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# Study of the miscibility of poly(styrene-co-4-vinylbenzoic acid) with poly(ethyl methacrylate) or with poly[ethyl methacrylate-co-(2-*N,N*-dimethylaminoethyl) methacrylate] by inverse gas chromatography

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## Abstract

Poly(styrene) is immiscible with poly(ethyl methacrylate). The introduction of a small amount of 4-vinylbenzoic acid units along poly(styrene) chains (PS-VBA) enhanced its miscibility with poly(ethyl methacrylate) (PEMA) or with poly[ethyl methacrylate-co-(2-*N,N*-dimethylaminoethyl) methacrylate] (PEMA-DAE), as observed from the appearance of a single composition dependent glass transition temperature for each binary system using inverse gas chromatography. The negative values of the apparent polymer-polymer interaction parameter,  $\chi_{23}^{app}$ , determined with different families of molecular probes, for three blend compositions and over a range of temperature confirm quantitatively the miscibility of these blends. The  $\chi_{23}^{app}$  values for PEMA(PS-VBA) and (PEMA-DAE)-(PS-VBA) blends are dependent of the chemical nature of the probes, the temperature and the blend composition.

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## 1. Introduction

The mixing of structurally different polymers is an easy and economical way to obtain new polymeric materials with a desirable combination of properties. It is well known that most polymer blends are immiscible [1], this is due to the small contribution of combinatorial entropy in mixing high molecular mass chains as well as to the endothermic heat of their mixing. Miscibility has been shown to be achieved if there is a favourable specific attractive

intermolecular interaction, such as hydrogen bonding [2–7], between the two components of a binary polymer blend.

Although polymer-polymer miscibility can be attested by a number of techniques such as differential scanning calorimetry, dynamic mechanical measurement, viscosimetry and dielectric measurement, inverse gas chromatography [8–12] (IGC), a reliable and useful method, provides detailed information on polymers such as glass-transition temperature, melt temperature, degree of crystallinity, diffusion constants of volatile probes in polymeric stationary phase, solubility parameters and surface energy, as well as polymer-solvent and polymer-polymer interaction parameters [13,14].

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In a previous report [15] poly(styrene-co-4-vinylbenzoic acid) containing 3.5, 6.5 and 7.4 mol% of acidic units was shown to be miscible over the entire range of composition with poly(ethyl methacrylate-co-4-vinylpyridine) as investigated by differential scanning calorimetry and Fourier transform infrared spectroscopy. In this study, IGC is used to analyse the miscibility of binary systems of poly(styrene-co-4-vinylbenzoic acid) containing 3.5 mol% of 4-vinylbenzoic acid (PS-VBA) with poly(ethyl methacrylate), (PEMA) and with poly[ethyl methacrylate-co-(2-*N,N*-dimethyl aminoethyl) methacrylate] (PEMA-DAE) having 12.8 mol% basic units, (PS-VBA)-(PEMA-DAE). Several probes, with different chemical nature and polarity, were used to determine glass transition temperatures and polymer-solute and polymer-polymer interaction parameters and to examine the contribution of the chemical nature of the probe, the temperature and the blend composition to the apparent polymer-polymer interaction parameter.

## 2. Experimental part

### 2.1. Materials

Styrene, (2-*N,N*-dimethylaminoethyl) methacrylate and ethyl methacrylate monomers (Merck, Darmstadt, Germany) were freshly distilled under reduced pressure just before use. 4-Vinylbenzoic acid (Fluka, Buchs, Switzerland) was recrystallized from water-ethanol (70:30) solution heated to 35–40 °C. The *n*-nonane, *n*-decane, *n*-dodecane, benzene, tetrahydrofuran (THF) and butanone (Fluka) probes were Chromatograde.

PEMA, PS-VBA and PEMA-DAE were prepared by free radical solution polymerization using 2,2'-azobisisobutyronitrile (Fluka) (1 g/kg) as initiator at 60 °C, under nitrogen as described elsewhere [3,15,16]. The polymers were purified by repeated dissolution/precipitation, isolated by filtration and dried to constant weight at 40 °C in a vacuum oven for several days.

### 2.2. Polymer characterization

The molar content of acidic group 4-vinylbenzoic acid (3.5 mol%) in PS-VBA copolymer was ob-

tained according to a standard titration [17] of the corresponding polymer solution in benzene-methanol (80:20 v/v) with a standardised sodium hydroxide solution (Fluka). The composition of PEMA-DAE copolymer [12.8 mol% of (2-*N,N*-dimethylaminoethyl) methacrylate] was determined from elemental analysis with a type EXETER Analytical Series CE 440 system (USA). The molecular masses of PS-VBA [number-average molecular mass ( $M_n$ ) 169 000, mass-average molecular mass ( $M_w$ ) 391 400,  $M_w/M_n=2.31$ ], PEMA ( $M_n=213 100$ ,  $M_w=385 900$ ,  $M_w/M_n=1.81$ ) and PEMA-DAE ( $M_n=124 500$ ,  $M_w=307 700$ ,  $M_w/M_n=2.47$ ) polymers were determined from THF solutions, by size-exclusion chromatography using a Waters GPC II (Massachusetts, USA) and poly(styrene) or poly(methyl methacrylate) standards.

### 2.3. IGC measurements

Measurements were made on a Hewlett-Packard 5730A gas chromatograph (Avondale, PA, USA) equipped with a flame ionization detector. Dried nitrogen was used as a carrier gas. The flow rate, 12 cm<sup>3</sup>/min, was measured at the end of the column with a soap bubble flowmeter, at room temperature. Column inlet and outlet pressures, read from a manometer, were used to correct retention volumes. Methane gas was used as a non-interacting marker to correct for dead volume in the column. A small quantity of solutes and marker ( $<10^{-7}$  l) were injected manually with a 1  $\mu$ l Hamilton syringe.

### 2.4. Column preparation

The support for the preparation of the chromatographic columns, Chromosorb W AW DMCS (60–80 mesh; Fluka) was coated with tetrahydrofuran polymeric solutions of the pure components and the blends in three mass proportions 2:1, 1:1 and 1:2 according to the soaking method of Al-Saigh and Munk [9]. Each impregnated stationary phase was then dried at room temperature to constant weight in a vacuum oven. The polymer loading was about 9%. It was packed into 150 cm stainless steel columns (Supelco, Saint Quentin, France), 0.3175 cm diameter. The columns were conditioned at  $T_g+50$  °C

Table 1  
Characteristics of the chromatographic columns

Polymer		Mass of support (g)	Mass of polymer (g)
PEMA		1.5970	0.1602
PEMA-DAE		1.6396	0.1644
PS-VBA		1.5233	0.1472
PEMA-(PS-VBA)	(2:1)	1.5453	0.1551
PEMA-(PS-VBA)	(1:1)	1.5456	0.1549
PEMA-(PS-VBA)	(1:2)	1.5447	0.1549
(PEMA-DAE)-(PS-VBA)	(2:1)	1.5184	0.1520
(PEMA-DAE)-(PS-VBA)	(1:1)	1.5525	0.1553
(PEMA-DAE)-(PS-VBA)	(1:2)	1.5630	0.1565

under nitrogen for 24 h prior to use. A summarized description of the columns is given in Table 1.

### 2.5. DSC measurements

The polymer blends PEMA-(PS-VBA) and (PEMA-DAE)-(PS-VBA) were prepared in three mass ratios (2:1, 1:1 and 1:2) by coprecipitation from THF solutions in an excess of light petroleum

(Fluka). The blends were dried in a vacuum oven at 60 °C for several days.

The glass transition temperature of the pure components and blends was measured with a Perkin-Elmer DSC-7 instrument (Norwalk, USA), previously calibrated with indium, at 20 K/min rate. The samples of 10–15 mg were preheated to 200 °C under nitrogen atmosphere and kept at that temperature for 10 min to ensure total elimination of solvent. The glass transition temperature was taken as the midpoint in the heat capacity change with temperature.

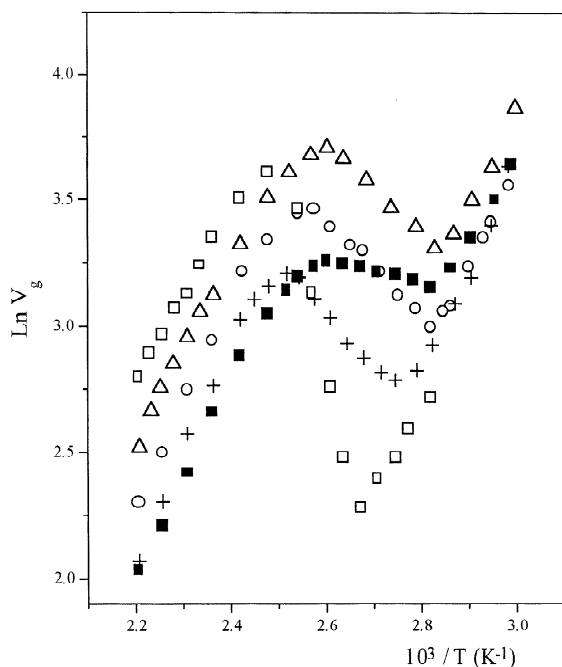


Fig. 1. Retention diagrams of PEMA-(PS-VBA) system using *n*-decane as molecular probe: 1:0 ( $\Delta$ ), 2:1 ( $\circ$ ), 1:1 ( $\blacksquare$ ), 1:2 ( $+$ ), 0:1 ( $\square$ ).

## 3. Results and discussion

### 3.1. Glass transition temperature

The specific retention volume of the solutes,  $V_g$  ( $\text{cm}^3/\text{g}$ ), used to describe the elution behavior of solutes, in pure PS-VBA, PEMA, PEMA-DAE and mixed PEMA-(PS-VBA), (PEMA-DAE)-(PS-VBA) stationary phases is calculated according to the following relationship:

$$V_g = 273.15(t_p - t_m)FJ \cdot \frac{P_0 - P_{\text{H}_2\text{O}}}{P_0 T_r w} \quad (1)$$

where  $t_p$ ,  $t_m$  are the probe and marker retention times, respectively,  $F$  is the gas carrier flow measured at the end of the column at  $T_r$ , room temperature,  $w$  is the mass of the polymeric stationary phase,  $P_{\text{H}_2\text{O}}$  is the vapour pressure of water at  $T_r$ , and  $J$  is the James and Martin factor, used to correct for the gas carrier compressibility defined as follows:

$$J = \frac{3}{2} \cdot \frac{[(P_i/P_0)^2 - 1]}{[(P_i/P_0)^3 - 1]} \quad (2)$$

where  $P_i$  and  $P_0$  are respectively the inlet and atmospheric pressures.

Typical retention diagrams,  $\ln V_g = f(1/T)$ , for the isolated components PEMA, PEMA–DAE, PS–VBA and their blends in different mass ratios using as low molecular mass probes *n*-decane and benzene, a non-solvent and solvent respectively of the polymer phases, are shown in Figs. 1–4. The obtained Z-shaped curves account for the change in the retention process of the probe by the stationary phase, switching from gas–solid to gas–liquid in the discontinuous region as induced by the increasing mobility of the polymeric chains going through the glass transition temperature. It was shown [18,19], by carrying out comparisons with other techniques of  $T_g$  determination, that the glass transition temperature value is best given by the first deviation from linearity of  $\ln V_g = f(1/T)$  curves. Each of the blends

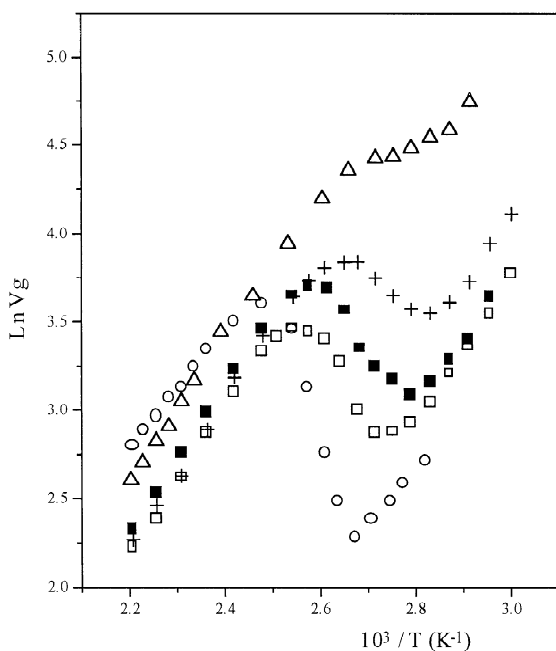


Fig. 2. Retention diagrams of (PEMA–DAE)–(PS–VBA) system using *n*-decane as molecular probe: 1:0 ( $\Delta$ ), 2:1 (+), 1:1 ( $\blacksquare$ ), 1:2 ( $\square$ ), 0:1 ( $\circ$ ).

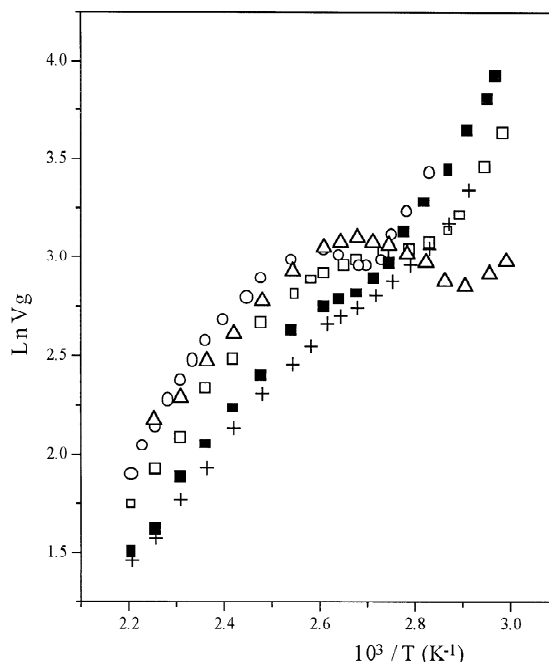


Fig. 3. Retention diagrams of PEMA–(PS–VBA) system using benzene as molecular probe: 1:0 ( $\Delta$ ), 2:1 ( $\square$ ), 1:1 (+), 1:2 ( $\blacksquare$ ), 0:1 ( $\circ$ ).

investigated is characterized by a single composition-dependent glass transition temperature, the value of which is intermediate between that of the pure components. Thus it is concluded that each binary system of PEMA–(PS–VBA) and of (PEMA–DAE)–(PS–VBA) forms a compatible blend. Moreover, the comparison of the values of  $T_g$  as deduced from DSC thermograms and IGC retention diagrams, Table 2, reveals that the  $T_g$ s detected with non-solvent, *n*-decane, as probe are closer than with solvent, benzene, to DSC values. Furthermore, the transition in the latter probe is less marked than in the former. We also note that the IGC values of  $T_g$  are located at lower temperatures than in DSC. This lowering, also observed by other authors [20], results from a phenomenon of plasticization and swelling of polymeric chains by the probe molecules; such an effect is more important with solvent than non-solvent probes. In order to establish the consequence of temperature on the homogeneity of each binary system and ascertain its miscibility the retention

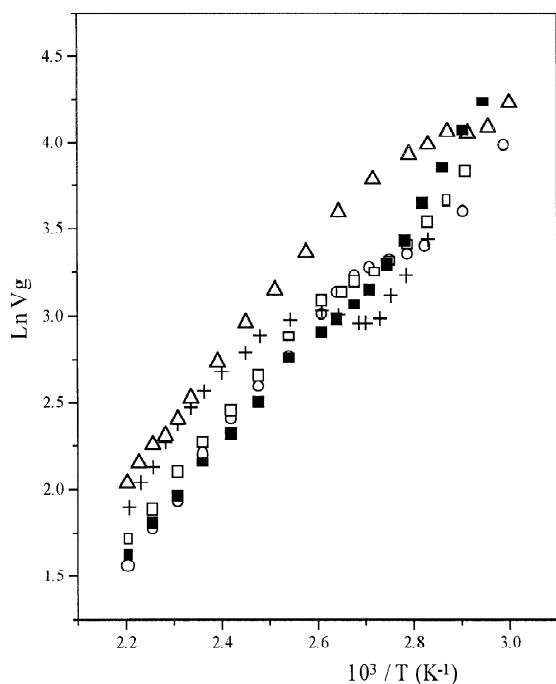


Fig. 4. Retention diagrams of (PEMA-DAE)-(PS-VBA) system using benzene as molecular probe: 1:0 ( $\Delta$ ), 2:1 ( $\circ$ ), 1:1 ( $\square$ ), 1:2 ( $\square$ ), 0:1 (+).

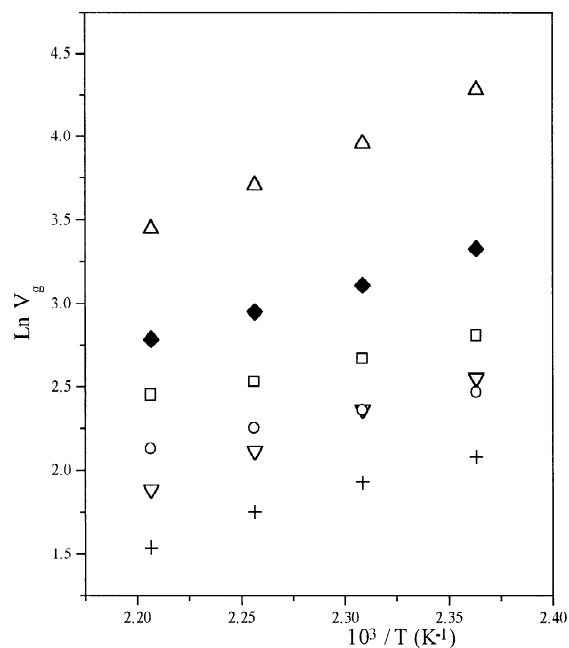


Fig. 5. Retention diagrams of PS-VBA in the 150–180 °C temperature range using different molecular probes: *n*-dodecane ( $\Delta$ ), *n*-decane ( $\blacklozenge$ ), *n*-nonane ( $\square$ ), benzene ( $\nabla$ ), THF ( $\circ$ ), butanone (+).

volume of each of six chemically different solute probes, through the stationary phase of the pure polymer components and their blends in three weight proportions, was monitored at selected temperatures

in the equilibrium region,  $T > T_g + 50$ . Plots of the retention diagrams in this temperature range, Figs. 5–13 are straight lines, as expected for stationary phases in a thermodynamic equilibrium state. The

Table 2  
Comparison of  $T_g$  values obtained by DSC and IGC techniques

Stationary phase	$T_g$ (°C)		DSC
	IGC		
	Benzene	<i>n</i> -Decane	
PEMA	–	–	62.0
PEMA-DAE	–	–	70.5
PS-VBA	93.5	101.9	109.0
PEMA-(PS-VBA) (2:1)	74.3	77.6	83.7
PEMA-(PS-VBA) (1:1)	79.6	81.8	90.9
PEMA-(PS-VBA) (1:2)	83.0	87.7	100.8
(PEMA-DAE)-(PS-VBA) (2:1)	75.6	80.6	87.3
(PEMA-DAE)-(PS-VBA) (1:1)	81.3	86.9	96.8
(PEMA-DAE)-(PS-VBA) (1:2)	85.2	93.7	101.5

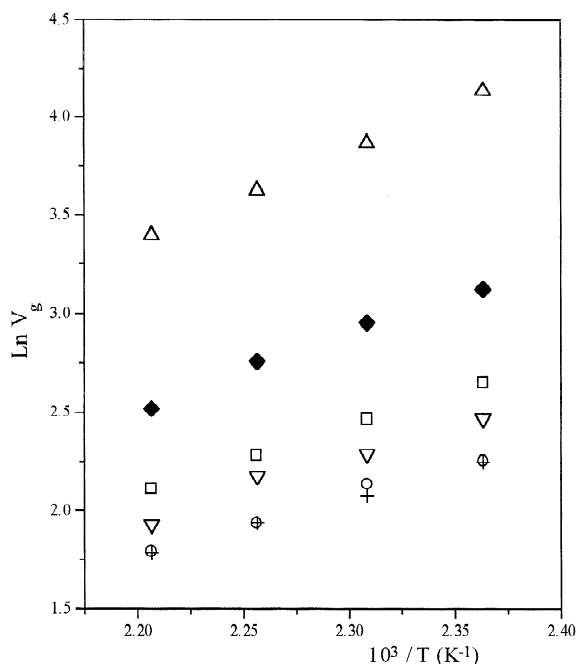


Fig. 6. Retention diagrams of PEMA in the 150–180 °C temperature range using different molecular probes: *n*-dodecane (Δ), *n*-decane (◆), *n*-nonane (□), benzene (∇), THF (○), butanone (+).

miscibility of the binary systems was then again checked qualitatively using the accumulated data by comparing the experimental retention volume of the polymer blends  $V_{g, \text{blend}}$  with that theoretically predicted from Eq. (3):

$$V_{g23}^{\text{the}} = W_2 V_{g12} + W_3 V_{g13} \quad (3)$$

where subscripts 1, 2 and 3 refer respectively to the probe and each one of the two polymer components,  $W_i$  and  $V_{g_{1i}}$  are, respectively, the mass fraction and the specific retention volume of each constituent of the blend. The negative deviation of the experimental specific retention volume of the blend from the mass average linear variation of the specific retention volumes of the pure constituents, observed as an illustration at the selected temperature of 180 °C in Figs. 14–15 for PEMA–(PS–VBA) and (PEMA–DAE)–(PS–VBA) for each molecular probe, is typical of a miscible blend.

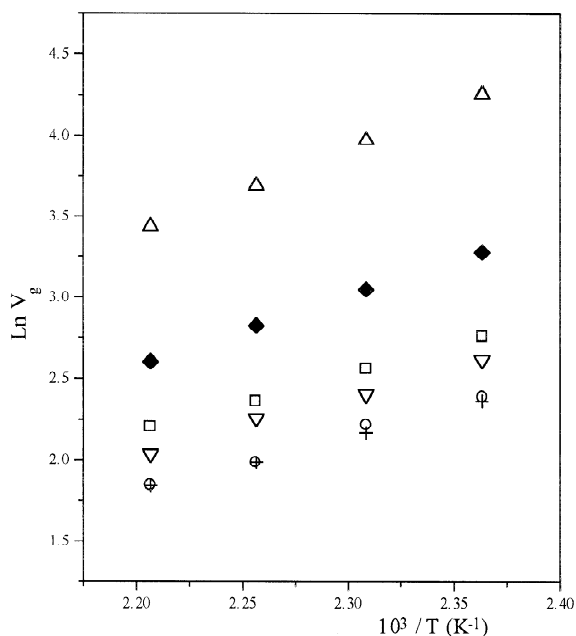


Fig. 7. Retention diagrams of PEMA–DAE in the 150–180 °C temperature range using different molecular probes: *n*-dodecane (Δ), *n*-decane (◆), *n*-nonane (□), benzene (∇), THF (○), butanone (+).

### 3.2. Thermodynamic study of the systems

At temperatures above  $T_g + 50$  °C, equilibrium bulk sorption is achieved and the polymer–solute and polymer–polymer–solute interaction parameters can be quantified in the studied binary mixtures.

### 3.3. Polymer–solute interaction parameter

The polymer–solute interaction parameters at infinite dilution of different probes were determined using the following relations [21,22]:

$$\chi_{1i} = \ln \left[ \frac{273.15 R v_i}{V_g^0 P_1^0 V_1} \right] - \left[ 1 - \frac{V_1}{M_i v_i} \right] - \frac{P_1^0}{RT} \cdot (B_{11} - V_1) \quad (4)$$

where  $P_1^0$ ,  $V_1$  are the solute saturation vapour pressure and liquid state molar volume, respectively, at  $T$  the column temperature,  $B_{11}$  refers to the second virial coefficient of the probe,  $v_i$  and  $M_i$  represent the

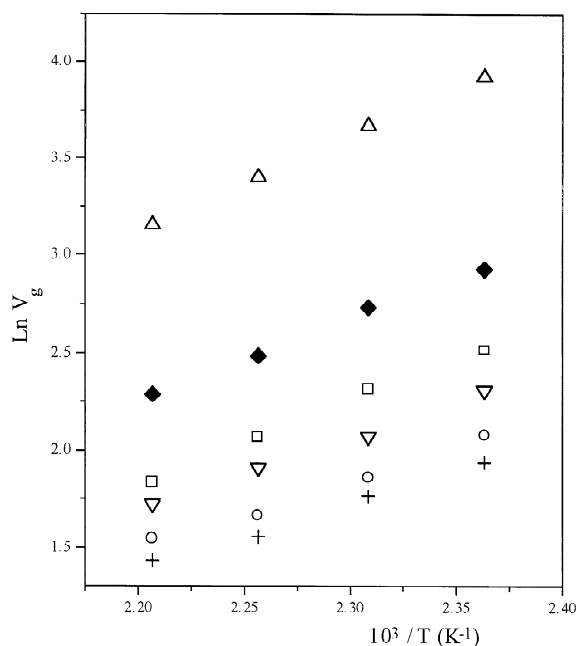


Fig. 8. Retention diagrams of PEMA-(PS-VBA) (2:1) blend in the 150–180 °C temperature range using different molecular probes: *n*-dodecane ( $\Delta$ ), *n*-decane ( $\blacklozenge$ ), *n*-nonane ( $\square$ ), benzene ( $\nabla$ ), THF ( $\circ$ ), butanone (+).

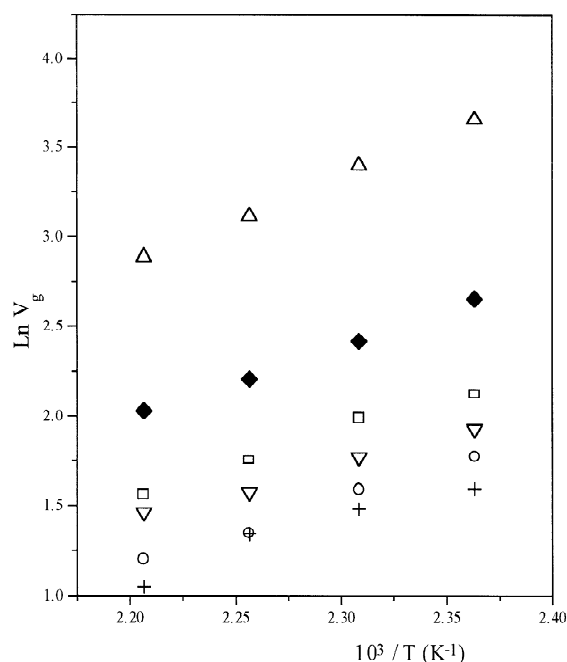


Fig. 9. Retention diagrams of PEMA-(PS-VBA) (1:1) blend in the 150–180 °C temperature range using different molecular probes: *n*-dodecane ( $\Delta$ ), *n*-decane ( $\blacklozenge$ ), *n*-nonane ( $\square$ ), benzene ( $\nabla$ ), THF ( $\circ$ ), butanone (+).

specific volume and molecular mass of the respective polymer  $i$ , and  $R$  is the gas constant.

From the values of  $\chi_{1i}$ , Table 3, it can be concluded that at the selected temperature range the polymer solubility in the six types of probe did change significantly, as compared to room temperature: the *n*-alkanes remain non-solvents and THF and benzene good solvents for PEMA, PEMA-DAE and PS-VBA, while butanone continues to be a good solvent for PEMA and PEMA-DAE but becomes a  $\theta$  solvent for the PS-VBA. It is worth noting that for the homologous *n*-alkane series the value of  $\chi_{1i}$  increases with the number of carbon of the probe at constant temperature, and that for each probe a rise in temperature improves the interaction with the polymeric chains.

### 3.4. Polymer-polymer interaction parameter

A quantification of the miscibility of these blends can be obtained by the calculation of the apparent

polymer-polymer interaction parameter  $\chi_{23}^{\text{app}}$ , which can be determined using the following equation:

$$\chi_{23}^{\text{app}} = \frac{1}{\phi_2 \phi_3} \left[ \ln \frac{V_{g23}}{W_2 v_2 + W_3 v_3} - \phi_2 \ln \frac{V_{g12}}{v_2} - \phi_3 \ln \frac{V_{g13}}{v_3} \right]$$

$$\phi_2 = \frac{W_2 v_2}{W_2 v_2 + W_3 v_3} \quad \phi_3 = \frac{W_3 v_3}{W_2 v_2 + W_3 v_3} \quad (5)$$

where  $v_i$ ,  $W_i$  and  $\phi_i$  are the specific volume, weight fraction and volume fraction, respectively of polymer  $i$ .

The values of the  $\chi_{23}^{\text{app}}$  parameter for the PEMA-(PS-VBA) and (PEMA-DAE)-(PS-VBA) blends are gathered in Tables 4 and 5. The negative values of  $\chi_{23}^{\text{app}}$ , determined in the temperature range [150–180 °C], using the various probes, indicate the occurrence of strong specific interactions between the polymer components which ensures the miscibility of these blends. Furthermore, its values in the studied range are found to be composition-dependent for

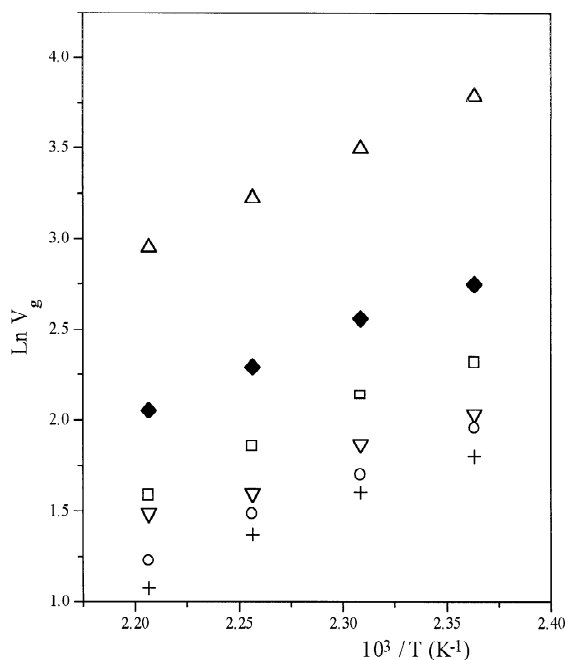


Fig. 10. Retention diagrams of PEMA–(PS–VBA) (1:2) blend in the 150–180 °C temperature range using different molecular probes: *n*-dodecane ( $\Delta$ ), *n*-decane ( $\blacklozenge$ ), *n*-nonane ( $\square$ ), benzene ( $\nabla$ ), THF ( $\circ$ ), butanone ( $+$ ).

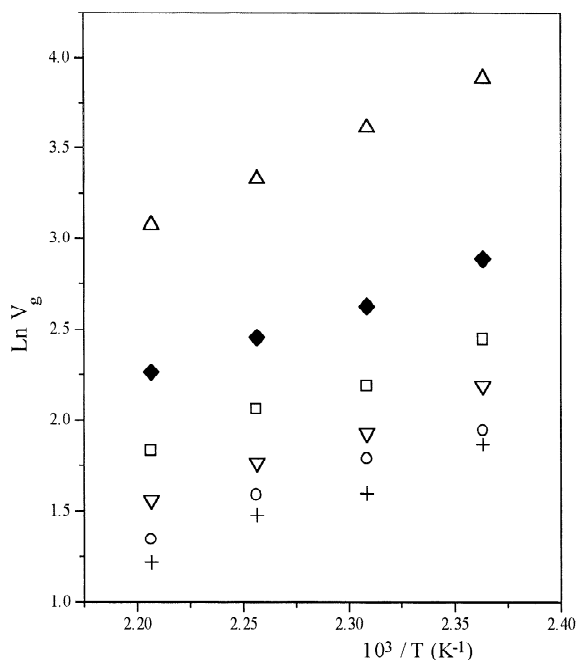


Fig. 11. Retention diagrams of (PEMA–DAE)–(PS–VBA) (2:1) blend in the 150–180 °C temperature range using different molecular probes: *n*-dodecane ( $\Delta$ ), *n*-decane ( $\blacklozenge$ ), *n*-nonane ( $\square$ ), benzene ( $\nabla$ ), THF ( $\circ$ ), butanone ( $+$ ).

both binary systems PEMA–(PS–VBA) and (PEMA–DAE)–(PS–VBA). The maximum of interaction between two components as reflected by the weakest values of  $\chi_{23}^{\text{app}}$  is observed with the blends containing an excess of PS–VBA (1/2 ratio).

Figs. 16–17 illustrate the evolution of  $\chi_{23}^{\text{app}}$  of PEMA–(PS–VBA) and (PEMA–DAE)–(PS–VBA) blends as a function of blend composition using various probes at the selected temperature of 170 °C; a similar behavior is observed for all the investigated temperature domain. It can be seen that  $\chi_{23}^{\text{app}}$  decreases with increasing temperature for the studied blend compositions and each of the six probes as a result of strong specific favourable polymer–polymer interactions. The densification of interacting sites can be due in one part to the disruption of the residual acid–acid dimeric interactions in favour of acid–ester or acid–nitrogen interactions and in the other part to an enhanced mobility of the chain segments with temperature facilitating the formation of hydrogen bonds which were initially far apart. In all cases,

it was observed that the  $\chi_{23}^{\text{app}}$  values exhibit a marked dependence on the probes, which is major problem encountered with the IGC technique [23–26].

According to Patterson and co-workers' [27,28] approach, the polymer–polymer interaction parameter is reflected all the more accurately as the term  $|\Delta\chi| = |\chi_{12} - \chi_{13}|$  would be the weakest possible and that the molecular probe develops the minimum of interactions with each of the two components of the polymers binary system. Our results show that, in the case of non-solvents, particularly at the maximum of interaction, at 1:2 weight ratio, the polymer–polymer interaction parameter follows the order:  $\chi_{23}^{\text{app}}$  (*n*-nonane) <  $\chi_{23}^{\text{app}}$  (*n*-decane) <  $\chi_{23}^{\text{app}}$  (*n*-dodecane).  $|\Delta\chi|$  evaluated for *n*-nonane, *n*-decane and *n*-dodecane molecular probes are of the same order of magnitude because they present a similar repulsion towards each polymers and the value of  $\chi_{23}^{\text{app}}$  obtained is most appropriate to interpret thermodynamic miscibility. On the other hand, we note that the phenomenon of preferential sorption of the probe



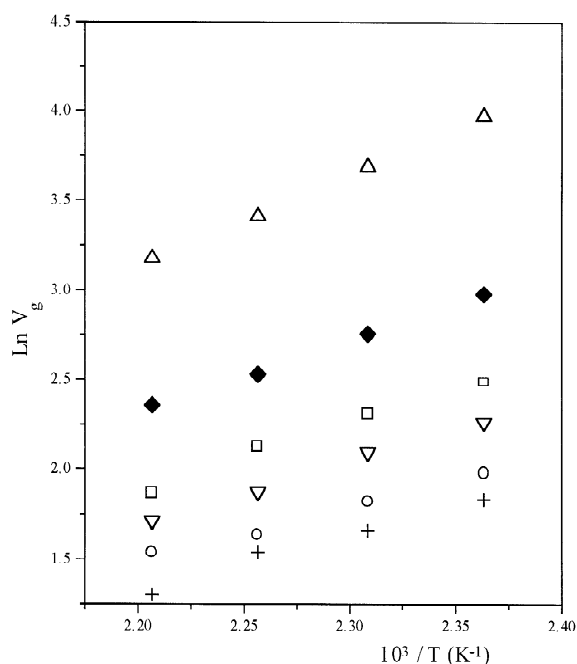


Fig. 12. Retention diagrams of (PEMA–DAE)–(PS–VBA) (1:1) blend in the 150–180 °C temperature range using different molecular probes: *n*-dodecane ( $\Delta$ ), *n*-decane ( $\blacklozenge$ ), *n*-nonane ( $\square$ ), benzene ( $\nabla$ ), THF ( $\circ$ ), butanone (+).

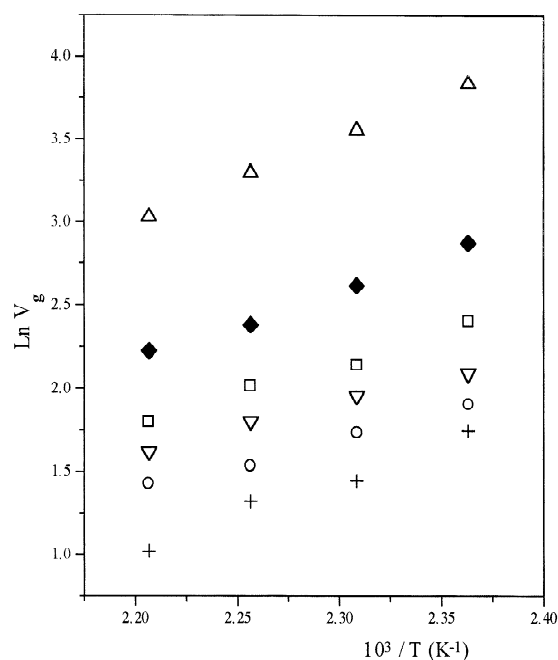


Fig. 13. Retention diagrams of (PEMA–DAE)–(PS–VBA) (1:2) blend in the 150–180 °C temperature range using different molecular probes: *n*-dodecane ( $\Delta$ ), *n*-decane ( $\blacklozenge$ ), *n*-nonane ( $\square$ ), benzene ( $\nabla$ ), THF ( $\circ$ ), butanone (+).

with respect to the two components leads to a reduction in the intensity of attractive interactions between the two polymers and affects the miscibility of the systems. It is the case of butanone, a mediocre solvent for the PS–VBA copolymer ( $\chi_{13} \cong 0.5$ ), which solvates in this temperature range preferentially PEMA ( $\chi_{12} < 0.5$ ), this behavior is reflected through slightly negative values of  $\chi_{23}^{\text{app}}$  of PEMA–(PS–VBA) system. A similar observation has already been reported in the literature [29]. In contrast, THF is a good solvent for the two components, its preferential solvation of PS–VBA chains ( $\chi_{13} < 0$ ) contributes to the disruption of the acid–acid dimeric interactions in favour of acid–ester or acid–nitrogen interactions, as reflected by more negative values of  $\chi_{23}^{\text{app}}$  for both PEMA–(PS–VBA) and (PEMA–DAE)–(PS–VBA) blends. The comparison of  $\chi_{23}^{\text{app}}$  values obtained with these systems at the composition of optimal interaction, 1:2 ratio, showed that at a given temperature and molecular probe, the  $\chi_{23}^{\text{app}}$  absolute values were larger for blends PEMA–(PS–

VBA) than for (PEMA–DAE)–(PS–VBA). This phenomenon can be attributed to fact that the bulky DAE units statistically distributed along the basic of PEMA–DAE copolymer chains might engender a steric effect and introduce an additional free volume, as compared to PEMA, and limit thereby the interactions with the acid copolymer.

#### 4. Conclusion

PS–VBA was found to be miscible with PEMA or PEMA–DAE. The detection of a single glass-transition temperature by IGC for each blend confirmed the miscibility of these systems over the entire range of composition. The negative deviation of retention volumes of the blends from the algebraic weight average  $V_{g23}^{\text{the}}$  of the pure components as well as the negative values of  $\chi_{23}^{\text{app}}$  confirm the established miscibility of these systems. This study showed that

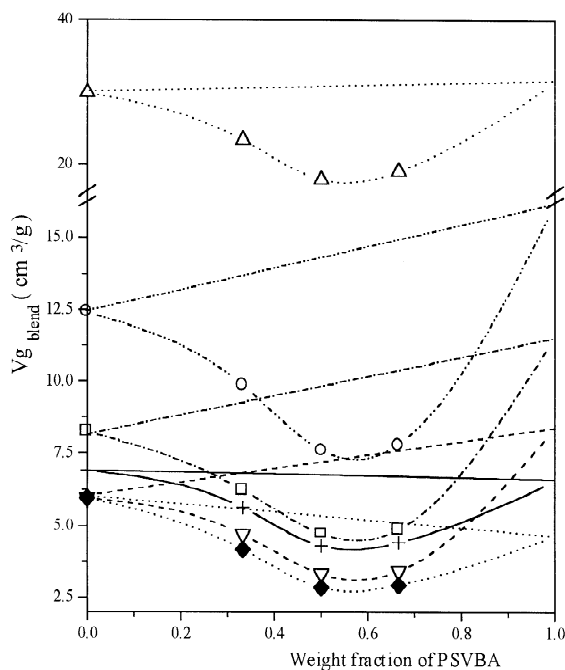


Fig. 14. Variation of the retention volume of PEMA-(PS-VBA) blends as a function of blend composition at 180 °C using various probes: *n*-dodecane ( $\Delta$ ), *n*-decane ( $\circ$ ), *n*-nonane ( $\square$ ), benzene (+), THF ( $\nabla$ ), butanone ( $\blacklozenge$ ).

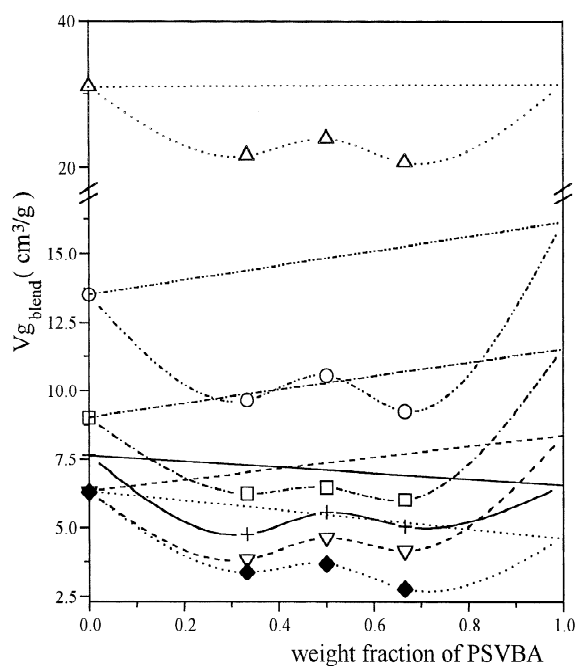


Fig. 15. Variation of the retention volume of (PEMA-DAE)-(PS-VBA) blends as a function of blend composition at 180 °C using various probes: *n*-dodecane ( $\Delta$ ), *n*-decane ( $\circ$ ), *n*-nonane ( $\square$ ), benzene (+), THF ( $\nabla$ ), butanone ( $\blacklozenge$ ).

$\chi_{23}^{app}$  depended of the nature of the probes, the temperature and the blend composition.

## 5. Nomenclature

$B_{11}$	second virial coefficient of the probe
$F$	gas carrier flow-rate
$J$	James and Martin factor
$M_i$	molecular mass of polymer $i$
$P_i$	inlet pressure
$P_0$	atmospheric pressure
$P_{H_2O}$	vapour pressure of water
$P_1^0$	saturation vapour pressure of the probe
$R$	gas constant
$T_p$	retention time of the probe
$t_m$	retention time of the marker
$T_g$	glass transition temperature
$T(T_r)$	(room) temperature

$V_{g23}^{the}$	theoretical retention volume of the polymer blend
$V_{g,blend}$	experimental retention volume of the polymer blend
$v_i$	specific volume of polymer $i$
$V_l$	liquid state molar volume of the probe
$V_g$	probe specific retention volume of the solute
$W$	mass of the polymeric stationary phase
$W_i$	mass fraction of polymer $i$
$\chi_{1i}$	polymer-solute interaction parameter
$\varphi_i$	volume fraction of polymer $i$
$\chi_{23}^{app}$	apparent polymer-polymer interaction parameter.

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Table 3  
Polymer–solute interaction parameter  $\chi_{1i}$  of PEMA, PEMA–DAE and PS–VBA

Polymer	Probe	150 °C	160 °C	170 °C	180 °C
PEMA	<i>n</i> -Nonane	1.03	0.97	0.91	0.85
	<i>n</i> -Decane	1.14	1.03	0.96	0.94
	<i>n</i> -Dodecane	1.23	1.17	1.09	1.02
	Benzene	0.19	0.18	0.11	0.18
	THF	0.20	0.13	0.14	0.12
	Butanone	0.32	0.29	0.23	0.20
PEMA–DAE	<i>n</i> -Nonane	0.93	0.89	0.85	0.77
	<i>n</i> -Decane	0.98	0.94	0.90	0.87
	<i>n</i> -Dodecane	1.11	1.08	1.04	0.99
	Benzene	0.05	0.08	0.04	0.09
	THF	0.06	0.05	0.11	0.08
	Butanone	0.21	0.21	0.19	0.15
PS–VBA	<i>n</i> -Nonane	0.95	0.83	0.72	0.57
	<i>n</i> -Decane	1.00	0.94	0.83	0.75
	<i>n</i> -Dodecane	1.15	1.14	1.08	1.04
	Benzene	0.18	0.17	0.24	0.30
	THF	0.05	−0.02	−0.08	−0.14
	Butanone	0.56	0.50	0.48	0.51

Table 4  
Apparent polymer–polymer interactions parameter  $\chi_{23}^{\text{app}}$  of PEMA–(PS–VBA) blends

Blend	Probe	150 °C	160 °C	170 °C	180 °C
PEMA–(PS–VBA) (2:1)	<i>n</i> -Nonane	−0.84	−0.96	−1.30	−1.74
	<i>n</i> -Decane	−1.16	−1.21	−1.48	−1.41
	<i>n</i> -Dodecane	−1.15	−1.00	−1.10	−1.14
	Benzene	−0.82	−1.07	−1.06	−0.80
	THF	−1.05	−1.58	−1.68	−1.57
	Butanone	−1.09	−1.14	−1.39	−1.18
PEMA–(PS–VBA) (1:1)	<i>n</i> -Nonane	−2.43	−2.31	−2.63	−2.90
	<i>n</i> -Decane	−2.28	−2.46	−2.59	−2.50
	<i>n</i> -Dodecane	−2.22	−2.07	−2.21	−2.14
	Benzene	−2.32	−2.22	−2.28	−1.77
	THF	−2.36	−2.68	−3.01	−3.03
	Butanone	−2.27	−2.07	−1.99	−2.44
PEMA–(PS–VBA) (1:2)	<i>n</i> -Nonane	−2.04	−2.12	−2.74	−3.48
	<i>n</i> -Decane	−2.36	−2.30	−2.75	−2.96
	<i>n</i> -Dodecane	−2.07	−2.00	−2.11	−2.22
	Benzene	−2.27	−2.15	−2.46	−1.88
	THF	−2.03	−2.71	−3.03	−3.63
	Butanone	−1.52	−1.70	−2.01	−2.49

Table 5  
Apparent polymer–polymer interactions parameter  $\chi_{23}^{app}$  of (PEMA–DAE)–(PS–VBA) blends

Blend	Probe	150 °C	160 °C	170 °C	180 °C
(PEMA–DAE)–(PS–VBA) (2:1)	<i>n</i> -Nonane	–1.45	–1.76	–1.57	–1.99
	<i>n</i> -Decane	–1.80	–1.94	–1.79	–1.75
	<i>n</i> -Dodecane	–1.65	–1.54	–1.63	–1.60
	Benzene	–1.75	–2.01	–1.93	–1.84
	THF	–2.07	–2.14	–2.16	–2.61
	Butanone	–1.73	–2.13	–1.87	–2.27
(PEMA–DAE)–(PS–VBA) (1:1)	<i>n</i> -Nonane	–1.17	–1.21	–1.26	–1.84
	<i>n</i> -Decane	–1.30	–1.29	–1.43	–1.35
	<i>n</i> -Dodecane	–1.20	–1.11	–1.15	–1.06
	Benzene	–1.27	–1.15	–1.23	–0.96
	THF	–1.81	–1.89	–1.93	–1.83
	Butanone	–1.54	–1.54	–1.30	–1.52
(PEMA–DAE)–(PS–VBA) (1:2)	<i>n</i> -Nonane	–1.79	–2.23	–2.10	–2.63
	<i>n</i> -Decane	–2.02	–2.17	–2.44	–2.30
	<i>n</i> -Dodecane	–2.01	–1.87	–1.86	–1.89
	Benzene	–2.21	–1.91	–1.64	–1.42
	THF	–2.50	–2.67	–2.86	–2.82
	Butanone	–1.94	–2.57	–2.32	–2.82

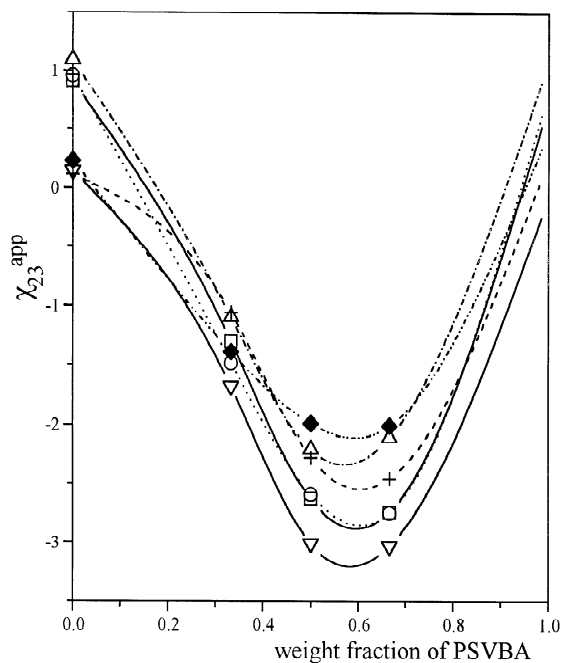


Fig. 16. Composition dependence of  $\chi_{23}^{app}$  at 170 °C for (PEMA–DAE)–(PS–VBA) blends using various probes: *n*-dodecane ( $\Delta$ ), *n*-decane ( $\circ$ ), *n*-nonane ( $\square$ ), benzene (+), THF ( $\nabla$ ), butanone ( $\blacklozenge$ ).

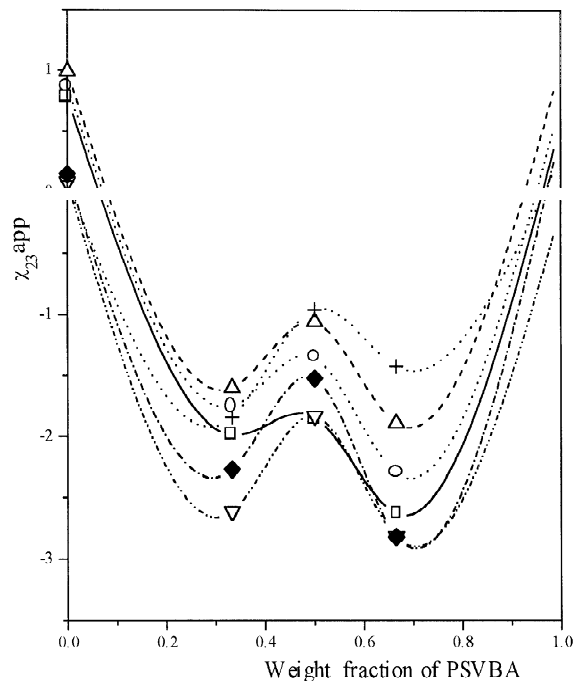


Fig. 17. Composition dependence of  $\chi_{23}^{app}$  at 170 °C for (PEMA–DAE)–(PS–VBA) blends using various probes: *n*-dodecane ( $\Delta$ ), *n*-decane ( $\circ$ ), *n*-nonane ( $\square$ ), benzene (+), THF ( $\nabla$ ), butanone ( $\blacklozenge$ ).

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