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Inverse Gas Chromatography. 6. Thermodynamics of Poly(ε-caprolactone)–Polyepichlorohydrin Blends

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ABSTRACT: Poly(ε-caprolactone) (PCL), polyepichlorohydrin, and their blends were studied at 80 °C by inverse gas chromatography (IGC). The retention behavior of the homopolymers and three blends (0.25, 0.5, and 0.75 PCL volume fractions) was characterized for 25 probes. Several new experimental and data reduction procedures were implemented to boost the data precision. In agreement with past work, the IGC-derived polymer–polymer interaction coefficients χ'_{23} and B_{23} showed an apparent dependence on the chemical nature of the probe. This dependence was regular and systematic with respect to probe structure and solvent strength. χ'_{23} values ranged from +0.08 for the *n*-alkanes to −0.27 for the good solvents. On the other hand, χ'_{23} and B_{23} did not vary with blend composition for a given probe. The observed dependence of the apparent polymer–polymer interaction parameter on probe is believed to result from the Flory–Huggins treatment improperly applied to ternary systems. A correlation was found to exist between the apparent B_{23} values and the Hildebrand solubility parameter of the probe. A procedure is suggested by which the intrinsic B_{23} interaction energy for the blend can be extracted from such a correlation. Accordingly, for the present blend, B_{23} was estimated to be about −2 cal/mL.

Introduction

The availability of a simple technique for characterizing polymer–polymer interactions in miscible blends would be of great value. Such capability is still nonexistent today. Among the handful of techniques useful for this purpose (vapor sorption, melting point depression analysis, scattering techniques) none is sufficiently simple and versatile to be considered a routine method.

For some time now, inverse gas chromatography (IGC) has held considerable promise for becoming a convenient tool for investigating polymer blend thermodynamics. In a pioneering work, Deshpande et al.[1] first suggested this possibility. Olabisi[2] immediately followed, reporting the first experimental work on a blend of poly(ε-caprolactone) and poly(vinyl chloride). Since then, a modest number of blend studies[3-9] that made use of the IGC technique have appeared in the literature. As more studies were reported, however, the technique faced increasing doubts due to the strong variability of the IGC-derived polymer–polymer interaction coefficient χ'_{23} with the probe used. In an effort to reevaluate the method, Al-Saigh and Munk[8] undertook a critical examination of the experimental aspects of IGC. They suggested that the apparent variability in χ'_{23} from probe to probe was partly caused by uncontrolled experimental artifacts and errors. Nevertheless, they further pointed out that part of the observed variation was real. This they attributed to an inadequate thermodynamic treatment from which the χ'_{23} value is derived—a position shared by a recent theoretical study.[10] Having realized that, we took a two-pronged approach to the problem. First, we have recognized that for obtaining meaningful interaction data on blends, an experimental precision superior to that of conventional polymer–solvent IGC work is demanded. A column-to-column reproducibility better than 1% appears to be the minimum requirement. A careful examination of the possible error sources has led us to implement a number of data acquisition and data reduction procedures to improve the data quality and reproducibility. In the second phase of the study, the dependence of χ'_{23} on probe structure is to be tackled from the viewpoint of thermodynamic modeling for a ternary system. It is believed that the current Flory–Huggins–Scott[11] treatment does not account for all the interactions present in the polymer–polymer–probe system, and this deficiency is responsible for the apparent probe dependence for polymer–polymer interaction properties.

We have selected for this study the blend poly(ε-caprolactone) (PCL)–polyepichlorohydrin (PECH). This blend is known miscible at all compositions from previous studies.[12,13] The miscibility in this system is believed to arise from a favorable interaction between chlorine in PECH and the carbonyl function in PCL. The blend was studied at 80 °C, about 100 °C above the glass transition of PECH and 20 °C above the melting point of PCL. This condition ensured that the system exhibited ideal chromatographic behavior over the entire composition range. The IGC retention behavior was measured for three blend compositions: 0.25, 0.5, and 0.75 PCL volume fractions. The purpose here was to check for any compositional dependence as well as to assess the overall data reproducibility. Twenty-five probes, representing a number of chemical group families, were used to facilitate the correlation of apparent χ'_{23} values with probe characteristics.

Theory

The elution behavior of a volatile substance (probe) on a gas chromatographic column is usually described by its specific retention volume, V_g, defined as

$$V_g = (V_r - V_0)/w = V_n/w \quad (1)$$

where V_r is the probe elution volume (eq 8), V_0 is the column void volume, and V_n is the net retention volume ($V_r - V_0$). w is the mass of the polymer on the column.

Throughout this paper, the subscript 1 will be used to denote the probe, while the polymer will be denoted by 2 or 3 corresponding to PCL and PECH, respectively. By combination of the Flory–Huggins theory with routine chromatographic calculations,[14,15] the expression for the residual free energy parameter of binary interaction, χ_{12}, can be written as

$$\chi_{12} = \ln (RTv_2/V_gV_1P^\circ_1) - 1 + V_1/M_2v_2 - (B_{11} - V_1)P^\circ_1/RT \quad (2)$$

The variables V_1 and P°_1 in eq 2 represent the probe molar volume in the liquid phase and saturated vapor pressure, respectively, B_{11} is the second virial coefficient of the probe in the gas phase, v_2 is the specific volume of the polymer

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at the experimental temperature, and R and T are the gas constant and absolute temperature. For most work involving high molecular weight polymers, the third term on the right-hand side in eq 2 may be omitted. Equation 2 has been a standard route for evaluating probe–polymer interaction parameters from IGC measurements. In the case of a polymer blend investigation, eq 2 is first applied to the two homopolymers for a given selection of probes, giving χ_{12} and χ_{13}. A similar analysis on the blend column yields the analogous parameter $\chi_{1(23)}$. From the Flory–Huggins theory as applied to a ternary system,[11] an expression for the free energy of mixing can be written as

$$\Delta G_{\mathrm{mix}} = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1\phi_2\chi_{12} + n_1\phi_3\chi_{13} + n_2\phi_3\chi_{23}] \quad (3)$$

where ϕ_i's and n_i's are the volume fractions and the numbers of moles of the pertinent system components and the χ_{ij}'s are the binary interaction coefficients. The polymer–polymer interaction coefficient χ_{23} is a rather cumbersome quantity to work with, as it embeds the large molar volume of the polymer within it. Instead, the related parameter χ'_{23} defined as

$$\chi'_{23} = (V_1/V_2)\chi_{23} \quad (4)$$

is employed to characterize the binary interaction between the two polymers. This interaction parameter is also usually normalized to the molar volume of the probe. A common way of expressing it is by the quantity B_{23}

$$B_{23} = RT\chi'_{23}/V_1 \quad (5)$$

The parameter χ'_{23} can be evaluated as

$$\chi'_{23} = (1/\phi_2\phi_3)[\phi_2\chi_{12} + \phi_3\chi_{13} - \chi_{1(23)}] \quad (6)$$

In eq 6, ϕ_2 and ϕ_3 are the volume fractions of the two polymers in the blend column. Comparison of eq 2 and 6 would reveal that all the terms in expression 2 must cancel out upon combination in eq 6 except those for the column-dependent partition coefficient term $\ln (V_g/v_2)$. This leads to a mathematically identical yet more simplified form of eq 6 which reads

$$\chi'_{23} = (1/\phi_2\phi_3)\left[\ln \frac{V_{g,\mathrm{blend}}}{W_2v_2 + W_3v_3} - \phi_2 \ln \frac{V_{g,2}}{v_2} - \phi_3 \ln \frac{V_{g,3}}{v_3}\right] \quad (7)$$

Here, the second subscript after V_g denotes the nature of the column and W_i's are the weight fractions of the two components in the blend. Use of eq 7 instead of eq 6 circumvents the necessity of having accurate probe thermodynamic data in order to evaluate χ'_{23}. Equation 7 also involves less round-off errors in the computations than does eq 6. Equation 7 assumes that all columns are studied under experimentally identical conditions, so that any experimental artifacts nearly cancel out in the data reduction.

Experimental Section

Materials. The poly(ϵ-caprolactone) sample used was purchased from Scientific Polymer Products. It had $\bar{M}_w = 37\,000$. The PECH sample was a B.F. Goodrich product: Hydrin 100, having $\bar{M}_w = 700\,000$. The chromatographic support was 60/80 mesh Chromosorb W, acid washed and treated with DCMS. The probes were all obtained from reputed suppliers and had a nominal purity of 99% or better. They were used without further purification. High-purity nitrogen was used as the carrier gas. Packed columns were prepared out of 157-cm-long strips of $^1/_4$-in.-o.d. copper tubing. The tubing was rinsed with methanol and oven-baked for 1 h at 100 °C prior to packing.

By use of 1.37 g/cm^3 as the density of PECH at 25 °C and thermal expansion data from van Krevelen,[16] the temperature dependence of PECH specific volume was obtained. For PCL, the volumetric data from Brode and Koleske's work[12] were used. The specific volumes thus derived for the two polymers at 80 °C were 0.9463 and 0.7607 cm^3/g for PCL and PECH, respectively.

Table I
Summary of Chromatographic Column Characteristics

column	PCL, g	PECH, g	PCL wt fractn	PCL vol fractn[a]	support, g	% load
1	0.5595	0	1	1	7.521	6.92
2	0.5588	0	1	1	7.392	7.10
3	0.3980	0.1661	0.7055	0.7487	7.423	7.06
4	0.3939	0.1678	0.7013	0.7449	7.318	7.13
5	0.2490	0.3107	0.4449	0.4993	7.261	7.16
6	0.2510	0.3137	0.4445	0.4989	7.346	7.14
7	0.1189	0.4462	0.2104	0.2490	7.300	7.18
8	0.1161	0.4340	0.2111	0.2497	7.326	6.98
9	0	0.5565	0	0	7.522	6.89
10	0	0.5615	0	0	7.278	7.16
11	0	0			7.666	0

[a] Volume fractions are based on specific volumes of 0.9463 and 0.7607 cm^3/g for PCL and PECH at 80 °C, respectively.

Column Preparations. Each of the homopolymer and blend samples was first weighed carefully and dissolved in about 100 mL of tetrahydrofuran (THF). The polymer sample was then deposited onto the support by employing a procedure described in an earlier work.[8] This coating technique was developed to combat the error associated with inaccurate determination of the polymer mass on the column. The polymer mass determination is believed to be one of the chief sources of systematic error in the specific retention volume data from IGC experiments. In the new coating procedure, the mass of polymer can be known with the same accuracy allowed by the initial weighing of the sample on an analytical balance.

Solvent residue was removed from the polymer-coated support by drying overnight in a vacuum oven at 100 °C. Prior to any retention measurements, each new column was conditioned in the chromatograph at 120 °C for 8 h, during which the carrier gas swept through the system until a low and steady base-line signal was established.

Five system compositions were studied: the two parent homopolymers and three blends 25, 50, and 75% PCL by volume. For each composition, two nominally identical columns were prepared. This was done in an effort to establish the column-to-column reproducibility in the retention data. The exact compositions of the columns used and other column data are summarized in Table I.

Data Acquisition. A modified Varian Aerograph Model 2100 GC unit was utilized for gathering all the elution data. A water-jacketed soap bubble flow meter was used to monitor the carrier gas flow rate at 25 °C. The precision in the flow-rate measurement was ±0.02 mL/min. Flow control was achieved by a thermostated needle valve preceded by another reducing valve connected to the nitrogen supply regulator. All experiments were performed at a nominal flow rate of 16 mL/min. A flame ionization detector (FID) was used throughout and methane served as marker. A more detailed description of the apparatus is given elsewhere.[8]

The gathering of the elution data was accomplished by a recently developed microcomputer-based data station. This was a custom-configured system in which the elution signal from the FID output was monitored by a Hewlett-Packard 3478 A digital voltmeter and was processed in real time by a Tandy 3000 Personal Computer. The microcomputer was interfaced to the volt meter via an IEEE-488 board manufactured by National Instruments. The injection instant was marked for each run by the press of a mouse button, which actuated the start of the elution data timing. All the programming for the data station was performed by us using GW-BASIC 3.2 in conjunction with the interfacing software supplied by National Instruments. The data acquisition configuration described above afforded a resolution of ±0.1 s in the elution time data and a signal-to-noise ratio of about 5×10^4 in the detector output reading for typical injections.

Data Reduction. The elution volume (V_r) data were all obtained from measurement of peak maximum positions, t_p. As the digital gathering of data was performed at a sampling rate of 2 reading/s, the precise value of t_p was determined from a quadratic curve fit of the time-slice data in the top section of the peak. V_r was calculated as

$$V_r = t_p F j \tag{8}$$

where F is the carrier gas volumetric flow rate at column temperature and column exit pressure and j is the pressure drop correction factor as routinely used in GC work.

The elution volume must be corrected with respect to column void volume V_0 in order to obtain the net and specific retention volumes as defined in eq 1. The marker (methane) elution volume is inaccurate as a measure of V_0 due to the methane retention on the column. To correct for this, the net retention volume of methane, V_n^m, was estimated from the retention behavior of higher normal alkanes. V_n^m was then used for computing a corrected column void volume, V_0, according to

$$V_0 = V_r^m - V_n^m \tag{9}$$

where V_r^m is the methane elution volume. The quantity V_n^m was estimated based on the linear relationship between ln V_n for n-alkane probes and the alkane carbon number. This correction for methane retention has been discussed in a recent paper[17] and in several other works.[18-21]

The apparent V_g values of eq 1 contain a contribution from the solid support. Usually ignored, the support retention has proved to be nonnegligible in most cases and must therefore be accounted for. We have found the support retention can contribute as much as 10% of the observed retention for a typical 7% polymer-loaded column. A paper devoted to this support retention phenomenon has appeared recently.[22] Correcting the retention data for support adsorption was performed by direct subtraction of the support retention from the apparent specific retention of the column, V_g^a, such that

$$V_g = V_g^a - V_n^s/w \tag{10}$$

in which V_n^s is the retention of the probe on the support as obtained from an independent experiment on the uncoated support. For best results, the support must be studied under conditions very similar to those of the polymer-coated columns. The assumption of retention additivity, which is inherent in eq 10, is strongly supported by experimental data.

The support retentions were not independent of the amount of probe injected. This concentration dependence varied with the chemical nature of the probe, being most pronounced for the strongly polar probes and almost negligible for the alkanes and other hydrocarbons. Within the region of sample sizes practical to IGC experiments, all the concentration dependences of the probes were found to obey the logarithmic relation

$$\ln V_n^s = a + b \ln A_p \tag{11}$$

where A_p, the peak area, is a measure of the probe sample size. The constants a and b are functions of temperature only, and have been found to correlate with temperature in an Arrhenius manner. The dependence of support retentions on peak area is illustrated for several probes in Figure 1. The data are plotted according to eq 11.

Since the retention on the support was a function of sample size, a sound algorithm for subtracting the support data from the coated-column data had to be devised. First, the support retention was characterized according to eq 11 for various probes. Next, for a given run on a coated column, the peak area was inserted into eq 11 to determine the support retention corresponding to that particular area. Then the computed V_n^s value was subtracted from the apparent retention according to eq 10. The validity of this subtraction routine is confirmed by retention data such as those shown in Figure 2 for acetone on a PECH-coated column. For an ideal linear isotherm, V_n should not depend on peak area. Looking at Figure 2 one finds both the uncorrected PECH V_n and the support V_n^s (line drawn from eq 11) show a significant dependence on area as described above, but the data after correction for the support are nearly independent of area.

The evaluation of the χ_{12} parameters (eq 2) requires critical property data (for the calculation of B_{11}) as well as Antoine vapor pressure coefficients and other constants. These data have been extracted, for the most part, from Dreisbach's compilation.[23] Additional data were obtained from Reid et al.[24] Calculation procedures for B_{11} and other quantities have been described in detail earlier.[8]

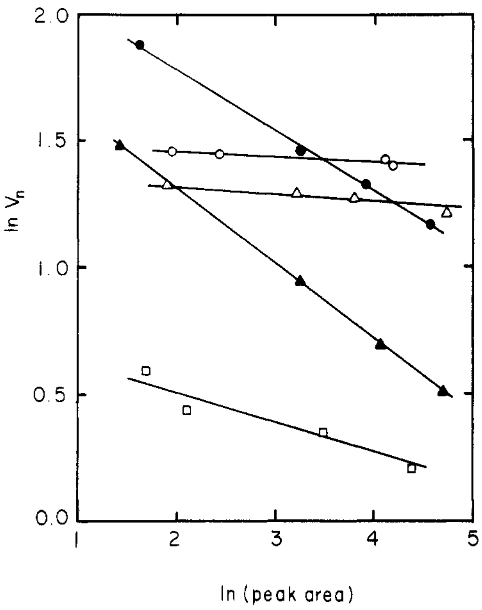

Figure 1. Dependence of net retention volume, V_n, on the amount of probe injected (represented by peak area) for uncoated Chromosorb W support: (▲) ethyl acetate; (●) propyl acetate; (○) n-octane; (△) toluene; (□) carbon tetrachloride.

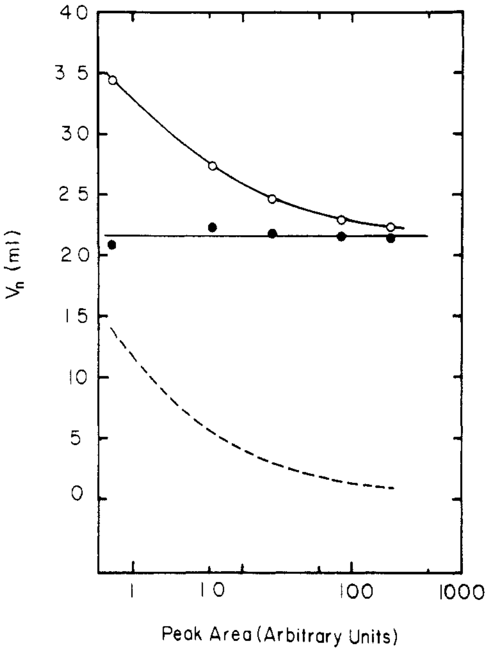

Figure 2. PECH-coated column at 80 °C. Dependence of net retention volume of acetone V_n on amount injected (peak area) before (○) and after (●) correcting the data for the support retention (dashed line).

Results and Discussion

In order to assess the degree of reproducibility among independent experiments, two nominally identical columns were prepared for each composition as is apparent from Table I. The V_g data for each pair of columns were found to differ by 0.5–1.5%. The observed differences were represented by a uniform staggering of the values for all the probes studied. For example, the V_g values for column 2 were about 1% smaller than their column 1 counterparts, and that was the case for essentially all probes. This kind

Table II
Specific Retention Volumes, V_g, of Various Probes on PCL, PECH, and Their Blends at 80 °C[a]

probe	code[b]	PCL vol fractn 0.0	0.25	0.5	0.75	1.0
pentane	NC5	3.43	4.23	5.13	6.11	7.48
hexane	NC6	6.96	8.65	10.49	12.79	15.59
heptane	NC7	13.73	17.18	20.99	25.78	31.68
octane	NC8	26.65	33.76	41.52	51.59	64.03
nonane	NC9	51.59	65.97	82.13	103.02	129.02
cyclohexane	CC6	19.88	23.32	26.84	31.09	36.37
cyclohexene	CHX	33.43	38.07	42.97	49.32	57.14
benzene	BNZ	69.84	74.50	81.05	91.65	106.30
toluene	TOL	141.52	152.40	166.90	190.15	222.97
pentyl chloride	CLP	74.35	83.51	94.57	110.15	131.01
butyl chloride	CLB	37.16	41.21	46.19	53.55	63.10
methyl chloroform	MCH	38.75	44.75	51.81	61.73	74.43
1,1-dichloroethane	D11	32.45	36.74	42.54	50.75	61.77
1,2-dichloroethane	D12	89.72	99.18	113.03	133.98	162.75
methylene chloride	CL2	29.09	33.50	39.60	47.94	60.02
chloroform	CL3	47.38	58.73	73.41	94.59	122.19
carbon tetrachloride	CL4	35.36	41.81	49.07	59.07	71.63
tetrahydrofuran	THF	61.52	61.46	61.88	64.16	68.23
1,4-dioxane	DOX	189.24	185.17	185.60	195.04	212.51
acetone	ACT	38.21	36.44	35.75	36.61	38.62
2-butanone	MEK	70.97	69.01	68.13	70.16	74.68
methyl acetate	MAC	33.42	33.85	34.34	36.67	40.38
ethyl acetate	EAC	52.03	52.73	54.11	57.88	63.86
propyl acetate	PAC	99.59	101.26	104.34	111.63	123.67
n-butyl acetate	NBA	193.45	199.90	208.07	224.55	251.63

[a] Units of V_g are mL/g. [b] As employed in Figure 4.

of error behavior pinpoints column preparation as the primary source of variability in IGC data. The variability of independent measurements (i.e., on two different days) for the same column has been reduced to better than 0.3%. It is this kind of precision that we believe is needed for successful use of IGC in polymer blend studies. This can be readily achieved by observing the data handling precautions described here. Also, in order to maximize the resolving power of the IGC technique in the study of blend systems, it is recommended that, whenever possible, probes having a relatively low volatility be favored over others, as such probes are subject to less error in the experimental V_g measurements than are the weakly retained volatile ones.

The V_g data appearing in Table II, which are used in all the subsequent thermodynamic calculations, are averages of the five column pairs studied. The reader should be reminded that all the V_g values reported in this work are not normalized to 0 °C as is customarily done by many workers in this field. The V_g values are inherent characteristics of the system from which probe–polymer interaction data can be directly computed. The quantity ln V_g is plotted in Figure 3 for selected probes against blend composition. As apparent in Figure 3, all the probe curves, except those for the alkanes, exhibited the downward curvature in the ln V_g values, which reflects the strength of the interaction between the two homopolymers in the blend. According to the formalism leading to eq 6 and 7, the value of χ'_{23} is measurable by the deviation of the experimental ln V_g line from the hypothetical logarithmic average for the two pure homopolymers, which characterizes the behavior of hypothetical noninteracting blends (dashed lines).

The apparent polymer–polymer interaction data at three blend compositions, as embodied in the parameters χ'_{23} and B_{23}, are presented in Table III. The observed variation in the χ'_{23} values among the three composition data for a given probe was less than 0.05. We attribute this variation to experimental errors, which would be expected from an error level of 1% in the V_g data. As such, the χ'_{23} and B_{23} values have been averaged over the three blend compositions and the average values appear in Table IV in final form. Along with these values, the χ_{12}, χ_{13}, and $\chi_{1(23)}$ values for the two homopolymers and the 50:50 blend, as well as the probe solubility parameters at 80. °C, are also tabulated. Since each column data were in themselves obtained by merging dual-column data, the final values of χ'_{23} and B_{23} given in Table IV are, in effect, averages

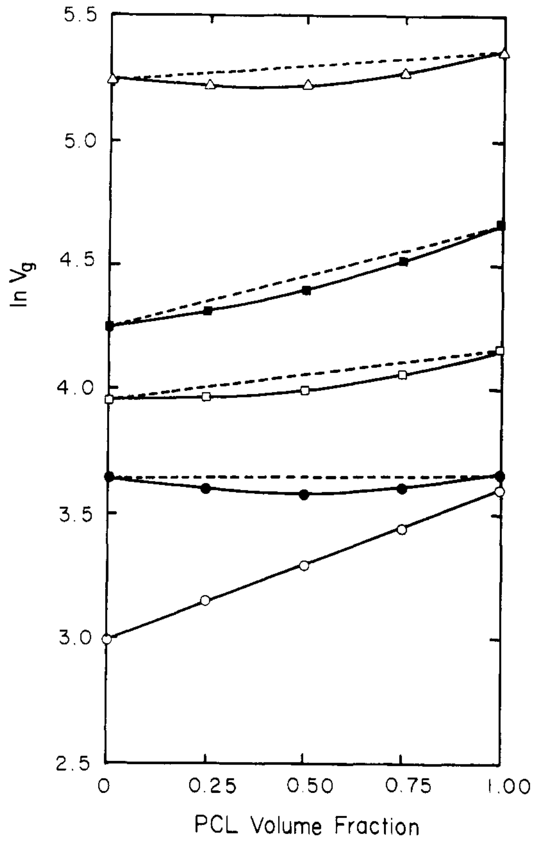

Figure 3. PECH–PCL blends at 80 °C. Logarithm of V_g plotted against PCL volume fraction for selected probes: (△) 1,4-dioxane; (■) benzene; (□) ethyl acetate; (●) acetone; (○) cyclohexane.

Table III
Apparent Polymer–Polymer Interaction Parameters χ'_{23} and B_{23} for PCL–PECH Blends at Three Blend Compositions (PCL Volume Fractions) at 80 °C

	χ'_{23}			B_{23}, cal/mL		
probe	0.25	0.5	0.75	0.25	0.5	0.75
pentane	0.10	0.08	0.00	0.6	0.4	0.0
hexane	0.11	0.05	0.06	0.6	0.3	0.3
heptane	0.11	0.05	0.05	0.5	0.2	0.2
octane	0.12	0.05	0.06	0.5	0.2	0.2
nonane	0.12	0.05	0.06	0.4	0.2	0.2
cyclohexane	0.07	0.02	0.00	0.4	0.1	0.0
cyclohexene	0.00	−0.04	−0.04	0.0	−0.3	−0.2
benzene	−0.19	−0.22	−0.20	−1.4	−1.6	−1.4
toluene	−0.19	−0.22	−0.21	−1.2	−1.4	−1.3
pentyl chloride	−0.11	−0.15	−0.13	−0.6	−0.8	−0.7
butyl chloride	−0.13	−0.16	−0.13	−0.8	−1.0	−0.8
methyl chloroform	−0.08	−0.12	−0.09	−0.5	−0.8	−0.6
1,1-dichloroethane	−0.17	−0.18	−0.15	−1.3	−1.4	−1.2
1,2-dichloroethane	−0.24	−0.24	−0.21	−1.9	−2.0	−1.7
methylene chloride	−0.19	−0.19	−0.19	−1.9	−1.9	−1.9
chloroform	−0.09	−0.12	−0.06	−0.8	−1.0	−0.5
carbon tetrachloride	−0.02	−0.08	−0.05	−0.1	−0.5	−0.3
tetrahydrofuran	−0.12	−0.16	−0.16	−0.9	−1.3	−1.3
1,4-dioxane	−0.25	−0.29	−0.27	−2.0	−2.3	−2.2
acetone	−0.25	−0.26	−0.24	−2.1	−2.3	−2.1
2-butanone	−0.20	−0.24	−0.24	−1.4	−1.7	−1.7
methyl acetate	−0.16	−0.25	−0.23	−1.3	−2.0	−1.9
ethyl acetate	−0.18	−0.23	−0.23	−1.2	−1.5	−1.5
propyl acetate	−0.18	−0.22	−0.23	−1.0	−1.3	−1.3
n-butyl acetate	−0.15	−0.21	−0.23	−0.8	−1.0	−1.1

Table IV
PCL–PECH Apparent Interaction Parameters χ'_{23} and B_{23} at 80 °C Averaged Over for All Blend Compositions, Along with the Probe–Polymer Binary Interaction Parameters[a] and Probe Solubility Parameters, δ_1, at 80 °C

no.[b]	probe	χ_{12}	χ_{13}	$\chi_{1(23)}$	χ'_{23}	B_{23}, cal/mL	δ_1, (cal/mL)$^{1/2}$
1	pentane	1.19	1.74	1.45	0.06	0.33	6.58
2	hexane	1.24	1.82	1.52	0.08	0.37	6.75
3	heptane	1.31	1.92	1.61	0.07	0.31	6.88
4	octane	1.39	2.04	1.71	0.08	0.30	6.98
5	nonane	1.47	2.16	1.80	0.08	0.28	7.08
6	cyclohexane	0.94	1.32	1.13	0.03	0.19	7.63
7	cyclohexene	0.61	0.92	0.78	−0.03	−0.18	7.94
8	benzene	0.04	0.23	0.19	−0.20	−1.48	8.50
9	toluene	0.06	0.30	0.24	−0.21	−1.28	8.31
10	pentyl chloride	0.35	0.70	0.57	−0.13	−0.70	7.77
11	butyl chloride	0.35	0.65	0.54	−0.14	−0.88	7.81
12	methyl chloroform	0.06	0.49	0.31	−0.10	−0.62	7.85
13	1,1-dichloroethane	−0.06	0.36	0.20	−0.17	−1.28	8.31
14	1,2-dichloroethane	−0.18	0.19	0.07	−0.23	−1.88	9.11
15	methylene chloride	−0.31	0.20	−0.01	−0.19	−1.90	9.24
16	chloroform	−0.51	0.22	−0.11	−0.09	−0.76	8.78
17	carbon tetrachloride	0.24	0.73	0.51	−0.05	−0.33	8.00
18	tetrahydrofuran	0.12	0.00	0.10	−0.15	−1.15	8.59
19	1,4-dioxane	0.11	0.00	0.13	−0.27	−2.15	9.54
20	acetone	0.48	0.27	0.44	−0.25	−2.18	9.01
21	2-butanone	0.35	0.18	0.33	−0.22	−1.62	8.55
22	methyl acetate	0.39	0.36	0.44	−0.21	−1.74	8.77
23	ethyl acetate	0.35	0.33	0.40	−0.21	−1.38	8.21
24	propyl acetate	0.32	0.32	0.38	−0.21	−1.18	8.09
25	*n*-butyl acetate	0.30	0.34	0.38	−0.20	−0.97	7.96

[a] Probe = component 1; PCL = component 2; PECH = component 3; (23) designates blend. [b] As used in Figure 5.

over six independent data sets.

The B_{23} values of Table IV, also shown diagrammatically in Figure 4, vary with the chemical nature of the probe in a rather systematic manner. By inspecting Table IV and Figure 4 for the χ'_{23} and B_{23} values, one finds that both quantities vary significantly with probe. From the definition of χ'_{23}, however, this quantity should be expected to vary mildly with the molar volume of the probe, and its variation, per se, should not be unexpected. A critical examination must therefore focus on B_{23} (which is normalized with respect to molar volume) as opposed to χ'_{23}. The probes used have been carefully selected to span a wide range of polarities. Alkanes, which are nonsolvents for the two homopolymers, gave small positive values for B_{23}, whereas the strongly polar probes like acetone, dioxane, and methyl acetate gave the lowest values. Within a given probe family, the apparent value of B_{23} increased progressively with increasing aliphatic content in the probe molecule. This applied for the acetates, for example, where B_{23} followed the order methyl < ethyl < propyl < *n*-butyl, and within the cyclic hydrocarbons in which the trend benzene < toluene < cyclohexene < cyclohexane was observed. The same was true for the ketones, cyclic ethers, and chloroalkanes. We have further found that the apparent B_{23} value can, in fact, be constructed for a given probe by using the concept of atomic group contributions. For example, the acetone value of −2.2 cal/mL can be computed as the sum of two methyl group contributions and one carbonyl with proper accounting for the approximate volume fraction for each group within the probe molecule. This approach seems to work well on a phenomenological level, but due to the lack of an obvious theoretical basis for it, we are not pursing its use at the present time.

As an alternate approach, we attempted to correlate the apparent B_{23} values with the Hildebrand solubility parameter of the probe. The apparent B_{23} values are shown in Figure 5 plotted against the δ_1 values for the 25 probes studied. These δ_1 values, also listed in Table IV, have been calculated from the Antoine temperature dependence coefficients of the vapor pressure data so that the δ_1 values can be obtained at the experimental temperature of 80 °C.

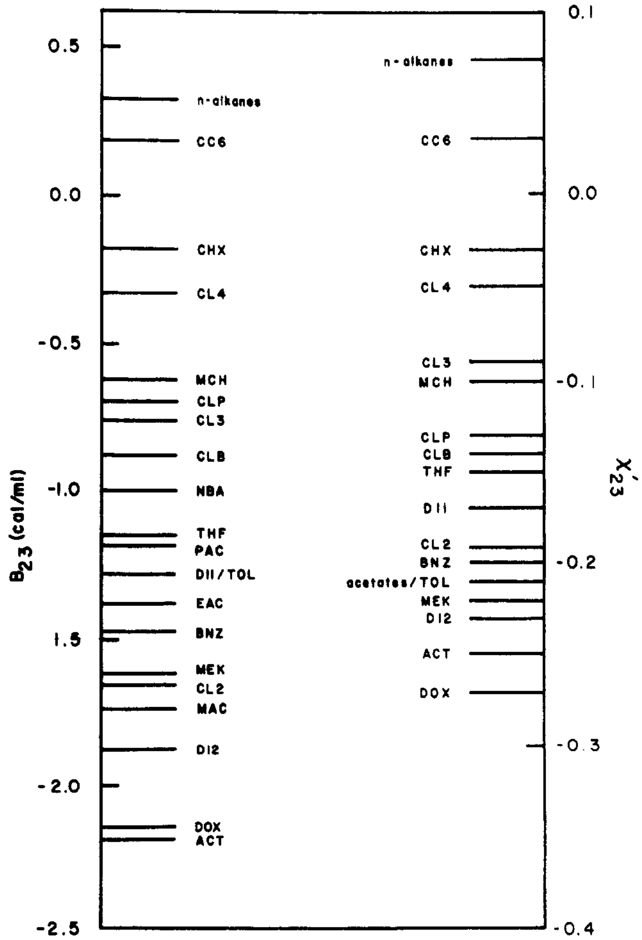

Figure 4. Apparent χ'_{23} and B_{23} values depicted for the various probes in ascending order in PECH–PCL blends at 80 °C. The three-letter codes represent the probes as defined in Table I.

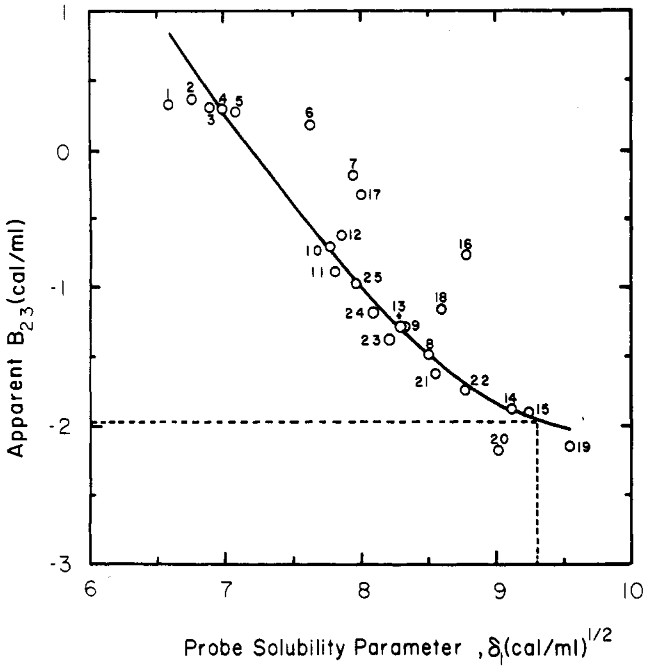

Figure 5. Apparent B_{23} values for PCL–PECH at 80 °C correlated against the Hildebrand solubility parameter of the probe. The numbers 1–25 represent the probes according to the assignments given in Table IV.

With the exception of very few probes, Figure 5 seems to reveal a very interesting correlation between apparent B_{23} values and probe solubility parameter. While it is difficult to judge the nature of this dependence from the extent of scatter in the points, a curve was drawn through the points as the most reasonable fit of the data without resorting to any regression procedures. It is important to note that the few major deviations of the data from the correlation line are well beyond the experimental errors associated with the B_{23} measurement. The experimental error in B_{23} has been estimated to be about ±0.25 cal/mL. The observed deviations are therefore due to a real thermodynamic effect which is not yet obvious to us. Based on the nature of this correlation, we have hypothesized that the probe result representative of the true B_{23} value for the blend is one which possesses the same solubility parameter as that of the blend (i.e., an athermal solvent). This stipulation necessitates that a good estimate of the solubility parameter for the blend be first made. This was done from the available χ_{12} data by using the method established by Guillet et al.[25,26] The solubility parameter for the blend which was obtained according to this treatment was in the neighborhood of 9.3 (cal/mL)$^{1/2}$. Inspecting Figure 5 again, one can obtain a B_{23} value of about −2 cal/mL corresponding to this solubility parameter value. This is a reasonable value for a blend exhibiting a moderate level of specific interaction between the homopolymers.

A number of works in this area are currently being undertaken to further probe the underlying significance of the B_{23} versus δ_1 correlation and to establish a standard procedure for obtaining binary interaction data on polymer blends. It is believed that having the ability to generate IGC data of enhanced precision and the possibility of correlating apparent B_{23} interaction data against probe properties will serve as important stepping stones in that direction.

Conclusions

A refined protocol for the acquisition and reduction of inverse gas chromatography data on miscible polymer blends was implemented. It was demonstrated that the adsorption of various probes on the inert chromatographic support contributes significantly to the observed retention on polymeric phases, and a procedure for eliminating this support contribution was described. Other experimental modifications and guidelines were also outlined. Reproducible values for the polymer–polymer interaction parameters χ'_{23} and B_{23} were found to be obtainable only when the specific retention volumes on individual columns can be measured to a precision of 1% or better. A systematic dependence of these parameters on probe structure and solvent strength was eminently present in the data, however. We have been successful in expressing this dependence as a correlation between the apparent B_{23} value and the Hildebrand solubility parameter for the probe. This correlation was further used in making an estimate of the true B_{23} for the blend based on the experimental data. This procedure, for the first time, offers a manageable way in which to treat IGC data on blends. We consider this a significant development toward obtaining reliable polymer–polymer interaction data from IGC measurements on miscible blends.

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Registry No. PCL (SRU), 25248-42-4; PCL (homopolymer), 24980-41-4; PECH (SRU), 61710-61-0; PECH (homopolymer), 24969-06-0; NC5, 109-66-0; NC6, 110-54-3; NC7, 142-82-5; NC8, 111-65-9; NC9, 111-84-2; CC6, 110-82-7; CHX, 110-83-8; BNZ, 71-43-2; TOL, 108-88-3; CLP, 543-59-9; CLB, 109-69-3; MCH, 71-55-6; D11, 75-34-3; D12, 107-06-2; CL2, 75-09-2; CL3, 67-66-3; CL4, 56-23-5; THF, 109-99-9; DOX, 123-91-1; ACT, 67-64-1; MEK, 78-93-3; MAC, 79-20-9; EAC, 141-78-6; PAC, 109-60-4; NBA, 123-86-4.

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