Nylon 6I consists of alternating polymethylene and aromatic segments. Since similar segments are isolated from one another, they respond to mechanical and dielectric oscillations in a similar manner.

Registry No. PEEK, 31694-16-3; (bisphenol A)(isophthalic acid)(terephthalic acid) (copolymer), 26590-50-1; (bisphenol A)(isophthalic acid)(terephthalic acid) (SRU), 39281-59-9; (hexamethylenediamine)(isophthalic acid) (copolymer), 25722-07-0; (hexamethylenediamine)(isophthalic acid) (SRU), 25668-34-2.

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Thermodynamic Characterization of Miscible Blends from Very Similar Polymers by Inverse Gas Chromatography. The Poly(ethyl acrylate)–Poly(vinyl propionate) System

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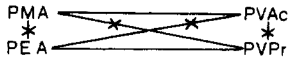
ABSTRACT: Thermodynamic interaction parameters for the interaction of poly(ethyl acrylate) (PEA) (component 2) and poly(vinyl propionate) (PVPr) (component 3) with themselves and separately with various probes (component 1), e.g., *n*-heptane, ethanol, benzene, toluene, methyl propionate (MP), acetone, ethyl acetate (EA), methyl ethyl ketone (MEK), ethyl propionate (EP), chloroform, 1,2-dichloroethane (EDC), and chlorobenzene, have been determined by the inverse gas chromatographic method (IGC) at four temperatures, 60, 80, 100, and 120 °C. The values of χ^*_H for the various polymer–probe interactions and their exchange interaction parameters (X_{1i}/s_1) as defined by the Flory–Prigogine theory have also been evaluated. These data have been analyzed to understand the nature of the interaction. $\chi^{*\prime}_{23}$ varies randomly with probes, assuming small positive or small negative values. The variation in sign is attributed to poor accuracy in the determination of a vanishingly small $\chi^{*\prime}_{23}$. The blends did not phase separate in the temperature region starting from the T_g's to the decomposition temperatures of the blends.

Introduction

Modern polymer solution theories[1-3] require that for a polymer–polymer system to be miscible in the absence of specific interactions not only should the exchange interaction energy be very close to zero but the differences in free volumes of the polymers must be very small also. In the absence of specific interactions, the exchange interaction energy would be positive. The exchange interaction energy or the X_{ij} parameter of the Flory–Prigogine theory may be written in terms of contact energies η_{ij} expressed per unit area of molecular contact[4]

$$X_{ij}/s_i = \tfrac{1}{2}(\eta_{ii} + \eta_{jj}) - \eta_{ij} \qquad (1)$$

where s_i is the molecular surface to volume ratio. The dispersion interaction η_{ij} may be approximated as the geometric mean of η_{ii} and η_{jj}, leading to a positive value for X_{ij} (endothermic mixing) which is unfavorable for solution. X_{ij} would be very small if the contact energies η_{ii} and η_{jj} are very close to each other, i.e., if the polymers are very similar. Recently, in our laboratory, several miscible polymer pairs have been discovered of which one component belongs to the polyacrylate family and the other to the poly(vinyl ester) family, viz., poly(methyl acrylate) (PMA) and poly(vinyl acetate) (PVAc),[5-7] poly(ethyl acrylate) (PEA) and poly(vinyl propionate) (PVPr),[8] and poly(phenyl acrylate) and poly(vinyl benzoate).[9] The degree of similarity required for miscibility could be anticipated from the following results. For example, six binary polymer pairs could be formed from the four polymers PMA, PEA, PVAc, and PVPr, as summarized in the following diagram



In the diagram the polymer pairs are linked by lines of which those not crossed turn out to be miscible. The components of the miscible pairs have one common feature; viz., their repeating units are isomeric esters differing only in the orientation of the COO group. The immiscible pairs differ only by one methylene group in their repeating units. The thermal expansion coefficients of the components of the miscible pairs are also very close to each other so that the equation-of-state effect contribution to ΔG_m remains very small.

Previously, the thermodynamic interaction for the PMA–PVAc system was studied in our laboratory by using the inverse gas chromatogrphic (IGC) method.[5] This paper is concerned with a similar study for the PEA–PVPr pair. The study also gave rise to the values of the thermodynamic interaction parameters of a number of probes with the neat polymers. These data are obtained at four temperatures, 60, 80, 100, and 120 °C, which allows the evaluation of χ^*_H used to interpret the polymer–probe interactions.

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Table I
GLC Column Parameters for the Stationary Phases

stationary phase	loading wt, %	wt of polym in column, g
PEA	10.40	0.9246
PVPr	10.11	0.9869
PEA:PVPr = 1:1 w/w	11.68	1.0323
PEA:PVPr = 3:1 w/w	10.72	0.9520
PEA:PVPr = 1:3 w/w	11.99	1.0670

Experimental Section

Materials. The PEA ($\bar{M}_n$ = 197 600) and PVPr ($\bar{M}_n$ = 49 000) used were whole polymers synthesized in the laboratory.[8] The solvents were of analytical reagent grade. They were purified by standard methods, dried over drierite, and distilled before use.

Preparation of Blends. The polymers in appropriate proportion were dissolved in acetone. They were then coprecipitated into petroleum ether and dried at 100 °C for 3 days in a vacuum oven.[5]

Inverse Gas Chromatography. The procedure described earlier[5] was followed except for the support loading for which the method of Klotz et al. was followed.[10] Acetone was the solvent used for making solutions of the polymer blends. Previous study showed that this solvent gave blend solutions which were homogeneous at all compositions.[11] Moreover, acetone-cast films of the blends of all compositions were clear. The coated support (Chromosorb W 60–80 mesh, acid washed, dimethyldichlorosilane treated) was dried in vacuum at 100 °C for 3 days. The percentage loading was determined by the calcination method (0.5 h at 300 °C and 2 h at 800 °C) with the usual blank correction.[12] Control experiments using known amounts of the two polymers mixed with the uncoated support gave analysis results accurate to 0.2%. The blend composition on the support was assumed to be the same as in the solutions used to coat the support. The details of the columns and the loadings are given in Table I.

The columns were purged at 130 °C overnight with a low flow rate of the carrier gas (argon). They were then left overnight for attainment of equilibrium at the experimental temperatures. When a measurement was performed, the flow rate was increased to the desired level by adjusting the inlet pressure of the column. A probe size of approximately 1 μL was used. For each probe the retention times obtained with three injections of the same probe size were averaged at each flow rate of carrier gas.

The basic parameter obtained in IGC experiments is the specific retention volume, V°_g, of the probes in milliliters per gram.[13] Under the experimental conditions used here V°_g for every polymer–probe combination varies to a small extent but randomly with flow rates. This small but random variation is attributable to experimental error and it may be concluded that V°_g is independent of flow rates. Hence the V°_g's were averaged rather than extrapolating them to zero flow rate. Each V°_g value subsequently used in evaluating interaction parameters thus represents an average of 12 experiments (three injections at each of four flow rates). The standard deviation in V°_g at the highest temperature, 120 °C, is within 2–3% and within 1–2% at the lower temperatures. The independence of V°_g on flow rate indicates that contribution of surface adsorption to retention time was negligible. Furthermore, the correlation coefficients of log V°_g versus $1/T$ linear least-square fit regressions were found to be very close to unity for each probe–column combination, which again indicates that equilibrium bulk sorption has prevailed in this work.[14]

Data Reduction. The polymer–solvent interaction parameters χ_{12} and χ_{13} were calculated by the relation[15]

$$\chi_{1i} = \ln \frac{273.15 R v_{i,\mathrm{sp}}}{P_1^0 V^\circ_{gi} V_1} - \frac{P_1^0}{RT}(B_{11} - V_1) - (1 - V_1/V_i) \qquad (2)$$

where the subscript 1 refers to the probe and i refers to either of the polymers, 2 or 3. V_1 and V_i are the molar volumes of the probe and the polymers, respectively, at the column temperature (T). P_1^0 and B_{11} are the vapor pressure and the second virial coefficient of the probe at the column temperature and R is the gas constant. The densities of the solvents at the column temperature were obtained from ref 16 and 17 as were the values of P_1^0. B_{11} values were obtained from O'Connel and Prausnitz.[18] The densities of the polymers at room temperature (32 °C) were measured by the buoyancy method[19] and the values are 1.112 and 1.106 g/mL for PEA and PVPr, respectively. Densities at column temperatures were obtained from these data with the knowledge of the thermal expansion coefficients (α), which in turn were determined in the following way. First, an estimate of α was obtained by using Bondi's correlation.[20] The values were then multiplied by a factor which is the ratio of the experimentally determined value reported for PVAc in the literature[21] to the theoretically calculated value obtained from Bondi's correlation.[20] The assumption was, of course, made that the ratio of the experimental value to the calculated value would be the same for the polymers under consideration as that for PVAc. The α values at 32 °C for PEA and PVPr ($\alpha_{\mathrm{PEA}} = 7.2 \times 10^{-4}$/°C and $\alpha_{\mathrm{PVPr}} = 7.4 \times 10^{-4}$/°C) so obtained were considered to be valid over the whole range of experimental temperatures.

Table II
Characteristic Parameters of the Solvents and Polymers at 25 °C

	v^*, mL/g	P^*, J/mL	T^*, K
PEA	0.7528[c]	502.60[d]	6355.40[c]
PVPr	0.7542[c]	501.391[d]	6242.27[c]
n-heptane	1.14[a]	382.27[a]	4840[a]
benzene	0.890[a]	572.91[a]	4780[a]
toluene	0.9180[b]	561.00[b]	5020[b]
methyl propionate	0.8455[e]	588.13[d]	4620[e]
acetone	1.02[a]	289.93[a]	5070[a]
methyl ethyl ketone	0.958[a]	568.94[a]	4590[a]
ethyl acetate	0.897[a]	485.53[a]	4820[a]
ethyl propionate	0.8624[e]	566.13[d]	4530[e]
chloroform	0.5460[a]	318.72[a]	5280[a]
1,2-dichloroethane	0.6560[a]	495.46[a]	5440[a]
ethanol	0.9955[b]	545[b]	4840[b]
chlorobenzene	0.734[a]	586.81[a]	5550[a]

[a] From ref 52. [b] From ref 15. [c] Calculated by using the Flory–Prigogine theory with computed α values at 32 °C. [d] P^* of the two polymers PEA and PVPr and of the two probes methyl propionate and ethyl propionate at 25 °C calculated by using the relation $P^* = \delta^2\tilde{V}^2$; δ's, the solubility parameters were taken from the literature[53] for ethyl propionate and methyl propionate whereas for the two polymers these parameters were determined from IGC χ_{1i}'s following ref 30. [e] Calculated by using the Flory–Prigogine theory; α values were obtained from literature.[17]

The polymer–polymer interaction parameter normalized to the size of the probe molecule, $\chi'_{23} = \chi_{23} V_1/V_2$ was obtained by using the relation[22,23]

$$\chi'_{23} = \frac{\chi_{23} V_1}{V_2} = \frac{1}{\Phi_2 \Phi_3} \ln \left[\frac{(v_{2\mathrm{sp}})^{\Phi_2} (v_{3\mathrm{sp}})^{\Phi_3} V^\circ_{g23}}{(w_2 v_{2\mathrm{sp}} + w_3 v_{3\mathrm{sp}})(V^\circ_{g2})^{\Phi_2} (V^\circ_{g3})^{\Phi_3}} \right] \qquad (3)$$

where the Φ_i, w_i, and $v_{i\mathrm{sp}}$ are the volume fraction, weight fraction, and specific volume, respectively. V°_{g2}, V°_{g3}, and V°_{g23} refer to the specific retention volumes of a probe with polymers 2 and 3 and the blend 23 as the stationary phases.

The parameters with asterisks were obtained by replacing in eq 2 and 3 the specific volumes by core specific volumes and the volume fractions by segment fractions Φ^*_i defined as

$$\Phi^*_i = w_i v_i{}^*{}_{\mathrm{sp}} / \sum w_i v_i{}^*{}_{\mathrm{sp}} \qquad (4)$$

where $v_i{}^*{}_{\mathrm{sp}}$ are reduction parameters per gram for volume, i.e., the specific core volumes.[15]

The exchange interaction parameter (X_{1i}) as defined by the Flory–Prigogine theory was calculated from a knowledge of χ^*_{1i} and the reduction parameters for pressure (P^*), volume (V^*), and temperature (T^*) of the components (listed in Table II) by using the explicit form of the relation between χ^*_{ij} and X_{ij} from Patterson and Delmas[24,25] as given below. For a binary mixture with component 1 at infinite dilution as in IGC

$$RT\chi^*_{12} = \frac{V^*_1 X_{12}}{\tilde{V}_2} + P^*_1 V^*_1 \left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}_2} + 3\tilde{T}_1 \ln \frac{\tilde{V}_1{}^{1/3} - 1}{\tilde{V}_2{}^{1/3} - 1} \right] \qquad (5)$$

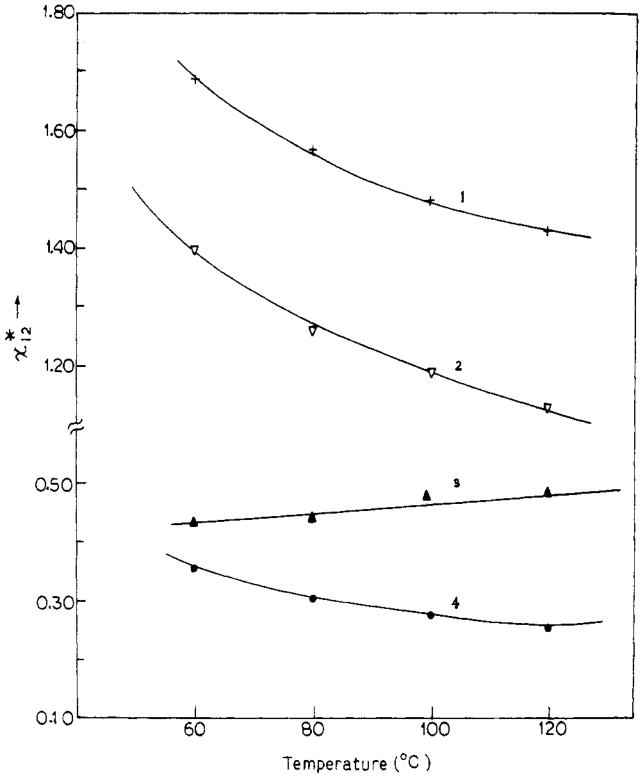

Figure 1. Variation of χ^*_{12} with temperature (curves 1–4 are for the probes *n*-heptane, ethanol, ethyl acetate, and methyl ethyl ketone, respectively).

where the first term is the interactional term and the second is the free volume term, P^*_1 and V^*_1 are the pressure and volume reduction parameters, and

$$\tilde{V} = V/V^* \tag{6}$$

$$\tilde{T} = T/T^* = (\tilde{V}^{1/3} - 1)\tilde{V}^{-4/3} \tag{7}$$

$$\tilde{V}^{1/3} = 1 + \frac{\alpha T}{3(1 + \alpha T)} \tag{8}$$

Similarly for a ternary system with a mixed stationary phase

$$RT\chi^*_{1(23)} = \frac{s_1 V^*_1}{\tilde{V}_0}\left[\left(\frac{X_{12}}{s_1}\right)\theta_2 + \left(\frac{X_{13}}{s_1}\right)\theta_3 - \left(\frac{X_{23}}{s_2}\right)\theta_2\theta_3\right] + P^*_1 V^*_1\left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}_0} + 3\tilde{T}_1 \ln \frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}_0^{1/3} - 1}\right] \tag{9}$$

where the first term is the interactional term and the second is the free volume term, $\tilde{V}_0$ is the reduced volume of the mixed stationary phase, s_i is the molecular surface to volume ratio, and θ_i is the surface fraction defined by

$$\theta_i = w_i v_i^* s_i / \sum w_i v_i^* s_i \tag{10}$$

Calculation of X_{ij} parameters using eq 5–10 was done by an iteration procedure following Su,[26] an outline of which is given in ref 27. The X_{ij} terms like their χ_{ij} counterparts are not symmetrical, being proportional to s_i. On the other hand, X_{ij}/s_i like χ_{ij}/V_i is independent of the molecular size. The sources of the various data needed for the above-mentioned calculations are listed in Table II. The segmental surface area per unit volume was estimated from the correlation of Bondi[20] and literature data.[28,29] V^* and T^* of the two polymers PEA and PVPr were obtained by using their respective α values (mentioned earlier) along with the relations (6)–(8). P^* values were calculated by using the relation $P^* = \delta^2\tilde{V}^2$, where δ, the solubility parameters of the polymers, was obtained at 25 °C from the IGC χ_{1i}'s following Guillet and Dipaola-Baranyi.[30] The χ_{1i} at 25 °C was obtained by extrapolation of the data obtained at 60, 80, 100, and 120 °C. δ values so calculated tallied well with those calculated theoretically by Small's method[31] and Hoy's group contribution data.[32]

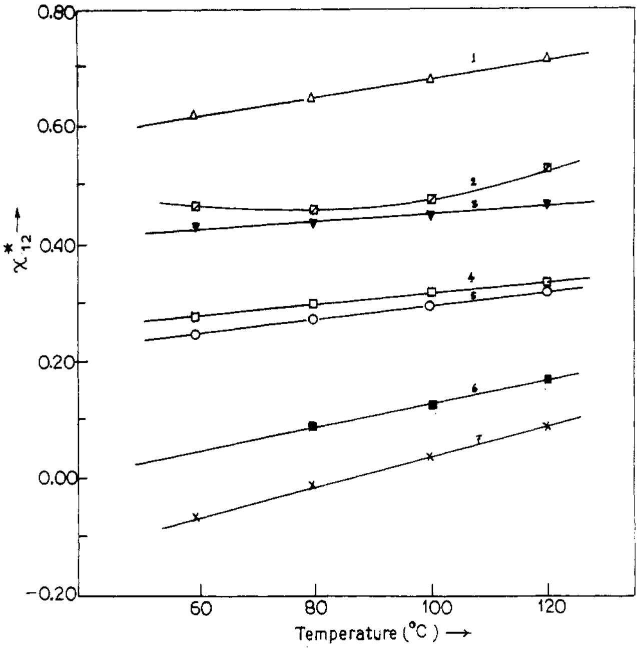

Figure 2. Variation of χ^*_{12} with temperature (curves 1–7 are for the probes acetone, ethyl propionate, methyl propionate, toluene, benzene, chlorobenzene, and 1,2-dichloroethane, respectively).

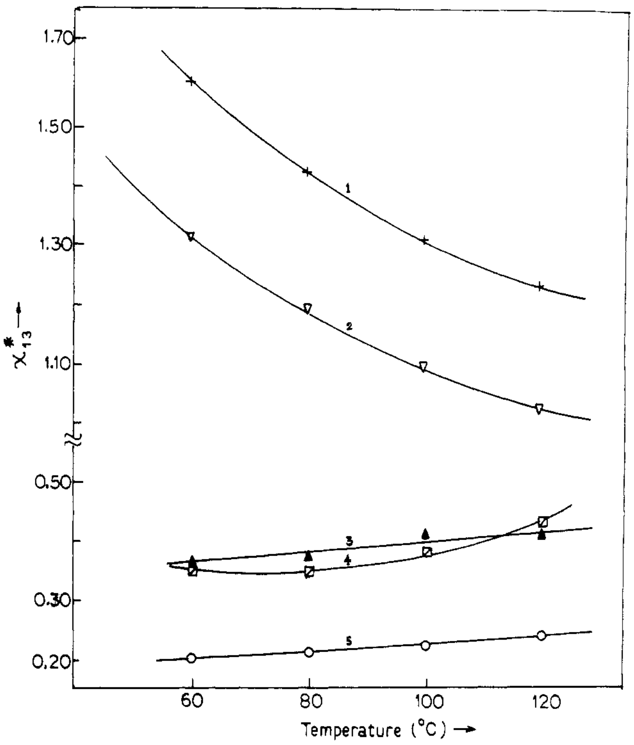

Figure 3. Variation of χ^*_{13} with temperature (curves 1–5 are for the probes *n*-heptane, ethanol, ethyl acetate, ethyl propionate, and benzene, respectively).

Results and Discussion

Polymer–Probe Interaction. Tables III and IV give the values of the thermodynamic parameters χ_{1i}, χ^*_{1i}, and X_{1i}/s_1 for the interaction of the probes (component 1) with the polymers PEA and PVPr (components 2 and 3, respectively) at 60, 80, 100, and 120 °C. The parameters with asterisks are the appropriate noncombinatorial free energy of mixing parameters as defined in the modern solution theories, which find increasingly greater usage. The temperature variation of χ^*_{1i} for most of the probes has been shown graphically in Figures 1–4. The figures reveal that the pattern for the variation of the interaction parameters

Table III
Thermodynamic Quantities of Interaction for the PEA (2)–Probe (1) System[a]

	60 °C			80 °C			100 °C			120 °C		
probe	χ_{12}	χ^*_{12}	$10^8 \times X_{12}/s_1$[b]	χ_{12}	χ^*_{12}	$10^8 \times X_{12}/s_1$[b]	χ_{12}	χ^*_{12}	$10^8 \times X_{12}/s_1$[b]	χ_{12}	χ^*_{12}	$10^8 \times X_{12}/s_1$[b]
n-heptane	1.58	1.69 ± 0.01	46.0	1.45	1.57 ± 0.006	45.6	1.35	1.48 ± 0.02	45.9	1.28	1.43 ± 0.02	47.2
benzene	0.15	0.25 ± 0.004	5.3	0.16	0.27 ± 0.02	6.77	0.17	0.29 ± 0.02	8.12	0.18	0.32 ± 0.02	10.1
toluene	0.20	0.28 ± 0.006	7.2	0.21	0.30 ± 0.01	3.6	0.22	0.32 ± 0.004	10.0	0.23	0.33 ± 0.01	11.4
methyl propionate	0.32	0.43 ± 0.003	9.5	0.31	0.43 ± 0.007	10.5	0.30	0.45 ± 0.007	11.7	0.30	0.47 ± 0.02	13.1
acetone	0.55	0.62 ± 0.02	31.6	0.55	0.65 ± 0.07	35.6	0.56	0.68 ± 0.03	40.1	0.57	0.72 ± 0.01	45.4
methyl ethyl ketone	0.24	0.35 ± 0.005	7.6	0.17	0.30 ± 0.01	5.3	0.12	0.27 ± 0.016	3.5	0.09	0.25 ± 0.007	2.5
ethyl acetate	0.36	0.43 ± 0.01	11.6	0.35	0.44 ± 0.02	12.9	0.37	0.48 ± 0.016	15.4	0.35	0.48 ± 0.02	16.2
ethyl propionate	0.34	0.46 ± 0.007	7.5	0.32	0.46 ± 0.006	7.4	0.32	0.47 ± 0.02	8.2	0.36	0.53 ± 0.01	10.7
chloroform	–0.64	–0.49 ± 0.008	–28.8	–0.56	–0.39 ± 0.008	–24.0	–0.47	–0.29 ± 0.02	–19.8	–0.39	–0.19 ± 0.03	–14.9
1,2-dichloroethane	–0.11	–0.06 ± 0.004	–4.8	–0.07	–0.01 ± 0.01	–2.2	–0.03	0.04 ± 0.02	0.45	0.00	0.09 ± 0.01	3.71
chlorobenzene				0.03	0.09 ± 0.005	2.6	0.06	0.12 ± 0.006	4.31	0.10	0.17 ± 0.02	7.04
ethanol	1.27	1.36 ± 0.006	95.1	1.16	1.26 ± 0.03	95.6	1.07	1.19 ± 0.06	97.0	1.00	1.13 ± 0.01	99.4

[a] The standard deviations shown for the parameters with asterisks are calculated by taking into consideration only the error in V°_g values and not in other values such as P°_1, B_{11}, etc. (see eq 2). [b] In unit of J/cm^2.

Table IV
Thermodynamic Quantities of Interaction for PVPr (3)–Probe (1) Systems

	60 °C			80 °C			100 °C			120 °C		
probe	χ_{13}	χ^*_{13}	$10^8 \times X_{13}/s_1$[a]	χ_{13}	χ^*_{13}	$10^8 \times X_{13}/s_1$[a]	χ_{13}	χ^*_{13}	$10^8 \times X_{13}/s_1$[a]	χ_{13}	χ^*_{13}	$10^8 \times X_{13}/s_1$[a]
n-heptane	1.48	1.57 ± 0.02	43.6	1.32	1.43 ± 0.002	42.0	1.19	1.32 ± 0.01	41.1	1.09	1.24 ± 0.03	41.0
benzene	0.10	0.20 ± 0.01	3.6	0.11	0.21 ± 0.006	4.4	0.11	0.22 ± 0.009	5.18	0.11	0.24 ± 0.03	6.5
toluene	0.12	0.19 ± 0.004	4.2	0.13	0.22 ± 0.008	5.6	0.15	0.24 ± 0.006	7.3	0.17	0.27 ± 0.012	8.8
methyl propionate	0.28	0.39 ± 0.01	8.3	0.25	0.38 ± 0.003	8.6	0.24	0.38 ± 0.003	9.11	0.23	0.39 ± 0.016	9.8
acetone	0.53	0.70 ± 0.003	32.4	0.50	0.59 ± 0.003	32.7	0.48	0.59 ± 0.017	35.2	0.47	0.60 ± 0.03	38.5
methyl ethyl ketone	0.20	0.31 ± 0.006	6.6	0.12	0.25 ± 0.016	3.6	0.06	0.20 ± 0.018	1.1	0.03	0.18 ± 0.024	–0.5
ethyl acetate	0.30	0.36 ± 0.007	9.7	0.29	0.37 ± 0.003	10.8	0.31	0.41 ± 0.012	13.1	0.29	0.41 ± 0.037	13.8
ethyl propionate	0.24	0.36 ± 0.01	4.5	0.23	0.35 ± 0.007	4.4	0.23	0.38 ± 0.013	5.2	0.27	0.43 ± 0.014	7.6
chloroform	–0.69	–0.55 ± 0.007	–30.8	–0.60	–0.44 ± 0.004	–26.3	–0.50	–0.32 ± 0.007	–21.4	–0.40	–0.21 ± 0.014	–15.7
1,2-dichloroethane	–0.14	–0.10 ± 0.007	–6.3	–0.09	–0.04 ± 0.006	–3.4	–0.05	0.02 ± 0.006	–0.4	0.00	0.07 ± 0.010	3.2
chlorobenzene				–0.06	–0.01 ± 0.003	–1.7	–0.03	0.03 ± 0.006	0.28	0.02	0.09 ± 0.006	3.3
ethanol	1.23	1.32 ± 0.002	93.8	1.10	1.20 ± 0.005	92.6	0.99	1.10 ± 0.006	92.2	0.90	1.03 ± 0.024	92.7

[a] In unit of J/cm^2.

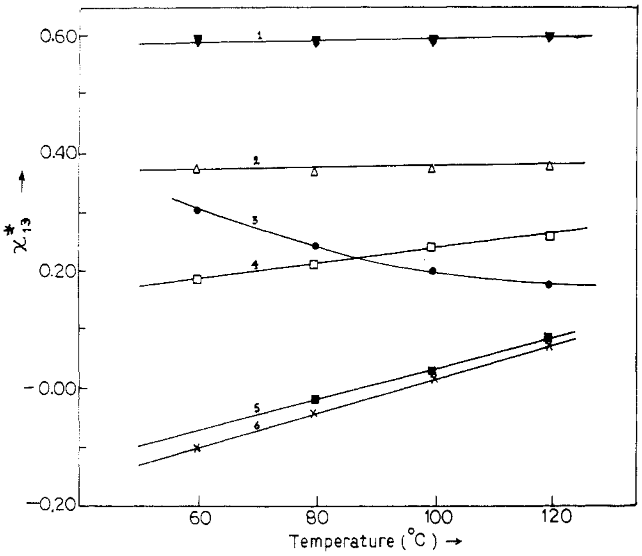

Figure 4. Variation of χ^*_{13} with temperature (curves 1–6 are for the probes methyl propionate, acetone, methyl ethyl ketone, toluene, chlorobenzene, and 1,2-dichloroethane, respectively).

with temperature is not similar for all probes. For example, the parameters with asterisks for PEA with chlorobenzene, EDC, chloroform, acetone, benzene, toluene, ethyl acetate (EA), methyl propionate (MP), and ethyl propionate (EP) increase linearly with temperature, whereas with n-heptane, ethanol, and MEK not only do the values decrease with temperature, the decrease is nonlinear too. From the slopes of the plots, the heats of dilution at any temperature between 60 and 120 °C as $\Phi_2 \rightarrow 1$ could be evaluated since

$$\Delta\bar{H}_1^\infty = RT\chi^*_H\Phi_2^2 \cong RT\chi^*_H \quad \text{(under IGC condition)} \qquad (11)$$

$$\chi^*_H = -T(d\chi^*/dT) \qquad (12)$$

The values of χ^*_H so obtained at the four temperatures are given in Tables V and VI. It is evident from these data that the heat of dilution is of negative sign (exothermic mixing) for all the probes except n-heptane, ethanol, and methyl ethyl ketone. The exothermic solutions do not necessarily indicate that specific interactions exist for all probe–polymer combinations. All or part of the heat evolved may originate from the differences in free volumes of the components of the mixture.[33,34] However, information about the existence of specific interactions is available from the values of X_{1i}/s_1, which is related to the change in energy for the formation of 1,2-contacts from 1,1- and 2,2-contact pairs. If specific interactions do exist between 1 and 2, X_{12} should be negative. But it should be noted also that the X_{ij} parameter as calculated from eq 5 using the IGC determined χ^*_{ij} is essentially a contact free energy parameter and not the contact energy parameter of the Flory–Prigogine theory. Thus X_{ij} may turn out to be positive even when specific interactions do exist because of the entropic contribution arising out of order created by specific interactions.[35] A negative value of X_{ij}, however, ensures the existence of specific interactions.

On the basis of these considerations the chlorinated solvents chloroform, EDC, and to a lesser extent chlorobenzene are found to interact specifically with PEA and PVPr. The nature of the specific interactions involving esters and chlorinated hydrocarbons has been discussed earlier.[5,36] With the aromatic hydrocarbon probes, viz., benzene and toluene, the exchange interaction parameter X_{1i}/s_1 is positive but small, indicating that there exist some specific interactions between these probes and PEA or PVPr. This may involve a donor–acceptor type of interaction: the aromatic nucleus with its π-electrons acting as a donor and the $>C^{\delta+}{=}O^{\delta-}$ group with its slightly positive charged carbon acting as the acceptor.[37] Evidence of such specific interactions between aromatic hydrocarbons and ketones, esters, and amides abound in the literature.[37-39] For many compatible polymer pairs of which one contains an aromatic ring and the other C=O or CO(=O) groups, the compatibility was explained to originate from such specific interactions.[40]

Table V
Values of χ^*_H for Probe (1)–PEA (2) Interaction

probe	χ^*_H 60 °C	80 °C	100 °C	120 °C
n-heptane	2.22	1.74	1.18	0.55
benzene	−0.41	−0.43	−0.46	−0.48
toluene	−0.32	−0.34	−0.36	−0.38
methyl propionate	−0.23	−0.24	−0.26	−0.27
acetone	−0.53	−0.56	−0.60	−0.63
methyl ethyl ketone	0.78	0.56	0.31	0.02
ethyl acetate	−0.31	−0.33	−0.35	−0.37
ethyl propionate	0.22	−0.25	−0.80	−1.38
chloroform	−1.66	−1.76	−1.86	−1.96
1,2-dichloroethane	−0.86	−0.92	−0.97	−1.02
chlorobenzene		−0.71	−0.75	−0.79
ethanol	1.73	1.53	1.28	0.99

Table VI
Values of χ^*_H for Probe (1)–PVPr (3) Interaction

probe	χ^*_H 60 °C	80 °C	100 °C	120 °C
n-heptane	2.61	2.09	1.55	0.94
benzene	−0.27	−0.28	−0.30	−0.32
toluene	−0.43	−0.46	−0.48	−0.51
methyl propionate	−0.04	−0.04	−0.04	−0.04
acetone	−0.05	−0.05	−0.05	−0.06
methyl ethyl ketone	1.11	0.83	0.50	0.13
ethyl acetate	−0.03	−0.03	−0.03	−0.04
ethyl propionate	0.34	−0.05	−0.60	−1.21
chloroform	−1.90	−2.01	−2.13	−2.24
1,2-dichloroethane	−0.97	−1.03	−1.09	−1.15
chlorobenzene		−0.93	−0.98	−1.03
ethanol	2.28	1.74	1.18	0.55

With the ester probes, MP, EA, and EP, the X_{1i}/s_1 values are positive, the lowest value (closer to the value for aromatic solvents) being obtained with EP. However, EP being an ester, there is no scope for specific interactions between it and the polymers which also contain ester functions. The low value of X_{1i}/s_1 for EP–PEA or EP–PVPr interaction therefore may be due to the dispersion interaction, being itself very small for these systems. In fact, EP being the hydrogenated monomer for both PEA and PVPr should yield a vanishingly small X_{1i}/s_1 value. The small nonzero value obtained may originate from an inaccurate assessment of the equation-of-state contribution to χ by the theory.[15,41]

The large difference in X_{1i}/s_1 values between the two ketonic probes acetone and MEK may also be instructive. The value for MEK is very much lower than for acetone. The small dispersion interaction with MEK may be due to its $[CH_2 + CH_3]/[CO]$ ratio becoming closer to the $[CH_2 + CH_3]/[COO]$ ratios in the repeating units of the polymers. Unlike acetone, MEK gives an endothermic solution in the temperature region studied, as the χ^*_H values (in Tables V and VI) would indicate. The exotherm in the case of acetone arises, in all probability, out of the differences in the free volume between the polymer and the solvent. The trend in the variation of χ^*_{1i} with temperature for MEK probe as shown in Figures 1 and 4 indicates that at temperatures somewhat higher than 120 °C, exothermic mixing would result with this probe too; i.e., the

Table VII
Thermodynamic Quantities of Interaction for PEA:PVPr = 1:1 w/w Mixture

	60 °C		80 °C		100 °C		120 °C	
probe	χ'_{23}	$\chi^{*\prime}_{23}$	χ'_{23}	$\chi^{*\prime}_{23}$	χ'_{23}	$\chi^{*\prime}_{23}$	χ'_{23}	$\chi^{*\prime}_{23}$
n-heptane	0.12	0.12 ± 0.09	0.06	0.06 ± 0.04	0.01	0.01 ± 0.10	−0.04	−0.04 ± 0.10
benzene	0.00	0.00 ± 0.03	0.02	0.02 ± 0.05	0.04	0.04 ± 0.05	0.05	0.05 ± 0.09
toluene	0.04	0.04 ± 0.02	−0.01	−0.01 ± 0.04	0.02	0.02 ± 0.03	0.05	0.06 ± 0.06
methyl propionate	−0.01	−0.03 ± 0.03	0.01	−0.01 ± 0.05	0.02	0.01 ± 0.09	0.04	0.03 ± 0.10
acetone	0.04	0.04 ± 0.07	0.00	0.00 ± 0.16	−0.03	−0.03 ± 0.10	−0.07	−0.07 ± 0.08
methyl ethyl ketone	−0.05	−0.05 ± 0.04	0.00	0.01 ± 0.06	0.05	0.05 ± 0.07	0.10	0.10 ± 0.10
ethyl acetate	−0.03	−0.03 ± 0.04	0.00	0.00 ± 0.07	0.04	0.04 ± 0.04	0.07	0.07 ± 0.09
ethyl propionate	−0.07	−0.07 ± 0.03	−0.01	−0.01 ± 0.03	0.03	0.03 ± 0.06	0.08	0.08 ± 0.08
chloroform	−0.01	−0.01 ± 0.03	0.04	0.04 ± 0.05	0.09	0.09 ± 0.06	0.14	0.14 ± 0.11
1,2-dichloroethane	−0.05	0.05 ± 0.03	0.05	0.05 ± 0.05	0.06	0.06 ± 0.08	0.11	0.11 ± 0.09
chlorobenzene			−0.08	−0.08 ± 0.06	−0.04	−0.04 ± 0.05	−0.01	−0.01 ± 0.04
ethanol	−0.07	−0.07 ± 0.03	0.03	0.03 ± 0.07	0.11	0.11 ± 0.14	0.20	0.20 ± 0.11

free volume contribution with MEK becomes important at higher temperatures.

The difference in interaction parameters χ^*_{12} and χ^*_{13} is small, although a variety of probes differing in polarity, hydrogen-bonding capability, and electron-donating or -accepting ability were used. This is expected since the two polymers are very similar in both physical and chemical properties.

Polymer–Polymer Interaction. The value of the polymer–polymer interaction parameter provides information about the nature of the interaction between the polymers. The 2,3-interaction parameter normalized to the size of the probe (χ'_{23}) allows a comparison of the interchange free energy for 2,3-segments with those for 1,2- and 1,3-segments on the same scale. However, better insight into the nature of the interaction could be obtained from the $\chi^{*\prime}_{23}$ values, which find increasingly greater usage. Table VII gives the values of χ'_{23} and $\chi^{*\prime}_{23}$ with their standard deviations for the 1:1 blend at 60, 80, 100, and 120 °C. The central values were obtained by using the mean V°_g values in eq 3. It is clear from the results that the error is very large so that a vanishingly small $\chi^{*\prime}_{23}$ assumes either small positive or small negative values randomly with variation in probe. The inaccuracy in IGC determined $\chi^{*\prime}_{23}$ values has been emphasized by almost all workers in this field.[15,42–44]

Similar results were obtained at other blend compositions, 1:3 and 3:1 w/w. Thus, the results may suggest that $\chi^{*\prime}_{23}$ has a value close to zero. Previously Su and Patterson[45] working with the polystyrene and poly(vinyl methyl ether) system found $\chi^{*\prime}_{23}$ values varying randomly with probes between +0.1 and −0.1. Similar results were obtained also by Nandi et al.[5] Considering the smallness of the values and the error in IGC, these workers concluded that the actual value was close to zero. The error also deters us from predicting the effect of temperature on miscibility from the $\chi^{*\prime}_{23}$ data at the various temperatures. The variation of $\chi^{*\prime}_{23}$ with probe falls within the error limit. In view of the large errors, no attempt was made to calculate the exchange interaction parameter X_{23}.

The critical value of χ'_{23} with the present blend system as calculated from the Flory–Huggins theory is 0.0025.[46] For the blend to be miscible in the absence of specific interactions $0.0025 > \chi'_{23} > 0$. It is quite expected that IGC with its inaccuracy may yield values that are opposite in sign for the χ'_{23} parameter (vide Table VII) whose theoretical value is such a small positive number. A straightforward approach of ascertaining miscibility would be to compare the V°_{g23} value with that theoretically predicted. For a phase-separated blend V°_{g23} should be equal to the arithmatic mean of V°_{g2} and V°_{g3},[22,23] i.e.

$$V^\circ_{g23} = w_2 V^\circ_{g2} + w_3 V^\circ_{g3} \qquad (13)$$

where w_i is the weight fraction. On the other hand, Ward et al.[22] pointed out that for a miscible blend with $\chi'_{23} = 0$, V°_{g23} becomes equal to the volume fraction weighted geometric mean of V°_{g2} and V°_{g3}, i.e.

$$V^\circ_{g23} = (V^\circ_{g2})^{\Phi_2}(V^\circ_{g3})^{\Phi_3} \qquad (14)$$

which follows from eq 3. In the present case the two equations yield V°_{g23} values which differ from each other by less than 0.1% due to the closeness of V°_{g2} and V°_{g3}. Hence with the 2% error in V°_g, this diagnostic test of ascertaining miscibility also proved ineffective.[27] The situation is quite different from that obtained with blend systems which owe their miscibility to strong specific interactions where χ'_{23} may assume large negative values. With such blend systems IGC has been used successfully to ascertain homogeneous mixing.[23,36,42,47–49] The effectiveness of IGC in ascertaining miscibility in blend systems under various situations has been discussed in detail in our recent review.[27]

However, better information about the miscibility may be obtained from the X_{12} and X_{13} values obtained with ethyl propionate probe. Ethyl propionate, being the hydrogenated monomer for both the polymers, may be approximated to represent a segment of both the polymers. Had it been so, the X_{12} and X_{13} values should be zero with this probe. However, an examination of the data given in Tables III and IV shows that barring the chlorinated hydrocarbon probes with which the polymers interact strongly and specifically, the X_{1i}/s_1 values for EP are among the lowest though not equal to the expected value of zero. The nonzero X_{1i}/s_1 values may be attributed, following Patterson et al., to the inaccurate assessment of the free volume contribution in χ^*_{1i}.[15,41] This result suggests that the exchange interaction energy (X_{23}) between the segments of the polymers must be very small.

Search for Critical Solution Temperatures. Modern solution theories predict the existence of both an UCST and a LCST for blend systems which are associated with a positive heat of mixing.[50] Since the heat of mixing for the present blend system is expected to be positive but vanishingly small, it would be of interest to look for these critical solution temperatures. To this end, the temperature of the blend films was increased from the T_g's of the blends to the decomposition temperatures (about 300 °C). The films were found to remain clear. The possibility of demixing of the blends at various temperatures was also checked by using differential scanning calorimetry by annealing the blends at several temperatures below the decomposition temperatures (starting from 250 °C) for 10 min, followed by quenching and subsequent scanning.[51] A single T_g for each blend was always obtained, proving thereby that no demixing occurs in the temperature region studied. Thus, it should be inferred that the UCST (if it exists) must occur at temperatures below the T_g and the LCST above the decomposition temperatures of the blends and hence they both remain experimentally inaccessible.

Registry No. PEA, 9003-32-1; PVPR, 25035-84-1; heptane, 142-82-5; benzene, 71-43-2; toluene, 108-88-3; methyl propionate, 554-12-1; acetone, 67-64-1; methyl ethyl ketone, 78-93-3; ethyl acetate, 141-78-6; ethyl propionate, 105-37-3; chloroform, 67-66-3; 1,2-dichloroethane, 107-06-2; chlorobenzene, 108-90-7; ethanol, 64-17-5.

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Probe Diffusion in Solutions of Low Molecular Weight Polyelectrolytes

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ABSTRACT: Probe diffusion coefficients (D) of polystyrene spheres ($0.019\ \mu\mathrm{m} \le R \le 0.38\ \mu\mathrm{m}$) were observed in solutions of neutralized and nonneutralized poly(acrylic acid)s ($5\ \mathrm{kDa} \le M_w \le 470\ \mathrm{kDa}$). Correlations were obtained between D and the probe radius, the background polymer's molecular weight, concentration (c), and degree of neutralization, and the solution ionic strength (I) and viscosity (η). D generally follows a stretched exponential $D = D_0 \exp(-\alpha c^\nu I^\beta)$. At low concentrations of nonneutralized polymer, D instead follows $D \sim 1 - kc^{1/2}$. Relations between M, α, ν, and γ are presented.

Introduction

The diffusion of polymer chains and globular probe species through polymer solutions is a complex phenomenon affording substantial information about polymer dynamics. Besides its current theoretical interest, polymer–probe interdiffusion occurs under many physical circumstances. For example, cell cytoplasm is a concentrated (~25 wt % solids) solution of aqueous polymers, almost all of which are polyelectrolytes. The inactive transport of proteins, metabolites, and other materials within the cell provides a natural example of probe diffusion in a concentrated polyelectrolyte system.

An effective approach for studying polymer diffusion is

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