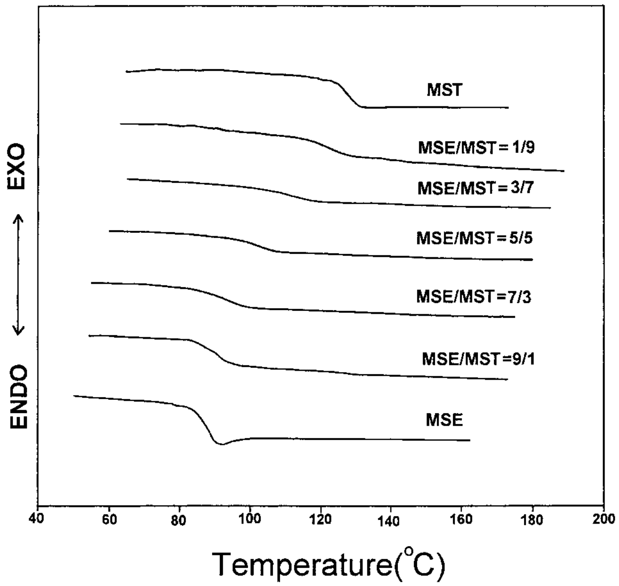


Figure 1. DSC thermograms of MSE/MST blends.

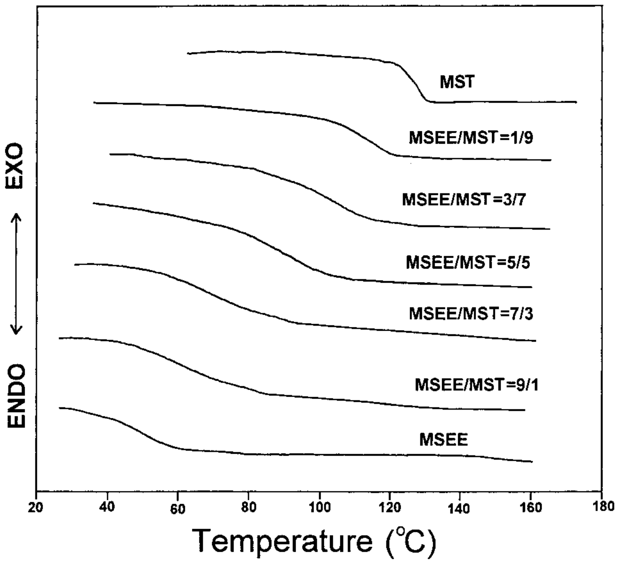


Figure 2. DSC thermogram of MSEE/MST blends.

curves show negative deviations from the semilogarithmic mixing rule, and the density vs blend composition curves indicate densification upon mixing. Normally a negative deviation of permeability and densification upon mixing can be observed when there are strong specific interactions, such as hydrogen bonding between two polymers,[5,38] or when there is a large unoccupied volume (or excluded volume) difference as discussed in the Introduction.[7,19,39] As MSE, MST, and MSEE all have ether backbones and methyl sulfone side groups, strong specific interactions are not possible. However, unoccupied volume differences can be expected, based on analysis of their structures and permeability coefficients.

The two methyl sulfone groups in MST are attached to a single carbon in the backbone, generating a very bulky, rigid substituent. This steric hindrance can generate a relatively large unoccupied, or excluded, volume at T_g. Since MSE and MSEE contain only one methyl sulfone group attached to backbone carbon, there is little, if any, steric hindrance to the polymer backbone. The unoccupied volumes of the polymers can be related to their permeability coefficients as discussed in the Introduction. That of MST is 10 times that of MSE and 3 times that of MSEE although the MSEE T_g is only 52 °C and the permeability measurements were made at 30 °C. This implies that MST has a larger unoccupied volume than either MSE or MSEE. The densification and the negative deviation of permeability seem to result from the packing of the flexible polymer into the larger unoccupied, or excluded, volume of the MST. The unoccupied volume difference is the driving force for miscibility.

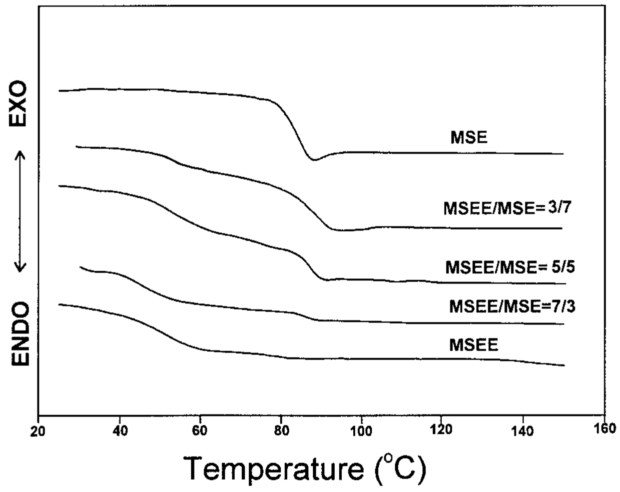


Figure 3. DSC thermogram of MSE/MSEE blends.

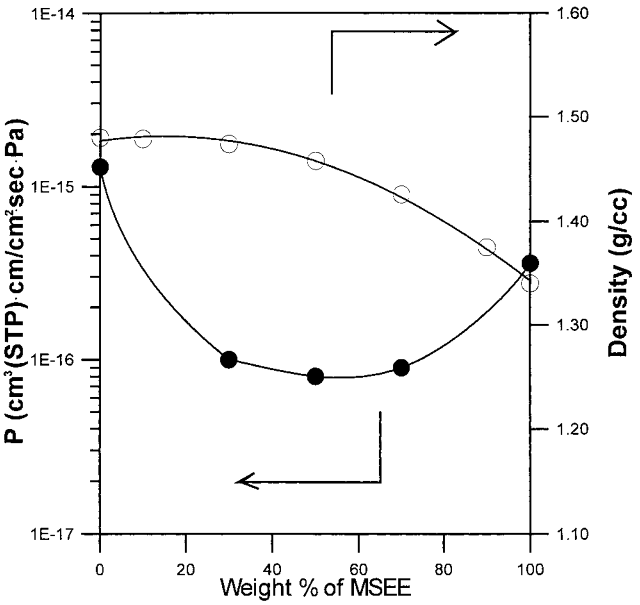


Figure 4. Oxygen permeability coefficients (●) and densities (○) of MSEE/MST blends.

Even though there are no permeability data for the polymers with longer alkyl side chains, the rationale of structure and unoccupied volume relationships used for MSE, MSEE, and MST implies that an (alkylsulfonyl)-substituted oxytrimethylene polymer (AST) should have a larger free volume than the analogous (alkylsulfonyl)-substituted oxyethylene homo- and copolymers (ASE and ASEE). Therefore, AST could be miscible with ASE and ASEE due to the unoccupied volume differences. Since little, if any, unoccupied volume differences are expected for AST pairs or ASE/ASEE pairs, there should little or no volume shrinkage in their blends and

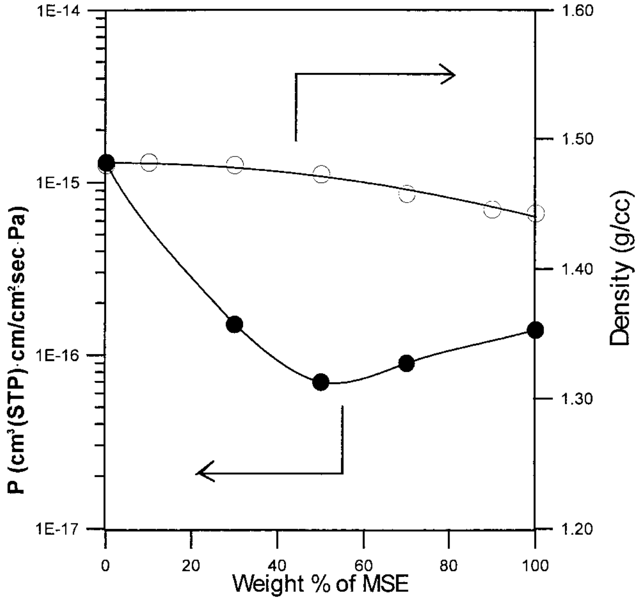


Figure 5. Oxygen permeability coefficients (●) and densities (○) of MSE/MST blends.

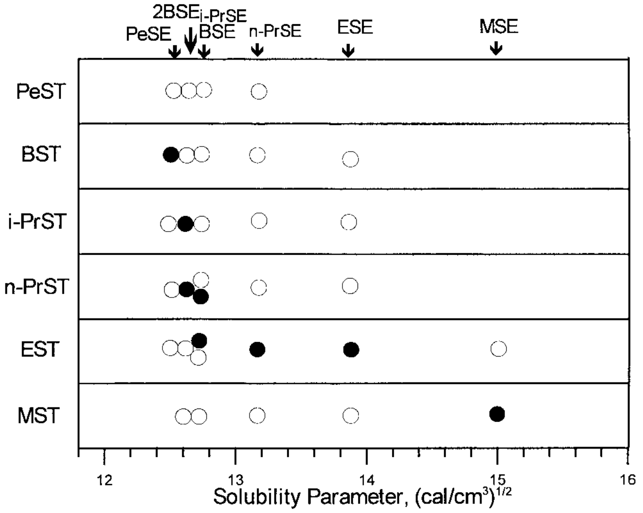


Figure 6. Miscibility diagram of AST/ASE blends: (●) miscible; (○) immiscible.

consequently no miscibility. Actually none of AST pairs and ASE/ASEE pairs were found to be miscible, even though in some cases the solubility parameters were very close. For example *i*-PrSE ($\delta = 12.7$ (cal/cm^3)$^{1/2}$) is not miscible with *n*-PrSEE, BSE, BSEE, or 2-BSE whose solubility parameters are 12.8, 12.7, 12.6, and 12.6 (cal/cm^3)$^{1/2}$, respectively. Similarly 2-BSE ($\delta = 12.5$ (cal/cm^3)$^{1/2}$) is not miscible with BSE, *i*-PrSEE, BSEE, PeSE, 2-BSEE, or PeSEE whose solubility parameters are 12.7, 12.6, 12.6, 12.5, 12.5, and 12.4 (cal/cm^3)$^{1/2}$ respectively. ASTs, on the other hand, were miscible with some ASEs or ASEEs. Table 4 summarizes the data for miscible and immiscible blends of ASTs.

Schematic diagrams for AST/ASE and AST/ASEE blends based in Table 4 are shown in Figures 6 and 7, respectively. It shows that a given AST is miscible with ASEs or ASEEs within a certain range of solubility parameters. The upper or lower limit for solubility parameters for miscible blends can be considered as the filled triangles (partially miscible) or the border between filled circles (miscible) and open circles (immiscible). For some cases, only the upper or lower solubility parameter limit is available. For example, EST is miscible with the ASEE series when the solubility parameter is 12.6 (cal/cm^3)$^{1/2}$ or higher, and BST is miscible with the

Table 4. Miscibility, Calculated Solubility Parameter, and Critical Solubility Parameter Difference ($\Delta\delta_{\text{crit}}$) of Poly[oxy-2,2-bis(alkylsulfonylmethyl)Trimethylene]s (ASTs)

	polymer (miscibility (cal/cm^3)$^{1/2}$)			estimated solubility param (cal/cm^3)$^{1/2}$	$\Delta\delta_{\text{crit}}$[a] (cal/cm^3)$^{1/2}$	$\Delta\delta_{\text{crit}}$[b] (cal/cm^3)$^{1/2}$
	miscible	partially miscible	immiscible			
MST	MSE (15.0) MSEE (13.2)		ESE (13.9) ESEE (13.0)	14.6	>0.4	>1.4
EST	ESE (13.9) *n*-PrSE (13.1) *i*-PrSE (12.7) MSEE (13.2) ESEE (13.0) *n*-PrSEE (12.8) *i*-PrSEE (12.6)		MSE (15.0) BSE (12.7) 2BSE (12.6) PeSE (12.5) BSEE (12.6) 2BSEE (12.5) PeSEE (12.4)	13.6	~0.9	~1.0
n-PrST	BSE (12.7) 2BSE (12.6) *n*-PrSEE (12.8) *i*-PrSEE (12.6) BSEE (12.6) 2BSEE (12.5) PeSEE (12.4)	ESEE (13.0)	MSE (15.0) ESE (13.9) n-PrSE (13.1) *i*-PrSE (12.7) PeSE (12.5) MSEE (13.2)	12.7	<0.1	~0.3
i-PrST	2BSE (12.6) *i*-PrSEE (12.6) BSEE (12.6) 2BSEE (12.5)	*n*-PrSEE(12.8) PeSEE (12.4)	ESE (13.9) *n*-PrSE (13.1) *i*-PrSE (12.7) BSE (12.7) PeSE (12.5) ESEE (13.0)	12.6	<0.1	~0.2
BST	PeSE (12.5) BSEE (12.6) PeSEE (12.4)		BSE (12.7) 2BSE (12.6) i-PrSEE (12.6)	12.4	<0.1	~0.1
PeST			PeSE (12.5) PeSEE (12.4)	12.2		

[a] Critical solubility parameter differences for ASE series. [b] Critical solubility parameter differences for ASEE series.

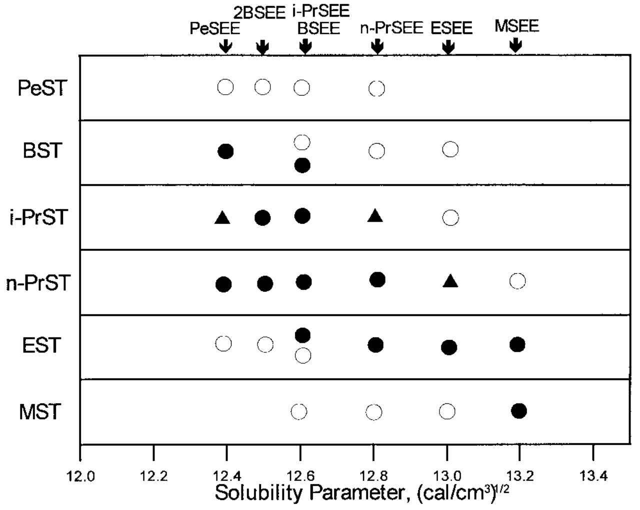
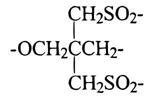


Figure 7. Miscibility diagram of AST/ASEE blends: (●) miscible; partially miscible (▲); and (○) immiscible.

ASEE series when the solubility parameter is lower than 12.8 (cal/cm^3)$^{1/2}$. For some cases, both upper and lower solubility parameter limits are available. EST is miscible with ASEs with solubility parameters of 12.7, 13.1, and 13.9 (cal/cm^3)$^{1/2}$ and is immiscible with ASEs with solubility parameters of 12.5, 12.7, and 15.0 (cal/cm^3)$^{1/2}$. So 12.7 (cal/cm^3)$^{1/2}$ can be considered as the lower limit. The upper limit is not well defined; it lies between 13.9 and 15.0 (cal/cm^3)$^{1/2}$. The upper and lower limits of *n*-PrST and *i*-PrST are rather clear. *n*-PrST is miscible with 2-BSE (12.6 (cal/cm^3)$^{1/2}$) and BSE (12.7 (cal/cm^3)$^{1/2}$), while it is not miscible with PeSE (12.5 (cal/cm^3)$^{1/2}$) and *i*-PrSE(12.7 (cal/cm^3)$^{1/2}$). The upper limit, 12.7 (cal/cm^3)$^{1/2}$, and lower limit, about 12.6 (cal/cm^3)$^{1/2}$, can be easily induced. Using the same rationale, upper and lower limits for *i*-PrST can be obtained from both the ASE series and the ASEE series. The ASE series has upper and lower limits of about 12.7 and 12.5 (cal/cm^3)$^{1/2}$, respectively; those from the ASEE series are 12.8 and 12.4 (cal/cm^3)$^{1/2}$, respectively. (These numbers are obtained by rounding off the fractions to one decimal place.) Using these upper and lower limits, the solubility parameters of *n*-PrST and *i*-PrST can be estimated as the average of upper and lower limits as the solubility parameter of the corresponding polymer. Those of *n*-PrST and *i*-PrST are 12.7 and 12.6, respectively.



$$\begin{array}{l} \quad\quad\;\; CH_2SO_2\text{-} \\ \quad\quad\quad | \\ \text{-}OCH_2CCH_2\text{-} \\ \quad\quad\quad | \\ \quad\quad\;\; CH_2SO_2\text{-} \end{array}$$

The molar attraction factor of the above group was calculated from eq 4 using the solubility parameters of *n*-PrST and *i*-PrST. Values of 2081 and 2096 (cal·cm^3)$^{1/2}$·mol^{-1} were obtained. An average value of 2089 was used as the molar attraction factor for this group. Using this value, the solubility parameters of MST, EST, BST, and PeST were then calculated; they were 14.6, 13.6, 12.4, and 12.2 (cal/cm^3)$^{1/2}$, respectively. These calculated solubility parameters seem to be reasonable, judging by the solubility parameter ranges of the miscible and immiscible polymers.

The critical solubility parameter differences ($\Delta\delta_{crit}$) were calculated using the calculated solubility parameters of the ASTs. They gave valuable information about the miscibility behaviors of the blends as follows.

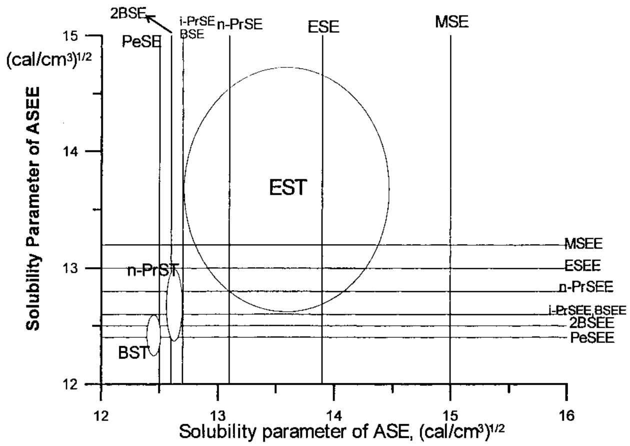


Figure 8. Miscibility windows for EST, *n*-PrST, and BST.

Two critical solubility parameter differences ($\Delta\delta_{crit}$) for the ASTs were calculated, one for the ASE series and the other for the ASEE series. For example the solubility parameter of EST is 13.6 (cal/cm^3)$^{1/2}$ and the lower limit solubility parameter for the ASE series is 12.7 (cal/cm^3)$^{1/2}$. The difference of 0.9 (cal/cm^3)$^{1/2}$ can be regarded as the $\Delta\delta_{crit}$ of EST with the ASE series. From ASEE series, a lower limit is also available, 12.6 (cal/cm^3)$^{1/2}$, and $\Delta\delta$ is 1.0 (cal/cm^3)$^{1/2}$. It can be regarded as the $\Delta\delta_{crit}$. Using the same procedure, $\Delta\delta_{crit}$'s of MST, *n*-PrST, i-PrST, BST, and PeST were calculated and are listed in Table 4. Two trends were found. The first is that the longer the side chain lengths of ASTs, the smaller $\Delta\delta_{crit}$. The second is that the $\Delta\delta_{crit}$'s from ASEE series are always higher than those from ASE series. Figure 8 shows these trends very well. The elliptical shapes of the miscibilty windows indicate that AST/ASEE blends show better miscibility than AST/ASE blends. The smaller size of ellipses for ASTs with longer side chains shows that the miscibility range decreases with increasing side chain length.

These trends can be rationalized from the unoccupied volume difference and consequent volume shrinkage upon mixing. MSE/MST and MSEE/MST blends show densification, and permeability/composition curves show negative deviations from the linear semilogarithmic mixing rule. A more positive deviation of density/composition curve and more negative deviation of permeability/composition curve (Figure 4) were observed for the MSEE/MST blends compared to those of the MSE/MST blends (Figure 5). This implies that the ability of MSEE to pack into the MST unoccupied, or excluded, volume is greater than that of MSE. Most likely, polymer chains with few side groups can fill the empty sites of MST more easily than those with more side groups. The polymer backbone of MSE has one methylsulfonylmethyl side group per repeat unit, while MSEE has a methylsulfonylmethyl side group per two repeat units on average. The same rationale should also hold generally for ASE/AST vs ASEE/AST blends. Better packing in the ASEE/AST blends can give greater volume contraction upon mixing, and this results in a more negative heat of mixing; polymers can be miscible with larger solubility parameter differences because the more negative heat of mixing offsets the more unfavorable contribution from the solubility parameter differences ($\phi_1\phi_2\chi$ where $\chi = V_R/RT\cdot(\delta_1 - \delta_2)^2$ in eqs 2 and 3) (see Introduction). The reason that $\Delta\delta_{crit}$ of AST with shorter side chains is larger that those of AST with longer side chains might be due to larger excluded

Table 5. Densities of 50/50 Blends

blend [polymer (density, g/cm^3)/ polymer (density, g/cm^3)]	blend density (g/cm^3)		density change (%)
	calculated[a]	experimental	
EST (1.391)/MSEE (1.340)	1.366	1.381	+1.1
EST (1.391)/ESEE (1.325)	1.258	1.272	+1.1
EST (1.391)/n-PrSE (1.292)	1.341	1.347	+0.4
EST (1.391)/n-PrSEE (1.310)	1.351	1.365	+1.0
n-PrST (1.314)/BSE (1.265)	1.290	1.298	+0.6
n-PrST (1.314)/2BSE (1.269)	1.292	1.312	+1.5
n-PrST (1.314)/*n*-PrSEE (1.310)	1.312	1.325	+1.0
n-PrST (1.314)/*i*-PrSEE (1.312)	1.313	1.336	+1.8
n-PrST (1.314)/BSEE (1.293)	1.314	1.323	+0.7
i-PrST (1.305)/*i*-PrSEE (1.312)	1.309	1.313	+0.3
i-PrST (1.305)/BSEE (1.293)	1.299	1.308	+0.7
i-PrST (1.305)/2BSE (1.269)	1.287	1.306	+1.5
i-PrST (1.305)/2BSEE (1.302)	1.304	1.327	+1.8
BST (1.298)/BSEE (1.293)	1.295	1.306	+0.8
BST (1.298)/PeSE (1.249)	1.274	1.297	+1.8

[a] Calculated using the linear additivity rule.

volume of, e.g., MST. Longer tails could partly fill the volume not available to the *gem*-disubstituted substituent, leaving less volume for the second polymer.

Melting enthalpy, measured from the heating DSC scan, for MST, *n*-PrST, PeST, and PENTON are 3.7, 12.4, 19.9, and 32.5 J/g, respectively. PENTON, which contains chloromethyl side chains, crystallizes very easily, while MST does not crystallize well, possibly due to the steric hindrance and diminished mobility of the main chain. As the AST side chain length increases, crystallinity increases because the steric effects are diminished and the backbone mobility increases; there may be only small unoccupied volume differences between the AST, ASE, and ASEE polymers with long side chains.

Table 5 shows the densities of the miscible blends; in every case, densification upon mixing is observed. However, no trends could be observed. The error for the density measurement is 0.5%, and the densification of the 50/50 blends ranged from 0.3 to 1.8%, so the trends might be buried in the noise. The volume shrinkage of MSEE/MST was quite large (densification for 50/50 blends was 3.4%, Table 3) and the densities were measured for several compositions. The densification for the MSE/MST blends was smaller but five compositions were measured. This made the results reliable. The densification difference between the two blend series was easily distinguished.

This is probably the first report that deals systematically with the polymer miscibility due to unoccupied volume differences and volume contraction. However, literature results also indicate that polymer pairs with large free (unoccupied or excluded) volume differences showed much more enhanced miscibility compared to those with smaller free volume differences. For example, TMPC/SAN, TMPC/(methyl methacrylate/styrene copolymer) (MMA−ST), and TMPC/(maleic anhydride/styrene copolymer) (MA−ST) blends were miscible with volume contraction within a certain range of copolymer compositions.[8,12,13,40] PC is known to be immiscible. Partial miscibility between PC and SAN with the very restricted range of 25−27 wt % AN has been reported.[41] Positron annihilation lifetime spectroscopy results by Jean et al.[19,20] showed that the mean unoccupied volume hole radius of TMPC is larger than that of PC. The larger size of unoccupied volume holes of TMPC compared to that of PC was explained as a substitution effect; the four side methyl groups attached to the phenyl groups in TMPC promote inefficient molecular packing compared to PC. If the compatibility of TMPC ($\delta = 9.5-10.5$ (cal/cm^3)$^{1/2}$) blend comes from polar−polar interactions or the closeness of the solubility parameters, PC ($\delta = 9.9-10.6$ (cal/cm^3)$^{1/2}$, slightly higher than that of TMPC) should be also miscible with these copolymers within a certain range of copolymer compositions.[3,33,42,43] (Solubility parameters of PAN, PS, PMMA, and PMA are 13.0−13.8, 9.1−9.3, 11.0, and 17.8 (cal/cm^3)$^{1/2}$ respectively,[3,33,42,44] and those of the copolymers can be calculated from the δs of the corresponding homopolymers using the linear additivity rule[3].) Similarly tetramethyl polyarylate and methyl-substituted polysulfone showed miscibility with SAN over a range of copolymer compositions.[45,46] However, polyarylate and polysulfone were not miscible with SANs.[3,47,48]

If we had the free volume data for all polymers from permeability measurement (indirect method), or positron annihilation spectroscopy or *PVT* data (direct method), the miscibility behavior as a function of the free volume differences could be more clearly understood. Still, using the limited data we have, the overall miscibility behaviors due to the free volume differences could be rationalized.

Conclusions

When the unoccupied, or excluded volumes of two miscible polymers are very different, volume contraction and negative heats of mixing in blends are expected when the solubility parameter difference between the two polymers is smaller than the critical solubility parameter difference. The volume contraction should not change the entropy of mixing since the flexible polymer is occupying an excluded volume that was part of the bulky polymer; the total volume available to the polymers remains almost unchanged even though the total interactions increase. On the basis of the structural factors and the permeability data, the unoccupied, or excluded, volumes of the AST series seem to be larger than those of the corresponding ASE or ASEE series. Many AST/ASEE and ASE/ASE polymer pairs were miscible with a large range of solubility parameter differences. However no AST was miscible with other ASTs and no ASE or ASEE was miscible with other ASEs or ASEEs even when $\Delta\delta \approx 0$, because these pairs seem to have similar unoccupied volumes or similar molecular flexibilities. ASTs were miscible with a broader range of ASEEs than with ASEs, This indicates polymer chains with fewer side groups (ASEE, one side group per two repeat units on average) can fill the empty sites (unoccupied or excluded volume) of AST more easily than those with more side groups (ASE, one side group per repeat unit). The critical solubility parameter differences of the above miscible blends ranged from >1.4 to 0.1 (cal/cm^3)$^{1/2}$ depending on the alkyl chain length. Such large $\Delta\delta$'s are generally found in blends with dipole−dipole interactions or weak to moderate hydrogen bonding. The energy liberated in a miscible blend due to volume contraction on mixing two polymers with very different unoccupied or excluded volumes can be as strong as that of hydrogen bonding.

Acknowledgment. Financial support of this work by Edison Polymer Innovation Corporation (EPIC) and Allied-Signal Corporation is gratefully acknowledged.

References and Notes

(1) Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: New York, 1978; Chapter 1.

(2) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer−Polymer Miscibility*; Academic Press: New York, 1979; Chapter 2.
(3) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing Co., Inc.: Lancaster, PA, 1991; pp 1−145.
(4) Utracki, L. A. *Polymer Alloys and Blends*; Hansen Publishers: New York, 1989; Chapter 1.
(5) Pedrosa, P.; Pomposo, J. A.; Calahorra, E.; Cortazar, M. *Macromolecules* **1994**, *27*, 102.
(6) Landry, C. J. T.; Coltrain, B. K.; Teegarden, D. M.; Ferrar, W. T. *Macromolecules* **1993**, *26*, 5543.
(7) Yee, A. F. *Polym. Eng. Sci*. **1977**, *17*, 213.
(8) Min, K. E.; Paul, D. R. *Macromolecules* **1987**, *20*, 2828.
(9) Lu, X.; Weiss, R. A. *Macromolecules* **1992**, *25*, 3242.
(10) Weeks, N. E.; Karasz, F. E.; MacKnight, W. J. *J. Appl. Phys.* **1977**, *48*, 4068.
(11) Kleiner, L. W.; Karasz, F. E.; MacKnight, W. J. *Polym. Eng. Sci*. **1979**, *19*, 519.
(12) Fernandes, A. C.; Barlow, J. W.; Paul, D. R. *Polymer* **1986**, *27*, 1788.
(13) Kim, C. K.; Paul, D. R. *Polymer* **1992**, *33*, 1630.
(14) Mitchell, G. R.; Windle, A. H. *J. Polym. Sci., Polym. Phys. Ed*. **1985**, *26*, 1967.
(15) Chin, Y. H.; Zhang, C.; Wang, P.; Inglefield, P. T.; Jones, A. A.; Kambour, R. P.; Bendler, J. T.; White, D. M. *Macromolecules* **1992**, *25*, 3031.
(16) Maconnachie, A.; Kambour, R. P.; White, D. M.; Rostami, S.; Walsh, D. J. *Macromolecules* **1984**, *17*, 2645.
(17) Kihara, H.; Seki, Y.; Hosoda, S. *Polym. Prepr*. **1990**, *31* (1), 548.
(18) Wellinghoff, S. T.; Koenig, J. L.; Baer, E. *J. Polym. Sci., Polym. Phys. Ed*. 1977, *15*, 1913.
(19) Liu, J.; Jean, Y. C.; Yang, H. *Macromolecules* **1995**, *28*, 5774.
(20) Jean, Y. C.; Yuan, J.-P.; Liu, J.; Deng, Q.; Yang, H. *J. Polym. Sci., Polym. Phys. Ed*. **1995**, *33*, 2365.
(21) Patterson, D. J. *Polym. Sci.: Part C* **1968**, *16*, 3379.
(22) Zeman, L.; Biros, J.; Delmas, G.; Patterson, D. *J. Phys. Chem*. **1972**, *76*, 1206.
(23) Siow, K. S.; G. Delmas, G.; Patterson, D. *Macromolecules* **1972**, *5*, 29.
(24) Patterson, D. *Macromolecules* **1969**, *2*, 672.
(25) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem*. **1976**, *80*, 2352.
(26) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem*. **1976**, *80*, 2568.
(27) Sanchez, I. C.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145.
(28) Tsujita, Y.; Kato, M.; Kinoshita, T.; Takizawa, A. *Polymer* **1992**, *33*, 773.
(29) Lee, J.-C.; Litt, M. H.; Rogers, C. E. *Macromolecules* **1997**, *30*, 3766.
(30) Collins, E. A.; Bares, J.; Billmeyer, F. W., Jr. *Experiments in Polymer Science*, Wiley-Interscience Pub.: New York, 1973; pp 146−153.
(31) Lee, J.-C.; Litt, M. H.; Rogers, C. E. *J. Polym. Sci., Polym. Phys. Ed*. **1998**, *36*, 754.
(32) Bosma, M.; Brinke, G. T.; Ellis, T. S. *Macromolecules* **1988**, *21*, 1465.
(33) Van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier Scientific Publishing Co., Inc.: New York, 1990; pp 189−225.
(34) Hoy, K. L. *J. Paint Technol*. **1970**, *42*, 76.
(35) Grulke, E. A. *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1989; p VII 519.
(36) *The Merck Index*, 10th ed.; Windholz, M., Ed.; Merck & Co., Inc.: Rahway, NJ., 1983; p 1286.
(37) *Aldrich, Catalog Handbook of Fine Chemicals*; Aldrich: Milwaukee, WI, 1996−1997; pp 1031 and 1399.
(38) Patel, K.; Manley, R. St. J. *Macromolecules* **1995**, *28*, 5793.
(39) Morel. G.; Paul, D. R. *J. Membr. Sci*. **1982**, *10*, 273.
(40) Chiou, J. S.; Paul, D. R. *J. Appl. Polym. Sci*. **1987**, *34*, 1503.
(41) Keitz, J. D.; Barlow, J. W.; Paul, D. R. *J. Appl. Polym. Sci*. **1984**, *29*, 3131.
(42) Pauly, S. *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1989; p VI 435.
(43) Chiou, J. S.; Paul, D. R. *J. Appl. Polym. Sci*. **1987**, *34*, 1037.
(44) Kim, C. K.; Paul, D. R. *Polymer* **1992**, *33*, 4929.
(45) Ahn, T. O.; Nam, B. U.; Lee, S.; Jeong, H. M. *Polym. Commun*. **1991**, *32*, 415.
(46) Ahn, T. O.; Ryu, C.-Y.; Sunwon, J. H.; Jeong, H. J. *Macromol. Rapid Commun*. **1994**, *15*, 265.
(47) Ahn, T. O.; Lee, Y. J.; Lee, S.; Jeong, H. M. *J. Macromol. Sci*. **1990**, *B29*, 91.
(48) Shaw, M. T. *J. Appl. Polym. Sci*. **1974**, *18*, 449.

MA971813J