An Approximate Method for the Determination of Polymer–Polymer Interaction Parameters of Incompatible Polymers in Solution

VENKATARAMAN NARASIMHAN,* ROBERT Y. M. HUANG, and CHARLES M. BURNS,† *Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada*

Synopsis

A method is developed, based on Scott's equations for ternary systems of two polymers and a mutual solvent, for the calculation of values of the polymer–polymer interaction parameter, χ_{23}, for systems in which both polymer–solvent interaction parameters χ_{12} and χ_{13} are not known *a priori*. Equilibrium phase studies were carried out on ternary systems of polystyrene, polybutadiene, and tetrahydrofuran or toluene at 23°C and 1 atm. Typical interaction parameter values (χ_{23}) calculated by this new method were compared with the values of χ_{23} determined earlier using standard equations and known χ_{12} values for these systems, and were found to agree very well. It is concluded that the technique presented in this article can be used for mixed polymer systems in good mutual solvents where neither polymer–solvent interaction parameter is known, for determining an approximate value of the χ_{23} parameter alone.

INTRODUCTION

There has been an ever growing interest in the studies relating to polymer–polymer incompatibility and subsequent phase separation during the last four decades. Numerous investigations dealing with polymer–polymer incompatibility in a common solvent have been conducted.[1-24] In particular, phase separation between the two incompatible polymers, polystyrene (PS) and polybutadiene (PBD), has industrial importance and has been studied in solutions by several workers.[11-14,18-21,24] In our laboratories, gel permeation chromatography (GPC) using sequential differential refractive index (RI) and ultraviolet absorbance (UV) detectors has been successfully used to give the analysis of the composition of each of the conjugate phases in the incompatible system of PS and PBD with tetrahydrofuran (THF) or toluene as mutual solvent.[21,25] A detailed discussion of the experimental procedures and of the determination of the tie lines, the binodal curve, and the plait point has been given in our earlier publications.[20,21,26]

In our earlier communications[25,27] typical values of the polymer–polymer interaction parameter (χ_{23}) determined from the quantitative analysis of mixtures of PS and PBD in THF and toluene using GPC were presented. This parameter is useful in characterizing the incompatibility of the two polymers. It should be noted here that the value of one of the single polymer–solvent

*Presently: Polymer and Engineering Consultant, Madras, India.
†To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 37, 1909–1919 (1989)

CCC 0021-8995/89/071909-11$$04.00

interaction parameters, χ_{12}, for the binary mixture of PS and solvent was obtained from the literature[28,29] and used in the equations to determine χ_{23}.

The object of the present work is to estimate χ_{23} for any system for which both single polymer–solvent interaction parameters χ_{12} and χ_{13} are unknown.

The theoretical basis for the determination of χ_{23} from phase equilibrium data, without *a priori* knowledge of both χ_{12} and χ_{13}, is discussed in the following section.

THEORY

The Flory–Huggins expression for the Gibbs free energy of mixing, ΔG_m, for a system consisting of two polymers and one solvent reads

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + (\chi_{12}\phi_1\phi_2 + \chi_{13}\phi_1\phi_3 + \chi_{23}\phi_2\phi_3)(m_1n_1 + m_2n_2 + m_3n_3) \quad (1)$$

where n_i is the number of moles of ith component in the mixture, ϕ_i is the volume fraction of ith component, χ_{ij} is the Flory–Huggins interaction parameter, and m_i is the ratio of the molar volume of i to that of the reference component (solvent). Subscripts 2 and 3 denote polymers 2 and 3, and 1 denotes the solvent. The chemical potentials of each component, as discussed by Tompa,[5b] can be obtained by differentiation of the Gibbs free energy of mixing with respect to n. Three equations can be obtained by equating the chemical potentials of each component in the conjugate phases. These equations are then simplified to give the following equations as obtained by Allen et al.[11] Denoting the two conjugate phases by single and double primes, we have

$$\chi_{23}[(\phi_2' - \phi_2'') - (\phi_1'' - \phi_1')] - \chi_{13}[(\phi_2' - \phi_2'') - (\phi_1'' - \phi_1')] + \chi_{12}[(\phi_2' - \phi_2'') + (\phi_1'' - \phi_1')] = \ln(\phi_1''/\phi_1') - (1/m_2)\ln(\phi_2''/\phi_2') \quad (2)$$

$$\chi_{23}[(\phi_3'' - \phi_3') + (\phi_1'' - \phi_1')] + \chi_{13}[(\phi_3'' - \phi_3') - (\phi_1'' - \phi_1')] - \chi_{12}[(\phi_3'' - \phi_3') + (\phi_1'' - \phi_1')] = (1/m_3)\ln(\phi_3''/\phi_3') - \ln(\phi_1''/\phi_1') \quad (3)$$

Thus, we have essentially only two equations [viz. eqs. (2) and (3)] but three unknowns (χ_{12}, χ_{13}, and χ_{23}) for a single equilibrium tie line. Hence the value of either χ_{12} or χ_{13} must normally be known in order to calculate χ_{23}. Otherwise, some assumptions will have to be made.

One such approach, as described in the following paragraphs, is to solve for the three interaction parameters using the tie lines in adjacent pairs. Two adjacent tie lines were taken. Thus we have the compositions of four phases, four applicable equations, and six unknown interaction parameters. The assumptions made to reduce the six unknown interaction parameters to four were:

1. χ_{12} remains essentially constant for the two adjacent tie lines.
2. χ_{13} also remains the same for the two tie lines.
3. χ_{23} varies, that is, the values of χ_{23} for the two tie lines are different.

We let $\chi_{23,A}$ and $\chi_{23,B}$ be the values of the two polymer–polymer interaction parameters for any two adjacent tie lines A and B, respectively. Using the subscripts A and B to indicate the equilibrium compositions of the phases corresponding to tie lines A and B, we can write eq. (2) as

$$\chi_{23,A}[(\phi_2' - \phi_2'') - (\phi_1'' - \phi_1')]_A - \chi_{13}[(\phi_2' - \phi_2'') - (\phi_1'' - \phi_1')]_A + \chi_{12}[(\phi_2' - \phi_2'') + (\phi_1'' - \phi_1')]_A = \ln\left[\frac{\phi_1''}{\phi_1'}\right]_A - \frac{1}{m_2}\ln\left[\frac{\phi_2''}{\phi_2'}\right]_A \quad (2a)$$

$$\chi_{23,B}[(\phi_2' - \phi_2'') - (\phi_1'' - \phi_1')]_B - \chi_{13}[(\phi_2' - \phi_2'') - (\phi_1'' - \phi_1')]_B + \chi_{12}[(\phi_2' - \phi_2'') + (\phi_1'' - \phi_1')]_B = \ln\left[\frac{\phi_1''}{\phi_1'}\right]_B - \frac{1}{m_2}\ln\left[\frac{\phi_2''}{\phi_2'}\right]_B \quad (2b)$$

Similarly eq. (3) gives

$$\chi_{23,A}[(\phi_3'' - \phi_3') + (\phi_1'' - \phi_1')]_A + \chi_{13}[(\phi_3'' - \phi_3') - (\phi_1'' - \phi_1')]_A - \chi_{12}[(\phi_3'' - \phi_3') + (\phi_1'' - \phi_1')]_A = \frac{1}{m_3}\ln\left[\frac{\phi_3''}{\phi_3'}\right]_A - \ln\left[\frac{\phi_1''}{\phi_1'}\right]_A \quad (3a)$$

$$\chi_{23,B}[(\phi_3'' - \phi_3') + (\phi_1'' - \phi_1')]_B + \chi_{13}[(\phi_3'' - \phi_3') - (\phi_1'' - \phi_1')]_B - \chi_{12}[(\phi_3'' - \phi_3') + (\phi_1'' - \phi_1')]_B = \frac{1}{m_3}\ln\left[\frac{\phi_3''}{\phi_3'}\right]_B - \ln\left[\frac{\phi_1''}{\phi_1'}\right]_B \quad (3b)$$

Thus we have four equations to solve simultaneously for the four unknowns, namely $\chi_{23,A}$, $\chi_{23,B}$, χ_{12}, and χ_{13}.

The assumption that χ_{12} and χ_{13}, respectively, remain the same for two adjacent tie lines seems to be a reasonable one in light of the literature values for χ_{12} as a function of concentration in the binary system PS–toluene.[28]

EXPERIMENTAL

The polymers used in this study were obtained from commercial sources. These polymers were employed as received with no further purification or pretreatment. The characteristics of the commercial PS samples supplied by Pressure Chemical Co. are given in Table I, and those of the PBD samples supplied by Phillips Petroleum Co. are given in Table II. The PS and PBD samples used are of narrow molecular weight distribution.

Toluene and THF were used as mutual solvents in the various systems studied, while THF was also used as the GPC eluent. Both solvents were "Baker-analyzed" reagent grade, supplied by J. T. Baker Chemical Co., and used as received.

A detailed discussion of the experimental procedure adopted for the quantitative analysis of the conjugate phases of the incompatible system of PS and

TABLE I
Characteristics of Polystyrene Samples

Sample	Supplier's data			Calculated data[a]		
	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
PS 9000	9.18	9.17	< 1.06	—	—	—
PS 37,000	33.0	36.0	< 1.06	36.8	32.0	1.15
PS 100,000	100.0	100.0	< 1.06	87.3	70.7	1.23
PS 110,000	110.0	110.0	< 1.06	123.6	107.8	1.15

[a]GPC measurements.

TABLE II
Characteristics of Polybutadiene Samples

Sample	Supplier's data[a]			Calculated data[b]		
	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
PBD 17 M[c]	17.0 ± 1.7	16.0 ± 1.6	1.06	—	—	—
PBD 170 M[d]	170.0 ± 17	135.0 ± 13	1.26	—	—	—
PBD 54941[e]	161.0	150	1.07	1.30	115.0	1.13

[a]Supplier's data for PBD 17 M, PBD 170 M, and PBD 54941 were provided by Phillips' Petroleum Co.
[b]GPC measurements.
[c]43.5% cis, 49.1% trans, 7.4% vinyl, 0.05% antioxidant.
[d]47.1% cis, 44.5% trans, 8.4% vinyl, 0.4% antioxidant.
[e]38% cis, 53% trans, 9.0% vinyl, 0.3% antioxidant.

TABLE III
Interaction Parameters for the PS 110,000/PBD 170 M/THF System

Tie line no.	Wt % solvent (mean)	Volume fraction of conjugate phases						χ_{12}[a]	χ_{13}	χ_{23}
		ϕ_1'	ϕ_2'	ϕ_3'	ϕ_1''	ϕ_2''	ϕ_3''			
1	79.49	0.809	0.023	0.169	0.823	0.169	0.009	0.445	0.472	0.008
2	80.41	0.820	0.022	0.159	0.830	0.164	0.007	0.445	0.466	0.010
3	85.97	0.881	0.011	0.108	0.870	0.126	0.004	0.445	0.415	0.014
4	91.12	0.924	0.011	0.065	0.920	0.074	0.007	0.445	0.419	0.020
5	93.41	0.940	0.015	0.045	0.944	0.043	0.014	0.445	0.462	0.022

[a]Schulz and Bauman.[29]

TABLE IV
Interaction Parameters for the PS 37,000/PBD 170 M/THF System

Tie line no.	Wt % solvent (mean)	Volume fraction of conjugate phases						χ_{12}[a]	χ_{13}	χ_{23}
		ϕ_1'	ϕ_2'	ϕ_3'	ϕ_1''	ϕ_2''	ϕ_3''			
1	79.16	0.817	0.014	0.170	0.809	0.185	0.006	0.428	0.40	0.023
2	78.97	0.810	0.013	0.177	0.812	0.184	0.004	0.428	0.412	0.024
3	79.94	0.816	0.021	0.163	0.825	0.174	0.001	0.428	0.44	0.024
4	86.59	0.877	0.021	0.102	0.886	0.112	0.003	0.428	0.44	0.029
5	88.18	0.887	0.024	0.089	0.905	0.092	0.003	0.428	0.471	0.026

[a]Schulz and Bauman.[29]

PBD in the presence of a mutual solvent, using GPC, has been given in our earlier publications.[20,21]

RESULTS AND DISCUSSION

The values for χ_{12}, χ_{13}, and χ_{23} calculated using adjacent tie lines (we call it the "two-tie line method") for different systems are presented in Tables III–IX. Also given in those tables are the χ_{23} values calculated using known χ_{12} (PS–solvent) values and presented earlier,[25] for the purposes of comparison.

There is a very good agreement between the χ_{23} values calculated by the two different methods. In general, the χ_{23} value calculated by the two-tie line method is slightly higher.

The χ_{13} and χ_{12} values, however, are greater than 0.5 and hence will have to be ignored. This higher value is perhaps related to the slightly higher

TABLE V
Comparison of Interaction Parameters PS 110,000/PBD 170 M/THF

Wt % solvent (mean)		Two-tie line method		
	χ_{23}	χ_{23}	χ_{12}	χ_{13}
79.49	0.008	0.010	0.63	0.63
80.41	0.010	0.011	0.59	0.60
85.97	0.014	0.016	0.80	0.85
91.12	0.020	0.021	0.55	0.54
93.41	0.022	0.024	0.55	0.54

TABLE VI
Comparison of Interaction Parameters PS 37,000/PBD 170 M/THF

Wt % solvent (mean)		Two-tie line method		
	χ_{23}	χ_{23}	χ_{12}	χ_{13}
79.16	0.023	0.023	0.63	0.62
78.97	0.024	0.024	0.67	0.65
79.94	0.024	0.024	0.38	0.40
86.59	0.029	0.029	0.57	0.56
88.18	0.026	0.033	0.57	0.56

TABLE VII
Comparison of Interaction Parameters PS 100,000/PBD 170 M/Toluene

Wt % solvent (mean)		Two-tie line method		
	χ_{23}	χ_{23}	χ_{12}	χ_{13}
82.00	0.010	0.015	0.61	0.62
87.43	0.019	0.020	0.61	0.60
90.36	0.023	0.024	0.57	0.56
90.68	0.021	0.024	0.57	0.56

TABLE VIII
Comparison of Interaction Parameters PS 37,000/PBD 170 M/Toluene

Wt % solvent (mean)		Two-tie line method		
	χ_{23}	χ_{23}	χ_{12}	χ_{13}
77.91	0.026	0.028	0.68	0.67
81.39	0.029	0.029	0.71	0.69
84.10	0.030	0.030	0.57	0.55
88.41	0.026	0.038	0.57	0.55

TABLE IX
Comparison of Interaction Parameters PS 100,000/PBD 54941/Toluene

Wt % solvent (mean)		Two-tie line methods		
	χ_{23}	χ_{23}	χ_{12}	χ_{13}
79.82	0.004	0.015	0.63	0.63
81.97	0.013	0.017	0.63	0.63
82.85	0.016	0.017	0.58	0.58
85.91	0.019	0.020	0.58	0.58
88.96	0.025	0.026	0.58	0.58

values of χ_{23} itself. It is also interesting to note that for a given tie line the values of χ_{12} and χ_{13} are very close. At any rate, for this PS–PBD system with toluene or THF as mutual solvents, the two-tie line method yields good approximate values for χ_{23}. This method should find use in mixed polymer systems in a good mutual solvent where neither polymer–solvent interaction parameter is known.

This method was applied to the systems of PS–PBD–THF in this study. The bimodals for six of the PS/PBD/THF systems studied are given in Figure 1.

The use of this approximate method ("two-tie line method") was felt to be better for obtaining χ_{12} values for very low molecular weights of PS than extrapolating the second-virial coefficient (A_2) values of the PS–THF binary system[29] to higher concentrations or taking higher order virial coefficients. The values of χ_{23} obtained for the different systems are plotted against total solvent concentrations in Figure 2. There seems to be a linear increase in χ_{23} with increasing solvent concentration (or, in other words, with decreasing total polymer concentration). This increase in χ_{23} appears to have a common slope for the different molecular weight combinations studied. These lines follow the same order in which their positions of the bimodals and plait points are found in Figure 1.

Since the different lines appeared to have a common slope, the data for the different systems were treated in a fashion to force a common slope for all the systems (Fig. 2). For this purpose an algorithm by Fletcher[30] was used. Thus the equation of the lines is

$$\chi_{23} = mC + b_i$$

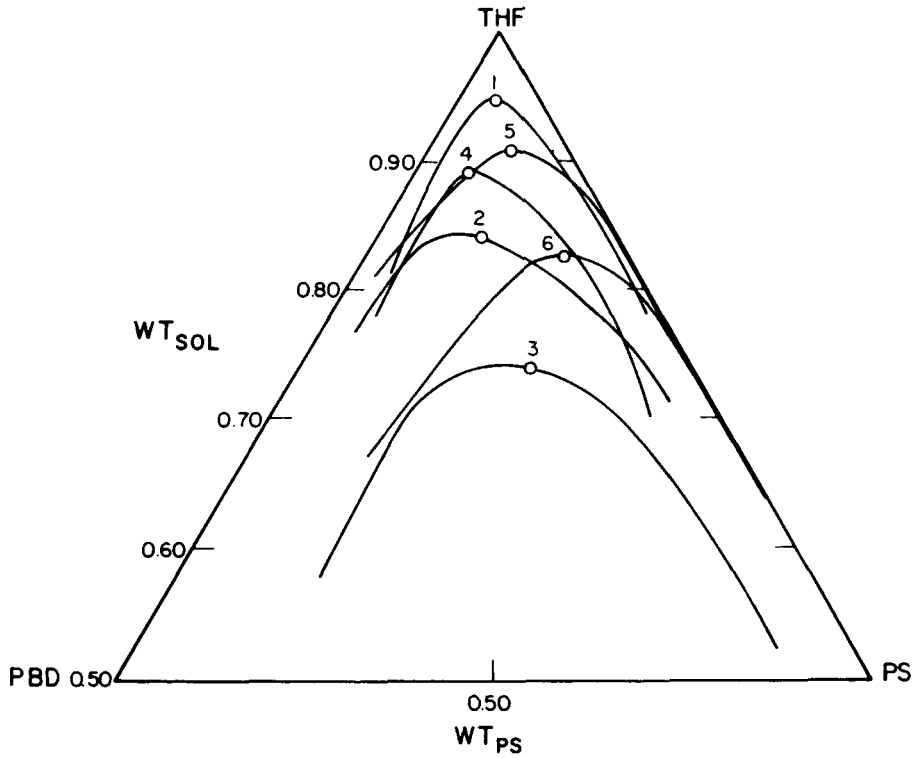

Fig. 1. Phase diagrams of the ternary systems studied at 23 ± 0.4°C and 1 atm. Binodal curves: (1) PS 110,000/PBD 170 M/THF; (2) PS 37,000/PBD 17 M/THF; (3) PS 9000/PBD 17 M/THF; (4) PS 110,000/PBD 17 M/THF; (5) PS 37,000/PBD 170/M/THF; (6) PS 9000/PBD 170 M/THF. (○) Plait points.

where χ_{23} = polymer–polymer interaction parameter, C = % solvent concentration (mean), m = common slope = 0.980, and b_i is the intercept which is different for each system. The calculated values are

$$b_1 = -0.068 \pm 0.004$$

$$b_2 = -0.036 \pm 0.023$$

$$b_3 = -0.012 \pm 0.007$$

$$b_4 = -0.046 \pm 0.019$$

$$b_5 = -0.053 \pm 0.032$$

$$b_6 = -0.027 \pm 0.038$$

The standard deviation of the slopes $\pm\sigma_{mi}$ found for $i = 1,\ldots,6$ were, respectively, 0.46×10^{-4}, 0.30×10^{-3}, 0.11×10^{-3}, 0.24×10^{-3}, 0.39×10^{-3}, and 0.53×10^{-3}.

The b_i values were plotted against the reciprocal of the molecular weight of the corresponding PS (Fig. 3) and two nearly parallel lines, one for each

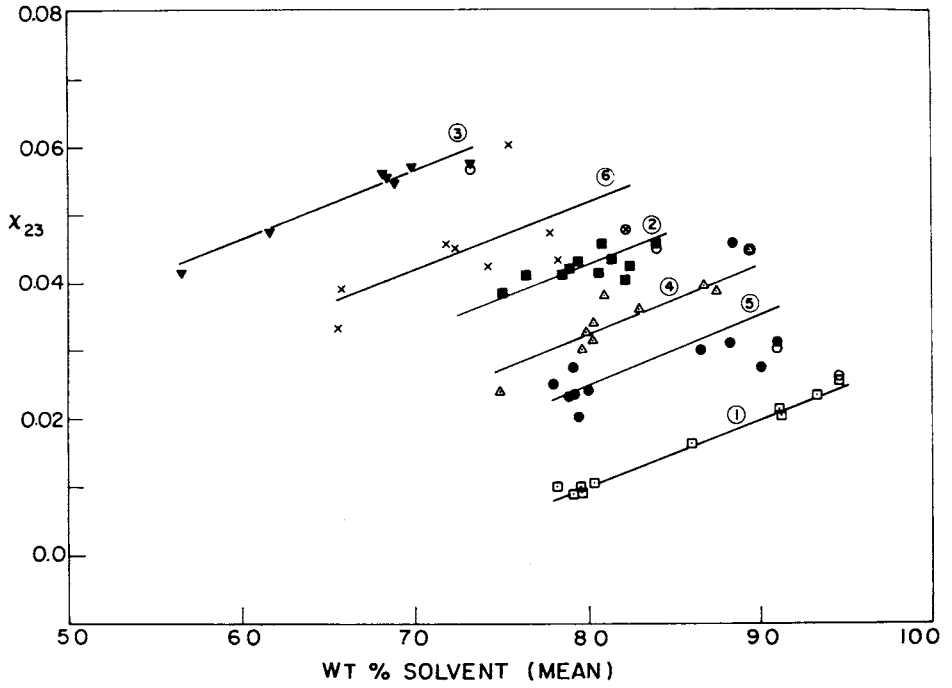

Fig. 2. Polymer–polymer interaction parameter χ_{23} as a function of mean solvent concentration at 23 ± 0.4°C and 1 atm. (1) PS 110,000/PBD 170 M/THF; (2) PS 37,000/PBD 17 M/THF; (3) PS 9000/PBD 17 M/THF; (4) PS 110,000/PBD 17 M/THF; (5) PS 37,000/PBD 170 M/THF; (6) PS 9000/PBD 170 M/THF. ⊗, ⊖, ●, ■, ⊟ and ⊜ are values of $\chi_{23,crit}$.

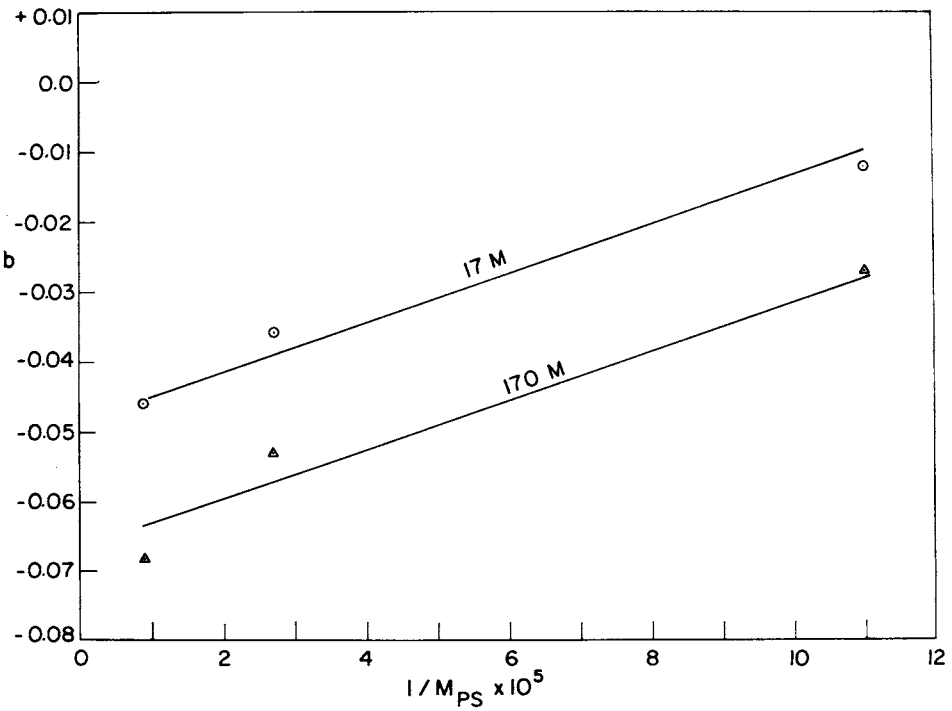

Fig. 3. The intercept b as a function of the reciprocal of the molecular weight of PS.

molecular weight of PBD, were obtained. Fletcher's algorithm[30] was applied to the data, and the common slope was found to be 351.70, indicating that the χ_{23} is decreasing with increasing molecular weight of the PS in the system. The standard deviations of the slopes $\pm\sigma_{mi}$ were, respectively, 52.10 and 82.87. The intercepts k_1 and k_2 were, respectively, -0.049 ± 0.0034 and -0.067 ± 0.0054.

Similarly these two intercepts may be plotted against the reciprocal of the molecular weight of PBD and a slope of 342.46 can be obtained, indicating that χ_{23} is also decreasing with increasing molecular weight of the PBD in the system.

CONCLUSIONS

Based on Scott's equations for ternary systems of two polymers and a mutual solvent, a method was developed for calculating values of the polymer–polymer interaction parameter (χ_{23}) for systems for which we do not have *a priori* knowledge of the two polymer–solvent interaction parameters, χ_{12} and χ_{13}. Ternary systems of PS–PBD and THF or toluene were studied. The χ_{23} values obtained by this new technique, in which the composition of conjugate solutions are used two at a time, were compared with χ_{23} values determined earlier using standard equations and known χ_{12} values from the literature. There is a very good agreement between the χ_{23} values calculated by the two different methods. In general, the χ_{23} calculated by this two-tie line method is slightly higher. The χ_{12} and χ_{13} values, however, are greater than 0.5 and cannot be accepted. Hence this two-tie line method can be used to determine a very good approximate value for χ_{23} alone. The advantage of this technique is that no prior knowledge of χ_{12} and χ_{13} is required.

The authors wish to thank Messrs. A. R. Telfer, N. Sri Namachchivaya, and V. Ramakrishnan for valuable help and discussions. Support from the Natural Sciences and Engineering Research Council of Canada is gratefully appreciated. One of the authors (V. N.) was supported in part by a Dean of Engineering Scholarship, University of Waterloo.

References

1. R. Koningsveld, *Adv. Colloid Interface Sci.*, **2**, 151 (1968).
2. P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941); **10**, 51 (1942).
3. M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941); *Ann. N.Y. Acad. Sci.*, **43**, 1 (1942).
4. R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).
5. H. Tompa, (a) *Trans. Faraday Soc.*, **45**, 1142 (1949); (b) *Polymer Solutions*, Butterworths, London, 1956, Chap. 7.
6. I. Prigogine, N. Trappeniers, and V. Mathot, *Discuss. Faraday Soc.*, **15**, 93 (1953); *J. Chem. Phys.*, **21**, 559 (1953).
7. D. Patterson, *Macromolecules*, **2**, 672 (1969).
8. R. H. Lacombe and I. C. Sanchez, *J. Phys. Chem.*, **80**, 2568 (1976).
9. A. Dobry and F. Boyer-Kawenoki, *J. Polym. Sci.*, **2**, 90 (1947).
10. R. J. Kern, *J. Polym. Sci.*, **21**, 19 (1956).
11. G. Allen, G. Gee, and J. P. Nicholsen, *Polymer*, **1**, 56 (1960).
12. S. G. Turley, *J. Polym. Sci. Part C*, **1**, 101 (1963).
13. T. R. Paxton, *J. Appl. Polym. Sci.*, **7**, 1499 (1963).
14. R. J. Angelo, R. M. Ikeda, and M. L. Wallack, *Polymer*, **6**, 141 (1965).
15. R. Kongingsveld, *Discuss. Faraday Soc.*, **49**, 144 (1970).
16. J. L. White, D. G. Salladay, D. O. Quisenberry, and D. L. MacLean, *J. Appl. Polym. Sci.*, **16**, 2811 (1972).

17. R. P. Parent and E. V. Thompson, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **18**, 505 (1977); **19**, 180 (1978); E. V. Thompson, *Am. Chem. Soc., Div. Org. Coat. Plast. Chem. Prepr.*, **40**, 751 (1979).

18. D. G. Welygan and C. M. Burns, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 339 (1973); *J. Appl. Polym. Sci.*, **18**, 521 (1974).

19. D. R. Lloyd and C. M. Burns, *J. Appl. Polym. Sci.*, **22**, 593 (1978).

20. D. R. Lloyd, V. Narasimhan, and C. M. Burns, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **20**, 897 (1979).

21. V. Narasimhan, D. R. Lloyd, and C. M. Burns, *J. Appl. Polym. Sci.*, **23**, 749 (1979).

22. G. M. Bristow, *J. Appl. Polym. Sci.*, **2**, 120 (1959).

23. D. Berek, D. Lath, and V. Durdovic, *J. Polym. Sci. Part C*, **16**, 659 (1967).

24. D. G. Welygan, M.A.Sc. thesis, University of Waterloo, 1973.

25. V. Narasimhan, R. Y. M. Huang, and C. M. Burns, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 1993 (1983).

26. D. R. Lloyd, V. Narasimhan, and C. M. Burns, *J. Liq. Chromatogr.*, **3**, 1111 (1980).

27. V. Narasimhan, R. Y. M. Huang, and C. M. Burns, *J. Polym. Sci., Polym. Symp.*, **74**, 265 (1986).

28. Th. Schote, *Eur. Polym. J.*, **6**, 1063 (1970).

29. Von G. V. Schulz and H. Bauman, *Makromol. Chem.*, **114** (2736), 122 (1968).

30. R. Fletcher, "FORTRAN Subroutines for Minimization by Quasi-Newton Methods," Report R 7125 AERE, Harwell, U.K., June 1972.

Received January 8, 1988
Accepted March 22, 1988