intense peaks at high masses which correspond in all cases to the molecular ion of the compound. This feature is characteristic of mass spectra of cyclic compounds and therefore permits an easy detection of these compounds by MS. Further peaks in the spectrum of oligomer I (Figure 2) originate from loss of CO (peak at m/z 736) and CO_2 (peak at m/z 720) from the molecular ion. A metastable peak corresponding to the latter fragmentation is found in the spectrum.

Cyclic urea II (Figure 3) is very stable to electron impact and the molecular ion is by far the most intense peak observed.

Compound III (Figure 4) shows loss of hydrogen from the molecular ion and loss of a neutral fragment of mass 57 from the molecular ion and from the M − 1 peak (ions at m/z 365 and 364, respectively). The neutral fragment lost probably corresponds to CH_3NCO. The same fragmentation pattern gives the peaks at m/z 787 and 786 in compound IV.

Loss of methyl isocyanate is an EI process similar to the very frequent loss of CO_2 observed in the EI spectra of cyclic esters, carbonates, and urethanes.[6,9,10]

As mentioned above, since the cyclic oligomers identified here are novel compounds, after their detection in the polycondensation mixtures, they were isolated from the polymers by solvent extraction and subsequent crystallization. The mass spectra of the pure compounds were identical with those shown in Figures 2–5, and the ^{1}H NMR spectra were in agreement with formulas I–IV (Table I).

Conclusion

The foregoing examples show the remarkable potential of MS in the detection of cyclic oligomers contained in polymeric samples. The unique advantage of this method consists in allowing simultaneous detection and identification of the cyclic oligomer, therefore eliminating the isolation and subsequent identification steps.

Furthermore, we have observed that when a linear programmed heating of the probe is used, the "retention times" of the cyclic oligomers (i.e., the peak appearance in the TIC curves) are quite constant.

This encourages further development of the MS method to the detection and separation of more complex oligomer mixtures. In the latter case, the use of single-ion curves (SIC),[8] corresponding to the intensity of a single mass ion, might prove very useful for increasing the "resolution" of this technique.

Acknowledgment. This work was partially supported by Consiglio Nazionale delle Ricerche (CNR), Rome.

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Gas Chromatographic Investigation of Poly(vinylidene fluoride)–Poly(methyl methacrylate) Blends

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ABSTRACT: Inverse gas chromatography was used to investigate the thermodynamic miscibility of molten poly(vinylidene fluoride)–poly(methyl methacrylate) blends. In addition to glass transition and melting point depression data, polymer–polymer interaction parameters, χ_{23}', were determined from the measured retention data for various polar and nonpolar probes in pure and mixed stationary phases of these polymers. Negative interaction parameters are observed in accordance with the well-known miscibility of these blends. The magnitude and the trend in the composition dependence of χ_{23}' are in excellent agreement with literature results obtained from small-angle X-ray scattering and calorimetry.

Introduction

There is currently a great deal of research interest in miscible polymer blends since such mixtures may represent a valuable and economical alternative to the use of copolymers.[3,4] However, truly miscible multicomponent polymer systems are rather infrequent. A thermodynamic study of polymer–polymer interactions can lead to an understanding of the resulting blend's miscibility and therefore to the selection of compatible polymer systems.

Recently, the usefulness of inverse gas chromatography (IGC) in the investigation of polymer–probe and polymer–polymer interactions has been widely recognized.[3,5] This method provides a fast and convenient way of obtaining thermodynamic data for concentrated polymer systems.

Mixtures of poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVF_2) have recently been the subject of great interest. A number of workers have reported evidence of true molecular mixing of these two polymers over a wide range of composition.[6–9] Calorimetric measurements and various spectroscopic techniques, including X-ray scattering,[7] Fourier transform infrared

0024-9297/82/2215-0885$01.25/0

Table I
Stationary Phase and Column Parameters

polymer or blend	loading, % (w/w)	wt of polymer, g	column length, cm
PVF_2	11.77	2.0600	152
PMMA	10.45	1.4490	119
PVF_2-PMMA blends			
25 wt % PVF_2	10.82	1.5342	119
50 wt % PVF_2	10.69	1.8271	144
75 wt % PVF_2	11.80	1.9634	152
90 wt % PVF_2	10.78	1.8615	152

spectroscopy,[10] and pulsed NMR spectroscopy,[11] have been used to investigate the compatibility of these blends. The PVF_2-PMMA system is one of the few for which thermodynamic interaction parameters have been measured. Both Nishi and Wang[6] (melting point depression studies) and Wendorff[7] (X-ray scattering studies) have reported negative interaction parameters (χ), which are indicative of the miscibility of PMMA and PVF_2.

Since IGC allows the determination of these interaction parameters, a comparative study of PVF_2-PMMA blends was undertaken as a function of blend composition.[12]

Experimental Section

Materials. All solutes were chromatoquality or reagent grade and were used without further purification. Poly(vinylidene fluoride) (PVF_2), Kynar 881, was supplied by Pennwalt Corp. in powder form. Poly(methyl methacrylate) (PMMA), Acrylite H-12, was supplied by the American Cyanamid Co. in pellet form. Chromosorb G (AW-DMCS treated, 70/80 mesh) was obtained from Johns-Manville.

Columns. The columns were prepared in the usual manner.[12,13] The polymers were coated from a hot *N,N*-dimethylformamide (DMF) solution onto Chromosorb G. All coatings were thoroughly dried in a vacuum oven for several days and resieved (70/80 mesh) before packing into 48-mm-i.d. copper columns. The total percent loading of polymer on the support was determined by calcination using a suitable blank correction. The relative concentration of polymers in the blends is assumed to be identical with that in the original solution prior to deposition on the inert support. The PVF_2 column was conditioned under nitrogen for 2 h at 230 °C. All other columns were conditioned at 200 °C because of base line instability at higher temperatures. The columns are described in Table I.

Instrumentation. IGC measurements were carried out with a Hewlett-Packard 5830 gas chromatograph which was equipped with a dual flame ionization detector and a cryogenic option (liquid N_2) for operation down to -50 °C. The oven temperature was measured with a Hewlett-Packard platinum resistance thermometer with a precision of ± 0.01 °C. Carrier gas (nitrogen) flow rates (5–20 $cm^3\ min^{-1}$) were measured from the end of the column with a water-jacketted soap bubble flowmeter. The net retention time of a probe (± 0.01 min) was determined from the peak maxima retention times for the probe and a methane marker. Column inlet and outlet pressures were read from a mercury manometer (± 0.05 mmHg). The experimental procedure has been described previously.[13,14]

Calorimetric measurements (DSC) were carried out with a DuPont 990 thermal analyzer. A scanning rate of 10 °C/min and sample sizes ranging from 5 to 10 mg were used.

Data Reduction. Specific retention volumes, V_g° (cm^3/g), were computed from the familiar expression of Littlewood et al.[15]

$$V_g^\circ = t_N F J / w_L \qquad (1)$$

where t_N is the net retention time for the probe, F is the carrier gas flow rate at 0 °C and 1 atm (STP), J is a correction factor for gas compressibility, and w_L is the weight of polymer in the column.

At temperatures above T_g, the magnitude of V_g° is a measure of the solubility of the probe in the stationary phase. By applying thermodynamic theory to gas chromatography, one can relate the measured V_g° to the weight fraction activity coefficient at infinite dilution of the probe, $(a_1/w_1)^\infty$, a fundamental parameter of solution thermodynamics which indicates deviation from ideal solution behavior.[16]

Table II
Comparison of Specific Retention Volumes and Weight Fraction Activity Coefficients for Various Solutes in PVF_2 and PMMA at 200 °C

	PVF_2		PMMA	
solute	V_g°, cm^3/g	$(a_1/w_1)^\infty$	V_g°, cm^3/g	$(a_1/w_1)^\infty$
acetophenone	32.53	6.32	41.21	4.96
cyclohexanone	15.94	5.46	16.11	5.38
N,N-dimethylformamide[a]	30.71	3.21	16.38	5.99
cyclohexanol	6.29	11.05	15.67	4.91
n-butylbenzene	5.09	23.93	13.99	8.67
tetralin	11.67	18.28	31.07	6.83
o-dichlorobenzene	9.30	11.12	24.56	4.18
1-chlorooctane	3.94	28.51[a]	10.65	10.51[a]
1-chlorodecane	6.58	37.78[a]	21.58	11.46[a]
n-tetradecane	3.22	145.97	15.05	31.14

[a] The values listed are not corrected for vapor phase nonideality of the probe.

$$\ln (a_1/w_1)^\infty = \ln (273.16R/V_g^\circ p_1^\circ M_1) - p_1^\circ(B_{11} - V_1)/RT \qquad (2)$$

where V_1, M_1, and p_1° refer to the solute molar volume, molecular weight, and saturated vapor pressure, respectively, R is the gas constant, T is the column temperature (K), and B_{11} is the second virial coefficient, which is used to correct for vapor phase nonideality of the probe. Values of B_{11} were estimated from corresponding equations of state.[17,18] Solute vapor pressures were obtained from Dreisbach's compilation.[19] Solute densities were obtained from various sources, including the compilations by Orwoll and Flory[20] and Timmermans,[21] as well as the International Critical Tables.[22]

From the Flory–Huggins treatment of solution thermodynamics,[23] one can obtain the χ parameter, which is a measure of the residual free energy of interaction between solute and polymer.[16] χ is determined from the relationship

$$\chi_{12} = \ln (273.16Rv_2/V_g^\circ p_1^\circ V_1) - (1 - V_1/V_2)\Phi_2 - p_1^\circ(B_{11} - V_1)/RT \qquad (3)$$

where v_2, V_2, and Φ_2 refer to the specific volume, molar volume, and volume fraction of the polymer. All other symbols have their usual meanings. For high molecular weight polymer and infinite dilution of probe the second term of eq 3 [i.e., $(1 - V_1/V_2)\Phi_2$] approaches 1.

It has been shown[24] using Scott's ternary solution treatment[25] of the Flory–Huggins theory that the overall interaction parameter between the volatile probe (1) and the binary stationary phase (2–3) is given by

$$\chi_{1(23)} = \ln [273.16R(w_2v_2 + w_3v_3)/V_g^\circ p_1^\circ V_1] - (1 - V_1/V_2)\Phi_2 - (1 - V_1/V_3)\Phi_3 - p_1^\circ(B_{11} - V_1)/RT \qquad (4)$$

where w_2 and w_3 refer to the weight fractions of PVF_2 and PMMA in the blend.

The volumetric data for the blends were determined by assuming that the specific volume of the blend is the weight average of the specific volumes of the parent homopolymers.[26,27]

Results and Discussion

Specific retention volumes, V_g° (cm^3/g), were measured for various probes in pure PVF_2, in pure PMMA, and in mixed stationary phases containing 25, 50, 75, and 90 wt % PVF_2. The molten blends were studied at 200 °C, a temperature well above the melting point of pure PVF_2.[6,8] The precision of the experimental V_g° is better than 3%.

Homopolymers. The poor solubility of many organic solvents in PVF_2 is illustrated by the measured thermodynamic interaction data for PVF_2 at 200 °C (Tables II

Table III
Excess Partial Molar Heats of Mixing ($\Delta\bar{H}_1^\infty$) for Various Solutes with PVF_2 between 190 and 230 °C

solute	$\Delta\bar{H}_1^\infty$, kcal/mol
acetophenone	−0.14
cyclohexanone	0.23
N,*N*-dimethylformamide[a]	−2.14
cyclohexanol	4.34
n-butylbenzene	1.58
tetralin	1.57
o-dichlorobenzene	1.45
1-chlorooctane[a, b]	1.92
1-chlorodecane[a]	2.57
n-tetradecane[c]	4.72

[a] The values listed are not corrected for vapor phase nonideality of the probe, since the B_{11} data were not available. [b] Between 190 and 220 °C. [c] Between 190 and 215 °C.

and III). Large activity coefficients (10 → 150), χ parameters (1 → 3), and endothermic excess heats of mixing ($\Delta\bar{H}_1^\infty$ = 1 → 5 kcal/mol between 190 and 230 °C) are observed for both aliphatic and aromatic probes. These nonsolvent probes have V_g° values less than 15 cm^3/g at 200 °C. The carbonyl-containing probes, however, are good solvents for PVF_2. Their interaction is characterized by smaller activity coefficients (3 → 6) and χ parameters (−0.6 → 0.2) and exothermic or nearly athermal excess heats of mixing (−2.0 → 0.2 kcal/mol). These probes are characterized by V_g° values between 15 and 40 cm^3/g. Except for acetophenone, cyclohexanone, and DMF, every other probe investigated showed a higher solubility in PMMA (Tables II and III). These results indicate that the presence of a carbonyl group in the probe is important in determining miscibility with PVF_2, which is in accord with previous reports that suggest that the carbonyl group is probably responsible for a specific interaction between PMMA and PVF_2.[10,28]

Polymer Blends. The miscibility of PVF_2-PMMA blends is confirmed by melting point depression, glass transition, and thermodynamic interaction data obtained by IGC. These results are in excellent agreement with previous investigations of miscibility using other techniques.

Melting Transition. Preliminary DSC experiments on the coated supports used for the IGC studies revealed melting endotherms for blends containing 50, 75, 90, and 100 wt % PVF_2. Retention diagrams for these blends (Figure 1) were therefore obtained by "probing" the stationary phases over a wide temperature range encompassing the melting regions observed by DSC. The probes used were *o*-dichlorobenzene (for PVF_2) and 1-chlorooctane (for the polymer blends). The melting point,[5] T_m, of pure PVF_2 (173 ± 2 °C) determined from IGC is consistent with the present as well as previously reported calorimetric data.[6,8]

The composition dependence of the melting point of PVF_2 is illustrated in Figure 2a. T_m decreases steadily with decreasing PVF_2 content. The maximum melting point depression is observed for a 50:50 mixture of PVF_2-PMMA. Blends containing less than 50% PVF_2 are amorphous.

Nishi and Wang[6] have demonstrated that the melting point depression of PVF_2 crystals in PVF_2-PMMA blends can be explained by Scott's[25] thermodynamic treatment for mixing a semicrystalline polymer with a miscible diluent. Their analysis indicates this behavior implies miscibility and allows for the calculation of the polymer-polymer interaction parameter. A χ value ca. −0.3 at 160 °C was reported.

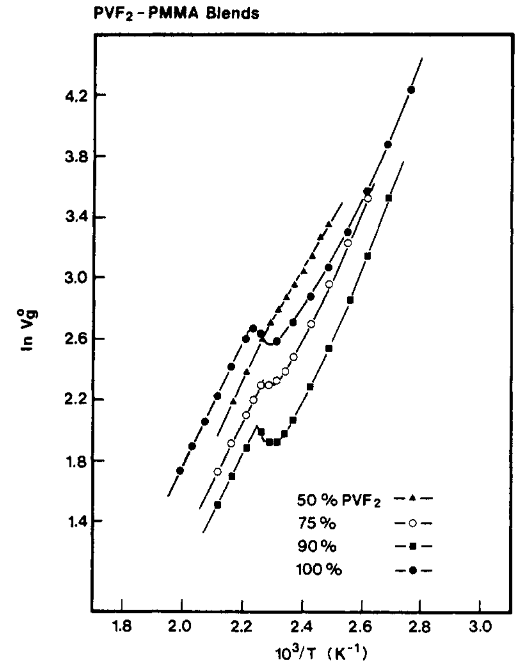

Figure 1. Retention diagrams for various PVF_2-PMMA blends in the melting region.

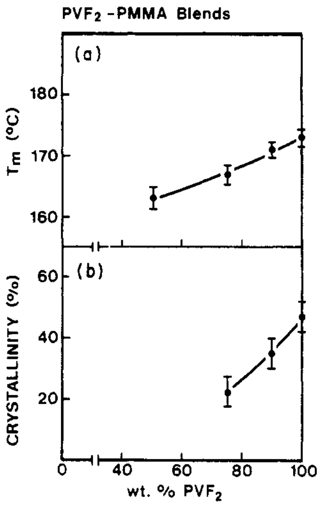

Figure 2. Composition dependence of (a) T_m and (b) percent crystallinity.

The crystalline content of a polymer is another parameter easily measured by IGC.[5] By extrapolating the linear portion of the retention diagram above T_m to lower temperatures, one can calculate the retention volume that corresponds to a hypothetical, completely amorphous polymer below T_m. The ratio of the measured V_g° to the extrapolated $V_g^{\circ *}$ at the same temperature will yield the weight percent crystallinity of the polymer or polymer blend:

$$\text{percent crystallinity} = 100(1 - V_g^\circ / V_g^{\circ *}) \qquad (5)$$

Figure 2b shows that the extent of crystallinity is a quasi-linear function of composition that decreases from ca. 50 ± 5% for pure PVF_2 to near zero for a PVF_2-PMMA blend containing 50 wt % PVF_2. The crystalline content of pure PVF_2 has been reported to lie between 50% and 68%.[8,29]

Glass Transition. Figure 3 illustrates the retention diagrams that were used to extract T_g data[5] for the various blends (*n*-alkanes were used as probes). Each of the blends investigated is characterized by a single, composition-de-

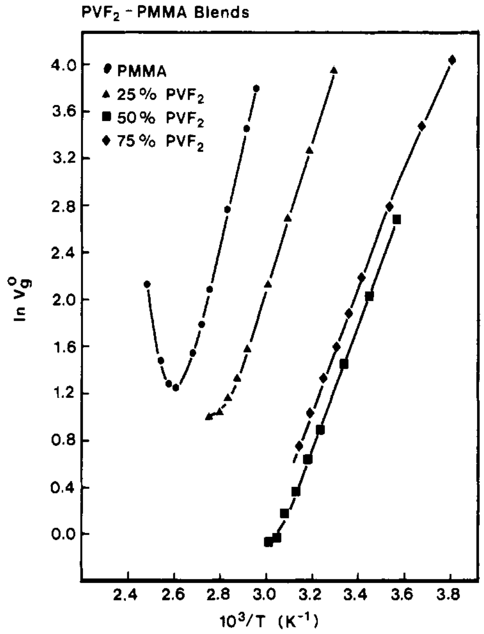

Figure 3. Retention diagrams for various PVF$_2$–PMMA blends in the vicinity of T_g. The probes used were n-C$_{12}$ for PMMA, n-C$_{10}$ for the 25 wt % PVF$_2$ blend, and n-C$_7$ for the 50 and 75 wt % PVF$_2$ blends.

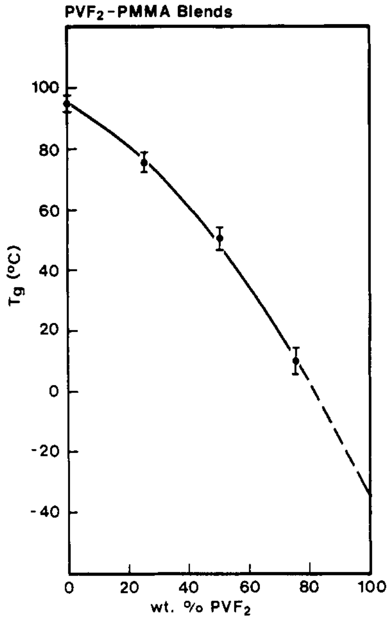

Figure 4. Composition dependence of T_g.

pendent T_g, indicating polymer–polymer miscibility (Figure 4). The T_g's of the 90% and 100% PVF$_2$ systems were not measured directly by IGC because of the lower temperature limit of the IGC experimental setup. Extrapolation of the curve in Figure 4 yields an estimate of −35 ± 5 °C for the T_g of PVF$_2$, in agreement with previously reported data[6,9] (ca. −45 °C).

The maximum deviation of the T_g–composition curve from linearity usually implies the existence of strong intermolecular interactions between the two polymers.[3] The present chromatographic findings are in excellent agreement with the calorimetric results reported by Nishi and Wang[6] for solution-cast films quenched from the melt as well as those reported by Noland et al.[9] for melt-mixed samples.

Thermodynamic Interaction Parameters. Figure 5 illustrates the dependence of $V_g°$ on blend composition for several of the probes. In general, consistently lower values of $V_g°$ are observed for the blends than predicted by addition of the homopolymer values. Negative deviations from linearity are therefore observed for these blends, which are reported to have strong polymer–polymer interactions. Our previous IGC work on some polymer blends with weak intermolecular interactions [polystyrene–poly(n-butyl methacrylate) blends] generally indicated only positive deviations from linearity (i.e., higher $V_g°$ values than predicted).[14]

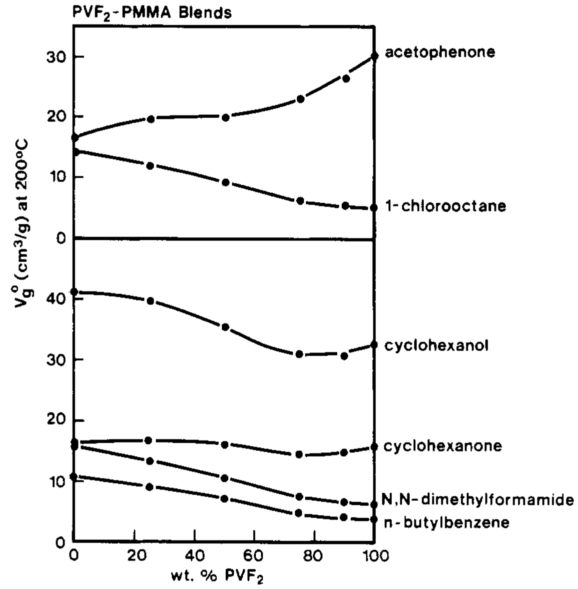

Figure 5. Composition dependence of $V_g°$ for various probes in PVF$_2$–PMMA blends at 200 °C.

Table IV
Flory–Huggins Interaction Parameters, χ, for Various Solutes in PVF$_2$, PMMA, and Their Blends at 200 °C

	wt % PVF$_2$					
solute	0	25	50	75	90	100
acetophenone	0.36	0.32	0.32	0.36	0.30	0.19
cyclohexanone	0.36	0.26	0.18	0.17	0.09	−0.04
N,*N*-dimethylformamide[a]	0.42	0.20	0.07	−0.18	−0.39	−0.59
cyclohexanol	0.19	0.28	0.39	0.63	0.69	0.70
n-butylbenzene	0.74	0.83	0.97	1.25	1.32	1.34
o-dichlorobenzene	0.44	0.56	0.69	0.93	1.01	1.01
1-chlorooctane[a]	0.94	1.04	1.15	1.41	1.51	1.52
1-chlorodecane[a]	1.04	1.14	1.34	1.65	1.77	1.82

[a] The values listed are not corrected for vapor phase nonideality of the probe.

The Flory–Huggins interaction parameter is an important measure of probe–polymer as well as polymer–polymer interaction. The probe–polymer interaction parameters (χ_{12}, χ_{13}, $\chi_{1(23)}$) were calculated from the measured $V_g°$ data for each system and are recorded in Table IV. χ parameters for carbonyl-containing probes decrease continually with increasing PVF$_2$ concentration (i.e., solvency increases). The opposite is true for the other probes. The interaction parameters in Table IV were used to evaluate the polymer–polymer interaction parameter (χ_{23}') for each blend composition:

$$\chi_{1(23)} = \chi_{12}\Phi_2 + \chi_{13}\Phi_3 - \chi_{23}'\Phi_2\Phi_3 \qquad (6)$$

where $\chi_{23}' = \chi_{23}V_1/V_2$ (i.e., χ_{23}' is normalized to the size of the probe molecule). Table V summarizes χ_{23}' values at 200 °C for various probes and blend compositions. As noted in previous chromatographic investigations of polymer–polymer miscibility, probe-to-probe variations are

Table V
Polymer-Polymer Interaction Parameters, χ_{23}', for Various PVF_2-PMMA Blends at 200 °C

	wt % PVF_2			
solute	25	50	75	90
acetophenone	0.55	−0.13	−0.51	−0.71
cyclohexanone	0.24	0.11	−0.33	−0.52
N,N-dimethylformamide	0.29	−0.20	−0.31	−0.45
cyclohexanol	0.03	−0.02	−0.46	−0.55
n-butylbenzene	0.12	0.01	−0.50	−0.59
o-dichlorobenzene	−0.01	−0.09	−0.50	−0.67
1-chlorooctane	0.06	0.08	−0.33	−0.60
1-chlorodecane	0.26	0.03	−0.47	−0.54

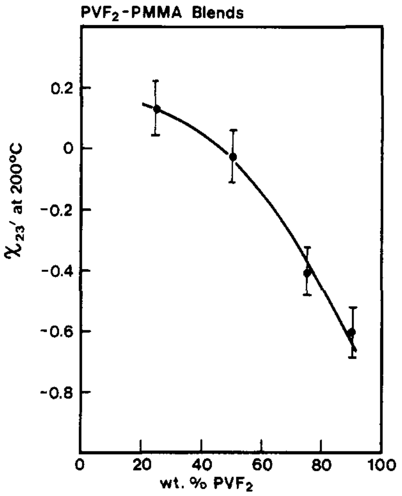

Figure 6. Composition dependence of the polymer–polymer interaction parameter for PVF_2-PMMA blends at 200 °C.

observed.[14,24,30,31] Possible reasons for such variations have been discussed by Su et al.;[30] these include nonrandom mixing of the two polymers or selective sorption of different probes on either component. It is therefore not surprising to see such probe-to-probe variations in the PVF_2–PMMA system. These blends are characterized by strong intermolecular interactions which probably prevent perfectly random mixing of the two components. In addition, the dissimilar solubility characteristics of PVF_2 and PMMA (Table IV) might also result in some nonrandom sensing of the polymer–polymer contacts by the probe molecules.

In order to represent the composition dependence of χ_{23}' concisely, the measured values for each blend were averaged for the eight probes and the resulting numbers plotted in Figure 6. In general, χ_{23}' becomes more negative (absolute value increases) with increasing PVF_2 content, i.e., from about 0.1 at 25 wt % PVF_2 to −0.6 at 90 wt % PVF_2. The negative interaction parameters measured indicate strong specific interactions, which ensure the miscibility of the two polymers. A similar composition dependence has been reported by Wendorff from small-angle X-ray scattering and melting point depression studies of melt-blended mixtures of PVF_2 and PMMA.[7] These trends have been attributed to effects of local structure (e.g., free volume, packing density) in the mixture. A composition-dependent polymer–polymer interaction parameter has also been observed in gas chromatographic investigations of poly(butyl methacrylate)–polystyrene blends,[14] poly(vinyl chloride)–plasticizer blends,[30] and poly(ethylene glycol) blends.[32]

Acknowledgment. We thank Dr. J. O'Reilly for suggesting this study and providing the polymers.

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