Macromolecules **1996,** *29,* 6629−6633

Enthalpy of Mixing for a Glassy Polymer Blend from CO_2 Sorption and Dilation Measurements

R. M. Conforti[†] and T. A. Barbari*

Department of Chemical Engineering, The Johns Hopkins University, Baltimore, Maryland 21218

M. E. Pozo de Fernandes[‡]

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

Received December 13, 1995; Revised Manuscript Received May 20, 1996[⊗]

ABSTRACT: Carbon dioxide sorption and dilation data were fitted with the glassy polymer lattice sorption model (GPLSM) to obtain segment−segment interaction parameters for poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), polystyrene (PS), and two PPO/PS miscible blends. These interaction parameters were then used to calculate the enthalpy of mixing for the two polymers. The resulting enthalpies were −0.2 and −1.1 cal/cm^3 for PPO/PS blends of 50/50 and 75/25 by weight, respectively, which compare favorably to those determined from measured heats of solution and from calorimetry with low molecular weight analogs.

Introduction

For miscibility in a binary polymer blend, specific interactions between the two polymers, such as strong polar forces or hydrogen bonding, are often necessary to compensate for the small entropic contribution associated with mixing long chain molecules. In these cases, the enthalpic contribution to the free energy of mixing is negative with a magnitude that reflects the strength of these interactions. Indirect methods must be used to determine the enthalpy of mixing since the direct calorimetric measurement for a polymer blend is not practical. For example, calorimetry with low molecular weight analogs can be used to estimate the enthalpy of mixing for a blend.[1−4] Alternatively, heats of solution can be measured in a mutual solvent from which the heat of mixing can be determined from Hess's law.[5] For crystallizable systems, melting point depression can be used to determine a polymer−polymer interaction parameter from which the enthalpy of mixing can be calculated.[6−9] Small angle neutron scattering (SANS)[27,28] and forward recoil spectrometry (FRES)[29] have also been used to determine interaction parameters. Lastly, small molecule probes can be used in either gas/vapor sorption experiments[10−12] or inverse gas chromatography[13−15] with a ternary thermodynamic model to determine a polymer−polymer interaction parameter and, hence, the enthalpy of mixing. The utility of this final approach depends on the ability of a particular thermodynamic model to describe the mixture. In this paper, a compressible lattice model developed specifically for gas sorption in glassy polymers is used to determine the enthalpy of mixing for a glassy polymer blend.

In addition to a negative enthalpy of mixing, blends of glassy polymers also exhibit a negative volume change of mixing which, in terms of a lattice representation, implies that the blend on the lattice is compressible or contains holes. In this paper and in our previous work,[16−18] the term compressible lattice refers to a lattice on which the system is compressible at a fixed lattice cell volume instead of one on which the lattice cell volume itself changes. The glassy polymer lattice sorption model (GPLSM), an activity coefficient model based on a compressible lattice, was developed to account for nonideal gas sorption behavior in glassy polymers.[16,17] In addition to its use to fit sorption isotherms in a number of glassy polymers, the model has been used to describe history-dependent phenomena such as gas conditioning[17] and sorption−desorption hysteresis.[18] Here, the model is extended to gas sorption in a miscible polymer blend with the aim of determining the enthalpy of mixing from a blend interaction parameter in the model.

To test this approach, the system of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polystyrene (PS) was chosen. This system is known to be completely miscible over the entire concentration range at low to moderate temperatures. In addition, miscibility does not rely on strong "chemical" interactions, such as hydrogen bonding, which are not included in the development of GPLSM. The PPO/PS system has been studied by most of the indirect methods mentioned above. Weeks et al.[5] used heats of solution data for PPO, PS, and their blends in *o*-dichlorobenzene to determine the enthalpy of mixing from Hess's law. Morel and Paul[10] measured CO_2 sorption isotherms in the PPO/PS system and then used parameters from the dual mode sorption model to determine a blend interaction parameter and the enthalpy of mixing. Very recently, Ziaee and Paul[30] used calorimetry with analogs of PPO and PS to determine the enthalpic interaction energy. In this paper, new experimental measurements of CO_2 sorption and dilation in PPO, PS, and two of their blends at 35 °C are used with GPLSM to determine a blend interaction parameter from which the enthalpy of mixing is calculated. The results are then compared to those obtained from these previous studies.

Background

Flory−Huggins theory, developed for an incompressible lattice on which there is no volume change of mixing, has been shown to be appropriate for gas−rubbery polymer mixtures, but inadequate for gas−

---

* To whom correspondence should be addressed.

[†] Present address: Polaroid Corp., 1265 Main St., Waltham, MA 01801.

[‡] Present address: Department of Chemical Engineering, Florida Institute of Technology, Melbourne, FL 32901.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

glassy polymer systems.[17] The glassy polymer lattice sorption model (GPLSM) was developed specifically to account for lattice compressibility in these systems. The expression for the free energy of mixing, ΔG_{mix}, from GPLSM is very similar to that resulting from Flory–Huggins theory, but the application to gas sorption in glassy polymers requires sorptive dilation (swelling) information for the gas–polymer mixture to account for the compressibility of the lattice.

For a compressible lattice containing gas molecules (N_g), polymer segments (N_r), and holes (N_h), ΔG_{mix} for GPLSM is given by[16,17]

$$\frac{\Delta G_{\text{mix}}}{kT} = N_g \ln \frac{N_g}{N_g + N_h} + N_h \ln \frac{N_h}{N_g + N_h} - N'_g \ln \frac{N'_g}{N'_g + N'_h} - N'_h \ln \frac{N'_h}{N'_g + N'_h} + \Psi \frac{N_g N_r}{N_g + N_r + N_h} + \frac{PV_s}{kT}(N_T - N_T^0 - N'_T) \quad (1)$$

where

$$\Psi = \frac{z}{kT}\left[\Gamma_{rg} - \frac{1}{2}(\alpha\Gamma_{gg} + \beta\Gamma_{rr})\right] \quad (2)$$

$$\alpha = \frac{N'_g}{N'_T}\left(\frac{N_T - N'_T}{N_r}\right) \quad (3)$$

and

$$\beta = \frac{FN_r}{N_T^0}\left(\frac{N_T - N_T^0}{N_g}\right) \quad (4)$$

N_T is the total number of lattice sites in the mixture ($N_g + N_r + N_h$), N_T^0 is the number of sites in the pure polymer ($N_r + N_h^0$), and N'_T is the number of sites in the pure gas ($N'_g + N'_h$). N'_g/N'_T is the fraction of sites in the pure gas occupied by gas molecules, and V_s is the molecular lattice-site volume. The parameter Ψ is analogous to the Flory χ parameter, and Γ_{rr}, Γ_{gg}, and Γ_{rg} represent segment–segment, gas–gas, and segment–gas interaction energies, respectively. Physically, α and β account for the compressibility of the lattice. F is the fraction of polymer segments that interact noncovalently, which for high molecular weight polymers, is given by

$$F = \frac{z - 2}{z} \quad (5)$$

where z is the coordination number.

The first two terms in eq 1 represent the combinatorial entropy associated with placing gas molecules on a lattice containing polymer segments and holes. The assumption here is that the polymer segments do not contribute to the combinatorial entropy of mixing for the glassy system. This assumption is similar to that made by others to describe the entropy of a polymer at temperatures below the glass transition[19–20] and is reasonable provided the mixture remains glassy. The second two terms represent the entropy of the pure gas. Since the lattice-site volume is chosen to be the close-packed volume of a gas molecule, the pure gas contains holes on its lattice. The fifth term is the internal energy contribution based on a mean-field approximation. The sixth and final term in eq 1 is the volume of mixing term for the compressible lattice. However, this term is small in magnitude compared to the others and is not included in the application of GPLSM.[16,17] The compressibility of the lattice is reflected primarily in the term for the internal energy.

Equation 1 can be developed into an activity coefficient model using the equations

$$kT \ln a_g = \left(\frac{\partial \Delta G_{\text{mix}}}{\partial N_g}\right)_{T,p,N_r} \quad (6)$$

$$a_g = \gamma_g \frac{N_g}{N_r} \quad (7)$$

$$\gamma_g^* = \frac{\gamma_g}{\gamma_g^\infty} \quad (8)$$

and

$$f_g = \gamma_g^* \frac{N_g}{N_r} H \quad (9)$$

where a_g is the activity of the gas in the polymer, γ_g and γ_g^* are the symmetrically- and asymmetrically-normalized activity coefficients for the gas in the polymer, respectively, f_g is the gas-phase fugacity, γ_g^∞ is the symmetrically normalized activity coefficient at infinite dilution, and H is the Henry's law constant.

The application of eq 6 to eq 1 results in a complex activity coefficient expression owing to the derivative, $\partial N_h/\partial N_g$. If the lattice were incompressible but contained holes, the number of holes would remain constant during sorption, this derivative would be zero, and a simple analytical expression would result. The GPLSM expression for γ_g^* and its application to the fitting of gas sorption isotherms are given elsewhere.[16–18] Gas concentration, C, in the typical units of cm^3(STP)/cm^3 polymer is converted to N_g/N_r for GPLSM using the equation

$$\frac{N_g}{N_r} = \frac{C\bar{V}_s}{22415}\frac{\hat{V}_{sp}}{\hat{V}_{oc}} \quad (10)$$

where $\hat{V}_{sp}$ and $\hat{V}_{oc}$ are the specific and occupied volumes, respectively, of the polymer, $\bar{V}_s$ is the molar lattice site volume, and 22 415 converts cm^3(STP) to moles. The occupied volume is determined from Bondi's group contribution method.[21] An appropriate equation of state is used to relate f_g to pressure.

Equation 1 can be applied to gas sorption/dilation in a polymer blend without modification if the blend is treated as a single component. The resulting segment–segment interaction energy, Γ_{rr}, can be written in terms of the homopolymer segment–segment interaction energies, Γ_{r1r1} and Γ_{r2r2}, according to

$$\left(\frac{N_r}{N_T^0}\right)^2 \Gamma_{rr} = \left(\frac{N_{r1}}{N_T^0}\right)^2 \Gamma_{r1r1} + \left(\frac{N_{r2}}{N_T^0}\right)^2 \Gamma_{r2r2} + 2\left(\frac{N_{r1}}{N_T^0}\right)\left(\frac{N_{r2}}{N_T^0}\right)\Gamma_{r1r2} \quad (11)$$

where N_T^0 is the total number of sites in the blend ($N_{r1} + N_{r2} + N_h^0$ and $N_r = N_{r1} + N_{r2}$. By equating the internal energy for a ternary mixture to that for a pseudobinary system consisting of gas molecules and blend segments, the segment−gas interaction energy for the pseudobinary system, Γ_{rg}, can be written as

$$\left(\frac{N_r}{N_T^0}\right)\Gamma_{rg} = \left(\frac{N_{r1}}{N_T^0}\right)\Gamma_{r1g} + \left(\frac{N_{r2}}{N_T^0}\right)\Gamma_{r2g} \qquad (12)$$

where Γ_{r1g} and Γ_{r2g} are segment−gas interaction energies for the two homopolymers. In terms of physical quantities, the site ratios in eqs 11 and 12 can be written as

$$\frac{N_{r1}}{N_T^0} = \frac{w_1\hat{V}_{oc1}}{\hat{V}_{sp}} \qquad (13)$$

and

$$\frac{N_{r2}}{N_T^0} = \frac{w_2\hat{V}_{oc2}}{\hat{V}_{sp}} \qquad (14)$$

where w_1 and w_2 are the weight fractions of each polymer in the blend, $\hat{V}_{sp}$ is the measured specific volume of the blend, and $\hat{V}_{oc1}$ and $\hat{V}_{oc2}$ are the occupied volumes of each homopolymer.

Assuming that the volume change of mixing the two polymers is small compared to the change in internal energy, the enthalpy of mixing per unit volume can be written as

$$\Delta H_{mix} = \frac{zFR}{2V_s}\left(\left(\frac{N_r}{N_T^0}\right)^2\frac{\Gamma_{rr}}{k} - \frac{N_{r1}}{N_T^0}\frac{N_{r1}}{N_{T1}^0}\frac{\Gamma_{r1r1}}{k} - \frac{N_{r2}N_{r2}}{N_T^0 N_{T2}^0}\frac{\Gamma_{r2r2}}{k}\right) \qquad (15)$$

where

$$\frac{N_{r1}}{N_{T1}^0} = \frac{\hat{V}_{oc1}}{\hat{V}_{sp1}} \qquad (16)$$

$$\frac{N_{r2}}{N_{T2}^0} = \frac{\hat{V}_{oc2}}{\hat{V}_{sp2}} \qquad (17)$$

It should be noted that $N_T^0 \neq N_{T1}^0 + N_{T2}^0$ because of the compressible nature of the lattice.

Experimental Section

Materials. Carbon dioxide (instrument grade, 99.99% purity) was obtained from Matheson Gas Products. Polystyrene (mol wt = 250 000) and poly(2,6-dimethyl-1,4-phenylene oxide) (mol wt = 244 000) were obtained from Scientific Polymer Products and Aldrich Chemical, respectively. Chloroform (98.9% purity), used as a film-casting solvent for the polymers and their blends, was obtained from J. T. Baker Analyzed. All materials were used as received.

Sample Preparation. The blends were prepared from 10 wt % solutions in chloroform at PPO/PS ratios of 0/100, 50/50, 75/25, and 100/0 by weight. Films of each composition were prepared by casting the solutions onto glass plates using a dual micrometer film casting knife. Immediately after casting, the plates were placed in an oven, preheated to 90 °C, under a slow air purge. The samples were heated for 15−20 min, removed from the oven, and allowed to cool at ambient conditions for approximately 30 min. The samples were then removed from the glass plates by immersion in water.

To remove residual solvent, the polymer films were mounted between steel supports and placed into a vacuum oven for 24 h at a temperature approximately 10 deg below the glass transition temperature of the blend. No orientation was observed in the films when examined through cross polarizers for birefringence. Using differential scanning calorimetry at 20 °C/min, a single glass transition temperature was determined for each blend, indicating complete miscibility. The films were uniform with a thickness of approximately 75 μm. Each film was cut into strips, 0.5 cm in width, for the gas sorption and dilation experiments. The strips for the dilation experiments were 13 cm in length. The densities of the polymer films at 35 °C were obtained by flotation in a pycnometer using aqueous solutions of calcium nitrate tetrahydrate.

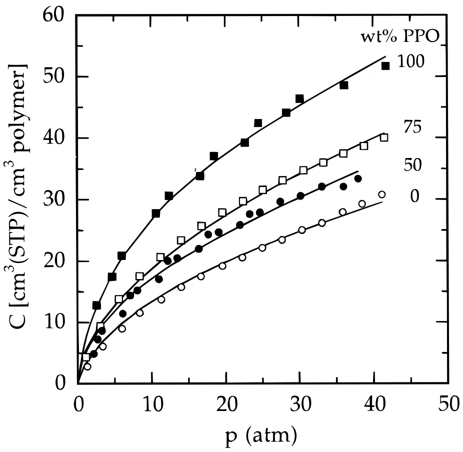

Figure 1. Sorption isotherms for CO_2 in PPO/PS blends at 35 °C. Curves represent GPLSM fits with parameters in Table 2.

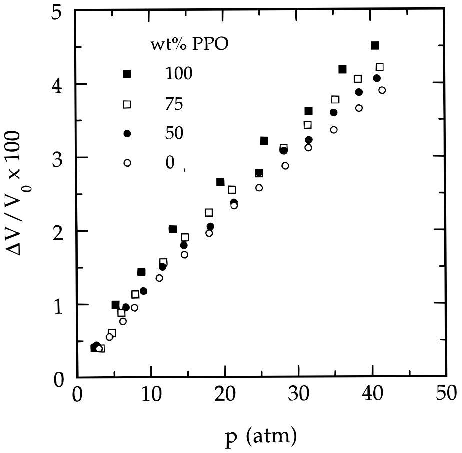

Figure 2. Dilation isotherms for CO_2 in PPO/PS blends at 35 °C.

Gas Sorption and Dilation. Gas sorption isotherms were measured at 35 °C using a single-transducer pressure decay method described in detail by Barbari[22] and Conforti.[23] Sorptive dilation isotherms at 35 °C were measured using a technique described by Wissinger and Paulaitis[24] which is based on changes in sample length. Volumetric changes were determined by assuming the samples were isotropic. The absence of birefringence in the polymer samples under cross polarizers was taken as verification of this assumption. Since gas sorption and dilation behavior in glassy polymers depends on the final pressure to which the polymer is exposed, all samples were "conditioned" for 24 h with CO_2 at 600 psia, a pressure higher than that used for either the sorption or dilation measurements.

Results and Discussion

Sorption and dilation isotherms for carbon dioxide in the PPO/PS blends at 35 °C are plotted in Figures 1 and 2, respectively. The measured CO_2 concentrations for this system are in excellent agreement with those

Table 1. Specific Volumes at 35 °C and Occupied Volumes for PPO, PS, and Two Blends

	$\hat{V}_{sp}$, cm^3/g	$\hat{V}_{oc}$, cm^3/g
PPO (1)	0.9259	0.7501
75 (1)/25 (2)	0.9276	0.7587
50 (1)/50 (2)	0.9294	0.7673
PS (2)	0.9425	0.7845

Table 2. GPLSM Parameters for CO_2 Sorption in PPO/PS Blends at 35 °C

	Γ_{rr}/k (K)	Γ_{rg}/k (K)	H (atm)
PPO(1)	−290	−381	60
75 (1)/25 (2)	−259	−369[a]	60
50 (1)/50 (2)	−218	−356[a]	76
PS (2)	−151	−333	155

[a] Calculated from eq 12.

Table 3. Enthalpies of Mixing at 35 °C for PPO (1)/PS (2) Blends from GPLSM, Heats of Solution (ΔH_{soln}), the Dual Mode Sorption Model, and Analog Calorimetry

	ΔH_{mix} (cal/cm^3)			
	GPLSM	ΔH_{soln}[5]	dual mode[10]	calorimetry[30]
50 (1)/50 (2)	−0.2	−1.3	−3.0	−0.3
75 (1)/25(2)	−1.1	−1.0	−2.3	−0.2

measured by Morel and Paul.[10] Nonideal mixing for the two polymers is reflected in the less-than-additive gas concentrations in the two blends. The dilation isotherms follow the same trend with increasing PPO content.

The experimental sorption data in Figure 1 were fitted with the glassy polymer lattice sorption model developed in eqs 1−10. For the lattice-site volume, the close-packed molecular volume of carbon dioxide from the Sanchez−Lacombe equation of state was used ($\bar{V}_s$ = 29.13 cm^3/mol).[16] Similarly, the value of the gas−gas interaction energy for CO_2 was taken from a fit of pure gas *PVT* data with the Sanchez−Lacombe equation of state ($\Gamma_{gg}/k = -402.6$ K).[25] The coordination number, z, and fraction of noncovalent interactions, F, were taken as 10 and 0.8, respectively. Measured specific volumes and occupied volumes from the Bondi group contribution method are listed in Table 1 for the PPO/PS system.

In previous applications of GPLSM, Γ_{rig} was taken as the geometric mean of Γ_{riri} and Γ_{gg} to demonstrate that the model could fit gas sorption isotherms with only two adjustable parameters, Γ_{riri} and H. However, it can be shown that if the geometric mean assumption is made for Γ_{rig} in a ternary system, then Γ_{r1r2} must equal the geometric mean of Γ_{r1r1} and Γ_{r2r2}, forcing a positive enthalpy of mixing according to eqs 16 and 20. Therefore, the geometric mean assumption was relaxed for the PPO/PS system. For pure PPO (1) and pure PS (2), three adjustable parameters were used, Γ_{riri}, Γ_{rig}, and H. Using eq 12, Γ_{rg} was calculated for each blend and the sorption data for the blends were fitted with Γ_{rr} and H as adjustable parameters. The resulting fits are shown in Figure 1 for the pure polymers and both blends, and Table 2 lists the corresponding GPLSM parameters.

The interaction energies in Table 2 can be substituted into eq 15 to calculate the enthalpy of mixing PPO and PS at 35 °C. The values for the 50/50 and 75/25 PPO/PS blends are given in Table 3 along with those obtained by Weeks et al.[5] using heats of solution in *o*-dichlorobenzene, by Morel and Paul[10] using CO_2 sorption with the dual mode sorption model for glassy polymers, and by Ziaee and Paul[30] using low molecular weight analogs. The value for the 75/25 blend from this study using GPLSM compares favorably with that determined from heats of solution, while the value for the 50/50 blend is in good agreement with the value from analog calorimetry.

The enthalpies of mixing calculated from the application of the dual mode sorption model to CO_2 isotherms in this blend system are much higher than those obtained from the application of GPLSM, from heats of solution, or from low molecular weight analog calorimetry. The dual mode model assumes that gas sorption occurs by two parallel mechanisms within a glassy polymer, equilibrium sorption into thermodynamically relaxed regions through a linear Henry's law expression and sorption into unrelaxed microvoids frozen into the polymer below its glass transition temperature through a Langmuir expression. Morel and Paul[10] used a mixing rule for the dual mode Henry's law parameter which assumes there is no volume change of mixing in the relaxed portion of the glassy blend. The interactions between PPO and PS which lead to the small negative enthalpy of mixing may also lead to a denser than expected dual mode Henry's law domain in the blend. Accounting for these negative deviations from ideality may lead to lower values of the blend interaction parameter used to calculate the enthalpy of mixing. GPLSM provides a framework from which these deviations can be considered.

Furthermore, the values of ΔH_{mix} from the dual mode model depend on the partial molar volume of CO_2 in the blend. Morel and Paul[10] use 55 cm^3/mol for this volume. More recent sorption and dilation data for CO_2 in rubbery polymers indicate that the partial molar volume for CO_2 is 46 cm^3/mol,[26] which would increase the values for the 50/50 and 75/25 blends to −3.6 and −2.8 cal/cm^3, respectively. Conversely, although the magnitude of Γ_{rr}/k in GPLSM depends on the molar lattice site volume, the interaction energy for the polymer per unit volume, $zF\Gamma_{rr}/k\bar{V}_s$, is constant. Therefore, the enthalpy of mixing calculated from eq 15 is independent of the lattice site volume.

Conclusions

Application of the glassy polymer lattice sorption model (GPLSM) to CO_2 sorption and dilation isotherms in the PPO/PS system results in values of segment−segment interaction energies from which reasonable values of the enthalpy of mixing are obtained. Although these are comparable to those from heats of solution data and from calorimetry with low molecular weight analogs, there is a large difference between the two blend compositions studied here (see Table 3). Given that the enthalpy of mixing is calculated by subtracting a weighted average interaction energy for the homopolymers from a blend interaction energy, it is imperative that accurate gas sorption and dilation data be measured to ensure values of these parameters that reflect the true nature of the interactions.

Of the two blends studied here with GPLSM, the enthalpy of mixing for the 50 (PPO)/50 (PS) system was consistent with low molecular weight analog calorimetry data while that for the 75 (PPO)/25 (PS) system was consistent with heats of solution data. Other blend systems, including those with hydrogen bonding, should be studied before final conclusions can be drawn from the approach presented here. However, it can be concluded that enthalpies of mixing for glassy polymer blends can be determined using ternary systems involving a small molecule provided an adequate thermodynamic model is used that reflects the unique physics of these systems.

Acknowledgment. The authors thank Professor Michael E. Paulaitis for the use of the high-pressure dilation equipment in his laboratory and for discussions related to the swelling measurements reported here.

References and Notes

(1) Cruz, C. A.; Barlow, J. W.; Paul, D. R. *Macromolecules* **1979**, *12*, 726.
(2) Walsh, D. J.; Higgins, J. S.; Zhikuan, C. *Polymer* **1982**, *23*, 336.
(3) Harris, J. E.; Paul, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1983**, *23*, 676.
(4) Harris, J. E.; Paul, D. R.; Barlow, J. W. *Adv. Chem. Ser.* **1984**, *206*, 43.
(5) Weeks, N. E.; Karasz, F. E.; MacKnight, W. J. *J. Appl. Phys.* **1977**, *48*, 4068.
(6) Harris, J. E.; Goh, S. H.; Paul, D. R.; Barlow, J. W. *J. Appl. Polym. Sci.* **1982**, *27*, 839.
(7) Aubin, M.; Prud'homme, R. E. *Macromolecules* **1980**, *13*, 365.
(8) Kwei, T. K.; Patterson, G. D.; Wang, T. T. *Macromolecules* **1976**, *9*, 780.
(9) Morra, B. S.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2243.
(10) Morel, G.; Paul, D. R. *J. Membr. Sci.* **1982**, *10*, 273.
(11) Masi, P.; Paul, D. R.; Barlow, J. W. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 15.
(12) Spencer, H. G.; Yavorsky, J. A. *J. Appl. Polym. Sci.* **1983**, *28*, 2837.
(13) Walsh, D. J.; McKeown, J. G. *Polymer* **1980**, *21*, 1335.
(14) DiPaola-Baranyi, G.; Fletcher, S. J.; Degre, P. *Macromolecules* **1982**, *15*, 885.
(15) Riedl, B.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2565.
(16) Conforti, R. M.; Barbari, T. A.; Vimalchand, P.; Donohue, M. D. *Macromolecules* **1991**, *24*, 3388.
(17) Barbari, T. A.; Conforti, R. M. *J. Polym. Sci., Polym. Phys. Ed.* **1992**, *30*, 1261.
(18) Conforti, R. M.; Barbari, T. A. *Macromolecules* **1993**, *26*, 5209.
(19) Gibbs, J. H.; DiMarzio, E. A. *J. Chem. Phys.* **1958**, *28*, 373.
(20) Chow, T. S. *Macromolecules* **1980**, *13*, 362.
(21) van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier Science Publishing: New York, 1991.
(22) Barbari, T. A. Ph.D. Dissertation, The University of Texas at Austin, 1986.
(23) Conforti, R. M. Ph.D. Dissertation, The Johns Hopkins University, 1992.
(24) Wissinger, R. G.; Paulaitis, M. E. *J. Polym Sci., Polym. Phys. Ed.* **1987**, *25*, 2497.
(25) Kiszka, M. B.; Meilchen, M. A.; McHugh, M. A. *J. Appl. Polym. Sci.* **1988**, *36*, 583.
(26) Fleming, G.; Koros, W. J. *Macromolecules* **1986**, *19*, 2285.
(27) Maconnachie, A.; Kambour, R. P.; Bopp, R. C. *Polymer* **1984**, *25*, 357.
(28) Maconnachie, A.; Kambour, R. P.; White, D. M.; Rostami, S.; Walsh, D. J. *Macromolecules* **1984**, *17*, 2645.
(29) Composto, R. J.; Mayer, J. W.; Kramer, E. J.; White, D. M. *J. Am. Phys. Soc., Phys. Rev. Lett.* **1986**, *57*, 1312.
(30) Ziaee, S.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.*, in press.

MA951838N