suggest that water absorption shifts the "20-Å wide-angle ionomer peak" into the small-angle X-ray region.

Delf and MacKnight[15] reported a small-angle X-ray scattering peak at an angle of 0.018 rad for ethylene–methacrylic acid ionomers ionized 60% with sodium and cesium but reported no peak for the lithium ionomer. The new data presented in this work would suggest that the low-angle peak they reported was caused by an overlap of the polyethylene crystalline lamellar peak and the "wide-angle X-ray ionomer peak" that shifted to smaller angles as a result of moisture absorption.

Conclusions[47]

This work introduces a new "aggregate" model for the morphology of ionomers. The model consists of small acid aggregates homogeneously distributed throughout the amorphous phase. The new model successfully correlates the physical properties and morphology of ionomer systems. As a result of this study several new conclusions can be drawn about the structure of ionomers. (1) The wide-angle "ionomer X-ray peak" Bragg spacing is a measure of the average distance between ionic scattering sites. (2) The degree of acid group aggregation in dry ionomers increases from dimers to trimers to tetramers up to septimers as the acid content in the copolymer increases. (3) Plasticization with water increases the extent of acid group aggregation. (4) Low-angle X-ray scattering results from crystalline lamellae in ethylene ionomers and from the "ionomer X-ray peak" shifted to lower angles as a result of water plasticization.

Acknowledgments. The authors thank Dr. E. A. Collins and Mr. D. G. Fraser of the B. F. Goodrich Chemical Co. and Mr. W. F. Brondyke of the E. I. du Pont de Nemours & Co. for supplying the butadiene copolymers and ethylene ionomers used in this study. We thank Mr. R. A. Horn of the Forest Products Laboratory for making the LAXS densitometer measurements. Finally we are grateful for partial federal support of this research through the National Science Foundation and the National Defense Education Act.

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(47) **Note Added in Proof.** In a recent note, F. L. Binsbergen and G. F. Kroon (*Macromolecules,* 6, 145 (1973)) have presented an explanation of the ionomer X-ray peak. Their interpretation, that the ionomer peak arises from constructive interference due to a most frequently occurring distance between nearest-neighbor clusters, is essentially identical with the "aggregate model" proposal of this paper.

Homopolymer and Random Copolymer Solubility in Styrene–α-Methylstyrene Systems

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ABSTRACT: We report on an experimental study of the solution properties of well-tailored homopolymers and copolymers of styrene and α-methylstyrene, prepared *via* the living polymer technique. In accord with earlier investigations, we found evidence of an increased copolymer solubility over that obtained by linear interpolation between the parent homopolymers. This effect is most pronounced in plots of Θ temperatures *vs.* composition which show minima. This phenomenon is also shown to be manifested in Flory–Huggins parameters obtained for moderately concentrated (3–25 vol %) toluene solutions. Comparison of our results with those available in the literature reinforce the notion that such increases in copolymer solubility are quite general, if not universal. The interactions accounting for the enhanced solubility were correlated in terms of an interunit interaction parameter χ_{ab}.

A major obstacle to a fundamental understanding of the processes controlling polymer solution thermodynamics is our lack of empirical knowledge of the molecular factors controlling the equilibrium state. For example, one would like to relate such molecular factors as functional group composition, repeat unit structure, copolymer composition, and tacticity to actual polymer solution behavior. This goal requires extensive thermodynamic data on model polymer solutions. In the current research we have studied the solution properties of a series of well-tailored homopolymers and random copolymers constructed from the closely related monomers styrene and α-methylstyrene. Differences in the solution properties of the materials of interest would pertain specifically to the number and location of the methyl group. The polymers were synthesized by the anionic living-polymer reaction to produce amorphous materials with fairly narrow molecular weight distributions. In addition the copolymers were homogeneous and random, and had compositions of 24, 50, and 69 wt % styrene.

Several groups of researchers have studied the thermodynamic and conformational properties of random copolymers in dilute solution.[1-6] The materials receiving the most attention are based on styrene and the various esters of acrylic and methacrylic acid. A salient finding to emerge from these studies is an increase in copolymer solubility over that exhibited by the parent homopolymers. The evidence for this enhanced solubility is summarized in Table I. The parameters directly and unambiguously measured are the second virial coefficient (A_2), the theta temperature (Θ), and the intrinsic viscosity ($[\eta]$), whereas the long-range interaction parameter (B) must be derived from still-imperfect two-parameter theories.[7] The param-

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(2) A. Kotera, T. Saito, Y. Watanabe, and M. Ohama, *Makromol. Chem.,* 87, 195 (1965).

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Table I
Experimental Evidence for Increased Solubility in Random Copolymers

Copolymers[a]	Solvent[a,b]	Measured Parameter[c]	Ref
S-MMA	D (g)	A_2 (1)	1
	Bu (m-a)	A_2 (1), [η]	
	N (m-b)	A_2 (1)	
MA-MMA	MEK (g)	A_2 (1)	2
S-AN	MEK (m-c)	A_2 (1)	3
S-MMA	CHl (p)	Θ(a), B	4
	2-EE (m-d)	Θ	
	T (g)	B	
	1-C-n-G (g)	B	
	DEM (g)	B	
S-MA	2-MCHl (p)	Θ (b)	5
	Be (g)	B	
	Bu (m-e)	B	
	DEM (m-e)	B	
MMA-BeA	DMF-MEK (g)	A_2 (o/1)	6
MAS-S	DMF-MEK (g)	A_2 (o/1)	
EA-MMA	DMF-MEK (g)	A_2 (o/1)	

[a] Abbreviations used are: A, acrylate; AN, acrylonitrile; Be, benzene, benzyl; Bu, butanone; CHl, cyclohexanol; 1-C-n-B, 1-chloro-*n*-butane; D, dioxane; DEM, diethyl malonate; DMF, dimethylformamide; E, ethyl; 2-EE, 2-ethoxyethanol; MEK, methyl ethyl ketone; 2-MCHl, 2-methylcyclohexanol; MA, methyl acrylate; MMA, methyl methacrylate; N, nitroethane; S, styrene; T, toluene. [b] Solvent quality symbols are: (g), a good solvent; (p), a poor (Θ) solvent; (m), a mixed-quality solvent; (m-a), fair for PMMA, poor for PS; (m-b), good for PMMA, nonsolvent for PS; (m-c), good for PS, nonsolvent for PAN; (m-d), poor for PMMA, nonsolvent for PS; (m-e), good for PMMA, poor for PS. [c] Measured parameters symbols are: (1) measured by light scattering; (a) determined in the limit $A_2 \rightarrow 0$; (b) determined by phase equilibria; (o) measured by τ_{oh} osmometry.

Table II
Polystyrene[a]

Sample No.	$\overline{M}_n \times 10^{-3}$	$\overline{M}_v \times 10^{-3}$	$\overline{M}_v/\overline{M}_n$
III-8	366	460	1.26
III-5	224	310	1.38
III-1	202	215	1.07
III-7	169	225	1.33
III-2	165	170	1.03
III-9	129	145	1.13
Pressure chemicals polystyrene	97.4		1.06[b]
III-6	50.9	73	1.43

[a] $T_{\text{sp}} = 100°$; $\alpha_c = 2.22 \times 10^{-4}$ deg^{-1}. [b] Material specification provided by Pressure Chemicals Inc.

eters A_2, [η], and B show a maximum with copolymer composition whereas Θ shows a minimum. Attempts to correlate expansion factors with composition have brought mixed results.[1-6]

This enhanced solubility was first discussed by Stockmayer *et al.*[1] who attributed the phenomenon to repulsive forces operating between the unlike monomer units. They suggested an equation of the following form to represent the Flory–Huggins interaction parameter for the copolymer

$$\chi_c = \chi_a w_a + \chi_b w_b - w_a w_b \chi_{ab} \tag{1}$$

where w is the weight fraction of monomer in the polymer, and χ is the Flory–Huggins parameter; subscripts a and b refer to the comonomers, and c to the copolymer; and χ_{ab} is a parameter characterizing a–b interactions. The term $w_a w_b \chi_{ab}$ causes χ_c to be different from that obtained by linear interpolation between the parent homopolymers.

Table III
Poly(α-methylstyrene)[a]

Sample No.	$\overline{M}_n \times 10^{-3}$	$\overline{M}_v \times 10^{-3}$	$\overline{M}_n/\overline{M}_n$
IV-5	278	300	1.08
IV-6	194	195	1.00
IV-1	142	127	0.90
IV-3	127	127	1.00
IV-2	122	120	1.01
IV-7	68.6	69	1.00
IV-8	56.7	59	1.04
IV-6	46.9	42	0.90

[a] $T_{\text{sp}} = 175°$; $\alpha_c = 1.44 \times 10^{-4}$ deg^{-1}.

Table IV
24% Styrene Copolymers[a]

Sample No.	Wt % Styrene	$\overline{M}_n \times 10^{-3}$	$\overline{M}_v \times 10^{-3}$	$\overline{M}_v/\overline{M}_n$
V-46	23.7	51.7	63	1.2
V-47	23.5	107.4	109	1.0
V-49	25.1	180	217	1.2
V-48	25.2	205	337	1.65

[a] $T_{\text{sp}} = 152°$; $\alpha_c = 2.0 \times 10^{-4}$ deg^{-1}.

Table V
50% Styrene Copolymers[a]

Sample No.	Wt % Styrene	$\overline{M}_n \times 10^{-3}$	$\overline{M}_v \times 10^{-3}$	$\overline{M}_v/\overline{M}_n$
V-36	47.9	106	150	1.4
V-37	53.0	163	245	1.5
V-38	50.0	253	305	1.2

[a] $T_{\text{sp}} = 141°$; $\alpha_c = 1.77 \times 10^{-4}$ deg^{-1}.

Enhanced solubility is predicted if χ_{ab} is positive, and its utility is predicated on its being independent of solvent or copolymer composition. Stockmayer *et al.*[1] calculated χ_{ab} from second virial and intrinsic viscosity relations; Benoit and Dondos[8] utilized intrinsic viscosity relations; and Mächtle[6] used second virial and specific volume data.

In this study three solution parameters were measured: (i) the second virial coefficient in toluene at 37°, (ii) the Θ temperature in methylcyclohexane, cyclohexane, and decalin, and (iii) the Flory–Huggins parameter (χ) in moderately concentrated toluene solutions (3–25 wt %) at 37°. The values of A_2 and Θ were obtained by membrane osmometry and phase separation, respectively; χ values were obtained by high-pressure osmometry. To our knowledge, we are the first to report χ values for concentrated copolymer solutions.

In accordance with the investigators cited in Table I, we found evidence of increased solubility for styrene–α-methylstyrene copolymers. We have correlated these results in terms of χ_{ab} to obtain values from all sources ranging from *ca.* 0.015 to 0.07.

Experimental Section

Polymer Preparation. The polymers were prepared *via* the anionic living polymer technique. An apparatus based on that of Wenger[9,10] was assembled from standard taper glassware parts. The reactions were run at −78° (the temperature of a Dry Ice–acetone mixture) in tetrahydrofuran under high vacuum (<20 μ before the addition of reactants) using sodium biphenyl as the initiator. In order to produce copolymers with uniform backbone composition, two precautions were followed. (i) The mixed mono-

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(8) A. Dondos and H. Benoit, *Makromol. Chem.*, **118**, 165 (1968).
(9) F. Wenger, *J. Amer. Chem. Soc.*, **82**, 4281 (1960).
(10) F. Wenger, *Makromol. Chem.*, **36**, 200 (1960).

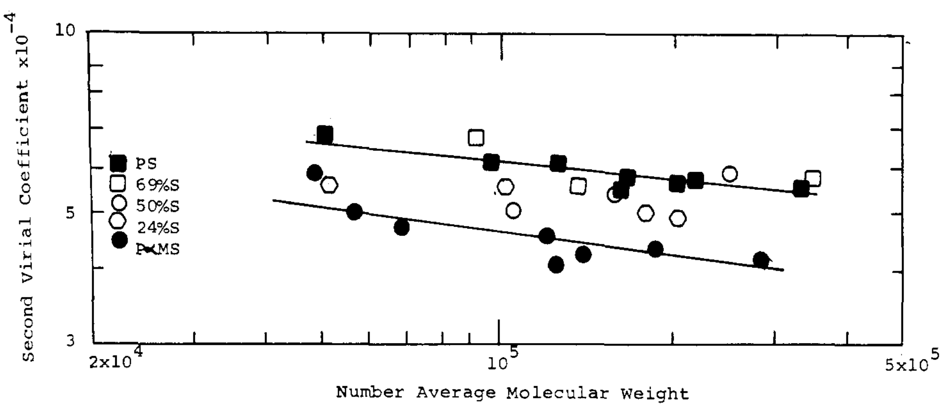

Figure 1.

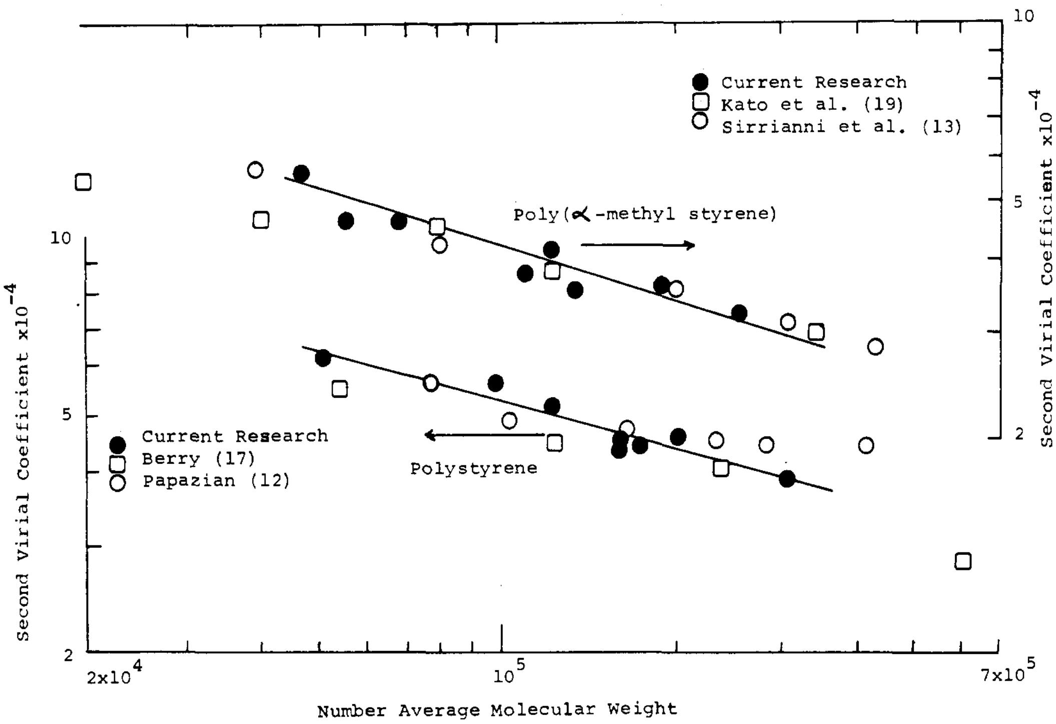

Figure 2.

mers were distilled slowly over a 6-hr reaction time into the reaction vessel. (ii) The monomer reservoir contained a large excess of monomer to prevent drift in monomer composition during distillation. The slow distillation time was necessary because styrene is considerably more reactive in copolymerization than α-methylstyrene.[11]

Polymer Characterization. The basic properties of the experimental materials are summarized in Tables II–VI. The copolymer compositions were determined by material balances of monomers around the reaction vessels. Three sets of copolymers (Tables IV–VI) were synthesized with average compositions of 24, 50, and 69 wt % styrene. Number-average molecular weights were determined *via* osmometry in toluene at 37° using a Mechrolab Model 501 high-speed osmometer (Hewlett Packard, Inc.) with S & S 08 membranes (Arro Laboratories, Joliet, Ill.).

Intrinsic viscosities were measured in toluene at 30.0° with Cannon-Ubbehlode viscometers having efflux times greater than 150 sec. Viscosity average molecular weights were computed for polystyrene and poly(α-methylstyrene) using the Mark–Houwink correlation with constants determined by Papazian,[12] and Sirrianni *et al.*,[13] respectively. Since the Mark–Houwink correlation constants have not been published for the copolymers, viscosity-average molecular weights M_v were computed from $\bar{M}_v = w_S\bar{M}_{vS} + w_{MS}\bar{M}_{vMS}$ where w_S and w_{MS} are weight fractions of styrene and α-methylstyrene in the copolymer and $\bar{M}_{vS}$ and $\bar{M}_{vMS}$ are the respective viscosity average molecular weights computed from the copolymer intrinsic viscosity. (The unperturbed molecular dimensions of the homopolymers and a 24 wt % styrene copolymer were the same within experimental error;[14] therefore, this approach should be valid).

Table VI
69 Wt % Styrene Copolymer

Sample No.	Wt % Styrene	$\bar{M}_n \times 10^{-3}$	$\bar{M}_v \times 10^{-3}$	$\bar{M}_v/\bar{M}_n$
V-42	70.5	90.5	121	1.3
V-44	70.4	139	220	1.6
V-45	67.6	352	402	1.15

[a] T_{sp} = 122°; $\alpha_c = 1.65 \times 10^{-4}$ deg^{-1}.

The ratio $(\bar{M}_v/\bar{M}_n)$ was used as a measure of the molecular weight distributions of these materials. The distributions of the homopolymers were quite narrow. The distributions of some of the copolymers were not as narrow as desired, but they proved adequate for our purposes.

Softening points (T_{sp}) and linear coefficients of expansion (α_c) below T_{sp} were measured with a Du Pont Model 941 thermome-

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(11) R. W. Lenz, "Organic Chemistry of Synthetic High Polymers," Interscience, New York, N. Y., 1967, p 433.

(12) L. A. Papazian, *Polymer*, 10, 399 (1969).

(13) A. F. Sirrianni, C. J. Worsfold, and S. Bywater, *Trans. Faraday Soc.*, 55, 2124 (1959).

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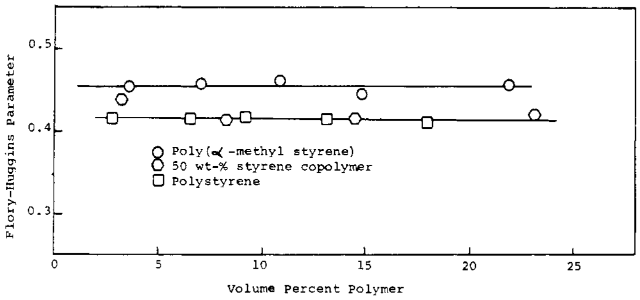

Figure 3.

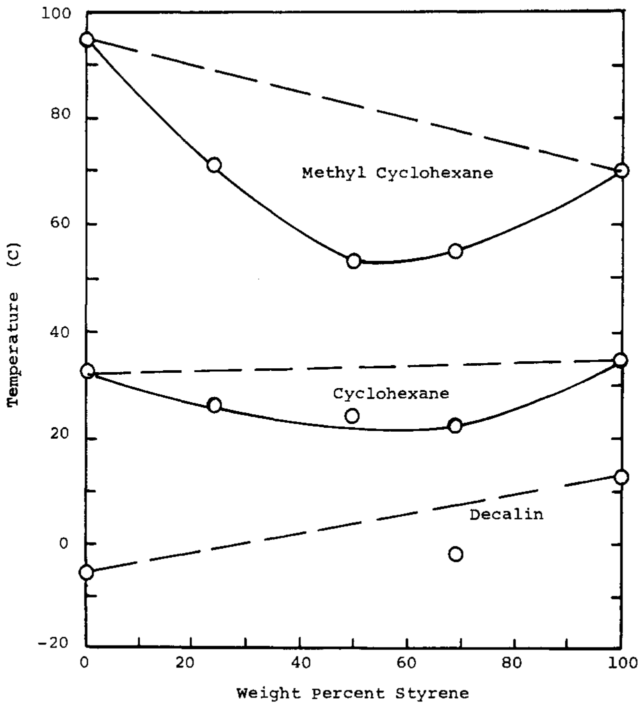

Figure 4.

chanical analyzer (E. I. du Pont de Nemours and Co., Wilmington, Del.). A 10-g probe weight, and a heating rate of 5°/min were used. The data appear in Tables II–VI. In accordance with the behavior of random copolymers, the softening point curves exhibited one break at T_{sp}, and the T_{sp} and α_c data displayed a linear variation with composition.

Measurement of Solubility. Second virial coefficients were determined for toluene solutions at 37° from the osmotic pressure (π) used to calculate $\bar{M}_n$. Plots of $(\pi/c)^{1/2}$ *vs.* c were used in addition to linear plots of (π/c) *vs.* c to facilitate comparison with literature results. The results, shown in Figures 1 and 2 (All data are tabulated in detail elsewhere.[14]) are linear on a log-log scale. The homopolymer data points are shown closed and the copolymer data points are shown open.

Flory-Huggins parameters of polymer solutions ranging from 3 to 25 wt % were determined for polystyrene, poly(α-methylstyrene) and a 50 wt % styrene copolymer in toluene at 37° using a high pressure osmometer similar to that of Flory and Daoust.[14,15] The materials were all about 100,000 in molecular weight. The results are plotted in Figure 3.

Θ temperatures were computed for cyclohexane, methylcyclohexane, and decalin solutions from critical temperatures determined by cloud-point measurements using a Flory–Schultz plot of $1/M^{1/2}$ *vs.* $1/T_c$. Since the copolymers had $(\bar{M}_v/\bar{M}_n)$ ratios of 1.0 to 1.6, the Flory–Schultz plots were smoother when viscosity average rather than number average molecular weights were used. These data are presented in Figure 4. The polystyrene data were obtained from the literature.[16]

Table VII
χ Values in Toluene: 0.2–25 vol %

Wt % Styrene	Dilute 0.2–1.0 vol %	Concn 3.0–25 vol %
0	0.460	0.454
50	0.432	0.412
100	0.413	0.414

Table VIII
χ_{ab} Values

Wt % Styrene	Eq 1 Toluene	Eq 6 CH	Eq 6 MCH	Eq 8 CH
24		0.022	0.028	0.026
50	0.07	0.0153	0.057	0.030
69		0.0287	0.061	0.046

Solubility

Second Virial Coefficients. As displayed in Figure 1 values of A_2 for polystyrene lie above those for poly(α-methylstyrene) indicating that polystyrene is more soluble in toluene than poly(α-methylstyrene). All the copolymer data points lie above those of poly(α-methylstyrene) and most of them lie between those of the homopolymers. Upon close examination, values of A_2 seem to increase with increasing styrene content at fixed molecular weight; however, the difference in A_2's between the homopolymers at fixed molecular weight is not much larger than experimental error. Figure 3 is a plot for comparison of A_2 *vs.* molecular weight containing the results of Papazian[13] and Berry[17,18] for polystyrene; Sirrianni[13] and Kato *et al.*[19] for poly(α-methylstyrene); as well as data from this research. As can be seen, our homopolymer data agree with those in the literature within experimental error.

Flory–Huggins Parameters. The data plotted in Figure 3 show χ to be a constant for all three polymers in the concentration range studied. Further, χ for polystyrene is smaller than that for poly(α-methylstyrene) which indicates, in agreement with the second virial coefficient data, that polystyrene is more soluble in toluene than poly(α-methylstyrene). For the 50–50 copolymer and polystyrene samples χ is about the same. That is, χ for the copolymer is smaller than that obtained by linear interpolation between the homopolymer values, indicating an increased copolymer solubility.

Compared in Table VII are average χ values computed from dilute solution osmometry data (for which χ is essentially constant) with the averages of those shown in Figure 3. The χ values are virtually identical for both dilute and moderately concentrated solutions. Hence, for these materials χ is constant up to about 25 vol %.

Bawn *et al.*[20] obtained vapor pressure data for polystyrene–toluene solutions over the concentration range 3–92 wt % at 25, 60, and 80°. They found the solvent activity to be independent of temperature. Flory[21] has plotted χ *vs.* v_2 between *ca.* 25 and 90 vol % based on these data. His plot plus ours provide a χ *vs.* v_2 relation over the entire composition range for polystyrene in toluene. The sets of data agree nicely at about 25 vol %, but our data show

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considerably less scatter than that obtained by vapor pressure measurements.

Theta Temperatures. As the data in Figure 4 indicate, Θ temperatures for the systems of interest exhibit minima in the midcomposition range. Commercial decalin was not a convenient solvent to use because gels tended to form at low temperatures which made critical temperature measurements difficult. Consequently, measurements were made only for the 69 wt % styrene samples. The decalin results followed the same pattern as those in cyclohexane and methylcyclohexane.

The variation in Θ with composition for cyclohexane and methylcyclohexane is curious. The order of solubility of the homopolymers is reversed and the increase in solubility for the copolymers is markedly increased when the solvent composition varies by only a methyl group.

Calculation of χ_{ab}. χ_{ab} was calculated directly from our high-pressure osmometry data in toluene *via* eq 1 as 0.07. Two techniques were devised to calculate χ_{ab} from Θ. First χ can be written in terms of its entropic and enthalpic components as

$$\chi = \chi_H + \chi_s \tag{2}$$

where Blanks and Prausnitz[22] have determined χ_s to be 0.34. At the Θ temperature where $\chi = 0.05$, $\chi_H = 0.16$. For the strictly enthalpic part $\chi_H T$ = constant. At any temperature other than Θ, we have

$$\chi_H = (0.16\Theta)/T \tag{3}$$

Combining eq 2 and 3 we obtain

$$\chi = 0.34 + \frac{0.16\Theta}{T} \tag{4}$$

If we assume χ_s to be the same for both homopolymers and copolymers, we can write for each of the components

$$\begin{aligned} \chi_a &= 0.34 + \frac{0.16}{T}\Theta_a \\ \chi_b &= 0.34 + \frac{0.16}{T}\Theta_b \\ \chi_c &= 0.34 + \frac{0.16}{T}\Theta_c \end{aligned} \tag{5}$$

Upon substitution in eq 1, and rearranging one obtains

$$\chi_{ab} = \frac{0.16}{T}(w_a\theta_a + w_b\theta_b - \theta_c)/w_a w_b \tag{6}$$

Values of χ_{ab} computed from eq 6 with $T = \theta_c$ are presented in Table VIII. Alternatively, using the well-known equation due to Flory[21]

$$\tfrac{1}{2} - \chi = \psi\left(1 - \frac{\theta}{T}\right) \tag{7}$$

combined with eq 1, one can derive

$$\chi_{ab} = \frac{1}{w_a w_b}\left[w_a\psi_a\left(\frac{\theta_a}{\theta_c} - 1\right) + w_b\psi_b\left(\frac{\theta_b}{\theta_c} - 1\right)\right] \tag{8}$$

Using $\psi_{PS} = 0.38$[12] and $\psi_{P\alpha MS} = 0.133$[23] the values shown in Table VIII were calculated. The significant difference in the ψ values used is probably an artefact resulting from their having been determined by different methods. (No ψ values for MCH are available so calculations could not be made for this solvent *via* eq 8.) If χ_{ab} is to be effective as a characterizing parameter, it should be independent of solvent and copolymer composition. The values shown in Table VIII are all within a fivefold range of each other, but there appears to be variation with both copolymer and solvent composition.

Table IX
χ_{ab} Values for Various Copolymer Systems

Copolymer	Solvent	χ_{ab}	Ref
P(S-MMA)	Bu	0.05	1
	D	0.07	
P(S-MMA)	Be	0.031	
	THF	0.046	8
	p-Xylene	0.053	
P(MA-BeA)	MEK	0.03	6
	DMF		
P(S-MMA)	MEK	0.05	
P(S-MA)	MEK	0.06	
	DMF		
P(MA-MMA)	MEK	0.08	
P(EA-MMA)	MEK	0.08	
	DMF		
P(MBA-MMA)	Acetone	0.08	

Values of χ_{ab} calculated by the investigators previously cited[1,6,8] are shown in Table IX for comparison. Our results plus those of Stockmayer *et al.*[11] and Dondos and Benoit[8] indicate a solvent dependence, whereas Machtle's[6] results indicate no such dependence.

Attempts to correlate our data in terms of solubility parameter theory are reported elsewhere.[14]

Summary

Comparison of our evidence for enhanced copolymer solubility with those in the literature (Table I) suggest that this phenomenon may be quite general. Evidence for increased polymer solubility comes from diverse polymer systems and solvents, and it is observed in a variety of parameters. Specifically, this phenomenon is observed in copolymer systems as chemically dissimilar as styrene and acrylonitrile and as chemically similar as styrene and α-methylstyrene or methyl acrylate and methyl methacrylate. Indeed, an increase in solubility produced by such an innocuous group as the methyl group is surprising. Furthermore, it has been observed in good solvents, Θ solvents and hydrogen-bonding solvents, and it is manifested in measurements of A_2, θ, and χ. Most of the evidence comes from dilute solution studies, but we have shown the phenomenon to prevail in moderately concentrated solutions as well.

The data were correlated in terms of χ_{ab} from eq 1 and compared with those previously calculated. Our values varied over a fivefold range in both composition and mode of calculation. Strictly speaking χ_{ab} should be independent of concentration and composition. The failure of χ_{ab} to be truly constant probably reflects its weak theoretical foundation as well as scatter in the data.

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