Miscibility of Poly(methyl acrylate) and Poly(vinyl acetate): Incompatibility in Solution and Thermodynamic Characterization by Inverse Gas Chromatography

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ABSTRACT: The miscibility of poly(methyl acrylate) and poly(vinyl acetate) has been studied. Glass transition temperature measurements indicated that the two polymers are miscible at all compositions. The incompatibility of the two polymers in solution with certain solvents (component 1) has been examined in light of the $|\Delta\chi|$ theory of Patterson et al. Determination of χ_{1i} values by the viscometric method using dilute polymer solutions showed that $|\Delta\chi|$ values are too small to enable the theory to predict a phase separation. On the other hand, $|\Delta\chi|$ values large enough to effect a phase separation obtain when solutions infinitely dilute with respect to the solvent molecules were used for the determination of χ_{1i} values by the inverse gas chromatographic (IGC) method. This calls for taking into account in the theory the composition dependence of χ_{1i}. Measurement of thermodynamic interaction parameters by IGC further revealed that miscibility in the binary polymer–polymer mixture is not caused by specific interactions and that there is a lack of "complementary dissimilarity" between the molecules of the two polymers. The LCST's of the polymer blends are probably situated at temperatures much higher than the degradation temperatures of the polymers and could not be determined. Also, no strong dependence of miscibility on molecular weights of the polymers was observed. These results are in agreement with the view that the exchange interaction energy is positive but small, as must be the free volume contribution to the free energy of mixing.

Introduction

Miscibility in polymer–polymer systems generally requires the existence of a strong specific interaction between the polymers. This situation arises because the combinatorial entropy of mixing for a given volume of solutions is exceedingly small for polymer–polymer mixtures in comparison to small-molecule mixtures due to the small number of molecules involved in the former systems. Consequently, a very small positive heat of mixing (which is usual in the absence of specific interactions) could result in immiscibility for the polymer–polymer systems. The above explanation based on the Flory–Huggins theory of polymer solutions is not, however, complete inasmuch as the rigid lattice model used in the theory leaves no scope for a volume change on mixing and thus does not take into account the properties of the components. Modern theories using the corresponding states model or the equation-of-state model aim at remedying this situation.[1-3] In brief, according to the modern theories the Gibbs free energy of mixing consists of three contributions originating from (1) the combinatorial entropy of mixing, (ii) the exchange interaction energy, and (iii) the equation-of-state or free volume difference between the components. The last, in general, is unfavorable for mixing and becomes more so with increasing temperature. This extra unfavorable factor makes it all the more imperative that a specific interaction such as hydrogen bonding, donor–acceptor interaction, charge transfer, etc., resulting in a negative exchange interaction contribution to the free energy of mixing, be a prerequisite for polymer–polymer miscibility. However, if the free volume contribution is very small, which is the case for polymers with very similar *P–V–T* properties, a small positive exchange interaction may still allow the net free energy of mixing to be negative. Of course, it should be noted that a negative free energy of mixing is a necessary but not sufficient requirement for complete miscibility. McMaster showed that miscible blends of very similar polymer molecules having a very small positive exchange interaction energy can exhibit both UCST and LCST behavior.[4] A few miscible polymer pairs are known where there are supposedly no specific interactions. Some examples are polystyrene–poly(*o*-chlorostyrene) and polystyrene–poly(α-methylstyrene), for each of which a strong molecular weight dependence of miscibility was noted.[5,6] It is expected that the pair poly(methyl acrylate) (PMA, component 2) + poly(vinyl acetate) (PVA, component 3) would also belong to this class. These two polymers are so similar in chemical constitution that one would expect only a very small positive exchange interaction contribution in the free energy of mixing. Their *P–V–T* properties are also not very different (as will follow from subsequent discussions) so that the unfavorable contribution to the free energy of mixing due to the free volume term would also be small. These two polymers are, therefore, likely to be miscible. However, there is ambiguity in the literature about their miscibility. Their well-mixed blends were found to exhibit single T_g's, indicating miscibility.[7] But they were found to be incompatible in certain solvents, e.g., toluene.[8] They were, therefore, considered to be immiscible also in the absence of solvent. However, according to the recent work of Patterson et al., polymer incompatibility in solution does not necessarily imply incompatibility in the absence of solvent.[9] According to their analysis a compatible polymer pair may appear incompatible in solution if the solvent in question interacts very differently with the two polymers. This effect, called the $|\Delta\chi|$ effect, was very successful in explaining incompatbility in some solutions of compatible polymer pairs.[9,10] However, as has been mentioned above, the polymers in the present case are so similar that one does not expect a significant $|\Delta\chi|$ effect with any solvent. One of the objectives of this paper is therefore to examine the validity of the $|\Delta\chi|$ effect for explaining polymer incompatibility in solution. A further objective is to study the thermodynamic interaction between the polymer molecules using the much used recent method of inverse gas chromatography.[11]

Experimental Section

Materials. PVA was supplied by Union Carbide Corp. It was fractionated into eight fractions, using benzene as the solvent and petroleum ether (40–60 °C boiling range) as the precipitant. The fractions were dried in a vacuum oven at 100 °C for 3 days. The second fraction ($\bar{M}_v$ = 141 420) has been used in most of the present work.

PMA was prepared by the solution polymerization of the monomer in benzene (20% (v/v)) at 60 °C under a nitrogen

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Table I
GLC Column Parameters

stationary phase	loading, % (w/w)	wt of polymer in column, g
squalene	8.05	0.5948
PMA(H)	15.07	1.4603
PVA	14.03	1.3046
1:1 (w/w) PMA + PVA	15.79	1.5310
1:3 (w/w) PMA + PVA	13.56	1.2607
3:1 (w/w) PMA + PVA	13.20	1.2191

atmosphere, using 2,2′-azobis(isobutyronitrile) (AIBN) as initiator (0.064% (w/v)). Three sets of polymerizations were carried out. In two of them dodecyl mercaptan was used as the chain-transfer agent to the extent of 0.065 and 0.13 M, respectively, to obtain low molecular weight polymers. The polymerizations were carried to 30% conversion. The third system, where no mercaptan was used, was difficult to control and the polymerization was stopped at 50% conversion. However, because of the low initial monomer concentration, the polymer concentration during polymerization never exceeded 10% so that the possibility of chain branching was rendered low. The polymers were isolated by precipitating them into petroleum ether. They were purified by the dissolution–precipitation technique. The isolated polymers were then fractionated, using benzene–petroleum ether as the solvent–precipitant system. The fractions were isolated by freeze-drying and finally dried as mentioned in the case of PVA. Two polymer fractions, one high molecular weight, designated PMA(H) ($\bar{M}_v$ = 705 940), and the other low molecular weight, designated PMA(L) ($\bar{M}_v$ = 28 370), have been used in the present work.

The solvents were in general analytical reagent grade materials. A few laboratory reagent grade solvents were used. They were purified and distilled before use.

Preparation of Blends. This was done by dissolving the required proportion of the polymers in benzene to make a maximum of 2.5 wt % polymer solution. The blends were then isolated by the freeze-drying method. The blend films were obtained by the solvent casting method over a taut cellophane surface. The blends and their films were dried at 100 °C for 3 days in a vacuum oven as described earlier.

Cloud Point Determination. Required amounts of polymer blends of known compositions and solvents were weighed into 6-mm Pyrex tubes. The tubes were evacuated to 0.1 torr and sealed. The cloud points (T_p) were determined visually. The temperature corresponding to the first appearance of definite haze on slow cooling (1 °C/3 h) of a clear solution is taken as T_p. The bath temperatures were controlled to ±0.01 °C. The T_p's were obtained within ±1 °C accuracy for PMA(L)–PVA–solvent systems, while for the other system, PMA(H) + PVA, they were obtained with somewhat lesser accuracy, e.g., ±2 °C.

Viscosity Determination. A Schurz–Immergut-type variable-shear viscometer[12] was used. The viscosity results were duly corrected for kinetic energy loss. Both shear correction and kinetic energy correction were small. Proper precaution to prevent moisture ingress in the viscometer was taken at subambient temperatures.

Glass Transition Temperature Measurement. This was done with a Perkin-Elmer DSC 2 instrument.

Inverse Gas Chromatography. A homemade dual-column gas chromatograph with a thermal conductivity detector was used. The gas flow rate was measured with a soap bubble flow meter. Argon was used as the carrier gas. The columns were 5-ft long copper tubes of $^1/_4$-in. o.d. The polymer (PMA(H), PVA, or their blends) were coated from a benzene solution (1.5% (w/v)) onto Chromosorb W (DMCS treated, acid washed, 60–80 mesh). After drying, the coated support was packed into the copper columns. The percent loading of the polymer on the support was determined by calcination at 1000 °C using a suitable blank correction. The relative concentrations of the polymers in the blends on the coated support were assumed to be identical with those in the original solutions used for deposition on the support. The column characteristics are given in Table I. The columns were purged at a temperature 10 °C above the experimental temperature for 5 h with a low flow rate of the carrier gas. They were then left overnight for attainment of equilibrium at the experimental temperature, and then the flow rate was increased to the desired level by adjusting the inlet pressure and the columns were further equilibriated at the new flow rate for a period of 2.5 h. A two-stage flow controller meant for a flame photometer (Carl Zeiss, Jena, West Germany) was used for accurate control of gas flow. A constant quantity of each probe (1 μL) was injected. The retention times were determined from the distance between air peak and sample peak and the chart speed. The latter was monitored at definite time intervals with a stopwatch. For each probe the average of triplicate readings of retention times was taken for a given flow rate of the carrier gas. The standard specific retention volumes ($V_g°$) were calculated in the usual manner[11,13]

Table II
$V_g°$ Data for the Squalene Column with Hydrocarbon Probes

probe	temp, °C	$V_g°$(exptl),[a] mL	$V_g°$(lit.), mL	lit. ref
n-hexane	55	130.4	130.4	14
	65	95.2	94.1	14
n-heptane	55	344.2	344.0	14
	65	242.5	236.7	14
benzene	78.5	91.9	95.0	15
toluene	78.5	232.7	238.0	15

[a] Our experimental data. The temperatures were actually 55.1 and 64.9 °C instead of 55 and 65 °C, respectively.

$$V_g = t_N F J / W_L \tag{1}$$

where t_N is the net retention time for the probe, F is the carrier gas flow rate at 0 °C and 1 atm, W_L is the weight of polymer in the column, and J is a correction factor for gas compressibility, as given by

$$J = \frac{3}{2}\,\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \tag{2}$$

where P_i is the inlet pressure and P_o is the outlet pressure. For each probe V_g values were determined at four different flow rates and extrapolated to zero flow rates to obtain $V_g°$. The instrument was standardized and checked against a squalene column before working with polymer columns. A comparison of our results with those of other workers using hydrocarbon probes is shown in Table II.

Data Reduction. The polymer–solvent interaction parameters (χ_{1i}) were calculated from the relation[11] applicable for polymers having a large number of segments

$$\chi_{1i} = \ln \frac{273.15 R v_{i,\mathrm{sp}}}{P_1° V_g° V_1} - \frac{P_1°}{RT}(B_{11} - V_1) - 1 \tag{3}$$

The standard specific retention volumes of the probes obtained with a column containing a homogeneous mixture of the two polymers ($V_{g,23}°$) were used together with the following relation to determine the interaction parameter χ_{23} between the two polymers:[11,16]

$$\chi_{1(23)} = \ln \frac{273.15 R(\omega_2 v_{2,\mathrm{sp}} + \omega_3 v_{3,\mathrm{sp}})}{P_1° V_{g,23}° V_1} - \frac{P_1°}{RT}(B_{11} - V_1) - 1 = \left[\left(\frac{\chi_{12}}{V_1}\right)\phi_2 + \left(\frac{\chi_{13}}{V_1}\right)\phi_3 - \left(\frac{\chi_{23}}{V_2}\right)\phi_2\phi_3\right] V_1 \tag{4}$$

where subscript 1 refers to the solvent and subscripts 2 and 3 refer to the respective polymers. V_i, ϕ_i, and ω_i represent the molar volume, volume fraction, and weight fraction of the components, respectively. $P_1°$ and B_{11} are, respectively, the vapor pressure and second virial coefficient of the solvent at the column temperature, and R is the gas constant. Values of these parameters were obtained or calculated from various sources. The densities of the solvents were obtained from ref 17 as were the values of $P_1°$. B_{11} values were obtained from O'Connel and Prausnitz.[18]

The new Flory–Prigogine exchange interaction parameter (X_{ij}) was calculated from a knowledge of reduction parameters for pressure (P^*), volume (V^*), and temperature (T^*) of the components along with the known values of χ_{ij}^*. The latter values

Table III
Characteristic Parameters for Solvents and Polymers at 298 K

material	v^*, cm^3/g	T^*, K	P^*, J/cm^3
PMA	0.7002^a	6762^a	632^a
PVA	0.7146^a	6668^a	607^a
n-octane	1.1204^b	4863^b	428^b
cyclohexane	1.0012^b	4719^b	531^b
benzene	0.8890^b	4708^b	620^b
toluene	0.9180^b	5026^b	561^b
ethanol	0.9955^c	4845^c	545^c
chloroform	0.5460^c	5280^c	320^c
MEK	0.9580^c	4590^c	571^c
ethyl acetate	0.8425^d	4393^d	489^e
acetone	0.9580^d	4368^d	292^e
1,2-dichloroethane	0.6249^d	4789^d	499^e

[a] Calculated; v^* and T^* were calculated from α values[19] using Flory's new theory, and P^* for PVA was obtained from the relation $P^* = \gamma\tilde{V}^2T$, V being the reduced volume. The pressure coefficient (γ) was obtained from ref 20 by extrapolation of the compresssibility coefficients (β) to 25 °C and taking $\gamma = \alpha/\beta$. For PMA, β or γ data are not available in the literature and so the P^* value was calculated from the solubility parameter (δ) using the relation $P^* = \delta^2\tilde{V}^2$ and then multiplying by a correction factor (obtained from a comparison of the P^* data of PVA determined by the two methods, viz., the γ method and the δ method). The δ values for both PMA and PVA used in the calculation were computed following Small's method[21] using the data of Hoy.[22] [b] From ref 16. [c] From ref 23. [d] Calculated from Flory theory, the α values were obtained from the density relations in ref 17. [e] From ref 24.

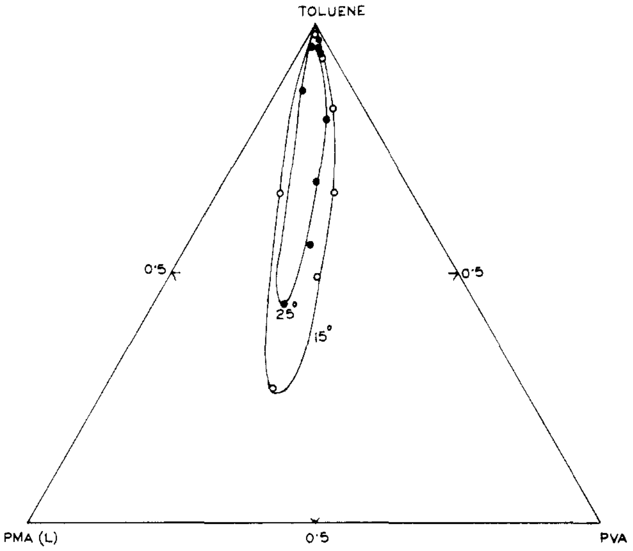

Figure 1. Ternary phase diagrams of the (PMA(L) + PVA)/toluene system at the indicated temperatures.

can be calculated easily by putting the core-specific volumes instead of the specific volumes ($v_{i,\mathrm{sp}}$) in 3 and 4 and replacing volume fraction (ϕ_i) by surface fraction (θ_i), where

$$\theta_i = (\omega_i v_i^* S_i)/\sum \omega_i v_i^* S_i \tag{5}$$

the v_i^* are the reduction parameters (per gram) for volume, and S_i is the molecular surface/volume ratio. The X_{ij} parameters can then be calculated by proceeding as in ref 16. These parameters when expressed per unit molecular surface (X_{ij}/S_i) become symmetrical and more meaningful. The sources of the various data needed for the above-mentioned calculations are listed in Table III, while the segmental surface area per unit volume was estimated from the correlation of Bondi.[25]

Results and Discussion

Both of the polymer pairs PVA + PMA(H) and PVA + PMA(L) were found to be miscible from T_g measurements. The blends in all compositions were found to exhibit single T_g's intermediate between the T_g values of the pure components. A prominent cusp exists in the T_g vs. composition curve around 0.45 weight fraction of PMA in the blend. This aspect will be dealt with in a separate publication.

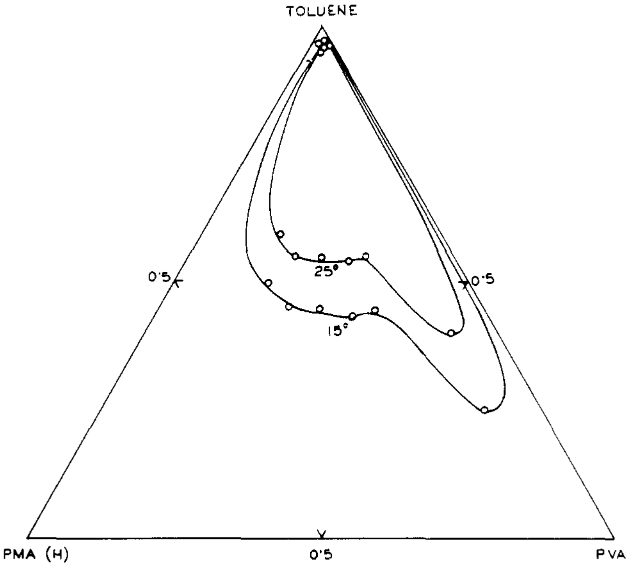

Figure 2. Ternary phase diagrams of the (PMA(H) + PVA)/toluene system at the indicated temperatures.

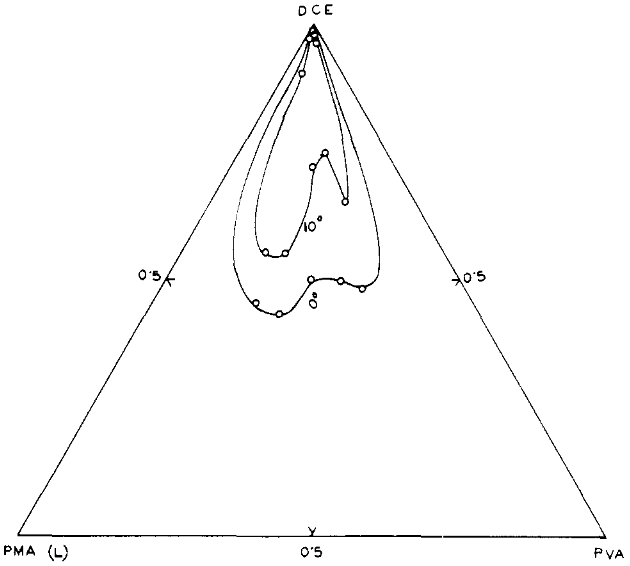

Figure 3. Ternary phase diagrams of the (PMA(L) + PVA)/DCE system at the indicated temperatures.

Incompatibility in Solution. The common solvent solubility of the blends was then studied. Of the four solvents used, viz., acetone, ethyl acetate (EtOAc), toluene, and 1,2-dichloroethane (DCE), no phase separation at any composition was observed in acetone even when the solutions were cooled to −60 °C. In EtOAc phase separation was observed at temperatures below −25 °C. Phase separation in the other two solvents was studied in some detail and is discussed below. Figures 1–3 respectively show the ternary phase diagrams for the polymer pairs PMA(L) + PVA and PMA(H) + PVA in the poor solvent toluene and for the former pair in the relatively good solvent DCE also. The phase diagrams contain closed immiscibility loops; i.e., the region inside the loop is phase separated but outside of it the polymers are miscible in the common solvent and the binaries are completely miscible. With increase in temperature the size of the loop decreases and vanishes at temperatures somewhat higher than those indicated on the narrowest loop in the figures, e.g., 35, 43, and 17 °C for Figures 1–3, respectively. The loops are bent toward the low molecular weight polymer. This effect is very prominent in Figure 2 for the (PMA(H) + PVA)/toluene system. Comparison of Figures 1 and 2 reveals that increasing the molecular weight leads to larger immiscibility gaps and brings in bimodality in the phase diagram. Bimodal phase diagrams are observed even for the low molecular weight system (PMA(L) + PVA)/DCE (Figure 3). These facts reveal that bimodality in cloud point curves (CPC) depends on the nature of the solvent and is promoted by increasing molecular weights of the polymers. Bimodal CPC curves are not uncommon. Aharoni[26] pointed out that in all such curves the trough always occurs at a polymer:polymer ratio of about 1:1. For the (PMA(L) + PVA)/DCE system this generalization seems to hold good. However, for the other system, i.e., (PMA(H) + PVA)/toluene, it does not. Of course, it must be pointed out that in Figure 2 the portion of the phase boundary under consideration is so flat and the experimental uncertainty is so large that it is difficult to locate the exact position of the trough. Aharoni attributed the appearance of a trough at 1:1 polymer ratio to the interaction between the two specifically interacting polymers being greatest at this ratio for compatible polymer pairs having specific interactions. This explanation does not apply for the present system, which is not endowed with specific interactions.

The phenomenon of incompatibility in solution of compatible polymer pairs has been explained by Patterson et al.[9,10] Using the Flory–Huggins solution thermodynamics theory, Patterson et al. have shown that phase equilibrium in ternary systems containing two polymers (components 2 and 3) and a solvent (component 1) depends not only on χ_{23} but also on any difference in the strengths of the polymer solvent interaction, i.e., on $|\Delta\chi| = |\chi_{12} - \chi_{13}|$. Closed-loop spinodals were theoretically constructed for systems consisting of compatible polymer pairs and a common solvent having a $|\Delta\chi|$ value greater than a certain minimum value.[9] The latter depends on the molecular weights of the polymers concerned. Subsequently, Prausnitz et al. reached similar conclusions based on the calculation of binodals.[27] Most of the observations made here except the bimodality in CPC have been predicted.[9] The occurrence of a closed loop in the CPC is common for compatible polymer pairs undergoing phase separation in solvents associated with high $|\Delta\chi|$ values. It is, therefore, of interest to examine the validity of the $|\Delta\chi|$ effect in the present case. As has been stated in the Introduction the polymers under consideration here are so similar in chemical nature and P–V–T properties (Table III) that a significant $|\Delta\chi|$ causing phase separation in solution is difficult to comprehend. To examine this aspect the χ_{1i}'s have been measured in this work both by viscometry and by IGC. The viscometric method uses the Stockmayer–Fixman equation[28]

$$[\eta] = KM^{1/2} + 0.51\phi_0\bar{v}_i^2(1 - 2\chi_{1i})M/V_1N_A \qquad (6)$$

where ϕ_0 is the Flory universal constant having the value 2.8×10^{23} cgsu, $\bar{v}_i$ is the specific volume of the polymer, and N_A is the Avogadro number. Accordingly, $[\eta]/M^{1/2}$ when plotted against $M^{1/2}$ should yield straight lines. From the slope of the lines χ_{1i}'s are estimated. Some representative plots are shown in Figure 4. The IGC method of determining χ_{1i} has been discussed earlier in the Experimental Section. The χ_{1i}'s determined by the two methods for the three solvents acetone, toluene, and DCE are compiled in Tables IV and V.

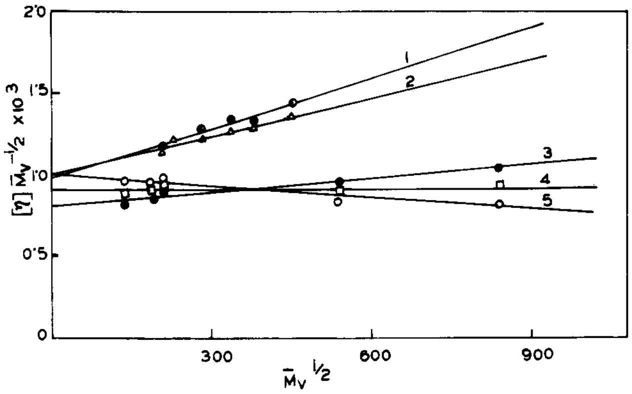

Figure 4. Typical Stockmayer–Fixman plots for PMA and PVA in toluene at different temperatures. Lines 1 and 2 are for the PVA–toluene system at 25 and 45 °C, respectively, and lines 3–5 are for the PMA–toluene system at 45, 25°, and 5 °C, respectively.

Table IV
χ_{1i} and $|\Delta\chi|$ Values at 25 °C As Determined by Dilute Solution Viscometry ($\phi_1 \rightarrow 1$)

solvent	χ_{12}	χ_{13}	$\Delta\chi$	$10^3\text{d}|\Delta\chi|/\text{d}T$,[a] K^{-1}
acetone	0.48	0.46	0.02	−0.5
toluene	0.50	0.47	0.03	−0.5
DCE	0.45	0.41	0.04	−0.3

[a] The data are based on the $|\Delta\chi|$ values at 5, 25, and 45 °C for toluene and DCE and at 5, 25, and 35 °C for acetone.

Table V
χ_{1i} and $|\Delta\chi|$ Values at 80 °C As Determined by IGC ($\phi_1 \rightarrow 0$)

solvent	χ_{12}	χ_{13}	$|\Delta\chi|$	$10^3 \times$ $\text{d}|\Delta\chi|/\text{d}T$,[a] K^{-1}
acetone	0.54	0.47	0.07	1.0
ethyl acetate	0.53	0.42	0.11	−4.0
toluene	0.60	0.52	0.08	−2.0
DCE	0.08	−0.01	0.09	−2.0

[a] Values based on measurements at two temperatures, 80 and 100 °C.

An examination of the data presented in Tables IV and V reveals that χ_{1i} values exhibit a composition dependence which is very large with DCE solvent. The variation of χ with composition is in general attributed to a difference in surface/volume ratio (S) of the two components,[29] which may be quite large for polymer–solvent systems. This explanation however does not appear to be adequate in the present case, particularly when the relative magnitude of the dependence of χ_{1i} with composition is compared for the two solvents DCE and toluene. For example, using Bondi's group contribution method, we find the values of S in Å^{-1} units to be 1.17 and 1.44 respectively for toluene and DCE while the two polymers have the same S value of 1.36 Å^{-1}. The above explanation requires that the dependence of χ_{1i} on composition be greater with toluene than with DCE. But the opposite is observed here.

Of particular interest here are the values of $|\Delta\chi|$. For the dilute polymer solutions $|\Delta\chi|$ is very low, having the highest value of 0.04 in DCE at 25 °C (Table IV). At the other extreme of solution composition $|\Delta\chi|$ is somewhat larger. Theoretical spinodals calculated following ref 9 reveal that with a value of $\chi_{23} = 0.004$, which is just below $\chi_{23}^{\text{cr}} = 0.0044$, a minimum $|\Delta\chi|$ value of 0.12 would be necessary for the occurrence of a miscibility gap for the low molecular weight system PMA(L) + PVA. Here toluene is used as the reference liquid for the determination of the segment numbers, r_i's, needed for the calculation.[30] For $\chi_{23} = 0$ the tolerated $|\Delta\chi|$ that would preclude phase separation is found to be 0.14 and 0.05 for the low and high molecular weight systems, respectively.

Table VI
Thermodynamic Quantities of Interaction for PMA[a]

	80 °C			100 °C		
probe	χ_{12}	χ_{12}*	$X_{12}/S_1 \times 10^8$, J cm^{-2}	χ_{12}	χ_{12}*	$X_{12}/S_1 \times 10^8$, J cm^{-2}
benzene	0.44	0.53	10.6	0.45 (0.49)	0.54	11.6
toluene	0.60	0.67	17.4	0.55 (0.63)	0.63	16.7
n-octane	2.36	2.45	43.7	2.24 (2.27)	2.33	44.0
cyclohexane	1.76	1.86	55.2	1.65 (1.62)	1.74	54.5
ethanol	1.19	1.28	56.2	1.09	1.17	54.7
acetone	0.54	0.67	21.9	0.61	0.74	26.3
MEK	0.52	0.62	11.6	0.48	0.59	10.9
ethyl acetate	0.53	0.66	9.7	0.48	0.61	8.3
1,2-dichloroethane	0.08	0.17	−0.2	0.09	0.18	−0.0
chloroform	−0.23	−0.17	−9.1	−0.16	−0.11	−6.9

[a] The values in parentheses are obtained from ref 32.

Table VII
Thermodynamic Quantities of Interaction for PVA[a]

	80 °C			100 °C		
probe	χ_{13}	χ_{13}*	$X_{12}/S_1 \times 10^8$, J cm^{-2}	χ_{13}	χ_{13}*	$X_{13}/S_1 \times 10^8$, J cm^{-2}
benzene	0.43 (0.44)	0.53	11.5	0.40 (0.34)	0.50	10.5
toluene	0.52 (0.56)	0.60	15.4	0.51 (0.51)	0.59	16.0
n-octane	2.56	2.65	48.2	2.14 (2.14)	2.23	42.6
cyclohexane	2.24	2.34	72.8	1.64 (1.56)	1.74	55.3
ethanol	0.99	1.08	47.2	0.96	1.05	48.6
acetone	0.47	0.60	19.6	0.52	0.66	23.1
MEK	0.44	0.53	9.1	0.45	0.56	10.5
ethyl acetate	0.42	0.55	7.1	0.45	0.58	8.2
1,2-dichloroethane	−0.01	0.08	−3.5	0.04	0.13	−1.8
chloroform	−0.27 (−0.19)	−0.22	−1.1	−0.18 (−0.11)	−0.14	−8.0

[a] The values in parentheses are obtained from ref 32.

The dilute solution $|\Delta\chi|$ values (Table IV) are smaller than the tolerated $|\Delta\chi|$ for all of the solvents in the temperature region indicated in Figures 1–3. Thus the $|\Delta\chi|$ theory does not seem to hold good. On the other hand, if one goes by the gas chromatographic data the $|\Delta\chi|$ theory proves to be validated. This would be evident from the following discussion. The temperature coefficient of $|\Delta\chi|$ reported in Table V is based on the $|\Delta\chi|$ data at two temperatures, viz., 80 and 100 °C. Assuming the same $\mathrm{d}|\Delta\chi|/\mathrm{d}T$ value to be operative below 80 °C, the calculated value of $|\Delta\chi|$ becomes sufficiently large to account for immiscibility at low temperatures for the three solvents toluene, DCE, and EtOAc. For example, at 25 °C $|\Delta\chi|$ for toluene is calculated to be 0.19, which is greater than the tolerated $|\Delta\chi|$ value of 0.14 for the low molecular weight system. Similar results obtain with DCE. With acetone as the solvent the temperature coefficient of $|\Delta\chi|$ is positive and the data in Table V may be used to find that the $|\Delta\chi|$ for this solvent will not exceed the tolerated $|\Delta\chi|$ even at very low temperatures. This is in accord with the experimental finding that no phase separation was observed in acetone even down to −65 °C. So far the agreement with the theory is good. However, it is not so for EtOAc. Using the data in Table V, one would find $|\Delta\chi|$ in this solvent to exceed the tolerated value at temperatures as high as 60 °C. But experimentally phase separation was observed only below −25 °C. This discrepancy points out that the $|\Delta\chi|$ theory, together with GLC χ parameters, gives good qualitative predictions. It should be noted, however, that for a quantitative test of the theory the $|\Delta\chi|$ values should be very accurate, particularly when one is dealing with small values. Unfortunately, GLC-determined χ values are not as accurate as the situation demands. This would be evident from the comparison of χ data as determined by us (reported in Tables VI and VII) and those determined by others given in parentheses in the same tables. Furthermore, since there is a significant dependence on composition of χ values, a rigorous test of the theory requires χ values appropriate for the compositions represented by the phase-separated regions. Such data are unavailable at the moment.

Thermodynamic Interaction. The thermodynamic interaction between the two polymers was next studied by inverse gas chromatography. Several polar and nonpolar solvent probes were used to determine the polymer–solvent interaction parameters using eq 3, and from these data and measurements using several polymer blends as stationary phases, values of the polymer–polymer interaction parameters (χ_{23}) for various blend compositions were evaluated by using eq 4. All these data are listed in Tables VI–IX. Some values obtained previously by workers[31,32] are shown in parentheses and these are in fair agreement with our values. Also reported in the tables are the values of χ_{ij}* and X_{ij}/S_i.

An examination of the χ_{1i} values (Tables VI and VII) reveals that for each probe $|\Delta\chi|$ is small, <0.1 say. Considering the wide variety of the probes with respect to polarity, hydrogen bonding, or donor–acceptor interaction capability, the closeness of the χ_{1i} values for any given probe indicates that the polymers are of very similar chemical nature and of similar *P–V–T* properties. The former determines the exchange interaction contribution and the latter the free volume contribution in χ_{1i}. Thus, the "complementary dissimilarity" character, which leads to specific interactions,[23] is absent between the two polymers under investigation.

The aliphatic (*n*-octane) or alicyclic (cyclohexane) hydrocarbons and the aliphatic alcohol (ethanol) used in this work are nonsolvents while the chlorinated hydrocarbons prove to be very powerful solvents. The aromatic hydrocarbons and the aliphatic esters are intermediate in solvent property. The very low and sometimes negative values of χ_{1i} for the chlorinated solvents may indicate the existence of specific interactions, presumably a hydrogen-bonding interaction between the ester group of the polymers and the acidic hydrogens of the chlorinated hydrocarbons.

Table VIII
Thermodynamic Quantities for Polymer–Polymer Interaction at 80 °C at Different Polymer Ratios (w/w)

	3:1 PMA + PVA			1:1 PMA + PVA			1:3 PMA + PVA		
probe	χ_{23}'	$\chi_{23}'^*$	$X_{23}/S_2 \times 10^8$, J cm^{-2}	χ_{23}'	$\chi_{23}'^*$	$X_{23}/S_2 \times 10^8$, J cm^{-2}	χ_{23}'	$\chi_{23}'^*$	$X_{23}/S_2 \times 10^8$, J cm^{-2}
benzene	0.20	0.20	7.3	0.02	−0.01	−0.4	0.02	0.02	0.8
toluene	0.27	0.27	8.9	0.08	0.08	2.6	0.02	0.02	0.5
n-octane	0.17	0.18	3.3	0.17	0.17	3.2	0.08	0.08	1.6
cyclohexane	0.28	0.28	3.8	0.00	−0.01	−0.0			
ethanol	0.04	0.04	1.6	0.17	0.17	7.4	−0.10	−0.10	−4.5
acetone	0.17	0.17	6.8	0.13	0.13	5.1	−0.16	−0.16	−6.6
MEK	0.30	0.26	8.4	0.21	0.16	5.3	0.06	0.06	−2.3
ethyl acetate	0.34	0.34	9.8	0.12	0.12	3.6	0.02	0.02	0.5
1,2-dichloroethane	0.28	0.29	10.6	−0.05	0.04	1.6	0.02	0.02	0.8
chloroform	0.11	0.11	4.2	−0.17	−0.17	−6.7	−0.14	−0.14	−5.4
av		0.214	6.97		0.068	2.17		−0.018	−1.46
sd		0.091	2.99		0.108	4.10		0.089	3.14

Table IX
Thermodynamic Quantities for Polymer–Polymer Interaction at 100 °C at Different Polymer Ratios (w/w)

	3:1 PMA + PVA			1:1 PMA + PVA			1:3 PMA + PVA		
probe	χ_{23}'	$\chi_{23}'^*$	$X_{23}/S_2 \times 10^8$, J cm^{-2}	χ_{23}'	$\chi_{23}'^*$	$X_{23}/S_2 \times 10^8$, J cm^{-2}	χ_{23}'	$\chi_{23}'^*$	$X_{23}/S_2 \times 10^8$, J cm^{-2}
benzene	0.06	0.06	2.3	0.06	0.06	2.4	−0.04	−0.04	−1.5
toluene	0.16	0.16	5.8	0.05	0.04	1.4	0.09	0.09	3.4
n-octane	0.16	0.16	3.1	0.12	0.12	2.3	0.00	0.01	0.1
cyclohexane	0.24	0.24	7.9	−0.11	−0.11	−3.4	−0.11	−0.11	−3.4
ethanol	0.02	0.02	0.9				0.15	0.15	7.0
acetone	0.07	0.07	3.0				−0.03	−0.00	−1.2
MEK	0.14	0.14	4.8	0.11	0.11	3.9	0.07	0.07	2.3
ethyl acetate	−0.02	−0.02	−0.5	0.06	0.06	1.9	−0.00	−0.01	−0.1
1,2-dichloroethane	0.08	0.08	3.3	0.07	0.07	2.9	0.09	0.09	3.6
chloroform	−0.09	−0.10	−4.0	0.10	0.09	3.6	−0.03	−0.04	−1.7
av		0.081	2.66		0.055	1.875		0.021	0.85
sd		0.099	2.89		0.072	2.29		0.078	3.16

However, the electronic interaction of the n,σ^* type between oxygen and chlorine atoms of the polymers and the probe, respectively, may also be responsible for such strong interactions.[23] It should be noted that the χ_{1i} values determined by the viscometric method using dilute polymer solutions in DCE discussed earlier in this paper do not reveal the existence of any specific interaction of the kind discussed here. On the other hand, the χ_{1i}^* parameters or the exchange interaction parameters, X_{1i}/S_1, both of which eliminate the equation-of-state effect, are more reliable guides and for the case under consideration they indicate the existence of specific interactions. However, the X_{1i}/S_1 values as determined by the IGC method may not in all cases represent the pure enthalpic contribution, due largely to the failure in estimating other noncombinatorial free energy contributions than the free volume effect. For example, in hydrocarbon systems effects such as orientational order are known to offer a positive contribution to χ.[33]

Of particular interest here is the χ_{12} value for the ethyl acetate probe. This probe may be looked upon as approximating a segment of PVA, itself being the hydrogenated monomer of PVA. The X_{12}/S_1 value for this probe may therefore furnish some idea about the nature of the interaction between PMA and PVA. The positive value of X_{12}/S_1 indicates, therefore, the absence of any specific interactions between PMA and PVA. Regarding the magnitude of X_{12}/S_1, we may only point out that this value might not reflect the true exchange enthalpy parameters and include also other noncombinatorial free energy contributions. That this may indeed be so is apparent from the similar positive value of X_{13}/S_1. If ethyl acetate may truly represent a segment of PVA, X_{13}/S_1 should be zero, provided it represents only the exchange enthalpy contribution.

Let us now examine the polymer–polymer interaction parameter. This parameter is normalized to the size of the probe molecule, $\chi_{23}' = \chi_{23} V_1/V_2$. Elimination of the contribution of the equation-of-state effect to χ_{23}' results in $\chi_{23}'^*$. For the polymers used here the P–V–T properties are not very different (Table III) so that the equation-of-state correction is small. We see that $\chi_{23}'^*$ parameters depend on the probe used. Such a phenomenon is quite common although not allowed in the theory. This is one of the drawbacks of the IGC method of χ_{23}' determination. Olabisi attributes this to the nonrandom distribution of the probes in the stationary phase due to its preferential affinity for one of the components.[23] However, such an explanation is hard to justify in the present system in view of the very similar chemical nature of the two polymers. Notwithstanding the dependence of X_{23}/S_2 on the probe, the results may still be used for comparative purposes. To this end, we averaged the values and these results along with the standard deviations are included in Tables VIII and IX. The average values are indeed positive and small except for the 1:3 PMA + PVA blend, an indication for a possible absence of specific interactions. The temperature dependence shows no definite trend. For two of the compositions, 3:1 and 1:1, the value decreases with increase in temperature from 80 to 100 °C while for the 1:3 blend it increases. The $\chi_{23}'^*$ parameters show a composition dependence at both 80 and 100 °C decreasing with increasing PVA in the blends. Such composition dependence is commonly observed with the IGC method.[23,34,35] With reference to the earlier discussion on the variation of χ with composition, one does not expect a significant composition dependence for χ_{23}' in view of the same value of the surface/volume ratio of the two very similar polymers used here (discussed earlier in this paper). With the $\chi_{23}'^*$ parameter, which is obtained by the elimination of the equation-of-state effect, the composition dependence should have been absent altogether. However, the fact that a significant composition dependence is observed even with $\chi_{23}'^*$ values casts doubt on the reliability of the method. Zacharius et al. found a similar composition dependence of χ values for polymer–polymer systems using the vapor sorption method. They have questioned the validity of the determination of the χ_{23} parameter for the solvent-free polymer blend from experimental data obtained using solvent probes.[5]

Attempts were made to determine the LCST by using films of neat blends of both PMA(L) + PVA and PMA(H) + PVA. They were clear even at 300 °C. The LCST probably lies at much higher temperature and could not be determined due to degradation of the polymers above 300 °C or so. Since the P–V–T properties of the polymers do not differ much (Table III), the free volume contribution to χ_{23}' is small. The LCST would, therefore, be expected at much higher temperature.

Finally, there is yet another aspect on which we would like to comment. With all the miscible polymer–polymer systems studied so far where there are no specific interactions, a strong dependence of miscibility on molecular weight has been observed.[5,6,34] This is understandable in view of the further decrease with molecular weight of the already low combinatorial entropy of solution for polymer–polymer systems. In the present case, however, such a dependence of miscibility on molecular weight was not observed. Both PMA(L) + PVA and PMA(H) + PVA were found to be miscible as evidenced by a single T_g at all blend compositions as well as closed-loop CPC curves in the ternary phase diagrams (Figures 1 and 2). The molecular weight of PMA(H) was 25 times as high as that of PMA(L). This exceptional situation is further indicative of the very similar chemical nature and P–V–T properties of the two polymers. These characteristics ensure that unfavorable noncombinatorial free energy contributions such as the exchange interaction contribution and the free volume contribution are sufficiently small.

Conclusion

This study shows that PMA and PVA are miscible in all proportions and that the miscibility is not effected by specific interactions between them. The absence of specific interactions has been inferred from inverse gas chromatography, which shows a lack of complementary dissimilarity between the polymers and that the polymer–polymer interaction parameter has a small but positive value. Unlike other known cases of polymer–polymer miscibility which are characterized by a small positive exchange interaction, the present system does not exhibit any significant dependence of miscibility on molecular weight. It has been inferred that for the polymer blend under investigation, not only the exchange interaction energy is small but the free volume contribution to the thermodynamic interaction is small also.

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Registry No. PVA (homopolymer), 9003-20-7; PMA (homopolymer), 9003-21-8; MEK, 78-93-3; benzene, 71-43-2; toluene, 108-88-3; *n*-octane, 111-65-9; cyclohexane, 110-82-7; ethanol, 64-17-5; acetone, 67-64-1; ethyl acetate, 141-78-6; 1,2-dichloroethane, 107-06-2; chloroform, 67-66-3.

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