stituted anhydroglucose units in HPC. For HPS, the retention data are given by

$$\ln V_g = -5.728 + 2493(1/T) + 490600(1/T)^2 \quad (8)$$

in the temperature range 15–75 °C, and the values for $-\Delta\bar{H}_m^\infty$ decreased from ~5 kJ/mol at 15 °C to ~2 kJ/mol at 75 °C. Thus the temperature dependence of $-\Delta\bar{H}_m^\infty$ for HPS apparently differs from that of HPC. We note that, unlike aqueous HPC solutions, HPS solutions in water showed no signs of phase separation when heated to 100 °C.

In comparing the HPS retention data with those for HPC,[3] we noted that the HPC measurements showed much greater experimental variation. This was due to the dependence of the measured retention volumes on sample size and to the consequent extrapolations to zero water peak height. (The HPS retention volumes were virtually independent of water concentration, as should be the case in the infinitely dilute region.) We now think that extrapolating to zero peak height and taking the difference between two fitted curves may have introduced errors which contribute to the apparent temperature dependence of $\Delta\bar{H}_m^\infty$ for water in HPC. Table II and the associated discussion in ref 3 should therefore be treated with caution; the trend is still thought to be correct, but the errors in $\Delta\bar{H}_m^\infty$ are larger than those listed. (We note that this problem only concerns the measurement of the partial molar heats of mixing of water with HPC at effectively zero water content reported in the previous paper.[3] The finite-concentration measurements in the present paper showed negligible kinetic effects, and, of course, no extrapolation to zero concentration was necessary.)

Supplementary Material Available: Experimental activities of water over HPC solutions (4 pages). Ordering information is given on any current masthead page.

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Miscibility of Acrylic Polymers in Polystyrene by Melt Titration

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ABSTRACT: The melt titration technique was used to determine the extent of miscibility in several polystyrene/polyacrylate (PMA, PEA, PBA) and polystyrene/polymethacrylate (PnBMA, PMMA) blends. The results were used in the Flory–Huggins theory of polymer solutions to calculate the interaction energy density. A theoretical value of the interaction energy density was obtained from the components' solubility parameters and the two values were compared. The Flory theory and Sanchez's lattice fluid theory, based on statistical thermodynamic principles, were used to predict the miscibility of the polystyrene/acrylic blends. The use of experimental values of the specific volume, the thermal expansion coefficient, and the thermal pressure coefficient was found to affect the miscibility predictions considerably. Finally, results from the melt titration technique were compared with predictions of these theories. The Flory treatment offered the best ranking of the experimental miscibilities, while the Sanchez theory correctly predicted the very low miscibilities (10^{-5} to 10^{-6}) found for all pairs.

Introduction

Miscibility in a two-component polymer system is required to obtain a homogeneous product, which is highly desirable for superior and predictable performance. Various theories have been developed to aid in predicting polymer–polymer miscibility[2,9] and its dependence on temperature, pressure, and concentration. For better appreciation of the performance of these theories, experimental miscibility data are essential. Unfortunately, very few data are available at present, which has led many scientists to investigate new methods for determining miscibility in polymer–polymer systems. We reported[1] earlier a melt titration technique for measuring the extent of miscibility in polymer blends.

In this work, polystyrene (PS) was chosen as one component and the extent of miscibility of poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(butyl acrylate) (PBA), poly(n-butyl methacrylate) (PnBMA), poly(methyl methacrylate) (PMMA), and poly(dimethylsiloxane) (PDMS) in polystyrene was determined by melt titration. From the known phase behavior of the polymer blends, the "Tompa interaction parameter" χ and "interaction energy density" $B = RT\chi/V_1$ were calculated. For comparison purposes, the interaction energy density was obtained from the difference in solubility parameters δ_i calculated from group contributions: $B = (\delta_1 - \delta_2)^2$.

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Table I
Miscibility Results from the Melt Titration Technique

polymer	polymer designation	M_w[a]	M_w/M_n	wt fraction in PS × 10^5	$n^{20}{}_D$
polystyrene	PS	520 000			1.592
poly(methyl acrylate)	PMA	200 000	3.16	3.8	1.473
poly(ethyl acrylate)	PEA	125 000	3.24	8.6	1.468
poly(butyl acrylate)	PBA	119 000	3.61	7.8	1.466
poly(*n*-butyl methacrylate)	PnBMA	320 000	4.35	5.0	1.483
poly(methyl methacrylate)	PMMA	160 000	1.10	0.39	1.490
poly(dimethylsiloxane)	PDMS	71 800	2.24	0.39	1.403

[a] M_w is the weight-average molecular weight obtained from the suppliers (for PS from GPC).

Equation-of-state parameters for the Flory theory and the lattice fluid theory were calculated from the specific volume, the thermal expansion coefficient, and the thermal pressure coefficient. Group contribution methods were also used for estimation of these quantities. A comparison of the experimental results and the predictions of these theories was then made.

Experimental Section

In a preceding note[1] the melt titration technique was described in detail.

The first component, polystyrene, was fed to an extruder used as a mixer. High shear in the extruder (50-rpm screw speed) ensures homogeneous mixing of the two polymers. The polymer melt was extruded into a slit die and then to a recycle tube which returned it to the hopper of the extruder.

The second polymer, dissolved in a volatile solvent (toluene, methylene chloride, or chloroform), was added slowly at a flow rate of 0.18 mL/min from a syringe pump to the hopper of the extruder. The high temperature (423 K) in the hopper and feed section of the extruder forces evaporation of most of the solvent from the blend (T_g = 396 K before, T_g = 389 K after, by dynamic mechanical analysis, Du Pont DMA-981). Since very low miscibilities are expected in polymer-polymer systems, low concentrations of the second component (0.002–0.02 g/mL) were used. The presence of a second phase in the mixture was detected by light scattering using a special die and optical system.[1,3] Initially the polymer film was clear, and no light from the detector was scattered, so a steady base line was obtained. The film became cloudy upon formation of a second phase at the miscibility limit of the second polymer in the first polymer. The intensity of the scattered light increased linearly as the concentration of the second component was increased. The miscibility of the second polymer in the first was calculated from the location of the cloud point (see Appendix).

All polymers used in this study were bought from commercial sources. The weight-average molecular weights of the polymer samples are listed in Table I. PMA and PEA were obtained from Aldrich Chemical Co. PBA, PnBMA, and PDMS were obtained from Scientific Polymer Products, Inc. PMMA was obtained from Polysciences, Inc. PS was a commercial product manufactured by the Dow Chemical Co. under the trade name Styron. All structures were checked by IR.

Results

All experimental runs were done at a melt temperature of 423 K. At this temperature the thermal and mechanical degradation of the polystyrene was negligible, as determined by solution viscosity. The fate of the second component is not possible to follow, but the low temperature and the continual supply of antioxidant should provide optimum conditions for the preservation of the molecular weight.

The results for the system polystyrene/poly(methyl acrylate) are shown in Figure 1. Two independent runs are shown on the same plot; both were done under the same conditions of temperature and pressure and with the same two polymer samples. The agreement in repeat runs is good and an average value of miscibility is used for further calculations. The difference in slopes is due to gain differences in the photocell unit. Miscibility results for all polymer pairs studied are shown in Table I.

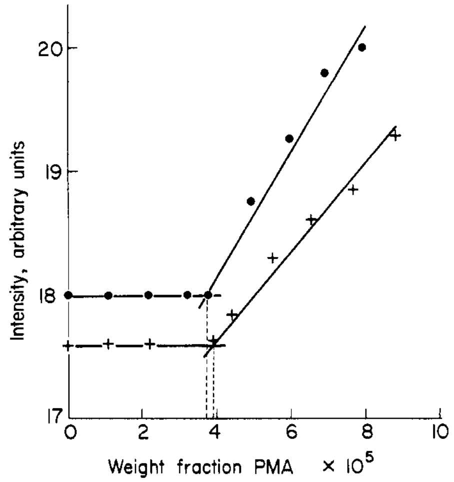

Figure 1. Melt titration result for the system polystyrene/poly(methyl acrylate).

Discussion

In this section an attempt has been made to compare the experimental results with the predictions of different theories of polymer blends. The equation-of-state theories, i.e., the Flory theory and the lattice fluid theory, have the advantage that the predictions of miscibility can be made from a purely theoretical approach; no experimental data other than the physical properties of polymers are required. Sanchez[10] has given a method for predicting, qualitatively, the miscibilities of polymer-polymer systems. This method was used to predict whether the miscibility in the polymer blends studied is favored or not.

For comparing the theoretical predictions with the experimental results, the Flory-Huggins theory was used to calculate the interaction energy density from the melt titration results. It must be pointed out that at a low concentration (1–10 ppm) of the second polymer, the polymer molecule may not mix segmentally with the first component and the application of the Flory-Huggins theory may be questionable; however, only relative values of the interaction energy density are important for comparison purposes.

Flory-Huggins Theory. The Gibbs free energy of mixing for two polymers is given by the following expression:[2]

$$\frac{\Delta G^M}{V} = RT\left[\frac{\phi_1}{V_1}\ln\phi_1 + \frac{\phi_2}{V_2}\ln\phi_2 + \frac{1}{V_s}\chi\phi_1\phi_2\right] \quad (1)$$

where V is the total volume, V_i is the molar volume of component i, ϕ_i is the volume fraction of component i, V_s is the molar volume of a segment, χ is the Tompa inter-

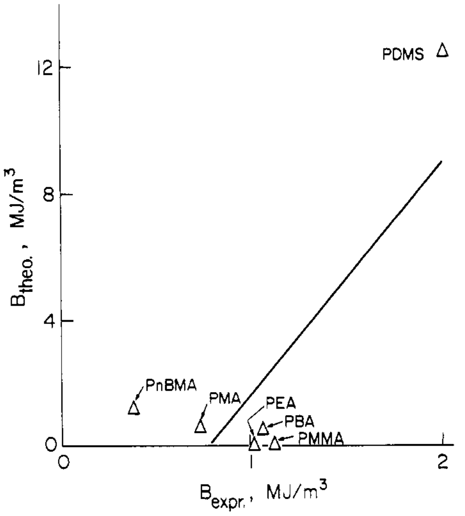

Figure 2. Correlation between experimental and theoretical values of the interaction energy density.

action parameter, R is the gas constant, and T is the absolute temperature.

For a two-component polymer–polymer system, the chemical potential can be obtained from the free energy of mixing. The phase equilibrium criteria then provide the following two equations for χ_1 and χ_2:[2,4]

$$\chi_1 = \frac{\ln\left(\dfrac{1-\phi_{2B}}{1-\phi_{2A}}\right) + \left(1 - \dfrac{1}{r}\right)(\phi_{2B} - \phi_{2A})}{(\phi_{2A})^2 - (\phi_{2B})^2} \qquad (2)$$

$$\chi_2 = \frac{\ln(\phi_{2B}/\phi_{2A}) + (1-r)(\phi_{2A} - \phi_{2B})}{(1-\phi_{2A})^2 - (1-\phi_{2B})^2} \qquad (3)$$

where A and B denote the two phases in equilibrium, ϕ_{2A} and ϕ_{2B} are volume fractions of component 2 on the boundary of the two-phase region, and r is the ratio of molar volumes ($r = V_2/V_1$). Also

$$\chi_1 = \chi_2/r \qquad (4)$$

The value of ϕ_{2A} was determined from the melt titration technique, and r, the ratio of the molar volumes of the two polymers, was calculated from the molecular weight and density. Equations 2–4 were solved simultaneously with the aid of a computer to obtain the value of the Tompa interaction parameter. The interaction energy density, B, is given by[5]

$$B = RT\chi_1/V_1 \qquad (5)$$

where χ_1 is the Tompa interaction parameter, V_1 is the molar volume of component 1, R is the gas constant, and T is the temperature.

The interaction energy density can also be estimated from the difference in solubility parameters of the two components by using the relationship[6]

$$B = (\delta_1 - \delta_2)^2 \qquad (6)$$

where δ_1 and δ_2 are the solubility parameters of components 1 and 2, respectively. The calculated values of χ_1 and B and the theoretical value of B from the solubility parameter difference are shown in Table II. Figure 2 shows the correlation between the experimental and theoretical values of the interaction energy density. For a large difference in solubility parameters calculated from the theory, we expect to get a large value for the interaction energy density from the experiment, indicating immiscibility. On the other hand, a small difference in solubility parameters does not necessarily mean miscibility for the polymers, since the B value from experiment is still too large for high miscibility.

Table II
Comparison of Experimental and Theoretical Values of the Interaction Energy Density

polymer pair	$\phi_{2A} \times 10^5$	χ_1	B, J/m^3 × 10^{-6} exptl	B, J/m^3 × 10^{-6} theor[a]
PS-PMA	3.4	28	0.80	0.57
PS-PEA	8.3	37	1.05	0.02
PS-PBA	7.7	38	1.12	0.52
PS-PnBMA	4.5	15	0.43	1.20
PS-PMMA	0.34	44	1.23	0.02
PS-PDMS	0.45	72	2.02	12.47

[a] Solubility parameter values from group contribution method (ref 7, p 143) and $\delta(T) = \delta(T_0)/[1 + \alpha(T - T_0)]$ (ref 8), where α is the thermal expansion coefficient, T is the temperature, and T_0 is room temperature (298 K).

Table III
Flory Equation-of-State Parameters

polymer	V_{sp},[a] cm^3/g	α[b] × 10^4, deg^{-1}	γ,[c] bar deg^{-1}	T^*, K	P^*, bar	V_{sp}^*, cm^3/g
PS	0.99	6.08	7.45	8080	4680	0.82
PMA	0.89	6.02	8.10	8130	5070	0.73
PEA	0.96	5.82	7.57	8290	4700	0.80
PBA	1.00	5.97	6.86	8160	4280	0.82
PnBMA	1.02	5.96	6.56	8170	4100	0.84
PMMA	0.90	6.25	7.34	7950	4650	0.73
PDMS	1.10	5.80	4.78	8310	2960	0.91

[a] $V_{sp}(T) = V_{sp}(T_0) + E_g(T_g - T_0) + E_r(T - T_g)$ for $T_g > T_0 = 298$ K or $V_{sp}(T) = V_{sp}(T_0) + E_r(T - T_0)$ for $T_g < T_0$, where E_g is the molar thermal expansivity in the glassy region and E_r is the molar thermal expansivity in the rubbery region.[d] [b] $\alpha = \rho E_r/M$ (ref 7), where ρ is the density and M is the molar weight.[d] [c] $\gamma = \alpha/\beta$ and $\beta \cong T\alpha/\delta^2$ (ref 2), where β is the isothermal compressibility.[d] [d] The values of E_g, E_r, ρ, and M were obtained from ref 7, pp 70–2.

"Equation-of-State" Theories. The two equation-of-state theories, namely, Flory's theory and the "lattice fluid" theory, represent promising alternatives to the solubility parameter approach for predicting polymer–polymer miscibility.[9] Therefore we thought it necessary to compare the experimental results with the predictions of these two theories.

Flory Theory. In the Flory theory, each component is characterized by three equation-of-state parameters: a characteristic temperature T^*, a characteristic pressure P^*, and a characteristic specific volume, V_{sp}^*. The three characteristic parameters can be calculated with the following equations:[10]

$$V_{sp}^* = V_{sp}\left(\frac{1 + T\alpha}{1 + 4T\alpha/3}\right)^3 \qquad (7)$$

$$P^* = \tilde{V}^2 T\gamma \qquad (8)$$

$$T^* = T(\tilde{V})^{4/3}/(\tilde{V}^{1/3} - 1) \qquad (9)$$

where V_{sp} is the specific volume, α is the thermal expansion coefficient [$\alpha = (\partial \ln V/\partial T)_p$], γ is the thermal pressure coefficient [$\gamma = (\partial P/\partial T)_V$], T is the temperature, and $\tilde{V}$ is the reduced volume ($\tilde{V} = V_{sp}/V_{sp}^*$). The values of V_{sp}, α, and γ were calculated from group contribution methods; they and the corresponding values of V_{sp}^*, T^*, and P^* are listed in Table III.

Table IV
Prediction of Miscibility by the Flory Theory: Characteristic Parameters from Group Contribution Methods

polymer pair	P_1^*/P_2^*	T_1^*/T_2^*	$\lvert T_1^* - T_2^* \rvert$, K	remarks
PS-PMA	0.92	0.99	50	favorable
PS-PEA	1.00	0.97	210	unfavorable
PS-PBA	1.09	0.99	80	favorable
PS-PnBMA	1.14	0.99	90	favorable
PS-PMMA	1.00	1.02	130	favorable
PS-PDMS	1.58	0.97	230	unfavorable

Table V
Prediction of Miscibility by the Flory Theory: Experimental Values of T^* and P^* for PS and Group Contribution Values for Other Polymers

polymer pair	P_1^*/P_2^*	T_1^*/T_2^*	$\lvert T_1^* - T_2^* \rvert$, K	remarks
PS[a]-PMA	0.99	1.02	170	favorable
PS-PEA	1.07	1.00	10	favorable
PS-PBA	1.17	1.02	140	favorable
PS-PnBMA	1.22	1.02	130	favorable
PS-PMMA	1.09	1.04	350	unfavorable
PS-PDMS	1.70	1.00	10	favorable

[a] Characteristic parameters for polystyrene are $T^* = 8300$ K, $P^* = 5020$ bar, and $V_{sp}^* = 0.83$ cm^3/g.

Table VI
Equation-of-State Parameters for the Lattice Fluid Theory

polymer	T^*, K	P^*, bar	V_{sp}^*, cm^3/g	V^*, cm^3/mol
PS	744	3870	0.90	16.0
PMA	747	4190	0.80	14.8
PEA	759	3890	0.87	16.2
PBA	750	3540	0.91	17.6
PnBMA	750	3390	0.93	18.4
PMMA	734	3840	0.81	15.9
PDMS	760	2450	1.00	25.8

To achieve significant miscibility of two polymers, the characteristic temperatures of the polymers must be very close to one another ($\Delta T^* < 200$ K). Larger ΔT^* differences can be tolerated if both $T_1^*/T_2^* > 1$ and $P_1^*/P_2^* > 1$; the combination $T_1^*/T_2^* > 1$ and $P_1^*/P_2^* < 1$ is very unfavorable. Unfortunately, the exact conditions on the T_1^*/T_2^* and P_1^*/P_2^* ratios have not yet been determined. Nevertheless, these general criteria[10,11] were used in determining the extent of miscibility in the polymer blends studied; the result is shown in Table IV. Clearly, the Flory theory seems to indicate favorable interaction among four pairs. Because the difference in characteristic temperatures is sensitive to the difference in the thermal expansion coefficients for the two polymers (a difference in the thermal expansion coefficients as low as 4% corresponds to a ΔT^* of about 200 K[10,11]), it is important that the method used for calculating or measuring α be accurate. Preferably, reliable experimental values of V_{sp}, α, and γ should be used for calculation of the equation-of-state parameters.

The experimental values at the desired temperature for V_{sp}, α, and γ were not found in the literature for all the polymers studied in this work; only values for PS,[13] PnBMA,[14] PMMA,[14] and PDMS[15] were found. Since this leads to only three pairs, it was very difficult to draw a conclusion from the results. In a trial to evaluate the effect of the method of calculation of V_{sp}, α, and γ on equation-of-state parameters, the characteristic parameters for polystyrene were calculated from the experimental values of V_{sp}, α, and γ. For the other polymers, the values were again those calculated from group contributions.

The same criteria described earlier were used to determine the extent of miscibility in the polymer blends studied. The results are shown in Table V. Clearly, the effect on the values of ΔT^* is tremendous. The values of ΔT^* for PS/PEA and PS/PDMS changed more than 200 K and now the miscibility is predicted to be favored in these pairs. This illustrates the importance of accurate experimental values of V_{sp}, α, and γ for the calculation of equation-of-state parameters.

Lattice Fluid Theory. As with the Flory theory, the lattice fluid theory is based on the configurational partition function for a system of polymeric molecules arranged on a lattice. Each component is characterized by three equation-of-state parameters: the characteristic specific volume V_{sp}^*, the characteristic temperature T^*, and the characteristic pressure P^*. Using the method described by Sanchez,[10] we calculated the equation-of-state parameters based on the values of V_{sp}, α, and γ from group contribution methods. Table VI shows the corresponding values of V_{sp}^*, T^*, P^*, and $V^* = RT^*/P^*$, where V^* is the characteristic molar volume.

The extent of miscibility in two polymers depends on the ratio of the two characteristic temperatures ($\tau = T_1^*/T_2^*$), the ratio of the characteristic molar volumes ($\nu = V_1^*/V_2^*$), and a dimensionless parameter ζ $(=\epsilon_{12}^*)/(\epsilon_{11}^*\epsilon_{22}^*)^{1/2}$, where ϵ_{ij} is the energy associated with species i interacting with species j. The polymers were designated component 1 and component 2 such that $\tau > 1$. For the case $\tau > 1$ and $\nu > 1$, ζ should satisfy the following two conditions:

$$0.95 < \zeta < 1.0 \tag{10}$$

and

$$\zeta > \zeta_{\min} = (3 + \tau)/4\tau^{1/2} \tag{11}$$

A value of ζ satisfying the inequalities (10) and (11) was assumed and $\nu_{\min}$ was calculated from the following equation:

$$\nu_{\min} = 2(1 - \zeta\tau^{1/2})/(3 + \tau - 4\zeta\tau^{1/2}) \tag{12}$$

If the calculated value of $\nu_{\text{calcd}} = V_1^*/V_2^*$ is greater than $\nu_{\min}$, then the miscibility is favored. On the other hand, if ν_{calcd} is less than $\nu_{\min}$, then the miscibility is not favored. The case $\tau > 1$ and $\nu < 1$ is very unfavorable for miscibility. Using these criteria,[10] we determined the extent of miscibility in the polymer blends studied; the result is shown in Table VII. The lattice fluid theory predicts that the miscibility is not favored in any of the polymer pairs

Table VII
Prediction of Miscibility by the Lattice Fluid Theory: Characteristic Parameters from Group Contribution Methods

polymer pair	τ	$\zeta_{\min}$	ζ_{assumed}	$\nu_{\min}$	ν_{calcd}	$\nu_{\min} - \nu_{\text{calcd}}$	remarks
PS-PMA	1.004				0.926		unfavorable
PS-PEA	1.020	0.995	0.996	3.24	1.014	2.226	unfavorable
PS-PBA	1.008	0.998	0.999	1.51	1.100	0.41	unfavorable
PS-PnBMA	1.008	0.998	0.999	1.51	1.150	0.36	unfavorable
PS-PMMA	1.013	0.997	0.998	1.83	1.004	0.826	unfavorable
PS-PDMS	1.021	0.995	0.996	3.24	1.610	1.63	unfavorable

Table VIII
Prediction of Miscibility by Lattice Fluid Theory: Experimental Values of T^* and V^* for PS and Group Contribution Values for Other Polymers

polymer pair	τ	$\zeta_{\min}$	ζ_{assumed}	$\nu_{\min}$	ν_{calcd}	$\nu_{\min} - \nu_{\text{calcd}}$	remarks
PS[a]-PMA	1.016	0.996	0.997	2.62	1.024	1.596	unfavorable
PS-PEA	1.000				0.936		unfavorable
PS-PBA	1.012				0.862		unfavorable
PS-PnBMA	1.012				0.828		unfavorable
PS-PMMA	1.034				0.953		unfavorable
PS-PDMS	1.000				0.589		unfavorable

[a] Equation-of-state parameters for PS are $T^* = 759$ K, $P^* = 4160$ bar, $V_{\text{sp}}^* = 0.91$ cm^3/g, and $V^* = 15.2$ cm^3/mol.

Table IX
Miscibility Ranking of the Polymer Blends for Various Theories

polymer pair	expt	Flory theory[a]	Flory theory[b]	lattice theory[a]	lattice theory[b]	solubility parameter method
PS-PnBMA	1	3	3	1	5	5
PS-PMA	2	1	5	6	1	4
PS-PEA	3	5	1	5	3	2
PS-PnBA	4	2	4	2	4	3
PS-PMMA	5	4	6	3	2	1
PS-PDMS	6	6	2	4	6	6
probability		0.88	0.50	0.54	0.67	0.40

[a] Equation-of-state parameters from group contribution methods. [b] Equation-of-state parameters for PS from experimental values of V_{sp}, α, and γ and from group contribution methods for other polymers.

studied. This is in good agreement with the very low values obtained from the melt titration technique; however, we point out that the prediction of the lattice fluid theory is very sensitive to the assumed value of ζ, which is a measure of deviation of the interaction between the molecules of two components from that between the molecules of individual components. As ζ approaches unity the value of $\nu_{\min}$ approaches 1, decreasing the difference between ν_{calcd} and $\nu_{\min}$; this situation is more favorable for miscibility.

For the reasons given earlier, the characteristic parameters for polystyrene were calculated based on the experimental values of the V_{sp}, α, and γ. For other polymers the values calculated from group contribution methods were used. On the basis of the criteria for the lattice fluid theory, the results for the extent of miscibility are shown in Table VIII. The calculated values of ν have changed considerably compared to the values obtained from group contribution methods, indicating again the importance of using accurate experimental values of V_{sp}, α, and γ for calculation of equation-of-state parameters.

Correlation between the Experimental Results and the Theoretical Predictions. To compare the experimental results with the predictions of the Flory theory and the lattice fluid theory, we ranked the polymer blends in order of their miscibility. The extent of miscibility was determined on the basis of interaction energy density values for the experimental results and basic Flory–Huggins theory. This procedure was designed to correct for the small differences in molecular weight of the second component. For the Flory equation-of-state theory, the extent of miscibility was determined on the basis of the difference in characteristic temperatures, while for the lattice fluid theory it was based on the difference in ν_{calcd} and $\nu_{\min}$. Table IX shows the ranking of the polymer blends for different theories. At the bottom of the table the probability that there is a correlation between the experimental data and the theoretical predictions is also shown; the rank correlation test was used to establish this probability.[16,17] There is a good correlation between the experimental results and the Flory theory, as compared to the lattice fluid theory and the solubility parameter method. This suggests that the difference in the characteristic temperatures is a good basis for ranking the extent of miscibility in polymer blends. The lattice fluid theory does have the advantage, however, that it correctly predicts very low miscibility for all blends studied, with the reservations expressed above.

Conclusion

In summary, the following conclusions can be drawn from this work:

1. The usefulness of the melt titration technique for determining miscibility in polymer blends has been demonstrated by using a series of acrylic polymers in polystyrene.
2. Very low miscibility, of the order of 10^{-5} to 10^{-6} (weight fraction), was observed in blends of polyacrylates and polymethacrylates in polystyrene and poly(dimethylsiloxane) in polystyrene.[3,18]
3. The melt titration technique provides a new route for determining the interaction energy density for polymer–polymer systems.
4. "Equation-of-state" theories (Flory theory and lattice fluid theory) are very sensitive to the values of the specific volume, the thermal expansion coefficient, and the thermal pressure coefficient used for calculation of the characteristic parameters.
5. There is a good correlation between the experimental results and the predictions of the Flory theory; the difference in the characteristic temperatures is a good criterion for ranking the miscibility in polymer blends, although more data are needed to set the exact condition on ΔT^*.
6. The lattice fluid theory predicts unfavorable interaction in the blends of polystyrene with polyacrylates and polymethacrylates, which is in good agreement with the results from melt titration technique.
7. The solubility parameter theory is able to distinguish correctly between poly(dimethylsiloxane) and the acrylics as a group but is unable to rank correctly the miscibilty

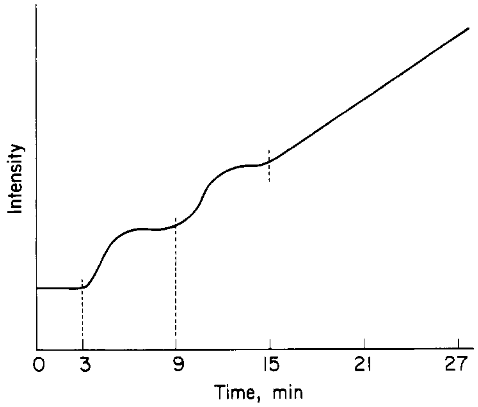

Figure 3. Intensity vs. time response for an immiscible blend.

of the acrylics in polystyrene.

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Appendix

In the melt titration technique the photocell unit records the intensity as a function of time. To obtain an intensity vs. concentration (or weight fraction) curve from the intensity vs. time data, the following procedure was adopted.

A typical intensity vs. time response for an immiscible blend is shown in Figure 3. The residence time in the extruder is 3 min, so the polymer film at the die is clear and intensity is constant. At the end of 3 min the second component, in the form of a second phase, is seen at the die and there is an increase in the scattered light or intensity. The concentration of the second component is approximately equal to the ratio of the flow rates of the two components. This concentration remains the same until the second component is recycled into the hopper of the extruder. At this time, the concentration at the inlet of the extruder is twice the ratio of the flow rates of the two components. The total residence time in the system for the polymer is 6 min, so there is an increase in the intensity after 9 min. It is observed that the intensity vs. time response becomes linear after about two residence times in the system. After this time the concentration of the second component is taken as an average. For quite miscible blends the curve is shifted to the right, and the miscibility limit is calculated from the shift in time.

The following equations are used to calculate the weight fraction of the second component (weight fraction (W) $\simeq$ concentration):

$$W = 0 \qquad 0 \leq t \leq 3 \tag{13}$$

$$W = M_2/M_1 \qquad 3 < t \leq 9 \tag{14}$$

$$W = 2M_2/M_1 \qquad 9 < t \leq 15 \tag{15}$$

$$W = (t-3)M_2/Z \qquad t > 15 \tag{16}$$

where t is the time corresponding to the location of the cloud point, M_2 and M_1 are the mass flow rates of components 2 and 1, respectively, and Z is the total quantity of component 1 in the system.

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Model Estimate for the Relaxation Time of the Counterion Distribution in the Radial Direction around a Rodlike, Charged Macromolecule

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ABSTRACT: A deviation of the equilibrium counterion distribution around a charged macromolecule, disappearing in a direction perpendicular to the chain, is investigated. To estimate the relaxation time τ of such a process, an approach, based on the Katchalsky cell model of polyelectrolyte solutions without salt, is developed and a steady-state counterion flow in the radial direction with respect to the macromolecular rod is considered. The results of a numerical analysis show for τ a remarkable independence of electrostatic interactions and values which lie close to those for free diffusion.

Introduction

Many properties of polyelectrolyte solutions reflect the strong interaction of the counterions with the macroions. The counterions concentrate in the vicinity of the polymer chain and stay there during a certain time, trapped in the strong electrostatic potential existing around the charged macromolecule. Lifson and Jackson[1] have studied the average time of association in relation to the problem of

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