

Thermodynamics of Polymer-Polymer-Solvent and Block Copolymer-Solvent Systems I. Experimental Measurements

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ABSTRACT: A new multiple-cell apparatus for vapor-liquid equilibria measurements in concentrated polymer solutions is described. Experimental data on vapor-pressure lowering for four polymer-polymer-solvent systems and one block copolymer-solvent system are reported. The Flory-Huggins χ interaction parameters for the corresponding polymer pairs are evaluated. For ternary systems, the results are expressed in terms of a parameter $\chi_{1,23}$ which reduces to the classical Flory-Huggins χ interaction parameter for the case of binary mixtures. Experimental data measured in this work are compared with existing literature data.

KEY WORDS Polymer Mixture / Block Copolymers / Sorption Isotherms /

Due to their technological importance, polymer blends have attracted considerable attention during the past decade. As it has been pointed out several times in the past,^{1,2} a complete miscibility in the segmental scale is not a *sine qua non* condition for a blend to have desirable physical properties. For thermodynamic reasons, most polymer pairs are immiscible and their "degree of compatibility" is of underlying importance to the microphase structure and, consequently, to the mechanical properties of the blend. The Flory-Huggins χ interaction parameter³ for the polymer pair plays a dominant role in explaining critical phase behavior of a compatible pair⁴ and in estimating interfacial tension and interfacial thickness for semicompatible or incompatible pairs.^{5,6}

Direct measurement of this parameter is not always possible and in this respect, the indirect "probing" vapor-pressure lowering technique⁷ is of great use. Although this technique cannot be directly used for an incompatible pair, it

may be of help if the polymers are replaced by their miscible oligomeric analogs. The information obtained in this latter case, assisted with suitable theoretical models of polymer solutions, may lead to an assessment of the interaction parameters for the actual polymeric case.

In this work we present experimental information regarding this interaction parameter for three compatible or semicompatible pairs and one block copolymer system. In a following publication these data will be treated with the non-random new-Flory theory of polymer solutions.⁸

Since there is no unanimity for the terminology of polymer mixtures, the terms compatibility and polymer-polymer miscibility are used here in the spirit of ref 1 and 2.

APPARATUS AND EXPERIMENTAL PROCEDURE

Bonner,⁷ in a comprehensive review article

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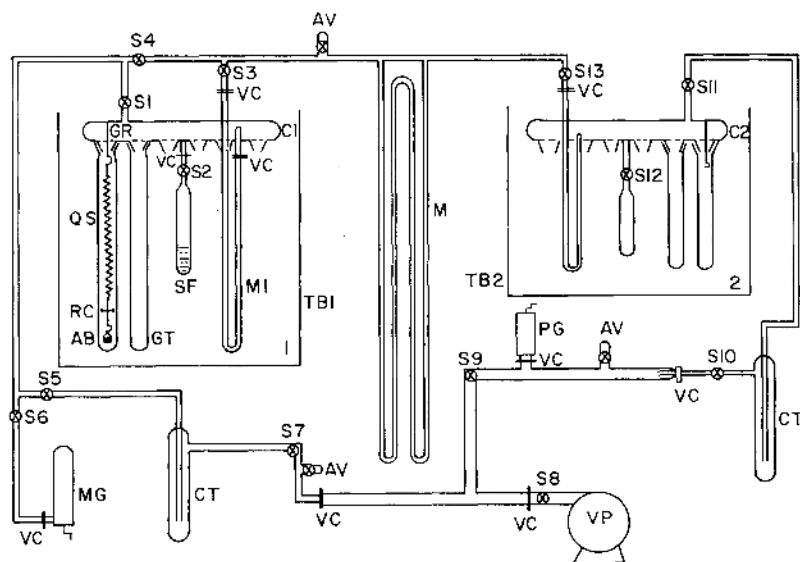


Figure 1. Sketch of the experimental apparatus. AB, aluminum baskets; AV, air valve; C1, C2, horizontal chambers; CT, cold trap; GR, glass rod; GT, glass tube; M, mercury manometer; MI, small null manometer; MG, McLeod gauge; PG, Pirani gauge; QS, quartz spring; RC, reference cross; S1 to S13, stopcocks; SF, solvent flask; TB1, TB2 thermostatic baths; VC, vacuum couplings; VP, vacuum pump.

has discussed the common experimental techniques for measuring vapor-liquid equilibria in concentrated polymer solutions. Dynamic techniques (gas-liquid chromatography) are useful for a fast determination of χ interaction parameters. However, for not well understood reasons, static and dynamic techniques may show a discrepancy as high as 20%.⁹ In this work we have used a static method and to compensate for the disadvantage of the long time required to reach equilibrium, we have constructed a multiple-cell apparatus which gives as many as twelve equilibrium points at a time.

Figure 1 gives an overall view of the equipment. Basically, it consists of two glass multi-cell units #1 and #2, the central mercury manometer M and the vacuum line extended from stopcock S1 through the vacuum pump, VP, to stopcock S11. Each unit consists of a horizontal chamber (C1 and C2) 35 mm O.D., 23.5 cm long, bearing six outlets (ground joints 24/29) to which there fit six vertical glass tubes (cells) GT, whose length varies from 20 to

48 cm. The horizontal chamber is also connected to a small mercury manometer M1, the solvent flask SF and the vacuum line. For reasons of clarity, only two vertical glass tubes are shown in each unit. From each glass rod GR, fused in the upper part of the horizontal chamber, a quartz spring QS, is hung, bearing in its lower end an aluminum basket AB, with the polymeric sample. The glass tubes GT, the solvent flask SF, and the small mercury manometer M1, are removable parts. Each of the units is immersed in a thermostatic bath TB1 and TB2. The bath temperature is monitored by means of a Hewlett Packard quartz thermometer, model 2801A, calibrated against a standard platinum thermometer by the NRC of Canada. During experiments, the temperature in the thermostatic baths was maintained constant to within ± 0.02 degrees. Up to 55°C the liquid of the baths was water, above this temperature, ethylene glycol was used.

The ability of the multi-cell units to maintain vacuum for several weeks was tested

before any runs were conducted. Both units were able to maintain better than 10^{-2} mmHg vacuum for four weeks. Although the ground joints were carefully and separately ground, a minute amount of high vacuum grease (Dow Corning) was used in the uppermost part of the ground joint.

Before each run the solvents were thoroughly degassed by the combination of distillation under vacuum and the freezing-thawing process.¹⁰ A Mettler H51 electric balance was used to determine the polymer ratio (w_{ip}) and the total mass m_p of the polymer sample loaded in each of the aluminum baskets for a given run. After the quartz springs, the aluminum baskets and the glass cells were placed in their positions, the system was evacuated. On each glass tube GT there was fused in a reference line, whose one sharp end was the reference point for all subsequent measurements of the spring displacements inside the tube. For this purpose, a cathetometer (Gaertner Scientific, Model 101 AT) was used. This model allows measurements of vertical height differences to 0.001 mm within a 100 mm working range. A certain amount of solvent vapor was charged to the multicell units in each run.

After the equilibrium was reached, the new heights of the reference crosses relative to their corresponding reference points in the glass tubes were measured and the vapor pressure was measured on the manometer M1. In case of different crown heights, the correction suggested by Thomson¹¹ was applied by linear interpolation and extrapolation in his tabulated values. In case the pressure was exceeding *ca.* 300 mmHg, the central manometer M was used. Corrections for the variation of mercury density with temperature¹² and for the weight of the gas phase above the mercury column have been applied. Overall error in pressure measurements is estimated to be less than 0.04 mmHg.

Both adsorption and desorption experiments were conducted in order to guarantee

equilibrium and check for casual leaks. With the above information, the mass of the solvent was simultaneously obtained at given solvent pressures P for different polymeric samples characterized by w_{2p} .

The quartz springs (Worden Quartz Products Inc., Houston, Texas) were calibrated under vacuum at all temperatures of interest against inert samples weighed with the Mettler electric balance to ± 0.01 mg. In the range of interest (from *ca.* 50 mg to *ca.* 300 mg total load) the extension was found to be linear with the load, the linear compliance ranging from about 0.14 mm mg^{-1} to about 1.1 mm mg^{-1} . The initial polymeric sample at the more sensitive springs was about 30 to 40 mg, while for the less sensitive it was about 100 to 140 mg; thus, somewhat, compensating for the lower sensitivity of the latter.

In order to account for errors due to buoyancy forces, in one of the aluminum baskets inert materials (small pieces of glass) were placed and the reference cross was followed with added solvent vapor. In most cases this correction was within experimental error. No vapor condensation was detected in any inert part of the unit.

Further details of the apparatus and experimental procedure have been given elsewhere.¹³

MATERIALS

The systems studied are the following:

1. Poly(vinyl chloride)-poly(ϵ -caprolactone)-carbon tetrachloride
- 2a. Polystyrene-poly(vinyl methyl ether)-benzene
- 2b. Polystyrene-poly(vinyl methyl ether)-chloroform
3. Poly(isobutylene)-*n*-heptadecane-*n*-pentane
- 4a. α , ω -methoxypoly(ethylene oxide)-benzene
- 4b. α , ω -alcoxypoly(ethylene oxide)-benzene
- 4c. Poly(ethylene oxide)-benzene

4d. *n*-tetracosane-benzene

All solvents were of the spectrograde type and used without further purification. Benzene was from American Chemicals Ltd. The manufacturer reports maximum impurities: 0.05% water and sulfur compounds (as S) 0.005%. Chloroform was from American Chemicals Ltd. Reported maximum impurities: acetone and aldehyde 0.005%, lead 0.05 ppm. *n*-Pentane was from Aldrich Chemical Co. Reported maximum impurities: water 0.02%. Carbon tetrachloride was from American Chemicals Ltd. Reported maximum impurities: sulfur compounds (as S) 0.005%.

The poly(vinyl chloride) and poly(ϵ -caprolactone) samples were two secondary standards and had been obtained from Scientific Polymer Products Inc. The poly(vinyl chloride) sample had a weight average molecular weight $M_w=77,300$ and a number average molecular weight $M_n=39,600$. The poly(ϵ -caprolactone) sample had a weight average molecular weight 33,000 and a number average molecular weight $M_n=10,700$. It was crystalline under normal conditions with a reported melting point $T_m=60^\circ\text{C}$.

Polystyrene sample was obtained from Pressure Chemical Co. with a molecular weight of 800 and a dispersion ratio $M_w/M_n=1.30$. Poly(vinyl methyl ether) sample (Gantrez 093) was obtained from GAF Corporation and had a viscosity average molecular weight 14,000 in benzene.^{4a} Two polyisobutylene samples were used, both from Polysciences Inc. The first had an average molecular weight 1350 and the second 2700. The poly(ethylene oxide) with $M_w=100,000$ was also from Polysciences.

The α,ω -methoxypoly(ethylene oxide) E600M (600 molecular weight) and the two copolymers (α,ω -hydroxypoly(ethylene oxide)) 18-45-18 and 21-45-21—the numbers indicating corresponding monomer units, were kindly provided by Professor C. Booth of the University of Manchester, U. K. The disper-

Table I. Thermodynamic data for pure solvents

Solvent	Temperature	Saturated vapor pressure	Second virial coefficient
	$^\circ\text{C}$	mmHg	$\text{cm}^3 \text{mol}^{-1}$
Benzene	25	94.99	-1570
Benzene	55	326.90	-1100
Benzene	70	550.82	-950
Carbon Tetrachloride	65	524.90	-1150
Chloroform	25	196.68	-1150
<i>n</i> -Pentane	25	512.54	-1260

sion ratios for the copolymer samples M_w/M_n were reported to be 1.06 for the 18-45-18 sample and 1.03 for the 21-45-21 sample. The *n*-tetracosane sample with a purity of about 97% was from Aldrich Chemical Co.

The poly(vinyl chloride)-poly(ϵ -caprolactone) mixture samples were prepared by dissolving the polymers in excess of tetrahydrofuran (2–3% solution) and very slowly removing the solvent under vacuum initially at 40°C and subsequently at 70°C . The samples were left under vacuum at that temperature for a few days until constant weight.

The polystyrene-poly(vinyl methyl ether) mixture samples were obtained by dissolving the polymers in excess of toluene (also 2–3% solution) whose removal was done initially at room temperature and subsequently at 50°C . All other mixtures were prepared by simple stirring.

Data for pure solvents obtained from the literature^{14,15} are reported in Table I.

DEFINITION OF THE $\chi_{1,23}$ PARAMETER

It is common practice in the literature to present data on vapor sorption by pure polymers in the form of the Flory-Huggins χ_{12} interaction parameters³ versus polymer volume fraction. In this study, the absorbant is a mixture of polymers, in the general case, and it

has been deemed necessary to use an analogous term $\chi_{1,23}$. This term considerably simplifies the presentation of data for ternary systems and provides with a general formalism for the treatment of polymer solutions.

The segment fraction of component i , with r_i segments per molecule and a characteristic specific volume $v_{sp,i}^*$, is defined as

$$\phi_i = \frac{m_i v_{sp,i}^*}{\sum_j m_j v_{sp,j}^*} = \frac{x_i r_i}{\sum_j x_j r_j} \quad (1)$$

For a binary mixture, the Flory-Huggins χ_{12} interaction parameter is defined in terms of the solvent activity a_1 , or the vapor pressure, p , by the relation

$$\begin{aligned} \ln a_1 &= \ln \frac{P}{P^0} + \frac{B(P-P^0)}{RT} \\ &= \ln \phi_1 + \left(1 - \frac{r_1}{r_2}\right) \phi_2 + \chi_{12} \phi_2^2 \end{aligned} \quad (2)$$

where subindex 1 denotes the solvent and subindex 2 the solute (polymer). For the solvent, usually r_1 is assumed to be unity. For a ternary system the solvent activity is given by¹⁶

$$\begin{aligned} \ln a_1 &= \ln \phi_1 + \left(1 - \frac{r_1}{r_2}\right) \phi_2 + \left(1 - \frac{r_1}{r_3}\right) \phi_3 \\ &\quad + (\chi_{12} \phi_2 + \chi_{13} \phi_3)(1 - \phi_1) - \chi'_{23} \phi_2 \phi_3 \end{aligned} \quad (3)$$

where

$$\chi'_{23} = \chi_{23}(\text{Flory-Huggins}) \frac{r_1}{r_2} \quad (4)$$

However, in the general case, χ_{12} and χ_{13} vary with composition and without a knowledge of this composition dependence eq 3 cannot be used for the evaluation of χ'_{23} parameter. It is important to observe that eq 3 may be used in the limiting case $\phi_1 \rightarrow 0$.

If x_{2p} indicates mole fraction of component 2 in the polymer mixture (zero solvent concentration) and similarly, x_{3p} for component 3, we may define r_{23} and ϕ_{23} as:

$$r_{23} = x_{2p} r_2 + x_{3p} r_3 \quad (5)$$

and

$$\phi_{23} = \phi_2 + \phi_3 = 1 - \phi_1 \quad (6)$$

In addition, $\chi_{1,23}$ is defined as

$$\chi_{1,23} = ((\chi_{12} \phi_2 + \chi_{13} \phi_3)(1 - \phi_1) - \chi'_{23} \phi_2 \phi_3) / \phi_{23}^2 \quad (7)$$

With these definitions, the solvent activity in the ternary may be written as

$$\ln a_1 = \ln \phi_1 + \left(1 - \frac{r_1}{r_{23}}\right) \phi_{23} + \chi_{1,23} \phi_{23}^2 \quad (8)$$

in direct analogy with eq 2. Equation 8 reduces to eq 2 for the binary case. The use of eq 8 has the advantage of allowing to report data on ternary systems regardless of the dependence of χ_{12} and χ_{13} on composition.

EXPERIMENTAL DATA

1. System: Chloroform (1)-Polystyrene (2)-Poly(vinyl methyl ether) (3) at 25°C

The system polystyrene-poly(vinyl methyl ether) for the high molecular weight case is a rather controversial one.^{2,4} In order to avoid enhancement of immiscibility by the solvent due to " $\Delta\chi$ effect",⁴ the mixture samples have been cast from toluene⁴ solutions. The segment fractions have been defined based on the characteristic specific volumes of the pure components (for chloroform⁸ $v_{sp,1}^* = 0.5124$ cm³ g⁻¹, for polystyrene¹⁷ $v_{sp,2}^* = 0.810$ cm³ g⁻¹ and for poly(vinyl methyl ether)⁴ $v_{sp,3}^* = 0.828$ cm³ g⁻¹).

Experimental data are reported in Table II. As it is shown by the values of the χ_{12} ($\chi_{1,23}$ when $w_{2p} = 1.0$) and χ_{13} parameters, the nature of the intermolecular interactions between solvent and the two polymers is considerably different. In Figure 2, the ratios $m_{\text{solvent}}/m_{\text{polymer}}$ versus P/P^0 are presented for samples characterized by different w_{2p} values.

The data on $\chi_{1,23}$ may now be used for an approximate estimation of the χ'_{23} interaction parameter for the limiting case of zero solvent

Table II. Vapor-pressure lowering data for the system: chloroform (1)-polystyrene (2)-poly(vinyl methyl ether) (3) at 25°C

$w_{2p} = 1.0$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	ϕ_{23} ($= \phi_2$)	$\chi_{1,23}$ ($= \chi_{12}$)	
0.1541	0.2421	0.9112	0.225	
0.1874	0.2815	0.8940	0.220	
0.2169	0.3146	0.8794	0.220	
0.2616	0.3605	0.8580	0.221	
0.3056	0.3992	0.8380	0.214	
0.3639	0.4481	0.8129	0.218	
0.3988	0.4725	0.7986	0.213	
0.4489	0.5074	0.7788	0.216	
0.4958	0.5357	0.7613	0.215	
0.5550	0.5662	0.7401	0.208	
0.6066	0.5938	0.7227	0.214	
0.6854	0.6280	0.6976	0.213	
$\chi_{1,23}^{\infty} = 0.230$				
$w_{2p} = 0.8012$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	ϕ_{23}	ϕ_2	$\chi_{1,23}$
0.2096	0.2421	0.8834	0.7046	-0.098
0.2518	0.2815	0.8631	0.6884	-0.091
0.2869	0.3146	0.8470	0.6755	-0.075
0.3417	0.3605	0.8229	0.6564	-0.061
0.3953	0.3992	0.8007	0.6386	-0.059
0.4631	0.4481	0.7742	0.6175	-0.038
0.5040	0.4725	0.7591	0.6054	-0.037
0.5642	0.5074	0.7378	0.5885	-0.028
0.6145	0.5357	0.7210	0.5751	-0.016
0.6792	0.5662	0.7004	0.5587	-0.010
0.7408	0.5938	0.6819	0.5439	-0.002
0.8261	0.6280	0.6578	0.5247	-0.009
$\chi_{1,23}^{\infty} = -0.150$				

Table II. (continued)

$w_{2p} = 0.6023$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	ϕ_{23}	ϕ_2	$\chi_{1,23}$
0.1914	0.1878	0.8929	0.5330	-0.338
0.2571	0.2421	0.8612	0.5140	-0.331
0.3059	0.2815	0.8391	0.5009	-0.316
0.3498	0.3146	0.8202	0.4896	-0.304
0.4123	0.3605	0.7946	0.4743	-0.281
0.4717	0.3992	0.7718	0.4607	-0.269
0.5481	0.4481	0.7443	0.4443	-0.241
0.5971	0.4725	0.7276	0.4343	-0.241
0.6621	0.5074	0.7067	0.4218	-0.223
0.7206	0.5357	0.6888	0.4112	-0.210
0.7914	0.5662	0.6684	0.3990	-0.190
0.8544	0.5938	0.6512	0.3887	-0.180
0.9468	0.6280	0.6275	0.3746	-0.163
$\chi_{1,23}^{\infty} = -0.427$				
$w_{2p} = 0.3337$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	ϕ_{23}	ϕ_2	$\chi_{1,23}$
0.2494	0.1878	0.8655	0.2845	-0.657
0.3283	0.2421	0.8302	0.2729	-0.635
0.3876	0.2815	0.8055	0.2648	-0.616
0.4369	0.3146	0.7860	0.2584	-0.591
0.5132	0.3605	0.7577	0.2491	-0.568
0.5829	0.3992	0.7336	0.2411	-0.551
0.6727	0.4481	0.7046	0.2316	-0.517
0.7277	0.4725	0.6880	0.2262	-0.513
0.8007	0.5074	0.6671	0.2193	-0.487
0.8658	0.5357	0.6496	0.2135	-0.467
0.9425	0.5662	0.6300	0.2071	-0.447
1.0172	0.5938	0.6121	0.2012	-0.428
1.1141	0.6280	0.5902	0.1940	-0.397
$\chi_{1,23}^{\infty} = -0.803$				

concentration. For this purpose, at the end of each subsection of the tables, the limiting value of $\chi_{1,23}^{\infty}$ is shown. These values were obtained by graphical extrapolation of the data on lower solvent concentration. It should be stressed that there is an uncertainty in this extrapolation, especially when the data do not show any clear trend. This is why values thus obtained should be considered to be only an approximate estimation of χ_{23}' .

In terms of these limiting quantities, χ_{23}' is

given by

$$\chi_{23}' = \frac{\chi_{12}^{\infty} \phi_2^{\infty} + \chi_{13}^{\infty} \phi_3^{\infty} - \chi_{1,23}^{\infty} (\phi_1^{\infty} \rightarrow 0)}{\phi_2^{\infty} \phi_3^{\infty}} \quad (9)$$

In eq 9, ϕ_2^{∞} and ϕ_3^{∞} are the segment fractions of components 2 and 3 respectively in the polymeric mixture.

From the limiting values of $\chi_{1,23}$ at zero solvent concentration and eq 9, the χ_{23}' parameter is approximately estimated as

Table II. (continued)

$w_{2p}=0.0$			
$m_{\text{soln}}/m_{\text{pol}}$	P/P^0	$\phi_{23} (= \phi_3)$	$\chi_{1,23} (= \chi_{13})$
0.3281	0.1878	0.8313	-1.027
0.4218	0.2421	0.7931	-0.990
0.4949	0.2815	0.7656	-0.972
0.5526	0.3146	0.7453	-0.940
0.6445	0.3605	0.7150	-0.916
0.7258	0.3992	0.6902	-0.894
0.8292	0.4481	0.6610	-0.851
0.8929	0.4725	0.6442	-0.845
0.9762	0.5074	0.6235	-0.812
1.0480	0.5357	0.6067	-0.785
1.1372	0.5662	0.5871	-0.763
1.2146	0.5938	0.5710	-0.730
1.3274	0.6280	0.5491	-0.698
$\chi_{1,23}^{\infty} = -1.238$			

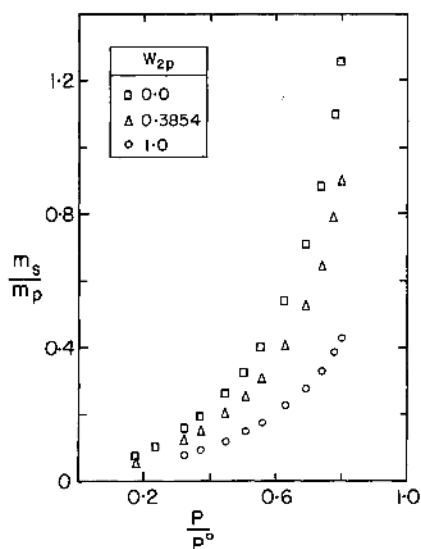


Figure 2. Sorption isotherm for the system chloroform (1)-polystyrene (2)-poly(vinyl methyl ether) (3) at 25°C.

w_{2p}	χ'_{23}
0.3337	0.21
0.6023	0.27
0.8012	0.51

2. System: Benzene (1)-Polystyrene (2)-Poly(vinyl methyl ether) (3) at 25°C

This system was studied in order to see the influence of the solvent probe in the χ'_{23} interaction parameter. The characteristic specific volume of benzene is $v_{sp,1}^* = 0.886 \text{ cm}^3 \text{ g}^{-1}$. Experimental data are reported in Table III. In this case, the difference $\chi_{12} - \chi_{13}$ is small compared to the previous case. From the limiting values of $\chi_{1,23}$ at zero solvent concentration, the following values are obtained for χ'_{23} .

w_{2p}	χ'_{23}
0.3337	-0.04
0.8012	0.32

In agreement with the $\Delta\chi$ effect, thoroughly discussed by Patterson and his collaborators (see for example ref 4a), results obtained using chloroform as a solvent suggest the polystyrene-poly(vinyl methyl ether) pair to be less compatible than results obtained when benzene is used as a solvent. On the other hand, in both cases the compatibility is shown enhanced with increasing poly(vinyl methyl ether) concentration. This result is in disagreement with the findings of Kwei *et al.*¹⁹ for the high molecular weight case. These authors have found considerably more negative values for χ'_{23} , although no specific interactions are involved in this pair. However, their samples had shown several symptoms of incompatibility. Pulsed NMR studies have shown that compatible polystyrene-poly(vinyl methyl ether) films can be described as microheterogeneous in which the polymeric chains, although being extensively mixed, are not completely mixed on the segmental scale. A 75% poly(vinyl methyl ether) film became opaque upon standing at room temperature for several weeks.

The discrepancies between the two works may be partly due to the differences in the molecular weights of the polymeric materials. If equilibrium and nonequilibrium states of

Table III. Vapor-pressure lowering data for the system: benzene (1)–polystyrene (2)–poly(vinyl methyl ether) (3) at 25°C

$w_{2p} = 1.0$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	$\phi_{23} (= \phi_2)$	$\chi_{1,23} (= \chi_{12})$	
0.1068	0.3185	0.8954	0.398	
0.1410	0.3815	0.8664	0.374	
0.1868	0.4552	0.8304	0.362	
0.2682	0.5543	0.7732	0.346	
0.3320	0.6177	0.7336	0.351	
0.4014	0.6650	0.6949	0.334	
0.4698	0.7053	0.6606	0.329	
0.5895	0.7584	0.6080	0.321	
0.7297	0.8025	0.5561	0.314	
0.8457	0.8303	0.5195	0.312	
0.9936	0.8580	0.4792	0.315	
1.1599	0.8775	0.4408	0.298	
$\chi_{1,23}^\infty = 0.415$				
$w_{2p} = 0.8012$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	ϕ_{23}	ϕ_2	$\chi_{1,23}$
0.1190	0.3274	0.8853	0.7061	0.313
0.1441	0.3738	0.8644	0.6894	0.306
0.1827	0.4383	0.8341	0.6653	0.308
0.2177	0.4891	0.8084	0.6448	0.310
0.2575	0.5401	0.7810	0.6230	0.316
0.2941	0.5785	0.7574	0.6041	0.315
0.3731	0.6454	0.7111	0.5672	0.310
0.4791	0.7146	0.6572	0.5241	0.316
0.5188	0.7302	0.6390	0.5097	0.301
0.6243	0.7761	0.5953	0.4748	0.308
0.9021	0.8481	0.5045	0.4024	0.305
$\chi_{1,23}^\infty = 0.311$				

Table III. (continued)

$w_{2p} = 0.3337$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	ϕ_{23}	ϕ_2	$\chi_{1,23}$
0.1167	0.3185	0.8883	0.2920	0.253
0.1495	0.3815	0.8613	0.2831	0.255
0.1958	0.4552	0.8258	0.2715	0.251
0.2735	0.5543	0.7724	0.2539	0.254
0.3392	0.6177	0.7323	0.2407	0.253
0.4007	0.6650	0.6985	0.2296	0.251
0.4640	0.7053	0.6667	0.2192	0.251
0.5648	0.7584	0.6217	0.2044	0.254
0.6954	0.8025	0.5717	0.1879	0.245
0.7859	0.8303	0.5415	0.1780	0.255
0.9064	0.8580	0.5059	0.1663	0.261
1.0342	0.8775	0.4729	0.1555	0.252
1.2686	0.9058	0.4225	0.1389	0.251
$\chi_{1,23}^\infty = 0.252$				
$w_{2p} = 0.0$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	$\phi_{23} (= \phi_3)$	$\chi_{1,23} (= \chi_{13})$	
0.1026	0.2791	0.9011	0.182	
0.1231	0.3185	0.8837	0.172	
0.1555	0.3815	0.8574	0.186	
0.2007	0.4552	0.8233	0.195	
0.2816	0.5543	0.7686	0.191	
0.3435	0.6177	0.7313	0.203	
0.4040	0.6650	0.6983	0.203	
0.4692	0.7053	0.6659	0.198	
0.6921	0.8025	0.5747	0.197	
0.7805	0.8303	0.5450	0.206	
1.0019	0.8775	0.4827	0.213	
1.1075	0.8913	0.4578	0.205	
1.2056	0.9058	0.4368	0.219	
$\chi_{1,23}^\infty = 0.158$				

this pair have close free energy values, chain entanglements in the high molecular weight case may lead to controversial conclusions.²⁰ Demixing may be favored thermodynamically, but kinetically it may be a very slow process.

3. System: Carbon tetrachloride (1)–Poly(vinyl chloride) (2)–Poly(ϵ -caprolactone) (3) at 65°C

The temperature chosen for this study is a few degrees above the melting point of poly(ϵ -

caprolactone). Before any injection of the solvent into the cell-units, the temperature of the thermostatic bath was kept at 100°C well above the glass transition temperature of poly(vinyl chloride) (near 87°C), for a few hours, in order to guarantee complete miscibility of the polymers. The characteristic specific volumes of pure components are²¹: for carbon tetrachloride $v_{\text{sp},1}^* = 0.487 \text{ cm}^3 \text{ g}^{-1}$, for poly(vinyl chloride) $v_{\text{sp},2}^* = 0.624 \text{ cm}^3 \text{ g}^{-1}$ and for poly(ϵ -caprolactone) $v_{\text{sp},3}^* = 0.769 \text{ cm}^3 \text{ g}^{-1}$

Table IV. Vapor-pressure lowering data for the system: carbon tetrachloride (1)-poly(vinyl chloride) (2)-poly(ϵ -caprolactone) (3) at 65°C

$w_{2p}=1.0$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	$\phi_{23} (= \phi_2)$	$\chi_{1,23} (= \chi_{12})$	
0.0557	0.3612	0.9583	1.331	
0.0885	0.4991	0.9354	1.288	
0.1287	0.6376	0.9087	1.270	
0.1659	0.7328	0.8854	1.250	
0.2099	0.8218	0.8592	1.237	
0.2434	0.8758	0.8404	1.229	
0.2702	0.9081	0.8258	1.218	
0.2999	0.9395	0.8103	1.209	
$\chi_{1,23}^{\infty} = 1.328$				
$w_{2p}=0.7653$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	ϕ_{23}	ϕ_2	$\chi_{1,23}$
0.0378	0.1991	0.9728	0.7060	1.103
0.0844	0.3612	0.9412	0.6831	1.013
0.1331	0.4991	0.9103	0.6606	0.995
0.1986	0.6377	0.8719	0.6327	0.983
0.2632	0.7328	0.8370	0.6074	0.967
0.3503	0.8218	0.7941	0.5763	0.950
0.4193	0.8758	0.7632	0.5538	0.947
0.4795	0.9081	0.7381	0.5356	0.939
0.5504	0.9395	0.7106	0.5157	0.927
$\chi_{1,23}^{\infty} = 1.025$				
$w_{2p}=0.4784$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	ϕ_{23}	ϕ_2	$\chi_{1,23}$
0.0619	0.1991	0.9587	0.4091	0.701
0.1283	0.3612	0.9180	0.3917	0.699
0.1994	0.4991	0.8781	0.3747	0.715
0.3004	0.6377	0.8271	0.3529	0.722
0.3989	0.7328	0.7827	0.3340	0.727
0.5310	0.8218	0.7301	0.3116	0.738
0.6509	0.8758	0.6882	0.2937	0.744
0.7445	0.9081	0.6587	0.2811	0.753
0.8760	0.9395	0.6212	0.2651	0.759
$\chi_{1,23}^{\infty} = 0.689$				

Experimental data are reported in Table IV. Data for poly(vinyl chloride) for solvent concentration below about 5% were deliberately

Table IV. (continued)

$w_{2p}=0.2171$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	ϕ_{23}	ϕ_2	$\chi_{1,23}$
0.0788	0.1953	0.9505	0.1745	0.502
0.1646	0.3612	0.9020	0.1657	0.526
0.2598	0.4991	0.8536	0.1568	0.541
0.3962	0.6377	0.7927	0.1456	0.553
0.5298	0.7328	0.7408	0.1361	0.569
0.7203	0.8218	0.6777	0.1245	0.585
0.8985	0.8758	0.6276	0.1153	0.600
1.0247	0.9081	0.5964	0.1096	0.609
1.2340	0.9395	0.5510	0.1012	0.624
$\chi_{1,23}^{\infty} = 0.493$				
$w_{2p}=0.0$				
$m_{\text{solv}}/m_{\text{pol}}$	P/P^0	$\phi_{23} (= \phi_3)$	$\chi_{1,23} (= \chi_{13})$	
0.0956	0.1991	0.9429	0.380	
0.1968	0.3612	0.8892	0.403	
0.3120	0.4991	0.8350	0.421	
0.4753	0.6377	0.7686	0.444	
0.6456	0.7328	0.7098	0.458	
0.8896	0.8218	0.6397	0.478	
1.1175	0.8758	0.5856	0.500	
1.3184	0.9081	0.5450	0.517	
1.6075	0.9395	0.4955	0.540	
$\chi_{1,23}^{\infty} = 0.363$				

discarded because it was suspected that this solvent quantity might not be enough to properly "plasticize" the polymeric sample. Figure 3 presents the ratio $m_{\text{solvent}}/m_{\text{polymer}}$ versus P/P^0 . The following values are obtained for χ'_{23} from the limiting values of $\chi_{1,23}$ at zero solvent concentration.

w_{2p}	χ'_{23}
0.2171	0.32
0.4784	0.35
0.7653	0.20

Olabisi²¹ has studied this system by gas-liquid chromatography at 120°C. For carbon tetrachloride-poly(vinyl chloride) he found $\chi_{12}=1.350$ and for carbon tetrachloride-

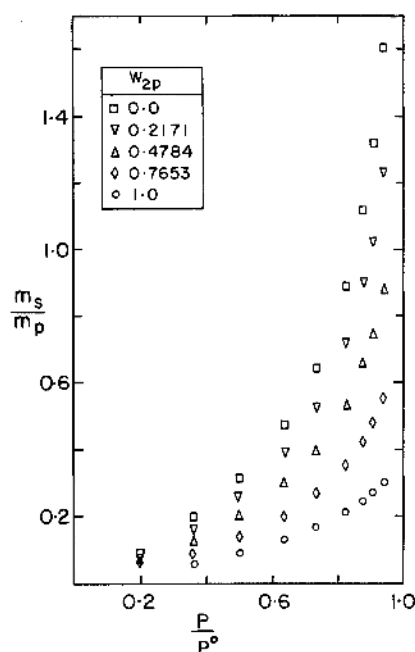


Figure 3. Sorption isotherm for the system carbon tetrachloride (1)-poly(vinyl chloride) (2)-poly(ϵ -caprolactone) (3) at 65°C.

poly(ϵ -caprolactone) he found $\chi_{13}=0.293$. Considering the difference in temperature, these values are in rather good agreement with the values obtained in this work (1.328 and 0.363 respectively). However, Olabisi's values of χ'_{23} are in surprisingly large disagreement with the values obtained in this work. For a mixture 50% poly(vinyl chloride) Olabisi found $\chi'_{23}=1.07$ and for 30% poly(vinyl chloride), $\chi'_{23}=1.31$. The trend of χ'_{23} with poly(vinyl chloride) concentration is the same in both studies. The discrepancy in χ'_{23} may be due to the difference in temperature and to the limitations of the techniques used. However, with most of the other solvents used as probes by Olabisi,²¹ estimated values of χ'_{23} were lower than those obtained in this study. With acetonitrile for example, a value of χ'_{23} as low as -0.46 was found by Olabisi.²¹ The somewhat higher value of χ_{13} estimated in this work may also be a cause of the discrepancies.

4. System: *n*-Pentane (1)-Polyisobutylene (2)-*n*-Heptadecane (3) at 25°C

Two polyisobutylene samples were used for assessing the effect of chain length on the solvent-polymer interaction parameter. The pure component characteristic specific volumes are^{22,23}: for *n*-pentane $v_{sp,1}^*=1.1828$ cm³g⁻¹, for polyisobutylene $v_{sp,2}^*=0.9493$ cm³g⁻¹ and for *n*-heptadecane $v_{sp,3}^*=1.063$ cm³g⁻¹. Experimental data are reported in Table V. Figure 4 shows the $m_{\text{solvent}}/m_{\text{polymer}}$ ratio versus P/P^0 .

From the limiting values of $\chi_{1,23}$ parameters the value of χ'_{23} is estimated to be -0.001 . Incidentally, the system polyethylene-polyisobutylene was predicted²⁴ by the solubili-

Table V. Vapor-pressure lowering data for the system: *n*-pentane (1) polyisobutylene (2)-*n*-heptadecane (3) at 25°C

$w_{2p}=1.0$ (MW _{PIB} =2700)			
$m_{\text{solvent}}/m_{\text{pol}}$	P/P^0	$\phi_{23} (= \phi_2)$	$\chi_{1,23} (= \chi_{12})$
0.0357	0.1913	0.9574	0.659
0.1075	0.4477	0.8819	0.642
0.0824	0.3723	0.9069	0.645
0.1327	0.5058	0.8582	0.623
0.1569	0.5582	0.8365	0.621
0.1965	0.6297	0.8033	0.620
0.2457	0.6932	0.7656	0.605
0.2885	0.7395	0.7356	0.603
0.3373	0.7792	0.7041	0.596
0.3713	0.8024	0.6837	0.592
$w_{2p}=1.0$ (MW _{PIB} =1350)			
$m_{\text{solvent}}/m_{\text{pol}}$	P/P^0	$\phi_{23} (= \phi_2)$	$\chi_{1,23} (= \chi_{12})$
0.0763	0.3235	0.9132	0.583
0.0920	0.3723	0.8971	0.585
0.1211	0.4477	0.8689	0.578
0.1484	0.5058	0.8440	0.569
0.1754	0.5582	0.8206	0.571
0.2236	0.6297	0.7821	0.562
0.2758	0.6932	0.7443	0.565
0.3279	0.7395	0.7100	0.560
0.3872	0.7792	0.6746	0.552
0.4284	0.8024	0.6520	0.550

$$\chi_{1,23}^{\infty}=0.593$$

Table V. (continued)

$w_{2p}=0.3854$ ($MW_{PIB}=1350$)				
$m_{\text{solvent}}/m_{\text{pol}}$	P/P^0	ϕ_{23}	ϕ_2	$\chi_{1,23}$
0.0569	0.1763	0.9381	0.3367	0.409
0.1226	0.3235	0.8755	0.3143	0.406
0.1510	0.3723	0.8509	0.3054	0.398
0.2028	0.4477	0.8095	0.2906	0.392
0.2513	0.5058	0.7742	0.2779	0.390
0.3016	0.5582	0.7407	0.2659	0.397
0.4016	0.6297	0.6821	0.2449	0.379
0.5196	0.6932	0.6238	0.2239	0.376
0.6385	0.7395	0.5743	0.2061	0.375
0.7900	0.7792	0.5217	0.1873	0.361
0.8947	0.8024	0.4906	0.1761	0.363
$\chi_{1,23}^{\infty}=0.415$				
$w_{2p}=0.0$				
$m_{\text{solvent}}/m_{\text{pol}}$	P/P^0	$\phi_{23} (= \phi_3)$	$\chi_{1,23} (= \chi_{13})$	
0.0729	0.1763	0.9249	0.311	
0.1037	0.2328	0.8965	0.299	
0.1586	0.3235	0.8500	0.313	
0.1962	0.3723	0.8208	0.306	
0.2630	0.4477	0.7736	0.310	
0.3292	0.5058	0.7319	0.307	
0.4019	0.5582	0.6910	0.307	
0.5406	0.6297	0.6244	0.291	
0.7098	0.6932	0.5587	0.289	
0.8827	0.7395	0.5045	0.288	
1.0989	0.7792	0.4499	0.277	
1.2532	0.8024	0.4176	0.282	
$\chi_{1,23}^{\infty}=0.315$				

ty parameter method to form a compatible blend.

5. A Block Copolymer-Solvent System

A different way for determining polymer-polymer interactions is by studying block copolymer-solvent systems. For such an information to be extracted, one has also to study the constituent homopolymer-solvent systems. For this purpose, a triblock copolymer has been chosen. Its end blocks, in one case, were $(\text{CH}_2)_{17}\text{CH}_3$ and, in the other, $(\text{CH}_2)_{20}\text{CH}_3$; while the central block was $(\text{CH}_2-\text{CH}_2-\text{O})_{45}$.

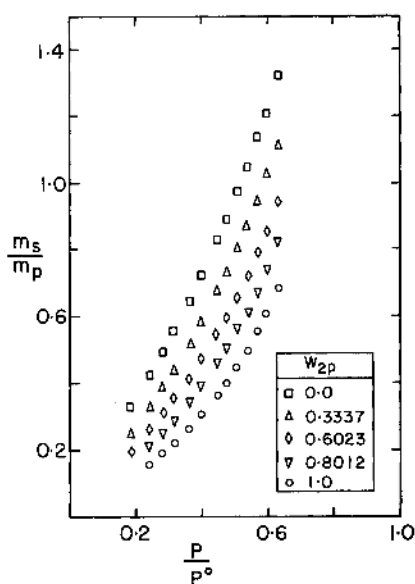


Figure 4. Sorption isotherm for the system *n*-pentane (1) -polyisobutylene (2) -*n*-heptadecane (3) at 25°C.

The copolymer-benzene systems have been studied at 55°C. The reported melting points²⁵ are: for the copolymer 18-45-18, $T_m=50^\circ\text{C}$ and for the copolymer 21-45-21, $T_m=54^\circ\text{C}$.

As model homopolymer for the end blocks, *n*-tetracosane has been chosen. For the central block, the α,ω -methoxypoly(ethylene oxide) with an average molecular weight 600 has been used at 55°C and a high molecular weight (100,000) poly(ethylene oxide) at 70°C. Pure component characteristic specific volumes are: for benzene²⁶ $v_{\text{sp},1}^*=0.8948 \text{ cm}^3 \text{ g}^{-1}$, for poly(ethylene oxide)²⁶ $v_{\text{sp},2}^*=0.7532 \text{ cm}^3 \text{ g}^{-1}$ and for *n*-tetracosane (by linear interpolation on the values reported in ref 23) $v_{\text{sp},3}^*=1.054 \text{ cm}^3 \text{ g}^{-1}$.

Experimental data are reported in Table VI. For the sake of comparison with data in the literature, in Table VII we present the data for the system benzene-poly(ethylene oxide) at 70°C as solvent activities *versus* weight fraction of benzene. As it is indicated in Figure 5, the three sets of data are in good agreement.

Table VI. Vapor-pressure lowering data for the system: benzene (1)–poly(ethylene oxide) (2)–*n*-tetracosane (3) at 55°C

$w_{2p} = 1.0$ (PEOM 600)			
$m_{\text{sol}}/m_{\text{pol}}$	P/P^0	$\phi_{23} (= \phi_2)$	$\chi_{1,23} (= \chi_{12})$
0.0916	0.2269	0.9019	0.110
0.1523	0.3340	0.8468	0.105
0.2790	0.4941	0.7511	0.105
0.4184	0.6098	0.6680	0.113
0.5974	0.7066	0.5849	0.125
0.8184	0.7818	0.5070	0.142
1.0892	0.8369	0.4359	0.152
$w_{2p} = 0.7494$ (21-45-21)			
$m_{\text{sol}}/m_{\text{pol}}$	P/P^0	ϕ_{23}	$\chi_{1,23}$
0.0795	0.2074	0.9210	0.104
0.1377	0.3254	0.8706	0.121
0.2471	0.4815	0.7894	0.116
0.2476	0.4815	0.7890	0.115
0.3655	0.5985	0.7170	0.122
0.5083	0.6559	0.6457	0.134
0.6503	0.7621	0.5875	0.144
1.0136	0.8574	0.4775	0.158
1.1776	0.8855	0.4402	0.180
$w_{2p} = 0.7740$ (18-45-18)			
$m_{\text{sol}}/m_{\text{pol}}$	P/P^0	ϕ_{23}	$\chi_{1,23}$
0.0797	0.2074	0.9201	0.094
0.1405	0.3254	0.8673	0.094
0.2478	0.4815	0.7874	0.107
0.2488	0.4815	0.7867	0.103
0.3657	0.5985	0.7151	0.115
0.5114	0.6959	0.6422	0.122
0.6577	0.7621	0.5825	0.128
0.7856	0.8037	0.5388	0.133
1.0108	0.8574	0.4759	0.155
1.1745	0.8855	0.4387	0.178
1.1840	0.8855	0.4367	0.171
$w_{2p} = 0.0$ (tetracosane)			
$m_{\text{sol}}/m_{\text{pol}}$	P/P^0	ϕ_{23}	$\chi_{1,23}$
0.0754	0.2074	0.9399	0.562
0.1327	0.3254	0.8988	0.566
0.2436	0.4815	0.8287	0.548
0.3721	0.5985	0.7600	0.536
0.5384	0.6959	0.6864	0.532
0.7303	0.7621	0.6174	0.516
0.9124	0.8037	0.5636	0.507
1.2731	0.8574	0.4807	0.508

Table VIa. Vapor-pressure lowering data for the system: benzene (1)–poly(ethylene oxide) (2) at 70°C

$w_{2p} = 1.0$ (PEO $M_w = 100,000$)			
$m_{\text{sol}}/m_{\text{pol}}$	P/P^0	$\phi_{23} (= \phi_2)$	$\chi_{1,23} (= \chi_{12})$
0.0641	0.2165	0.9292	0.242
0.1403	0.3945	0.8571	0.237
0.2330	0.5438	0.7832	0.242
0.3243	0.6430	0.7219	0.241
0.3889	0.6962	0.6840	0.244
0.5433	0.7830	0.6078	0.242
0.6340	0.8208	0.5704	0.252
0.8092	0.8687	0.5099	0.254

Table VII. Benzene activity in benzene–poly(ethylene oxide) solution at 70°C

Weight fraction of benzene w_1	Activity a_1
0.0603	0.2207
0.1231	0.4004
0.1890	0.5499
0.2449	0.6486
0.2730	0.7014
0.3880	0.8244
0.4773	0.8715

DISCUSSION AND CONCLUSIONS

The apparatus for vapor-sorption measurements used in this work reduces considerably the time required for a complete study of the system. This is due to the simultaneous measurements of samples containing different proportions of the polymers. However, the time required for the measurement of a single system still may be quite large. For example, the runs for the measurement of the system benzene–polystyrene–poly(vinyl methyl ether) lasted for nearly forty days. This long experimental time and the relatively low solvent vapor pressure may account for the relatively large scatter of the experimental data measured for this system.

Although, as shown by calibration of the apparatus,¹³ the $\chi_{1,23}$ data reported in this

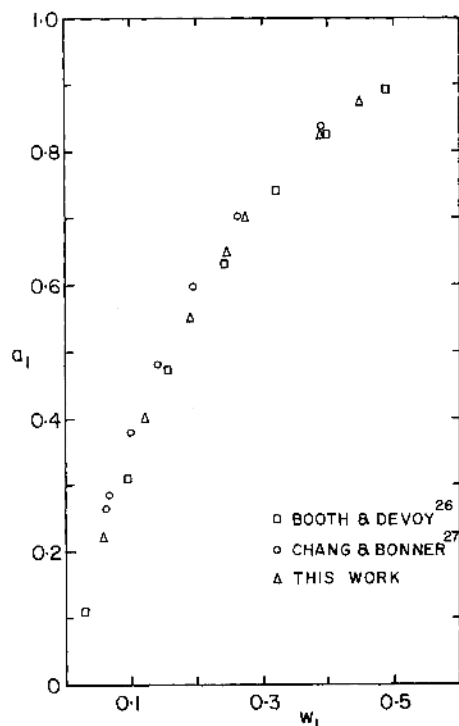


Figure 5. Activities of benzene versus solvent weight fraction for the system benzene (1)-poly(ethylene oxide) (2) at 70°C.

work is as good as that of similar studies reported in the literature, the values of χ'_{23} should be taken with caution. Extrapolation of the $\chi_{1,23}$ values for the limiting case of zero solvent concentration is probably the main cause of uncertainty in the value of χ'_{23} obtained. From the systems measured in this work, this is particularly valid for the system benzene-polystyrene-poly(vinyl methyl ether) due to the large scatter in $\chi_{1,23}$ values mentioned above. Positive values of χ'_{23} obtained for this system are questionable since they would indicate incompatibility between the polystyrene and the poly(vinyl methyl ether). In addition to the error in χ'_{23} introduced by the extrapolation of $\chi_{1,23}$ values, in static indirect methods, as the one used in this work, the solvent used for the study may affect the value of χ'_{23} .²¹ This effect has been discussed in the text for the system poly(vinyl chloride)-

poly(ϵ -caprolactone).

Further studies using oligomeric analogs may help in explaining the discrepancies in the information extracted from indirect methods as the probing technique used here. With oligomeric analogs the possibility of having nonequilibrium states may be minimized and, in addition, heats of mixing may be measured allowing a direct assessment of pair interactions.

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NOTATION

a_1	= activity of component 1
B	= second virial coefficient ($\text{cm}^3 \text{mol}^{-1}$)
m_i	= mass of component i (g)
P	= pressure (mmHg)
R	= gas constant
r	= number of segments per molecule
r_{23}	= quantity defined by eq 5
T	= temperature (K)
$v_{\text{sp},i}$	= specific volume of component i ($\text{cm}^3 \text{g}^{-1}$)
$v_{\text{sp},i}^*$	= characteristic specific volume of component i ($\text{cm}^3 \text{g}^{-1}$)
w_{ip}	= weight fraction of component i in the polymer mixture
x_i	= mole fraction of component i

Greek Letters

ϕ_i	= segment fraction of component i
ϕ_{23}	= quantity defined by eq 6
χ_{ij}	= Flory-Huggins interaction parameter
χ'_{ij}	= quantity defined by eq 4
$\chi'_{1,23}$	= quantity defined by eq 7

Superscripts

0	= quantity pertaining to pure component
∞	= quantity at zero solvent concentration

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