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# Random Copolymers: Their Solution Thermodynamics as Compared with That of the Corresponding Homopolymers

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Vapor pressure data (at 50 °C) of solutions of poly(methyl methacrylate) [PMMA], polystyrene [PS], and poly(styrene-*ran*-methyl methacrylate) [P(*S-*ran**-MMA)], with different weight fractions  $f$  of styrene units, in either CHCl<sub>3</sub>, acetone [AC], methyl acetate [MeAc], or toluene [TL] were evaluated with respect to the dependence of the Flory–Huggins interaction parameter  $\chi$  on polymer concentration and on  $f$ . For all solutions under investigation,  $\chi$  varies considerably with the composition of the mixture, and only for four of them [CHCl<sub>3</sub>/PS, AC/PMMA, MeAc/PS, and TL/P(*S-*ran**-MMA)  $f = 0.5$ ] is this dependence linear; another four systems exhibit a minimum [CHCl<sub>3</sub>/PMMA, CHCl<sub>3</sub>/P(*S-*ran**-MMA)  $f = 0.5$ , TL/PMMA, and TL/PS], and only one [MeAc/PMMA] shows a maximum. With the exception of CHCl<sub>3</sub>/P(*S-*ran**-MMA) and  $f = 0.5$ , the  $\chi$  values of the copolymers do not fall reasonably between the data obtained for the corresponding homopolymers. In most cases, the incorporation of a small fraction of the monomer that interacts less favorably with a given solvent suffices to make the copolymer behave very similar to the worse soluble homopolymer. In order to rationalize these multifaceted findings, we have modeled the results by means of an expression for  $\chi$ , which accounts explicitly for the chain connectivity of polymers and for the capability of the components to change their molecular conformation upon mixing. This approach yields a consistent picture of the present results; it reproduces the effects of polymer concentration on  $\chi$  quantitatively by means of three physically meaningful parameters. The modeling of the influences of copolymer composition requires one additional term for each of these parameters.

## Introduction

The interaction of random copolymers with low molecular weight liquids is of fundamental practical importance because such materials are increasingly used for manifold purposes. These are for instance: as packaging and coating materials, as separation membranes, as drug-delivery systems, and as bio-compatible materials for medical applications. In all these cases, sorption phenomena play an important role, and it is, therefore, mandatory to have access to accurate equilibrium vapor pressure data.<sup>1</sup> For a more general and comprehensive understanding of random copolymers, it would be highly desirable to develop theoretical means to calculate their interaction with a certain solvent within the entire composition range from the mere knowledge of the thermodynamic behavior of the corresponding homopolymers in this particular solvent and the comonomer content of the random copolymer.

According to the present state of the art, we are far from a satisfactory understanding concerning the thermodynamics of solutions of random copolymers. The majority of the still rather small number of experimental studies<sup>2,3</sup> covers limited composition ranges only. With the most frequently applied method of vapor pressure measurements, information for dilute and moderately concentrated solutions is inaccessible as well as for too concentrated solutions because the measurements become very inaccurate. This means that these data must be complemented by the results of other techniques in order to obtain the total information. On the dilute side, these are primarily osmosis and light scattering; inverse gas chromatography can be used for compositions close to the polymer melt. An interesting new ellipsometric method,<sup>4</sup> also supplying thermodynamic data, was

reported recently. On the theoretical side, equation of state models<sup>2,3,5–8</sup> and clustering functions<sup>3,9,10</sup> have so far been primarily used to describe the experimental findings.

In view of the unsatisfying situation portrayed above, we have undertaken this systematic experimental and theoretical study. First of all, we wanted to obtain some notion concerning the effects of changes in the copolymer composition on their interaction with a given solvent. For the measurements, we have chosen solutions of poly(styrene-*ran*-methyl methacrylate) [P(*S-*ran**-MMA)] of different compositions in various solvents, because reliable experimental data are already available from the literature.<sup>1</sup> The fact that these authors have performed vapor sorption experiments in contrast to our determination of vapor pressures does not impede the comparison of the results as long as equilibria are established; the differences lie exclusively in the experimental procedures. The theoretical description uses a comparatively new approach,<sup>11–13</sup> which describes complex composition dependencies of Flory–Huggins interaction parameters for homopolymer solutions and polymer blends (two chemically different kinds of segments) by means of four physically meaningful parameters, out of which two can usually be eliminated. The starting point for the present modeling of the solutions of random copolymers (three chemically different kinds of segments) is the assumption that these parameters can be calculated from the corresponding parameters of the homopolymers by means of a simple mixing rule with respect to the monomer content.

In this context, it appears advisable to talk about the expected minimum number of parameters required for a quantitative description of copolymer solutions. If one (unrealistically) assumes that Flory–Huggins interaction parameters do not depend on composition, systems of the present type consisting of a solvent and two types of polymer segments require an absolute minimum of three parameters, two for polymer solvent contacts and one for contacts between the chemically different

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**Table 1. Molecular Weights and Polydispersities of Polymer Samples as a Function of Weight Fraction of Styrene (*f*) in the Sample**

<i>f</i> weight fraction of PS	<i>M<sub>w</sub></i> (kg/mol)	<i>M<sub>n</sub></i> (kg/mol)	<i>M<sub>w</sub>/M<sub>n</sub></i>
0.0 (PMMA)	100	90.9	1.10
0.1	133	84.8	1.57
0.2	103	80.5	1.27
0.5	90	75.0	1.20
0.83	50.7	34.2	1.49
1.0 (PS)	94.9	89.3	1.06

**Table 2. Values of the Refractive Index, *n<sub>0</sub>*, and Refractive Index Increments, *dn/dc*, Measured at 50 °C as a Function of Weight Fraction of Styrene in the Sample**

<i>f</i>	solvent	<i>n<sub>0</sub></i>	<i>dn/dc</i>
0.0 (PMMA)	MeAc	1.3450	0.1323
0.0 (PMMA)	TL	1.4792	0.0100
0.1	TL	1.4792	0.0271
0.2	TL	1.4792	0.0334
0.5	TL	1.4792	0.0630
0.83	TL	1.4792	0.0981
1.0 (PS)	TL	1.4792	0.1180

polymer segments. Allowing for the well-documented (usually nonlinear) concentration influences on the Flory–Huggins interaction parameters leads to a total of nine parameters. For the present study, it should, however, be kept in mind that six of them are not adjusted but taken from independent measurements with the solutions of the two corresponding homopolymers in the same solvent. Moreover, one of the remaining three parameters can normally be eliminated using a general interrelation between two of them, so that we end up with two adjustable parameters per system. The central question we wanted to answer by means of the present work was: Why does monomer A dominate the thermodynamic behavior of a given random copolymer in one solvent, whereas monomer B turns out to be decisive for another solvent?

## Experimental Section

**Materials and Refractive Data.** Four poly(styrene-*ran*-methyl methacrylate) [P(S-*ran*-MMA)] samples with molecular weights between 50 and 133 kg/mol (Table 1) were commercial products purchased from PSS (Polymer Standard Service, Germany). Poly(methyl methacrylate) [PMMA] and polystyrene [PS] samples with similar molecular weights were obtained from Polysciences Inc. (Germany). The samples were dried at 40 °C in a vacuum oven for 3 days before use. Toluene [TL] and methyl acetate [MeAc] were of p.a. grade and purchased from Fluka.

Table 2 collects the refractive indices of the solvents and the refractive index increments for the different homopolymer and copolymer solutions required in the context of the light-scattering measurements.

**Apparatuses and Procedures.** Vapor pressure measurements were carried out as described in the literature<sup>14,15</sup> by means of an apparatus consisting of the headspace-sampler Dani HSS 3950, Milano (Italy), and a normal gas chromatograph Szimadzu GC 14B, Kyoto (Japan). This procedure gives access to the amount of the volatiles in a constant volume of the vapor phase, which is in thermodynamic equilibrium with the polymer solution. From these data, it is possible to calculate the partial pressures of the volatiles.

Light-scattering measurements were performed with a modified (SLS, G. Bauer, Freiburg, Germany) static light-scattering apparatus Fica 50 (Sofica, Paris) using a laser (632 nm) and measuring angles from 20° to 145°. Polymer (copolymer) solutions with concentrations in the range of 0.2–2 g/dL were

prepared 1 day in advance and kept at 50 °C in an oven. Prior to measurements, they were filtered through a 0.45 μm membrane filter (Millipore) directly into the thoroughly cleaned optical cells (Helma, Müllheim, Germany) and thermostatted in the light-scattering apparatus for 15 min. The refractive index of the solvent (*n<sub>0</sub>*) was determined by means of an Abbé refractometer, Carl Zeiss, Germany. The refractive index increments (*dn/dc*), measured at 50 °C by means of an instrument described in the literature,<sup>16</sup> are listed in Table 2.

For the vapor pressure measurements, we have prepared samples with weight fractions of the polymer ranging from 0.41 to 0.84 and a total volume of 2 mL in crimp top vials of 10 mL by loading the polymer with solvent via the gas phase in these vials, which were then sealed with airtight septa. In order to guarantee the attainment of thermodynamic equilibrium, the polymer–solvent mixtures were kept in an oven at 50 °C for 2 weeks, agitating them by means of a rolling mixer.

The reproducibility of the data was checked in multiple headspace extractions by means of five independent measurements for each sample. The amount of solvent vapor decreases from extraction to extraction. To obtain the equilibrium vapor pressure for the initial composition, the measured peak area was plotted as a function of the number of extractions. The linearly extrapolated value for the first extraction was taken for the determination of interaction parameters. The experimental error in the vapor pressures was typically on the order of 1–2%.

## Theory

**Phenomenology.** For the evaluation of the experimental data, we have used weight fractions, *w*, instead of the usual volume fractions, *φ*, to quantify the polymer concentration of the mixtures. This often practiced procedure eliminates the necessity of accounting for nonzero volumes of mixing and for changes in the composition variable if the temperature is varied due to dissimilar thermal expansion coefficients of the components. With the present systems, the differences in the interaction parameters *wχ*, obtained with *w* and *χ*, resulting for *φ* as a composition variable, remain negligible.

The following relation was employed to calculate Flory–Huggins interaction parameters

$$\chi \approx {}_w\chi = \frac{\ln(p/p_o) - \ln(1 - w) - (1 - 1/N)w}{w^2} \quad (1)$$

*p<sub>o</sub>* stands for the vapor pressure of the pure solvent, and *N* gives the number of polymer segments defined in terms of the molar volume of the solvent. For nonideal behavior of the vapor, fugacities must be used instead of the directly measured vapor pressures. The solvents under investigation do not require such corrections. With rising dilution, the above-stated experimental inaccuracies in *p/p<sub>o</sub>* become too large for a reliable determination of *χ<sub>o</sub>*, the limiting value of *χ* for *φ* → 0. In this case, the second osmotic virial coefficients *A<sub>2</sub>*, obtained from osmotic or light-scattering experiments, yield the required information via

$${}_w\chi_o \approx \chi_o = \frac{1}{2} - A_2 \rho_2^2 \bar{V}_1 \quad (2)$$

*ρ<sub>2</sub>* represents the density of the polymer, and *̄V<sub>1</sub>* is the molar volume of the solvent. For the present systems, the difference in the *χ* values calculated on the basis of *w* or *φ* remains within experimental error.

**Modeling.** Numerous experimental results have clearly demonstrated that *χ* is not independent of composition but does normally vary considerably and in a complex manner with that

variable. The simplest way to account for that feature consists of a series expansion of  $\chi$  with respect to the polymer concentration. This purely descriptive procedure is, however, not very helpful in increasing understanding of the molecular reasons of a particular dependence and for predictive purposes. For that reason, many other sophisticated approaches have been proposed (see, for instance, ref 17). We have, some years ago, suggested a comparatively simple modification of the Flory–Huggins theory, which accounts for two features that were initially overlooked, namely, chain connectivity and conformational response. The former effect results from the fact that the segments of a given macromolecule cannot spread out over the entire volume of a system, and the latter effect represents a consequence of the flexibility of polymer chains, which offers the solute additional routes to minimize the Gibbs energy. To a lesser extent, even solvent molecules may change their conformation as their molecular surrounding is altered. The central equations of this approach, which divides the process of dilution into two clearly separable steps, are recalled below.

Equation 3 represents a slightly simplified version of the original relation,<sup>12</sup> which amalgamates the two initially separate parameters  $\zeta$  (conformational response) and  $\lambda$  (intramolecular solvent/segment interaction parameter for isolated polymer coils) into one, such that very complex composition dependencies can be modeled by means of only three adjustable parameters

$$\chi = \frac{\alpha}{(1 - \nu w)^2} - \zeta \lambda (1 + 2w) \quad (3)$$

$\alpha$  quantifies the effect of opening an intersegmental contact (belonging to different solute molecules) in the limit of infinite dilution by inserting a solvent molecule between them without allowing the newly formed structures to rearrange. The chemical equilibrium is only reached in a second step of dilution, in which the components relax into their equilibrium conformation. The parameter  $\zeta \lambda$  accounts for the contribution to the Flory–Huggins interaction parameter resulting from this step of dilution, again in the limit of vanishing polymer concentration. The relation for  $\chi_o$  consequently reads

$$\chi_o = \alpha - \zeta \lambda \quad (4)$$

$\nu$ , the third parameter of eq 3 and the factor 2 of the second term (representing a simplification for typical vinyl polymers), describes the composition dependence of  $\chi$  caused by the variable environment of the components of the mixture. The physical meaning of  $\nu$  is clearly related to but not necessarily identical with the volume-to-surface ratios of polymer segments and solvent molecules. Details concerning the suitability of eq 3 for a better understanding of experimental observations and for the modeling of polymer solutions and polymer mixtures can be obtained from the literature.<sup>18–25</sup>

In order to apply the present approach to solutions of random copolymers, the different parameters  $\pi$  ( $\alpha$ ,  $\zeta \lambda$ , and  $\nu$ ) of eq 3 must be a function of  $f$ , the weight fraction of B-monomers a copolymer A-*ran*-B contains. For this purpose, we use the following relation to hold true

$$\pi_{AB} = \pi_A(1 - f) + \pi_B f + \pi^E f(1 - f) \quad (5)$$

According to this equation, the different parameters  $\pi_{AB}$ , referring to the copolymer of composition  $f$ , are made up of the corresponding homopolymer parameters,  $\pi_A$  and  $\pi_B$ , plus an excess term  $\pi^E$ , quantifying the extra effects resulting from the presence of two types of monomeric units in the copolymer chain.

Insertion of the parameters for the copolymers as formulated in eq 5 into eq 3 yields

$$\chi = \frac{\alpha_A - (\alpha_A - \alpha_B - \alpha^E)f - \alpha^E f^2}{\{1 - [\nu_A - (\nu_A - \nu_B - \nu^E)f - \nu^E f^2]w\}^2} - \{(\zeta \lambda)_A - [(\zeta \lambda)_A - (\zeta \lambda)_B - (\zeta \lambda)^E]f - (\zeta \lambda)^E f^2\}(1 + 2w) \quad (6)$$

From this expression, it becomes immediately obvious that the composition dependence of the interaction parameter for a given copolymer ( $f = \text{const}$ ) and a given solvent normally does not interpolate linearly between the corresponding dependencies for the two homopolymers. This is not even the case if all excess parameters  $\pi^E$  become zero (i.e., if all  $f^2$  members vanish), because of the expression  $(\nu_A - \nu_B)f$  in the denominator of the first term of eq 6.

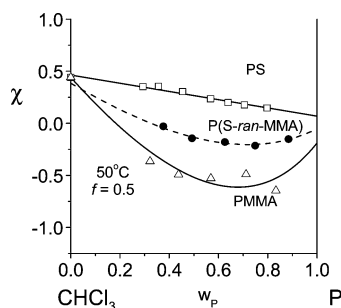
## Results and Discussion

We first evaluate vapor pressure data published for solutions of the homopolymers (PMMA and PS) and for a random copolymer with  $f = 0.5$  in the following three solvents: chloroform, acetone (AC), and methyl acetate (MeAc).<sup>1</sup> After that, we present our own results for the homopolymers and for four different compositions of the copolymer obtained with the solvent toluene. In all cases, the temperature was 50 °C. In order to avoid adulterations of the results by a possible glassy solidification of the mixtures at very high polymer concentrations,<sup>23</sup> we have omitted these data points in our evaluation. It appears interesting to compare the errors for sorption experiments with that of vapor pressure measurements. In the former case, the authors report an error in the weight of vapor-saturated polymer sample of  $\sim 0.05\%$ ; in view of the data scattering in the different vapor pressure curves, it appears, however, very probable that the overall errors are comparable to ours (a few percent).

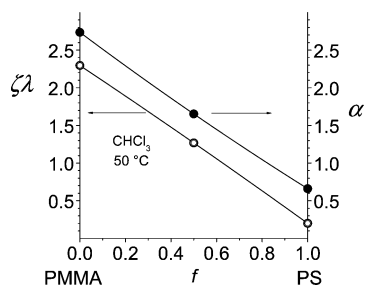
When comparing the solution behavior of random copolymers with that of the corresponding homopolymers, the most obvious question refers to the differences in the thermodynamic quality of a given solvent for the homopolymers and its consequences for the performance of the different copolymers. Such a comparison of solvent quality is, however, not trivial in view of the very diverse composition dependencies of the Flory–Huggins interaction parameters: If the  $\chi$  values for polymer A and solvent 1 are at all compositions less than those of polymer B and solvent 1, this means that the dilution tendency is in the former case more pronounced than in the latter case. According to this point of view, solvent 1 is better for polymer A than for polymer B. However, despite this situation, the system 1/polymer A may exhibit a miscibility gap, in contrast to the system 1/polymer B, because of a particular shape of the function  $\chi(w)$ . In view of this feature, which can be observed with the naked eye, one is inclined to state that solvent 1 is worse for A than for B, despite the fact that the Gibbs energy of the system 1/A is still further diminished upon demixing. According to the present considerations, we assess the quality of a given solvent for the different polymers by the direct comparison of the Flory–Huggins interaction parameter and do not account for the curvatures of  $\chi(w)$ . On the basis of this criterion, CHCl<sub>3</sub>, AC, and MeAc are more favorable for PMMA, whereas TL is a better solvent for PS than for PMMA.

**Chloroform.** With this solvent, the  $\chi$  values decrease within the solvent side of the composition range (cf. Figure 1) for all polymers. For PS, this trend is maintained up to the pure polymer, whereas PMMA and the copolymer exhibit a mini-

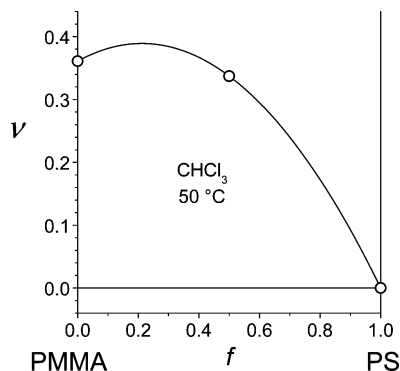




**Figure 1.** Composition dependence of the Flory-Huggins interaction parameter  $\chi$  (based on weight fractions  $w_P$  of the polymer P) for the solutions of the indicated polymers in chloroform at 50 °C. In all graphs of this type, the curves are calculated according to eq 1.



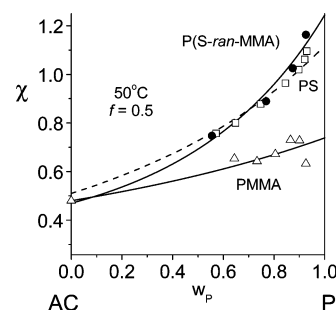
**Figure 2.** Dependence of the system specific parameters  $\alpha$  and  $\zeta\lambda$  of eq 3 on  $f$ , the weight fraction of styrene the polymers contain. In all graphs dealing with the dependence of the parameters of eq 3 on the composition of the copolymer, the curves are calculated according to eq 5.



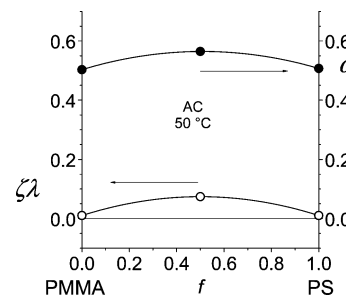
**Figure 3.** Same as Figure 2 but for the parameter  $\nu$ . In all graphs dealing with the dependence of the parameters of eq 3 on the composition of the copolymer, the curves are calculated according to eq 5.

mum, i.e.,  $\chi$  rises again upon an increase of the polymer concentration. Nonlinear dependencies of the present kind are no rarity but are frequently observed and conceivable on the basis of the theoretical considerations leading to eq 3. The system-specific parameters of the homopolymers are presented in Table 3; the corresponding data for the copolymers can be seen in Figures 2 and 3. Chloroform is the only solvent out of the four under investigation for which  $\chi(w)$  of the copolymer interpolates almost linearly between the curves for the homopolymers.

Figure 2 shows how the parameters  $\alpha$  and  $\zeta\lambda$  of eq 3 depend on the weight fraction,  $f$ , of styrene. How the parameter  $\nu$  changes is depicted in Figure 3. The experimental uncertainty of  $\alpha$  and  $\zeta\lambda$  is normally on the order of a few percent only, whereas it becomes considerably larger for small  $\nu$  values. This is so because of the difficulty to quantify a tiny deviation from linearity in  $\chi(w)$ . For that reason,  $\nu$  is not adjusted but set to zero in cases like  $\text{CHCl}_3/\text{PS}$  where the data can be represented by a straight line.



**Figure 4.** As in Figure 1 but for the solvent acetone.



**Figure 5.** As in Figure 2 but for the solvent acetone.

**Table 3.** Collection of System Specific Parameters; In All Cases, the Temperature Is 50 °C

solvent	PMMA			PS			excess parameters (eq 5)		
	$\alpha$	$\nu$	$\zeta\lambda$	$\alpha$	$\nu$	$\zeta\lambda$	$\alpha^E$	$\nu^E$	$\zeta\lambda^E$
$\text{CHCl}_3$	2.74	0.36	2.30	0.66	0.00	0.20	-0.18	0.63	0.08
AC	0.49	0.20	0.01	0.51	0.34	0.01	0.24	0.49	0.26
MeAc	-0.14	0.70	-0.47	0.30	0.00	-0.2	2.40	0.00	1.83
TL	1.01	0.41	0.56	1.33	0.38	0.90	-2.64	-0.75	-2.83

For  $\text{CHCl}_3$ , the parameters  $\alpha$  and  $\zeta\lambda$  vary almost linearly with  $f$ ; in consequence, the corresponding excess parameters formulated in eq 5 are very small (cf. Table 3). In the light of the present approach, this means that the monomeric neighborhood of the polymer chains does not distinctly influence the effects of separating two contacting monomeric units belonging to different macromolecules (by the inserting a solvent molecule keeping all conformations unchanged) or the subsequent conformational relaxations into the equilibrium state. In other words: the effects are approximately additive in the range of pair interaction between the solute molecules where the experimentally accessible quantity  $\chi_o$  is equal to  $\alpha - \zeta\lambda$  (cf. eq 4).

In contrast to the additivity of  $\alpha$  and  $\zeta\lambda$ , the parameter  $\nu$  deviates markedly from a linear dependence on  $f$ . The positive  $\nu^E$  value indicates that the curvature of  $\chi(w)$  for the copolymer is larger than that calculated from additivity. In view of the primarily geometrical nature of this parameter, such a behavior can be tentatively interpreted in terms of changes in the mutual accessibility of monomeric units and solvent molecules due to the modified neighborhood.

**Acetone.** The most obvious observation with this solvent lies in the similarity of the interaction parameters of  $\text{CHCl}_3$  with the homopolymer PS and with the P(S-ran-MMA) of  $f = 0.5$  (cf. Figure 4). The presence of only 50 wt % of styrene units increases the small  $\chi$  values for the interaction with PMMA to the considerably larger values for the interaction with PS.

The following two graphs, respectively, depict the composition dependence of the parameters  $\alpha$  and  $\zeta\lambda$  to  $\nu$  again. According to Figure 5, these parameters vary only moderately with  $f$  in the case of AC; the corresponding excess parameters

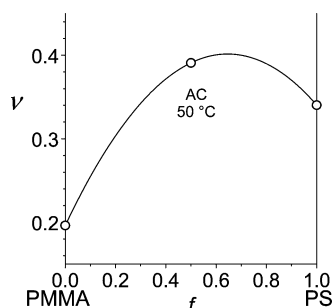


Figure 6. As in Figure 3 but for the solvent acetone.

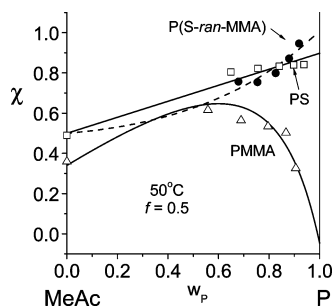


Figure 7. Like Figure 1 but for the solvent methyl acetate.

are, in both cases, positive. The very small  $\zeta \lambda$  of the homopolymers indicate that AC is, according to an alternative definition of the theta conditions,<sup>20</sup> almost a theta solvent for both homopolymers; indeed, the  $\chi_o$  values reported for PS and PMMA are very close to 0.5 (one of the well-established characteristics of theta systems).<sup>26,27</sup>

Like with  $\text{CHCl}_3$ , the parameter  $\nu$  as a function of  $f$  exhibits a pronounced maximum as shown in Figure 6. The outcome of this positive  $\nu^E$  value can be seen in Figure 4 from the more pronounced curvature of  $\chi(w)$  for P(S-ran-MMA) as compared with PS.

**Methyl Acetate.** The most striking feature of the  $\chi(w)$  functions for this solvent consists of the pronounced maximum observed with PMMA. So far, there are only two examples known for such a behavior. In both cases, the solvent is water. The systems are water/dextran<sup>19</sup> and water/bovine serum albumin.<sup>28</sup> The modeling of this shape requires a particular combination of negative  $\alpha$  values (favorable contact formation) in combination with negative  $\zeta \lambda$  values (unfavorable conformational relaxation). For MeAc, it suffices, like with AC, that P(S-ran-MMA) contains 50% styrene to behave thermodynamically almost like the homopolymer PS.

The parameters  $\alpha$  and  $\zeta \lambda$  for MeAc pass a distinct maximum, which is considerably more pronounced than for AC. The positive  $\alpha^E$  means that contact formation becomes considerably more unfavorable in the middle range of  $f$  than for the homopolymers; the positive  $\zeta \lambda^E$ , on the other hand, imply that this adverse effect of the first step of dilution is partly compensated by a more favorable second step. Like all previous solvents, MeAc is a much better solvent for PMMA than for PS, for which a theta temperature (endothermal mixing) of 43 °C is reported.<sup>29</sup> The  $f$  dependence of the parameter  $\nu$ , governing the curvature of  $\chi(w)$ , is practically linear for MeAc, in contrast to chemically very similar AC (see Figures 7–9).

**Toluene.** For the systems dealt with so far, information on the interaction parameters of P(S-ran-MMA) was only available for  $f = 0.5$ . We have, therefore, studied solutions of this copolymer with different compositions in a further solvent at the same temperature. In order to ease the comparison with the previous results and to keep the curves distinguishable, we

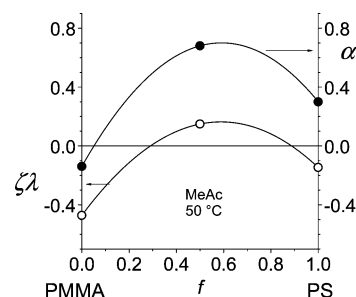


Figure 8. Like Figure 2 but for the solvent methyl acetate.

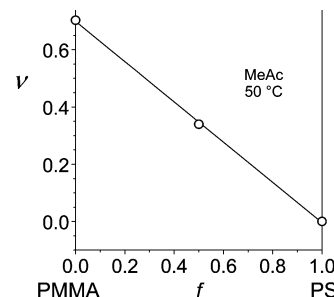


Figure 9. Like Figure 3 but for the solvent methyl acetate.

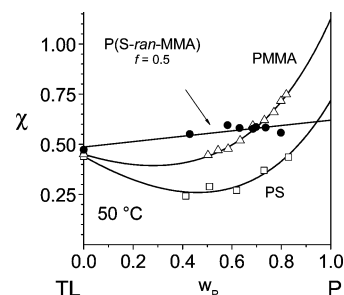


Figure 10. Like Figure 1 but for the solvent toluene.

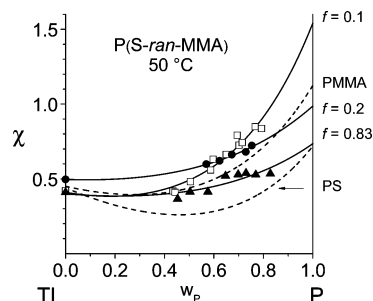


Figure 11. Like Figure 1 but for the solvent toluene: full lines, copolymers ( $f$  values are given in the graph); broken lines, homopolymers.

present the homopolymers and the copolymer with  $f = 0.5$  first (Figure 10). The data for the other three compositions are shown in Figure 11.

According to the data shown in Figure 10, toluene is the only solvent of the four under investigation for which the interaction with PS is more favorable than that with PMMA. The augmentation of the  $\chi$  values caused by the replacement of only a moderate fraction of MMA units by S units is for TL even more pronounced than for AC or MeAc. In this case, <10 wt % suffices to raise  $\chi(w)$  of P(S-ran-MMA) in the region of high polymer concentrations over the dependence for PS (cf. Figure 11). From the shapes and relative locations of the curves for different  $f$  values, it is almost impossible to rationalize the effects of changing copolymer composition. However, an evaluation along the same lines as those applied to the published data yields a clearer-cut picture as demonstrated in Figures 12 and 13.

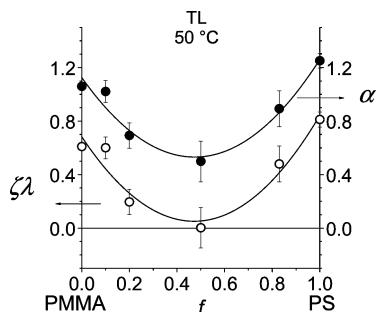


Figure 12. As in Figure 2 but for the solvent toluene.

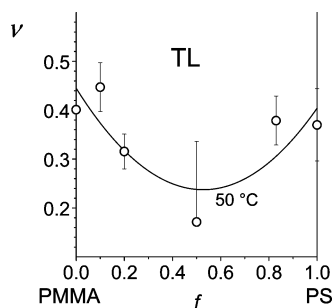


Figure 13. As in Figure 3 but for the solvent toluene.

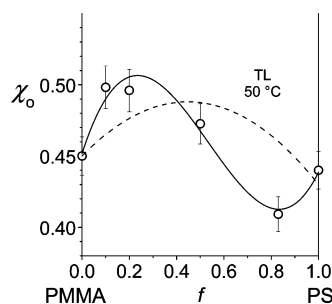


Figure 14. Dependence of the limiting value of the Flory-Huggins interaction parameter for infinite dilution (obtained from light-scattering experiments) on the weight fraction  $f$  of polystyrene the polymer contains. The full curve is modeled by a series expansion of  $(2f - 1)$  up to the third term; the broken curve is calculated according to eq 2 by means of the  $\alpha$  and  $\zeta\lambda$  values obtained from the adjustment of the individual dependencies  $\chi(w)$ .

The rather complex behavior of copolymers of different compositions results from the fact that each of the three system-specific parameters of eq 3 varies with  $f$  in its own characteristic manner. With toluene,  $\alpha$  and  $\zeta\lambda$  pass a minimum as a function of  $f$  (cf. Figure 12), in contrast to AC and MeAc, which exhibit a maximum, and  $\text{CHCl}_3$ , which exhibits linear dependencies. The observation that  $\zeta\lambda$  approaches zero for  $f = 0.5$  implies that TL becomes a theta solvent for the copolymer of this composition.

Toluene is the only solvent for which  $\nu(f)$  passes a minimum; for the present system, it is difficult to establish the precise function because of the little curvature of the different  $\chi(w)$  dependencies, as indicated in Figure 13 by the larger error bars. For further discussion, the system-specific parameters of all systems under investigation are collected in Table 3.

From light-scattering experiments with TL and the present homo- and copolymer in the range of pair interactions, we also have obtained detailed information on the variation of  $\chi_o$  (eq 2) with  $f$ . The results presented in Figure 14 evince a complex dependence of  $\chi_o$  on the composition of the copolymers. Because of the point of inflection of this function, terms up to  $f^3$  are required for its modeling. The curve shown in the graph corresponds to a series expansion with respect to  $(2f - 1)$ , by

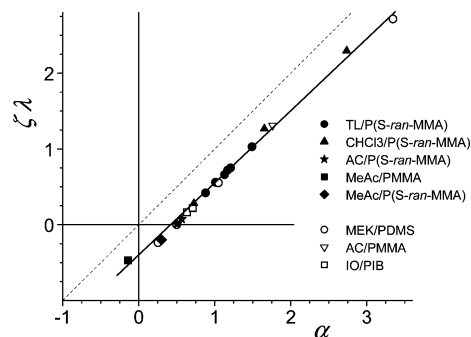


Figure 15. Interrelation of  $\zeta\lambda$  and  $\alpha$  for the present polymers (full symbols) and for some homopolymers (open symbols) taken from the literature.<sup>11</sup> MEK/PDMS (methyl ethyl ketone/poly(dimethylsiloxane)), IO/PIB (isooctane/poly(isobutene)), AC/PMMA.

analogy with the Redlich-Kister equation,<sup>30</sup> up to the third member.

In order to check the consistency of these data obtained from dilute solutions with the information resulting from the modeling of the composition dependencies of  $\chi$ , we have assembled  $\chi_o$  from the independently determined  $\alpha$  and  $\zeta\lambda$  values according to eq 4. Although the agreement is reasonable in view of the different experimental uncertainties, it is clear that the representation of  $\alpha(f)$  and  $\zeta\lambda(f)$  by the second-order polynomials of eq 5 cannot yield the points of inflection observed with  $\chi_o(f)$ .

**Elimination of One Parameter.** According to general experience, the parameters  $\alpha$  and  $\zeta\lambda$  are not independent of each other. This finding is conceivable from the physical meaning of these parameters:  $\alpha$  quantifies the effects resulting from the opening of an intermolecular intersegmental contact, keeping the conformation of all components constant, whereas  $\zeta\lambda$  measures the effects of the conformational relaxation. Because of the identical molecular environments, the contribution of the second step of the attainment of the equilibrium should be proportional to the contribution of the first step. Upon plotting  $\zeta\lambda$  as a function of  $\alpha$ , one indeed obtains a common line for all systems studied so far, including rather exotic mixtures like water/cellulose ( $\zeta\lambda \approx 52$ ). Figure 15 shows a blowup of this interrelation for the range of parameters covered by the present homo- and copolymers.

## Conclusions

Experimental data for solutions of poly(styrene-*ran*-methyl methacrylate) of variable composition and for solutions of the corresponding homopolymers in solvents of different polarity were evaluated by means of an approach accounting explicitly for chain connectivity and conformational variability of the components. The main implications of this study are, in the following, briefly recapitulated.

The first item concerns the thermodynamic quality of the solvents of different polarity for the homopolymers PMMA and PS, which are also dissimilar in their polarity. In terms of the  $\chi$  values measured for a given constant polymer concentration, the polar solvents  $\text{CHCl}_3$ , AC, and MeAc are expectedly more favorable for PMMA than for PS, whereas the nonpolar TL is a better solvent for PS than for PMMA. The shape of the functions  $\chi(w)$  varies considerably. For AC/PMMA, MeAc/PS  $\chi$  increases linearly; for AC/PS, it increases more than linearly, whereas it decreases linearly for  $\text{CHCl}_3$ /PS. With three of the systems, one observes minima in  $\chi(w)$ , namely, for TL/PMMA, TL/PS, and  $\text{CHCl}_3$ /PS; only MeAc/PMMA exhibits a maximum. On the basis of eq 3, this diversity of composition influences is

easily comprehensible, if one keeps in mind that they are made up of two separate contributions. The normally nonzero parameter  $\nu$  of the first term of this relation (which is primarily determined by the differences in the shapes of monomeric units and solvents molecules) leads to a nonlinear composition dependence of  $\chi$ , where the magnitude of this contribution increases as the absolute values of the parameter  $\alpha$  rise. The second term of eq 3 adds a linear dependence, quantified by the parameter  $\zeta \lambda$ . The great diversity of the functions  $\chi(w)$  results from the fact that all three parameters of the present approach may be positive, negative, or zero.

The next aspect concerns the solvent qualities for the different copolymers. Keeping the analysis for the homopolymers in mind, one is not too surprised that the naive interpolation of the  $\chi$  values for the copolymers according to their composition between the data of the corresponding homopolymers is at variance with the experimental observations. Only for the system  $\text{CHCl}_3/\text{poly}(\text{styrene-}r\text{-ran-methyl methacrylate})$  with  $f = 0.5$ , the composition dependence lies reasonably between the  $\chi(w)$  curves of the homopolymers. All other solvents are for the copolymer of the same composition approximately as bad as for the less favorably interacting homopolymer (PS in the case of AC and MeAc; PMMA in the case of TL). In the case of the system TL/P(S-*ran*-MMA), studied in greater detail, the presence of only 10 wt % of styrene units suffices to raise  $\chi$  to values that are, within the range of high polymer concentration, larger than that of the system TL/PS.

Another central issue pertains to the dependence of the different system-specific parameters  $\pi$  on  $f$ , the composition of the copolymer. Within experimental error, a series expansion up to the second term in  $f$  (cf. eq 5) suffices to model the results. Linear dependencies, corresponding to  $\pi^E = 0$ , are exceptions and only observed for the parameters  $\alpha$  and  $\zeta \lambda$  with  $\text{CHCl}_3$  and for  $\nu$  with MeAc.  $\alpha(f)$  and  $\zeta \lambda(f)$  exhibit maxima for the polar solvents AC and MeAc, whereas minima are observed for TL. Unlike the composition dependencies  $\alpha(f)$  and  $\zeta \lambda(f)$ , the leading terms yielding  $\chi_o = \alpha - \zeta \lambda$ , which are for a given solvent always qualitatively equal, the function  $\nu(f)$  may differ. This parameter, standing for nonlinear composition dependencies of  $\chi$ , passes a maximum for  $\text{CHCl}_3$  and AC and a minimum for TL.

The present study shows that the observed complex dependencies of the Flory–Huggins interaction parameter on polymer concentration and on the fraction of the different monomeric units the copolymers contain can be well-modeled by eq 3 without exception. The collection of parameters presented in Table 3 discloses another interesting feature, namely, the fact that all three excess parameters  $\pi^E$  exhibit the same sign for the three systems for which the behavior of the copolymer is dominated by the monomeric unit showing the less favorable interaction with the solvent. For  $\alpha$  and  $\zeta \lambda$ , this means that an adverse excess contact formation is counteracted by a favorable conformational relaxation (acetone and methyl acetate) or, conversely, a favorable excess contact formation goes along with an adverse conformational relaxation (toluene). In the case of chloroform, being the only solvent under investigation for which the interaction parameters of the random copolymer interpolate reasonably well between that of the corresponding homopolymers, both excess quantities lead to a reduction of the Gibbs energy of mixing. One can speculate that this particularity is due to the exceptionally large differences in the  $\alpha$  and  $\zeta \lambda$  values of the two homopolymers in this solvent. In view of the still limited experimental material, it must, however, remain open to which extent these interpretations are generally valid.

Another item that deserves additional attention to draw nearer to the central goal of calculating the thermodynamic behavior of random copolymers as a function of their composition from that information for the parent homopolymers concerns the interaction between the two types of monomeric units. Although the impact of this parameter is necessarily at least contained in  $\alpha^E$  and  $\zeta \lambda^E$ , it is presently impossible to learn more about its specific role, because  $\chi_{\text{PS/PMMA}}$  was kept constant. The next logical step would, therefore, consist of an extension of the investigation to random copolymers made up of monomeric units, which interact much less favorably than styrene and methyl methacrylate.

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