

Estimation of the Interaction Parameter between Polystyrene and Poly(*p*-chlorostyrene) from Osmotic Pressure Measurements

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ABSTRACT: The composition dependences of the osmotic second virial coefficients A_2 for the mixtures of polystyrene (PSt) and poly(*p*-chlorostyrene) (PClSt) and for the block copolymers of ABA and BAB types (A, PSt; B, PClSt) were studied in toluene, 2-butanone (MEK), and cumene solutions. All the samples were prepared by anionic polymerization and they are close in molecular weight which is *ca.* 35×10^4 . It was found that in toluene and MEK, plots of A_2 vs. composition obtained for the polymer mixtures and for the block copolymers of ABA and BAB types fell on a single curve in the respective solvents, whereas in the selective solvent, cumene, A_2 value of the polymer mixtures was smaller than that of the block copolymers with the same composition. The thermodynamic interaction parameter χ_{AB} between PSt and PClSt was estimated from A_2 data, according to the theories of dilute polymer solutions; the χ_{AB} values obtained from A_2 for the ternary system of PSt-PClSt-solvent were 0.086 (in toluene) and 0.063 (in MEK), and those from A_2 for the block copolymer solutions were 0.076 (in toluene), 0.064 (in MEK) and 0.063 (in cumene). $\chi_{AB} = 0.070 \pm 0.016$ was obtained as the average.

KEY WORDS Interaction Parameter / Polystyrene / Poly(*p*-chlorostyrene) / Styrene-*p*-Chlorostyrene Triblock Copolymer / Ternary System / Osmotic 2nd Virial Coefficient / Composition Dependence / Dilute Solution /

It has been known that diblock and triblock copolymers composed of a pair of incompatible homopolymers exhibit intra-chain phase separation because of repulsive interactions between unlike blocks giving rise to multiphase structures in solid state.^{1a,c} In the study of solution properties of block copolymers, the great attention has been concentrated on the question of segregation of blocks of different chemical species in recent years.^{1b,d} If such segregation of blocks occurred in a block copolymer in solution, its conformation could not be approximated with a random coil model.

We have previously investigated the conformational behavior of the styrene-*p*-chlorostyrene (St-ClSt) triblock copolymers in several solvents² and obtained the results leading

to a conclusion that procedures and theories originally developed for homopolymer solutions are applicable to the St-ClSt block copolymers in non-selective solvents such as toluene and 2-butanone (MEK) and their conformations in these solvents could be approximated with a statistical random coil form.^{2a,b,d} However, the results obtained for the St-ClSt block copolymers in a selective solvent such as cumene were less conclusive^{2a,b,d} and it was suggested that the conformation in cumene may change from a random coil form to a segregated form by lowering the temperature.^{2c,e}

Investigation of interactions between component homopolymers can lead to a better understanding of the properties of block copolymers. In this paper, in order to estimate

the interaction parameter χ_{AB} between PSt and PClSt, the composition dependences of osmotic second virial coefficients A_2 were studied on the mixtures of polystyrene (PSt) and poly(*p*-chlorostyrene) (PClSt) in toluene, MEK and cumene, and also on the St–ClSt triblock copolymer solutions.

EXPERIMENTAL

Materials

PSt, PClSt, and the St–ClSt triblock copolymers were prepared by the anionic polymerization technique; polymerization was carried out in tetrahydrofuran at -78°C under 10^{-6} mmHg, using sodium naphthalene as the initiator.^{2a} The products were purified by fractional precipitation from benzene/methanol. The gel permeation chromatography analysis showed that the molecular weight distribution of the polymer samples was narrow. The composition of the block copolymers was determined by analysis of chlorine. The characteristics of the samples are shown in Table I.

Measurements

Osmotic pressures π for PSt, PClSt, the PSt–PClSt mixtures and the St–ClSt block copolymers were measured in toluene and MEK at 30.0°C and in cumene at 55.0°C ,

using a Hewlett-Packard high speed membrane osmometer Model 502. The second virial coefficient, A_2 , was obtained according to the following equation,³

$$(\pi/c)^{1/2} = (RT/\bar{M}_n)^{1/2} (1 + \bar{M}_n A_2 c/2) \quad (1)$$

where c is the concentration (g dl^{-1}), \bar{M}_n is the number average molecular weight, R is the gas constant and T is the absolute temperature.

Viscosities of PSt, PClSt, and the St–ClSt block copolymers were measured using Ubbelohde dilution viscometers with negligible kinetic energy corrections. Intrinsic viscosities $[\eta]$ were determined according to Huggins' equation,⁴ which were shown in Table I.

The partial specific volumes \bar{v}_p of PSt and PClSt in the three solvents were determined from density measurements by an Anton-Paar Density Meter Model DMA-50. The results are as follows.

	$\bar{v}_p/\text{cm}^3 \text{g}^{-1}$		
	Toluene (30.0°C)	MEK (30.0°C)	Cumene (55.0°C)
PSt	0.914	0.905	0.937
PClSt	0.778	0.770	0.788

Table I. Characteristics of PSt, PClSt, and the St–ClSt block copolymers^a

Sample	Composition St mol. frac.	$\bar{M}_n \times 10^{-4}$	$[\eta]/\text{dl g}^{-1}$		
			Toluene (30.0°C)	MEK (30.0°C)	Cumene (55.0°C)
PSt	1.000	34.1	1.284	0.688	1.137
PClSt	0.000	33.0	0.557	0.603	0.354
BAB-1	0.650	37.9	1.249	0.874	1.017
BAB-2	0.467	32.5	0.958	0.737	0.773
BAB-3	0.372	36.8	1.003	0.811	0.770
ABA-1	0.655	37.4	1.279	0.824	1.074
ABA-2	0.509	35.6	1.106	0.834	0.937
ABA-3	0.311	29.9	0.887	0.723	0.714

^a BAB and ABA are the St–ClSt block copolymers (A, PSt; B, PClSt).

Interaction Parameter between PSt and PClSt in Solutions

Table II. Second virial coefficients A_2 for the ternary systems and polymer-solvent interaction parameter χ of PSt and PClSt^a

Sample	Composition St. wt. frac.	$A_2 \times 10^4 / \text{cm}^3 \text{ mol g}^{-2}$			χ		
		Toluene	MEK	Cumene	Toluene	MEK	Cumene
PSt	1.000	3.73	1.15	2.90	0.371	0.478	0.379
PClSt	0.000	1.20	1.72	-0.20 ₃	0.460	0.447	0.505
PSt-PClSt mixture	0.786	3.41	1.51	2.38	$(A_2)_{AB} \times 10^4 / \text{cm}^3 \text{ mol g}^{-2}$		
	0.593	2.99	1.70	1.92			
	0.434	2.64	1.78	1.39	Toluene	MEK	Cumene
	0.272	2.30	1.76	0.84 ₀			
	0.133	1.75	1.82	0.37 ₈	3.19 ± 0.08	2.05 ± 0.06	(2.65 ± 0.07) ^b

^a Measurements were made in toluene and MEK at 30.0°C and in cumene at 55.0°C.^b Calculated from eq 2 using A_2 data for the BAB copolymers.**Table III.** Second virial coefficients A_2 and the interaction parameters χ_{cop} for the St-ClSt block copolymers^a

Sample	$A_2 \times 10^4 / \text{cm}^3 \text{ mol g}^{-2}$			χ_{cop}		
	Toluene	MEK	Cumene	Toluene	MEK	Cumene
BAB-1	3.02	1.68	2.19	0.383	0.453	0.398
BAB-2	2.62	1.78	1.65	0.400	0.449	0.425
BAB-3	2.23	1.75	1.37	0.411	0.446	0.438
ABA-1	3.00	1.68	2.27	0.382	0.455	—
ABA-2	2.73	1.82	1.85	0.392	0.446	—
ABA-3	2.14	1.85	1.52	0.415	0.443	—

^a Measurements were made in toluene and MEK at 30.0°C and in cumene at 55.0°C.

RESULTS AND DISCUSSION

Composition Dependences of A_2

The second virial coefficients, A_2 , for the PSt-PClSt mixtures and the St-ClSt block copolymers of ABA and BAB types were measured in toluene and MEK at 30.0°C, and in cumene at 55.0°C, which are given in Tables II and III. The solvents chosen for this study are different in a nature towards the homopolymers of two components. Thus, toluene is a good solvent for PSt but a rather moderate solvent for PClSt; MEK is a moderate solvent for both of PSt and PClSt; cumene is good for PSt but poor for PClSt ($\theta = 59.0^\circ\text{C}^5$).

The second virial coefficient A_2 for the ternary system of A polymer-B polymer-

solvent can be expressed as functions of composition by the following equation⁶

$$A_2 = w_A^2(A_2)_{AA} + w_B^2(A_2)_{BB} + 2w_A w_B(A_2)_{AB} \quad (2)$$

where w_A and w_B are the weight fractions of A and B in the polymer mixtures, $(A_2)_{AA}$ and $(A_2)_{BB}$ are the A_2 for the homopolymers of A and B, and $(A_2)_{AB}$ means the A_2 corresponding to the interactions between A and B polymer chains in the given solvent. In eq 2, it is assumed that extents of contributions of A-A, B-B, and A-B interactions can be represented as a product of weight fractions. This assumption will be adequate if a distribution of segments of two polymers is statistically random in the given solvent.

Figures 1-3 show the A_2 data presented as

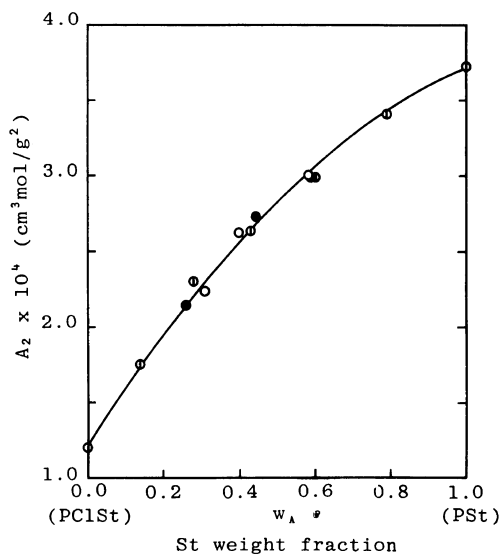


Figure 1. Composition dependences of second virial coefficients A_2 for the PSSt-PClSt mixtures and the St-ClSt block copolymers in toluene at 30.0°C. (○), the PSSt-PClSt mixtures; (●), the ABA copolymer; (○), the BAB copolymer; (—), values calculated from eq 2.

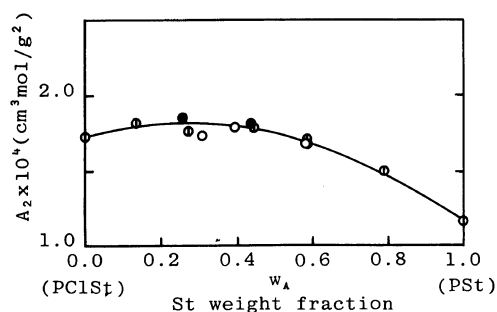


Figure 2. Composition dependences of second virial coefficients A_2 for the PSSt-PClSt mixtures and the St-ClSt block copolymers in MEK at 30.0°C. Symbols same as in Figure 1.

functions of composition. Molecular weights of all the samples used for the measurements are close enough so that the relatively minor dependence of A_2 on \bar{M}_n can be ignored. It was found that in toluene and MEK solutions, plots of A_2 vs. composition obtained for the polymer mixtures and for the block copolymers of ABA and BAB types fitted in a single curve. Such results suggest that the conformations of PSSt and PClSt block chains in the

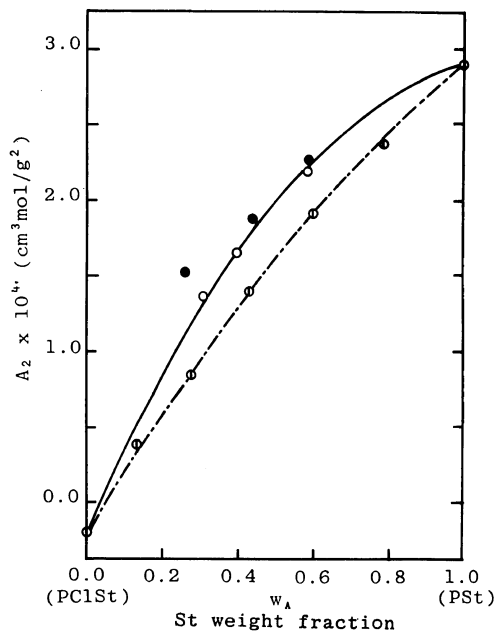


Figure 3. Composition dependences of second virial coefficients A_2 for the PSSt-PClSt mixtures and the St-ClSt block copolymers in cumene at 55.0°C. (---), experimental fit to the data. Symbols same as in Figure 1.

respective types of the copolymers are similar to those of PSSt and PClSt chains respectively in the polymer mixture solutions. This supports our previous conclusion that the conformations of the St-ClSt block copolymers of ABA and BAB types in toluene and MEK could be approximated with a random coil form in which domains of unlike segments overlap to a great extent allowing heterocontacts.^{2a,b,d} In such cases, eq 2 could be applicable to express A_2 's for the block copolymers as well as for the polymer mixtures. On the other hand, the results obtained in cumene were different from those in toluene and MEK. In Figure 3, it was noted that plots of A_2 vs. composition for the respective types of the block copolymers and for the polymer mixtures obtained in cumene could be expressed by two separate curves but not a single one; the value of A_2 for the polymer mixtures was smaller than that for the block copolymers with the same composition. It is supposed in

cumene, that PClSt chain is rather shrunk whereas PSt chain takes a more extended conformation and domains of PSt and PClSt chains are less overlapped, which makes A-B contacts few. This trend should be higher in the polymer mixtures than in the block copolymers. This may be a cause that the value of A_2 for the polymer mixtures in cumene was smaller. Plots of A_2 vs. composition for the ABA copolymers were rather scattered, especially for the sample of the highest ClSt content. Our previous studies showed that conformational anomalies may occur for the block copolymers in cumene depending on composition and type of the copolymers, and temperature, and such anomalies are more likely to occur for the ABA copolymers than for the BAB copolymers, and also for the copolymers with higher ClSt contents.^{2c} The anomalies might be caused by intra- and intermolecular associations in the block copolymer solution and in such a case, the assumption of a random distribution of the segments could not be valid. This should be a cause of the scatter of A_2 data for the ABA copolymers. Thus, eq 2 should not be a good approximation for the polymer mixtures and for the ABA copolymers.

Polymer-Solvent Interaction Parameter

According to theories of dilute polymer solutions, A_2 is generally given by the following equation relating to the thermodynamic interaction parameter χ of a polymer with a solvent,

$$A_2 = (\bar{v}_p^2/V_s) \left(\frac{1}{2} - \chi \right) h(z/\alpha^3)$$

with

$$z = (3/2\pi \langle r_0^2 \rangle)^{3/2} \beta n^2 \quad (3)$$

where V_s is the molar volume of the solvent, $\langle r_0^2 \rangle$ is the unperturbed mean square end-to-end distance of the polymer, β is the excluded volume, n is the number of segments in a chain and α is the expansion factor related

to the statistical radius. Several forms of $\alpha(z)$ consistent with $h(z/\alpha^3)$ have been reported. Equations proposed by Kurata-Yamakawa and by Yamakawa-Tanaka are as follows⁷

$$h(z/\alpha^3) = 0.547[1 - (1 + 3.903 z/\alpha^3)^{-0.4683}]/(z/\alpha^3) \quad (4)$$

and

$$\alpha^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \quad (5)$$

We obtained the viscosity-radius expansion factor α_η from viscosity data in Table I and $[\eta]_0$ values previously determined.⁸ Thus, the statistical-radius expansion factor α was calculated from the z value obtained by using the relation,⁷ $\alpha_\eta^3 = 1.05 + 0.87z$.

By applying the relations 3 to 5 to A_2 data, the interaction parameters of PSt and PClSt with toluene, MEK and cumene were estimated, which are given in Table II. The values of χ obtained from PSt and PClSt in toluene are 0.371 and 0.460, respectively. They are close to the values of 0.383 (PSt) and 0.483 (PClSt) which were previously estimated by Ogino *et al.*⁹ from A_2 data.

Polymer-Polymer Interaction Parameter

The interaction parameter χ_{AB} between PSt and PClSt was estimated in two different ways. The first one is an estimation from A_2 for the ternary system of PSt-PClSt-solvent and the second, from A_2 for the block copolymers in solution.

According to Krigbaum-Flory, $(A_2)_{ij}$ in eq 2 for the A polymer-B polymer-solvent ternary system is expressed as follows¹⁰

$$(A_2)_{ij} = \frac{\bar{v}_i \bar{v}_j}{2V_s} (1 - \chi_{is} - \chi_{js} + \chi_{ij}) h(z_{ij}/\alpha_{ij}^3) \quad (6)$$

$$(\chi_{ii} = 0) \quad (i, j = A \text{ or } B)$$

and then

$$(A_2)_{AA} = \frac{\bar{v}_A^2}{V_s} \left(\frac{1}{2} - \chi_{AS} \right) h(z_{AA}/\alpha_{AA}^3) \quad (6a)$$

$$(A_2)_{BB} = \frac{\bar{v}_B^2}{V_s} \left(\frac{1}{2} - \chi_{BS} \right) h(z_{BB}/\alpha_{BB}^3) \quad (6b)$$

$$(A_2)_{AB} = \frac{\bar{v}_A \bar{v}_B}{2V_s} (1 - \chi_{AS} - \chi_{BS} + \chi_{AB}) h(z_{AB}/\alpha_{AB}^3) \quad (6c)$$

where \bar{v}_A and \bar{v}_B are the partial specific volumes for the homopolymers, A and B, χ_{AS} and χ_{BS} are the interaction parameters for the homopolymers of A and B, respectively with solvent, and α_{AB} and z_{AB} are the quantities related to the interactions between A and B polymers in the given solvent.

The interaction parameter χ_{AB} can be estimated from $(A_2)_{AB}$ by using eq 6c, provided that the value of $h(z_{AB}/\alpha_{AB}^3)$ is known. An estimation of $h(z_{AB}/\alpha_{AB}^3)$ is rather a problem and it involves a fundamental difficulty. Our estimation at present was carried out as follows. Values of z for copolymers, z_{cop} , were estimated from α_η by the relation used for the case of homopolymers.¹¹ Then, the z_{AB} values were calculated using z_{cop} values for the copolymers, z_{AA} for PSt and z_{BB} for PClSt, according to the following equation given by Benoit *et al.*,¹²

$$z_{cop} = x_A^2 z_{AA} + x_B^2 z_{BB} + 2x_A x_B z_{AB} \quad (7)$$

where x_A and x_B are the mole fractions of A and B, respectively, in the copolymers. And then, the values of $h(z_{AB}/\alpha_{AB}^3)$ in eq 6c were evaluated by combining eq 4 and 5 using the z_{AB} values obtained.

As already pointed out, eq 2 could be applicable to A_2 data for the PSt-PClSt mixtures in toluene and MEK but not to those in cumene. The values of $(A_2)_{AB}$ in toluene and MEK were determined by applying eq 2 to all A_2 data by a least square method. The results are shown in Table II. The values of χ_{AB} estimated from these values by using eq 4 to 7 are given in Table IV.

The interaction parameter χ_{cop} of the block copolymers with solvents can be evaluated if the relations 3 to 5 could apply to A_2 data obtained for the block copolymers. An evaluation of χ_{cop} was attempted by using the same procedures as used for the homopolymer

solutions and the results are given in Table III.

For the interaction parameter χ_{cop} of a binary copolymer with a solvent, Stockmayer *et al.* proposed the following equation¹³

$$\chi_{cop} = x_A \chi_{AS} + x_B \chi_{BS} - x_A x_B \chi_{AB} \quad (8)$$

which assumes that (a) the distribution of segments of two components A and B in solution is statistically random; (b) solvent molecules and both kinds of monomer units have the same volume. The assumption (a) will not be so erroneous for the block copolymers in toluene and MEK but (b) should be invalid as it is generally not correct. Nevertheless, it was found that eq 8 can adequately express the experimental values of χ_{cop} as a function of composition; the χ_{AB} value determined from eq 8 were independent of composition, and the curve calculated by inserting this χ_{AB} value

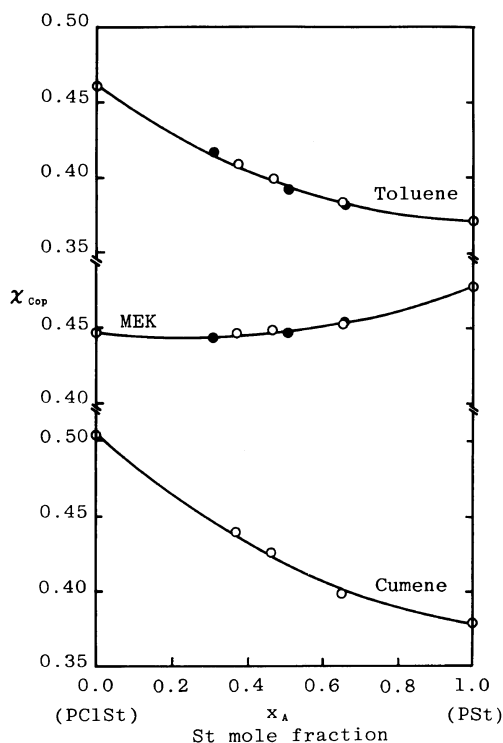


Figure 4. Plots of the interaction parameter χ_{cop} vs. composition for the St-ClSt block copolymers. (—), values calculated from eq 8. Symbols are same in Figure 1.

Table IV. The interaction parameter χ_{AB} between PSt and PClSt

Method	Solvent	χ_{AB}	
			Average
From osmotic 2nd virial coefficients, A_2			
Ternary system	Toluene	0.086	0.070 \pm 0.016
	MEK	0.063	
	Cumene	—	
Block copolymer	Toluene	0.076	
	MEK	0.064	
	Cumene	0.063	
From intrinsic viscosities, $[\eta]$			
Block copolymer	Toluene	0.098	0.087 \pm 0.012
	MEK	0.075	
From solubility parameters, δ			
	—	0.061	

into eq 8 showed a reasonably good agreement with the experimental values of χ_{cop} as shown in Figure 4. The values of χ_{AB} determined from χ_{cop} in the three solvents, toluene, MEK and cumene, are shown in Table IV.

In the estimations of χ_{AB} , V_s in eq 3 and 6 was assumed as 100 (cm³) instead of employing molar volumes of the respective solvents, since χ_{AB} should be different in each of the solutions depending on the solvent only through its molar volume if we use molar volumes of each solvent for V_s , 107.5 (cm³) for toluene, 90.8 (cm³) for MEK and 144.5 (cm³) for cumene.

In Table IV, it is noted that an agreement between the χ_{AB} values obtained from A_2 for the polymer mixture solutions and those from χ_{cop} for the block copolymer solutions was rather satisfactory, while there are some discrepancies between the χ_{AB} value obtained in toluene and that in MEK and cumene. Comparing with toluene and cumene, MEK should be a more favorable solvent for estimating χ_{AB} from A_2 of the PSt–PClSt mixtures since MEK has a similar nature towards PSt and PClSt,¹⁴ *i.e.*, $\chi_{AS}=0.478$ and $\chi_{BS}=0.447$, and the assumptions in eq 2 and 8 will be better approximations for the PSt–PClSt–

MEK system than for the PSt–PClSt–toluene system, which may lead to a conclusion that the χ_{AB} value in MEK will be more reliable than that in toluene and cumene. However, we have to take accounts of some other causes producing the discrepancies among the figures of χ_{AB} . Experimental inaccuracies in determining A_2 are naturally a cause of them and besides, an uncertainty in the $h(z/\alpha^3)$ values would be more significant, and an error in χ_{cop} produces a rather great difference in χ_{AB} . Moreover, theoretical limitations of the procedures also cause an uncertainty of χ_{AB} . From these points of view, it is hard to say which is a better value for χ_{AB} . $\chi_{AB}=0.070 \pm 0.016$ was obtained as the average.

For the purpose of comparison, χ_{AB} values evaluated from intrinsic viscosities are also shown in Table IV. These values were obtained using our previous data^{2b} by assuming the following equation for the excluded volume parameter β_{cop} for the block copolymers,^{2b} which is equivalent of eq 8 for χ_{cop} and has the same limitations,

$$\beta_{cop} = x_A \beta_{AA} + x_B \beta_{BB} + 2x_A x_B \Delta \beta_{AB} \quad (9)$$

with

$$\Delta \beta_{AB} = \beta_{AB} - (\beta_{AA} + \beta_{BB})/2$$

where β_{AA} , β_{BB} , and β_{AB} are the parameters characterizing A–A, B–B, and A–B interactions in the given solvent. $\Delta \beta_{AB}$ is related to χ_{AB} by the equation

$$\Delta \beta_{AB} = (V_s/N) \chi_{AB} \quad (10)$$

where N is Avogadro number.

The χ_{AB} value in the last row in Table IV is that calculated from the Hildebrand–Scott solubility parameters, δ_A for PSt and δ_B for PClSt. By assuming that polymer–polymer interaction is mostly enthalpic rather than entropic, χ_{AB} could be expressed as¹⁵

$$\chi_{AB} = \frac{V_r}{RT} (\delta_A - \delta_B)^2 \quad (11)$$

where V_r is a reference volume. Equation

11, with the solubility parameters of 9.03 (cal cm^{-3}) for PSt and $9.63 (\text{cal cm}^{-3})^{1/2}$ for PCIS_t, $V_r=100 (\text{cm}^3)$ and $T=298 \text{ K}$ gives $\chi_{AB}=0.061$,¹⁶ which is rather in a good agreement with the experimental χ_{AB} value obtained in MEK and cumene solutions from this study.

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