

Polymer–polymer interaction parameter determined by inverse gas chromatography*

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Inverse gas chromatography was employed to determine the apparent polymer–polymer interaction parameter $\chi'_{23,app}$ for the following blends using them as binary stationary phases: poly(vinyl acetate)–poly(n-butyl methacrylate) at 100 and 120°C, poly(vinyl acetate)–atactic poly(vinyl isobutyl ether) at 70°C, and poly(n-butyl methacrylate)–atactic poly(vinyl isobutyl ether) at 70°C. The interaction parameter $\chi'_{23,app}$ depended significantly on the chemical nature of the solvent (probe) used and the composition of the stationary phase. The lowest values of $\chi'_{23,app}$ were obtained when aromatic and chlorinated-alkane probes were eluted on stationary phases having weight fractional compositions of the component polymers in the range 0.4–0.6. The results predict a better compatibility for poly(n-butyl methacrylate)–atactic poly(vinyl isobutyl ether) than for the other blends.

(Keywords: polymer compatibility; Flory–Huggins interaction parameter; gas chromatography)

INTRODUCTION

In 1974 Deshpande *et al.*² described for the first time an inverse gas chromatographic (i.g.c.) method to study thermodynamic interactions in polymer blends and binary mixtures of a non-volatile compound with a polymer. Olabisi³ has also suggested independently a similar technique in which three columns are prepared—two from homopolymers and a third from a blend of the same polymer samples. The retention volume of a solvent 'probe' is then determined on the three columns under identical conditions. The measured retention data are used to derive interaction parameters (χ) for the probe–polymer (1–2), probe–polymer–polymer (1–2–3) and polymer–polymer (2–3) systems using the classical Flory–Huggins expression for the change in free enthalpy of mixing (ΔG_{mix}) in conjunction with the Scott–Tompa equation^{4,5} for ternary mixtures. The thermodynamic interaction in a ternary system is expressed as a combination of the pair interaction parameters, which have been implicitly assumed to be independent of the composition of the stationary phase. The polymer–polymer pair interaction energy parameter χ'_{23} is further assumed also to be independent of the chemical nature of the probe used. However, in all i.g.c. studies^{2,3,6–21} reported so far, χ'_{23} has exhibited a significant dependence on these factors. In order to explain the probe-to-probe variation of χ'_{23} in i.g.c. studies, Al-Saigh and Munk¹⁹ have introduced, in the expression for ΔG_{mix} , a surface fraction term (σ_i) and also a surface interaction parameter (γ_{ij}) similar to X_{ij} used earlier by Deshpande *et al.*²; but the presumption about the 'composition independence' of γ_{ij} has been retained. However, they have suggested the addition of a phenomenological function (g_T) of the composition of the mixture in the equation for ΔG_{mix} .

Recently, Su and Fried²² have suggested that the 'composition dependence' of the polymer–polymer interaction parameter may contribute to χ'_{23} in a manner independent of the probe used. They have included the phenomenological composition dependence in the interaction terms (g_{ij}) in the Flory–Huggins free-energy expression, which should account for the 'probe dependence' also. Although these modifications are significant contributions to i.g.c., they include scarcely available molecular parameters in the equations for χ'_{23} , and do not provide any clue to the physical significance or experimental evaluation of the elusive parameter g_{23} or χ'_{23} . Therefore, the polymer–polymer interaction parameter has to be computed from the retention data using the original expressions^{2,3}. We shall use an additional subscript 'app' with the interaction parameters in order to emphasize that the measured χ_{ij} are apparent parameters and that they are sensitive to both the composition of the blend and the chemical nature of the probe.

In the present work, we have studied these effects on $\chi'_{23,app}$ for binary mixtures (blends) of poly(vinyl acetate) (PVAc), poly(n-butyl methacrylate) (PnBMA) and atactic poly(vinyl isobutyl ether) (PVIBE). The probes differ significantly in their chemical nature and solvent power for the polymers. We have demonstrated earlier^{23–25} that the present polymer–probe pairs yield reliable thermodynamic data at and above 70°C.

EXPERIMENTAL

Materials

The polymer samples were the same as used elsewhere^{23–25}. Their properties^{23–26} are given in Table 1. The probes were analytical or chromatography grade solvents. Their abbreviations to be used in this work are given in Table 2.

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Table 1 Polymers and their properties

Property	PVAc ^{24,26}	PnBMA ²³	PVIBE ²⁵
\bar{M}_n	6700	91 300	2340
\bar{M}_v	40 000	372 000	8600
T_g (°C)	30	18	-55
Specific volume, v_i (ml g ⁻¹)			
70°C	0.86789	1.00040	1.15402
100°C	0.88740	1.02486	
120°C	0.90020	1.04011	

Table 2 Probes and their abbreviations

Probe	Abbreviation
n-Hexane	nC ₆
n-Heptane	nC ₇
n-Octane	nC ₈
iso-Octane	iC ₈
Cyclohexane	cC ₆
Dichloromethane	CH ₂ Cl ₂
Chloroform	CHCl ₃
Carbon tetrachloride	CCl ₄
Benzene	C ₆ H ₆
Toluene	Tol

Columns

The polymer pairs were dissolved in a mutual solvent (benzene) in which they showed neither phase separation nor turbidity at processing temperatures between ambient and 60°C. After homogenization of the solution, the mixed polymer stationary phase was deposited onto the support surface by continuous stirring and slow evaporation of benzene at 50°C under partial vacuum in a Rotavapor, following a common procedure and precautions. The PVAc-PnBMA mixed stationary phase was coated on Chromosorb P, AW, DMCS, 80/100 mesh, and the other mixed phases were coated on Chromosorb W, AW, DMCS, 80/100 mesh. The coated support was finally dried to constant weight in a vacuum oven; then it was sieved and packed in annealed copper tubing (90 cm × 0.625 cm). The composition of the mixed stationary phase and the mass ratio of the stationary phase to the support were adjusted prior to the coating process. The final column loading was estimated by ashing the coated and uncoated supports in triplicate under identical conditions at 550°C in an oven. In order to obtain retention data independent of the column loading, the mass ratio of the stationary phase to the support was kept above 0.12 following our earlier results²³⁻²⁵.

Chromatography

The gas chromatograph apparatus and the experimental procedure to measure the specific retention volume (V_g^0) of probes at infinite dilution on the polymer stationary phases were the same as described elsewhere¹⁷. Air was used as the internal marker and hydrogen as the carrier gas. The experimental error in V_g^0 was less than 1.5%. At the infinite dilution limit of the probes, the elution peaks were found to be symmetric and narrow, and V_g^0 was independent of the amount of probe used. However, V_g^0 decreased linearly with increase in the flow rate (F) of carrier gas. This effect, though small in

magnitude, was enhanced with an increase in the fractional concentration of PnBMA in PVAc, and of PVIBE in the other blends. In the case of PVAc-PnBMA blend, the flow-rate effect had diminished at 120°C. The extrapolated values of V_g^0 at zero flow rate, therefore, were employed to compute various interaction parameters as described below.

Data treatment

Flory-Huggins χ parameters characterizing the interactions of the vapour-phase probe (1) with each of the two polymers (2) and (3), and with their mixture (2-3), are determined from the retention data using three well-known equations^{2,3,27}:

$$\chi_{12} = \ln \left(\frac{273.16 R v_2}{V_{g,2}^0 P_1^0 V_1} \right) - \left(1 - \frac{V_1}{M_2 v_2} \right) - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (1)$$

$$\chi_{13} = \ln \left(\frac{273.16 R v_3}{V_{g,3}^0 P_1^0 V_1} \right) - \left(1 - \frac{V_1}{M_3 v_3} \right) - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (2)$$

$$\chi_{1(23)} = \ln \left(\frac{273.16 R (w_2 v_2 + w_3 v_3)}{V_{g,blend}^0 P_1^0 V_1} \right) - \left[\left(1 - \frac{V_1}{M_2 v_2} \right) \phi_2 + \left(1 - \frac{V_1}{M_3 v_3} \right) \phi_3 \right] - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (3)$$

where $R = 6.23732 \times 10^4$ ml min⁻¹; P_1^0 , V_1 and B_{11} are, respectively, the partial molar pressure, molar volume and second virial coefficient of the pure probe vapour; v_i and \bar{M}_i are, respectively, the specific volume and number-average molecular weight of polymer (i); w_i is the weight fraction and ϕ_i is the volume fraction of polymer (i) in the mixed stationary phase; the second subscript of V_g^0 identifies the nature of the column. The second term in the square brackets in equation (3) is reduced to unity for high-molecular-weight stationary phases^{2,19}. (Equation (2) is identical to equation (1), and is written above merely for clarity in the discussion.) The parameter $\chi_{1(23)}$ is affected by the interaction between the component polymers themselves, corresponding to χ_{23} , so that^{4,5}

$$\chi_{1(23)} = \phi_2 \chi_{12} + \phi_3 \chi_{13} - \phi_2 \phi_3 \chi_{23} (V_1/V_2) \quad (4)$$

In equation (4), the quantities χ_{12} , χ_{13} and $\chi_{23} V_1/V_2$ are all normalized to the size of the probe molecule (1). Since the component (2) is polymeric, χ_{23} becomes an inconveniently large quantity, hence the utility of the probe normalized parameter which is redefined as^{2,28}

$$\chi'_{23} \equiv (V_1/V_2) \chi_{23} \quad (5)$$

If parameters χ_{12} , χ_{13} and $\chi_{1(23)}$ are known (e.g. via equations (1) to (3)), χ'_{23} may be calculated from equation (4) as the only unknown². We shall call this method I. In the present work, the values of χ_{1i} and $V_{g,i}^0$ for the homopolymers were taken from the previous studies²³⁻²⁵ on the same polymer samples under identical conditions; P_1^0 , V_1 and B_{11} were derived from the physical constants of pure probes²⁹; $\chi_{1(23)}$ was determined from $V_{g,blend}^0$ using equation (3); and then χ_{23} was derived from equation (4).

Alternatively, χ'_{23} may be determined by using equation (6) below, which is obtained by manipulating

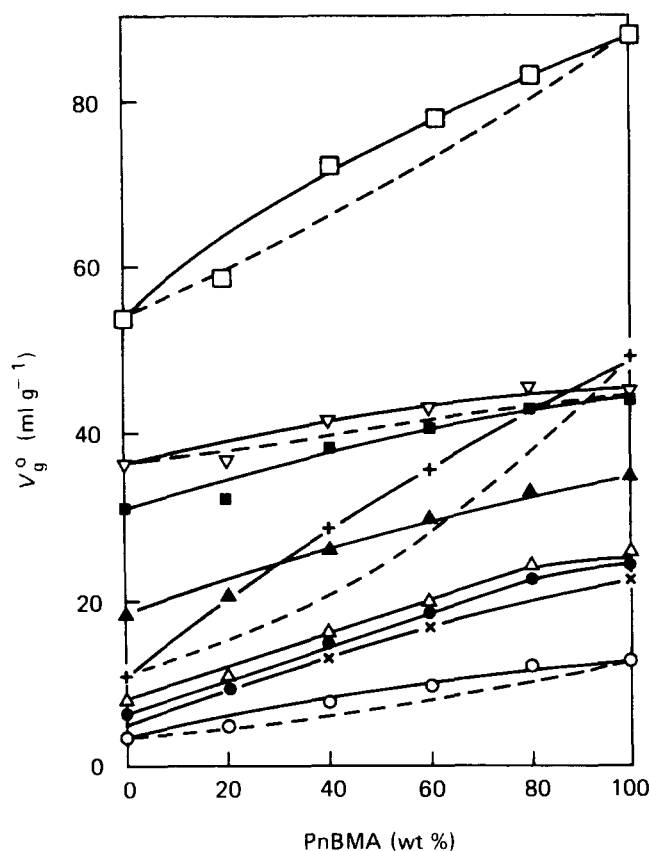


Figure 1 Dependence of probe retention volume on the composition of PVAc-PnBMA mixed stationary phase at 100°C: probes are n-hexane (○), n-heptane (●), n-octane (+), iso-octane (×), cyclohexane (△), chloroform (▽), carbon tetrachloride (▲), benzene (■) and toluene (□); the broken curves for n-hexane, n-octane, chloroform and toluene show the data predicted from equation (7)

equations (1) to (5) to cancel the common terms¹⁹:

$$\chi'_{23} = \frac{1}{\phi_2 \phi_3} \left[\ln \left(\frac{V_{g, \text{blend}}^0}{w_2 v_2 + w_3 v_3} \right) - \phi_2 \ln \left(\frac{V_{g,2}^0}{v_2} \right) - \phi_3 \ln \left(\frac{V_{g,3}^0}{v_3} \right) \right] \quad (6)$$

We shall call this method II.

As compared with method I, method II is believed to yield a more reliable value of the polymer-polymer interaction parameter in the sense that it saves many intermediate steps in computation and does not require *a priori* information about M_i , P_1^0 , V_1 and B_{11} , thus limiting the sources of error to the observable quantities only, i.e. V_g^0 , w_i and v_i . Therefore, the results computed by using equation (6) are presented in this publication. However, the results are not significantly different from those obtained by using method I since the physical constants of the probes were known accurately. As mentioned earlier, the additional subscript 'app' has been used with all χ parameters to indicate that they are sensitive to the composition of a given system and the nature of the probe employed.

RESULTS AND DISCUSSION

PVAc-PnBMA blend

The absolute values of the specific retention volumes of most of the probes on the mixed PVAc-PnBMA

stationary phase are small. Nevertheless, the following trends could be observed without any difficulty. The values of V_g^0 of alkane probes have increased linearly with increase in the weight fraction of PnBMA (w_3) in the mixed phase, and those of the other probes have increased nonlinearly (Figures 1 and 2). The changes are more regular at 120°C than at 100°C especially in the case of polar probes. For a random and homogeneous mixture of truly compatible polymer pairs, one may treat χ'_{23} as zero and rewrite equation (6) as below to predict $V_{g, \text{blend}}^0$ from the retention data of homopolymers:

$$V_{g, \text{blend}}^0 = (w_2 v_2 + w_3 v_3) (V_{g,2}^0 / v_2)^{\phi_2} (V_{g,3}^0 / v_3)^{\phi_3} \quad (7)$$

In this study, equation (7) has yielded lower values of $V_{g, \text{blend}}^0$ than the experimental data. This is illustrated by the broken curves for selected probes in Figures 1 and 2, which are slightly convex towards the composition axis.

The value of $\chi'_{1(23), \text{app}}$ has decreased nonlinearly from $\chi'_{1i, \text{app}}$ for pure PVAc to that for pure PnBMA as w_3 is raised to 0.8 (Table 3).

The polymer-polymer interaction parameter displays an extreme dependence on both the chemical nature of the probe and the composition of the blend (Tables 4 and 5). Although the trends in $\chi'_{23, \text{app}}$ are the same, there is a clear difference in the values of this parameter for different families of probes. Chloroform, carbon tetrachloride, benzene and toluene have yielded small values, indicating good miscibility for the blend. At 100°C, however, the unusually low values of $\chi'_{23, \text{app}}$ at 20 wt % PnBMA could not be explained, where the observed retention data were

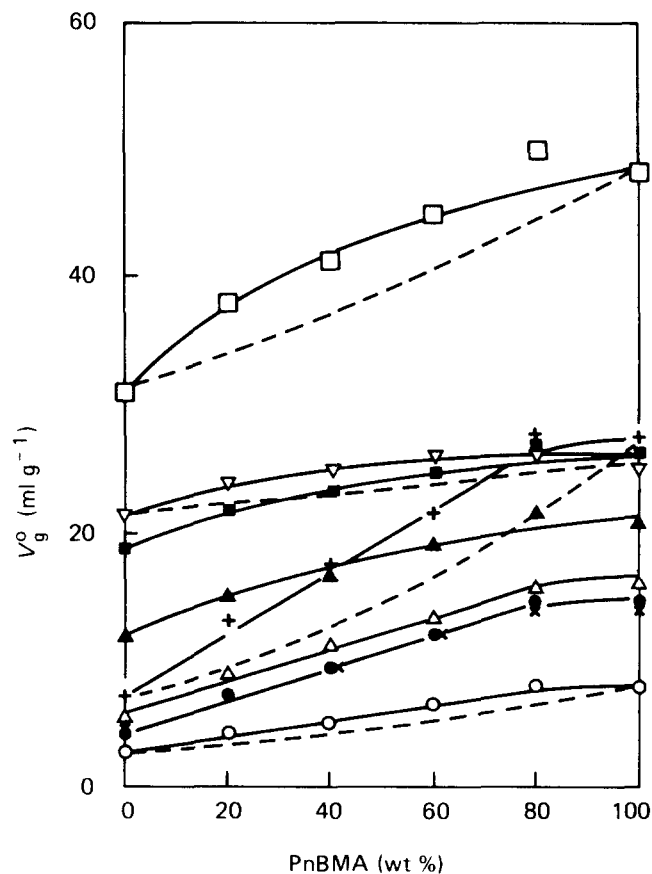


Figure 2 Dependence of probe retention volume on the composition of PVAc-PnBMA mixed stationary phase at 120°C: details are the same as in Figure 1

also smaller than the predicted values by $1.0 \pm 0.1 \text{ ml g}^{-1}$. The use of alkane probes has resulted in large positive values of $\chi'_{23, \text{app}}$. There are more unfavourable polymer-polymer interactions at higher temperature and at higher weight fractions of PnBMA in the blend. This means that the incompatibility of PVAc and PnBMA has increased under these conditions.

Patterson and coworkers^{30,31} and Hsu and Prausnitz³² have discussed the idea that the compatibility of polymers in solution should reflect not only the interaction between the polymers themselves (χ'_{23}) but also any difference between the interactions of the solvent with the polymers. They have called it a ' $\Delta\chi$ effect', so that

$$\Delta\chi = |\chi_{12} - \chi_{13}| \quad (8)$$

Thus, in addition to the high values of $\chi'_{23, \text{app}}$, the large ' $\Delta\chi$ effect' is also partly responsible for the incompatibility of PVAc and PnBMA in ternary solutions in an alkane

solvent (Tables 4 and 5). One may similarly argue that the compatibility of the blend should improve if an aromatic or a chlorinated aliphatic solvent is used to cast the blend or to prepare a ternary solution. This aspect will be investigated by using different techniques in future. There are other factors which might also contribute to the experimentally observed probe-to-probe variation of $\chi'_{23, \text{app}}$. Although the present results are not sufficient to confirm their effect, it is worth mentioning them below.

(i) Specific or H-bonding type interactions in some of the present polymer-probe systems²³⁻²⁵ might cause either short-range ordering or non-random mixing in their ternary solutions.

(ii) The values of $\chi_{12, \text{app}}$ and $\chi_{13, \text{app}}$ indicate that all probes interact more strongly with PnBMA than with PVAc (Tables 4 and 5). Then one may expect preferential sorption in microdomains rich in PnBMA in the blend.

(iii) Polymers may not be mixing at the molecular level as assumed in the theory⁹.

(iv) Certain sites of the polymer(s) may not be available to the probe molecules for interaction for some unknown reasons.

Table 3 Values of $\chi_{1(23), \text{app}}$ for various probes at different compositions of PVAc-PnBMA at 120°C

Probe	PnBMA ^a (wt %)					
	0 ^b	20	40	60	80	100 ^c
nC ₆	1.74	1.23	1.08	0.88	0.70	0.75
nC ₇	1.85	1.33	1.10	0.90	0.74	0.74
nC ₈	1.98	1.37	1.13	0.94	0.75	0.75
iC ₈	1.90		1.06	0.88		0.73
cC ₆	1.35	0.96	0.78	0.63	0.48	0.48
CHCl ₃	-0.03	-0.12	-0.12	-0.13	-0.15	-0.05
CCl ₄	0.67	0.47	0.37	0.28	0.19	0.26
C ₆ H ₆	0.36	0.25	0.22	0.17	0.12	0.19
Tol	0.50	0.33	0.28	0.22	0.14	0.19

^a In stationary phase; ^b Ref. 24; ^c Ref. 23

PVAc-PVIBE blend

This blend was studied only at 70°C and at two compositions for comparison with the other blends. The results show similar trends as in the case of PVAc-PnBMA (Table 6). The experimental values of $V_{\text{g, blend}}^0$ are higher than those predicted by equation (7), the difference being a minimum in the case of chloroform and aromatic probes and a maximum in other cases. The values of $\chi'_{23, \text{app}}$ determined by using chloroform and the aromatic probes indicate good compatibility for the blend. Carbon tetrachloride and the alkane probes show a strong ' $\Delta\chi$

Table 4 PVAc-PnBMA blend at 100°C: dependence of $\chi'_{23, \text{app}}$ on probe nature and composition of the blend

Probe	PVAc ²⁴ , $\chi_{12, \text{app}}$	PnBMA ²³ , $\chi_{13, \text{app}}$	PnBMA (wt %) in PVAc, $\chi'_{23, \text{app}}$				$ \Delta\chi $
			20	40	60	80	
nC ₆	1.930	0.743	0.450	0.967	0.921	1.279	1.151
nC ₇	2.035	0.753	0.844	1.167	0.929	1.227	1.278
nC ₈	2.143	0.771		1.252	1.033		1.362
iC ₈	2.165	0.779		1.315	1.197		1.386
cC ₆	1.562	0.550	0.194	0.748	0.818	1.132	1.012
CHCl ₃	-0.109	-0.175	-0.189	0.202	0.181	0.414	0.066
CCl ₄	0.712	0.222	-0.243	0.302	0.324	0.419	0.490
C ₆ H ₆	0.369	0.162	-0.203	0.235	0.219	0.265	0.207
Tol	0.513	0.179	-0.110	0.323	0.269	0.247	0.334

Table 5 PVAc-PnBMA blend at 120°C: dependence of $\chi'_{23, \text{app}}$ on the probe nature and composition of the blend

Probe	PVAc ²⁴ , $\chi_{12, \text{app}}$	PnBMA ²³ , $\chi_{13, \text{app}}$	PnBMA (wt %) in PVAc, $\chi'_{23, \text{app}}$				$ \Delta\chi $
			20	40 ^a	60 ^a	80	
nC ₆	1.746	0.748	1.669	0.938	0.984	1.570	0.998
nC ₇	1.856	0.743	1.564	1.117	1.082	1.413	1.113
nC ₈	1.977	0.749	1.903	1.252	1.120	1.477	1.228
iC ₈	1.903	0.730		1.352	1.225		1.173
cC ₆	1.351	0.488	1.153	0.793	0.750	1.085	0.863
CHCl ₃	-0.033	-0.048	0.446	0.338	0.386	0.698	0.019
CCl ₄	0.671	0.258	0.624	0.503	0.556	0.983	0.413
C ₆ H ₆	0.362	0.191	0.437	0.313	0.352	0.717	0.171
Tol	0.500	0.185	0.607	0.382	0.404	0.797	0.315

^a Ref. 17

Table 6 PVAc–PVIBE blend at 70°C: specific retention volumes V_g^0 (ml g⁻¹) of some probes, and the corresponding interaction parameters

Probe	PVIBE (wt %) in blend									Δχ
	PVAc, ^a		PVIBE ^{25, b}	30			50			
	V _{g,2} ⁰	χ _{12,app}		χ _{13,app}	V _{g,blend} ⁰	χ _{1(23),app}	χ _{23,app}	V _{g,blend} ⁰	χ _{1(23),app}	
nC ₆ ^c		2.20	0.53	19.0	1.10	2.16	28.0	0.77	1.94	1.67
nC ₇ ^c		2.29	0.54	42.5	1.12	2.33	62.0	0.82	1.91	1.76
nC ₈	22.0	2.45	0.59	93.0	1.16	2.68	141.0	0.80	2.39	1.86
iC ₈	17.5	2.56	0.52	36.5	1.15	2.93	54.5	0.81	2.40	2.04
cC ₆	14.0	1.90	0.36	38.5	0.93	1.79	54.5	0.64	1.55	1.54
CHCl ₃	83.0	−0.21	−0.10	93.5	−0.18	0.05	102.5	−0.22	0.30	0.11
CCl ₄	28.5	1.11	0.22	58.5	0.51	1.20	73.0	0.34	1.08	0.89
C ₆ H ₆	64.5	0.52	0.30	85.0	0.33	0.46	94.5	0.29	0.42	0.22
Tol	103.5	0.60	0.28	176.5	0.41	0.31	204.0	0.33	0.35	0.32

^a Extrapolated from higher-temperature data in Refs. 23 and 24; ^b $V_{g,3}^0$ in Table 7; ^c χ_{23,app} determined by method I**Table 7** Specific retention volumes $V_{g,blend}^0$ (ml g⁻¹) of various probes on PnBMA–PVIBE mixed stationary phase at 70°C

Probe	PVIBE ^a (wt %)				
	0 ^b	20	41.43	50	100 ^c
nC ₆	22.55	26.28	30.30	31.91	41.26
nC ₇	51.76	60.06	69.00	72.57	93.38
nC ₈	126.69	141.87	158.20	164.72	202.74
iC ₈	32.84	43.11	54.16	58.57	84.30
cC ₆	42.86	50.96	59.67	63.15	83.43
CH ₂ Cl ₂	47.22	46.58	45.89	45.61	44.00
CHCl ₃	112.47	111.02	109.45	108.83	105.18
CCl ₄	76.43	80.15	84.16	85.76	95.08
C ₆ H ₆	102.79	103.81	104.90	105.34	107.88
Tol	234.11	236.44	238.94	239.95	245.78

^a In stationary phase; ^b Ref. 23; ^c Ref. 25

effect' and yield large positive values of χ_{23,app}. In the composition range studied, χ_{23,app} has decreased with an increase in the weight fraction of PVIBE, except in the case of chloroform.

PnBMA–PVIBE blend

Although the retention data of the homopolymers differ widely, $V_{g,blend}^0$ has not changed appreciably with composition in the range investigated (Table 7). A simple calculation would show that, unlike in the case of previous blends, the experimental results are almost the same as or slightly lower than those predicted by equation (7). The values of χ_{23,app} are mostly negative despite a substantial 'Δχ effect' associated with many probes (Table

8); they decrease with an increase in the weight fraction of PVIBE. These results suggest strong, specific or polar-polar type interactions between PnBMA and PVIBE, and hence a compatible blend for all compositions irrespective of the solvent (probe) used.

The present results lead to the conclusion that the observed dependence of χ_{23,app} on the composition of the blend and the chemical nature of the probe is real. The stationary phases having the polymer-to-polymer ratio in the range 0.4–0.6 have yielded lower values of χ_{23,app} particularly when chloroform and the aromatic probes were used. The results predict a better compatibility for PnBMA–PVIBE than for the other blends. The present work, once again, demonstrates the potential of i.g.c., which should be exploited fully by realizing its two major advantages. First, any number of solvents that differ widely in their chemical nature and solubility characteristics can be used as probes even when their molecular properties are unknown. Secondly, a large body of thermodynamic data required for testing of new theories can be obtained with ease under extreme conditions of temperature and composition of blends.

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Table 8 PnBMA–PVIBE blend at 70°C: dependence of χ_{23,app} on the probe nature and composition of the blend

Probe	PnBMA ^{23,} χ _{12,app}	PVIBE ^{25,} χ _{13,app}	PVIBE (wt %) in PnBMA, χ _{23,app}			Δχ
			20	41.4	50	
nC ₆	0.975	0.526	-0.380	-0.735	-0.706	0.449
nC ₇	0.969	0.536	-0.296	-0.771	-0.923	0.433
nC ₈	0.898	0.586		-0.769	-0.860	0.312
iC ₈	1.292	0.523	0.376	-0.340	-0.868	0.769
cC ₆	0.871	0.358	0.198	-0.514	-0.756	0.513
CH ₂ Cl ₂	0.029	0.248	0.407	0.204	0.146	0.219
CHCl ₃	-0.317	-0.101	0.160	0.034	-0.006	0.216
CCl ₄	0.289	0.222	-0.380	-0.304	-0.432	0.067
C ₆ H ₆	0.194	0.296	-0.008	-0.016	-0.158	0.102
Tol	0.187	0.282	-0.080	-0.068	-0.097	0.095

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