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Dependence of Solvent Quality on the Composition of Copolymers: Experiment and Theory for Solutions of P(MMA-*ran*-*t*-BMA) in Toluene and in Chloroform

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The interaction of toluene with P(MMA-*ran*-*t*-BMA) and with the corresponding homopolymers was determined via vapor pressure measurements at 30, 50 and 70 °C. A unified thermodynamic approach served for the modeling of the results. It is capable of describing the behavior of the different solutions by means of two adjustable parameters, one representing the effective number of solvent segments and the other accounting for the interactions between the components. The solvent quality of toluene passes a maximum, a minimum and another maximum upon an increase of the *t*-BMA content of the copolymer at all temperatures. A similar behavior is discernable from vapor pressure data of chloroform published for the same copolymers. The heats of mixing for toluene depend strongly on temperature; at 50 °C they are all endothermal with the exception of PMMA, for which the value obtained from vapor pressures at 30 °C agrees very well with published caloric data.

1 Introduction

A given solvent in combination with a certain type of random copolymer may exhibit largely different thermodynamic quality depending on the mixing ratio of the comonomers. It can be completely miscible with the polymer in certain ranges of copolymer composition, whereas it can phase separate in others. A better understanding of the thermodynamics for solutions of random copolymers as a function of their comonomer composition would certainly be of great interest for basic research as well as for industrial applications.

Only little experimental material can be found on this matter in the literature[1-3]. An early work[1] deals with the system cylcohexanone/poly(methyl methacrylate-*ran*-*n*-butyl methacrylate) and uses osmotic and caloric measurements up to a maximum of 27 wt% polymer. The

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authors describe and discuss their results in terms of the classical Flory-Huggins theory extended to multicomponents. The other two contributions are more recent and the experimental information stems from vapor pressure measurements. One[2] is dedicated to solutions of poly(methyl methacrylate), polystyrene, and poly(styrene-ran-methyl methacrylate), with different weight fractions of styrene units, in either CHCl3, acetone, methyl acetate, or toluene. The other[3] studies the system chloroform/poly(methyl methacrylate-*ran*-*tert*-butyl methacrylate). The results are in both cases modeled by means of an approach eliminating some deficiencies of the original Flory− Huggins theory. It accounts for hitherto ignored consequences of chain connectivity and considers the ability of macromolecules to rearrange after mixing with the solvent to minimize the Gibbs energy of the system. In contrast to the situation described for copolymer solutions, a larger number of studies is dealing with blends of homopolymers and random copolymers in view of the industrial interest in such systems. Some of them report experimental data and their theoretical interpretation[4-6], others deal preferentially with the modeling[7-13].

We have undertaken the present study to broaden the general knowledge concerning the thermodynamic solution behavior of random copolymers and to test a unified thermodynamic approach[14], which is according to the present experience generally applicable, independent of the molecular and chemical architecture of the components and of other dissimilarities, like electrical charges. Here we wanted to check the universality of this concept by applying it to solutions of random copolymers.

2 Experimental

Samples of the homopolymers poly(methyl methacrylate) (PMMA) and poly(*t*-butyl methacrylate) (P-*t*-BMA), and of the corresponding random copolymers (P(MMA–*ran*–*t*-BMA) with weight fraction of *t*-butyl methacrylate (f) in the sample of 0.2, 0.5 and 0.8 (Table 1) were commercial products purchased from Polymer Standard Service, Germany. The samples were dried at 50 °C in a vacuum oven before use. The solvents toluene (TL) and chloroform ($CHCl_3$) were of p.a. grade and purchased from Fluka.

Table 1 Molecular weights, polydispersities and densities of (co)polymer samples as a function of *f*, the weight fraction of *t*-butyl methacrylate.

f	M_w (kg mol^{-1})	M_n (kg mol^{-1})	M_w/M_n	ρ (g cm^{-3}) 30 °C	ρ (g cm^{-3}) 50 °C	ρ (g cm^{-3}) 70 °C
0.0 (PMMA)	99.4	92.1	1.08	1.1819	1.1768	1.1709
0.2	164	67.8	2.43	1.1515	1.1464	1.1407
0.5	196	84.7	2.32	1.1060	1.1009	1.0954
0.8	329	155	2.12	1.0604	1.0554	1.0502
1.0 (P-*t*-BMA)	101	95.1	1.06	1.0301	1.0250	1.0199

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 g dL^{-1} to 2 g dL^{-1} were prepared one 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 results obtained for homo- and copolymer samples at 50 °C are given in Table 2.

Table 2 Refractive Index (n_o), refractive index increment (dn/dc), second virial coefficient (A_2) and Flory-Huggins interaction parameter at infinite dilution (χ_o) as a function of weight fraction of *t*-butyl methacrylate (*f*) for toluene at 50 °C.

f	n_o	dn/dc	$10^4 \times A_2$ (mol mL g^{-2})	χ_o
0.0 (PMMA)	1.4792	0.0100	3.2872	0.4500
0.2	1.4760	0.0110	4.609	0.4336
0.5	1.4715	0.0130	2.980	0.4603
0.8	1.4669	0.0148	6.168	0.4245
1.0 (P-*t*-BMA)	1.4588	0.0161	11.27	0.3701

Vapor pressure measurements were carried out as described in the literature [15] 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.

For the vapor pressure measurements, samples with weight fractions of the polymer ranging from 0.37 to 0.85 and a total volume of 2 mL were prepared 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 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%.

3 Theoretical background

The approach was first formulated for the Gibbs energy of dilution, in view of the fact that it is the solvent activity (normally obtained via vapor pressure measurements over a wide range of compositions) which yields the required thermodynamic information in most cases. The following simple phenomenological expression[16] turned out to be suited best for the quantitative description of the composition dependence of the base molar chemical potential of the solvent $\Delta\overline{\overline{G}}_{solv}$

$$\frac{\Delta\overline{\overline{G}}_{solv}}{RT} = \ln\frac{p}{p_o} = \left(z-k\right)w + b\,w^2 + c\,w^2\left(1-2w\right) + z\ln\left(1-w\right) \tag{1}$$

which is for the sake of convenience formulated in terms of weight fractions w instead of the frequently used volume fractions. Out of the four system specific parameters this relation contains two (k and z) which are characteristic for the components of the mixture. The parameter k refers to the high molecular weight solute and z to the solvent. In the light of lattice theories k and z can be interpreted as the inverse of the numbers of segments the polymer and of the solvent respectively. In the practical application of the above relation the parameter k is calculated from the known molar masses of the polymer and that of the solvent according to

$$k = \frac{M_{solvent}}{M_{polymer}} \tag{2}$$

whereas z is treated as adjustable parameter. According to experience z is normally on the order of unity[14]; depending on the particular system it may however assume values as low as 0.1 and as high as 10 and even more. The parameters b and c characterize the mixture; b constitutes a binary (differential) interaction parameter between the components and the parameter c is only required if the presence of a second macromolecule in the immediate vicinity of a polymer/solvent contact causes extra effects.

Eqn (1) yields the following relation[14] for the base molar Gibbs energy of mixing, $\Delta\overline{\overline{G}}$

$$\frac{\Delta\overline{\overline{G}}}{RT} = z(1-w)\ln(1-w) + k\,w\ln w + b\,w(1-w) - c(1-w)w^2 \tag{3}$$

For the present study eqn (3) needs to be rewritten to account for the fact that one and the same solvent results in different effective numbers of segments depending on the solute, i.e. on the parameter f. For a comparison of the experimental observations it is mandatory to define the segment for all subsystems in the same manner. For that purpose we are setting the z value of the solvent by definition unity, i.e. we divide eqn (3) by z, as formulated below

$$\begin{aligned}\frac{\Delta\overline{\overline{G}}{}^{*}_{mix}}{RT} = {} & \frac{z}{z}(1-w)\ln(1-w) + \frac{k}{z}w\ln w + \frac{b}{z}w(1-w) - \frac{c}{z}(1-w)w^2 \\ & (1-w)\ln(1-w) + k^{*}w\ln w + b^{*}w(1-w) - c^{*}(1-w)w^2\end{aligned} \tag{4}$$

The asterisks in the above expression serve as a reminder for the fact that the Gibbs energy of mixing now refers unfailingly to *one mol of segments*, where the size of the segment is defined by the molar mass of the solvent. This procedure establishes a common basis for the discussion, because the amount of matter is identical for the solutions of all copolymers in a given solvent.

The condition for the minimum of the Gibbs energy calculated from eqn (4) reads

$$\begin{aligned}&\frac{d\left(\Delta\overline{\overline{G}}{}^{*}_{mix}/RT\right)}{d\,w} = \\ &= k^{*}\ln(w) - \ln(1-w) + 3c^{*}w^{2} - 2w(b^{*}+k^{*}) + b^{*} + c^{*} - 1 = 0\end{aligned} \tag{5}$$

The enthalpies of mixing can be calculated by means of the following relation

$$\frac{\Delta \overline{\overline{H}}^{*}}{RT} = T\left[\frac{d\,k^{*}}{dT}\,w\ln w + \frac{d\,b^{*}}{dT}\,w\left(1-w\right)\right] \tag{6}$$

4 Vapor pressures and their modeling

All experimental data of the copolymer solutions of present interest in either toluene or in chloroform[3] can be modeled quantitatively by means of eqn (1). Only two parameters need to be adjusted, because *k* is given by the molar masses of the components (eqn (2)) and *c* can be set zero.

4.1 Toluene

Fig. 1 shows the reduced vapor pressures measured in the case of toluene at 70 °C. The dependencies obtained for the other temperatures look very similar. The parameters describing them quantitatively are reported in Table 3.

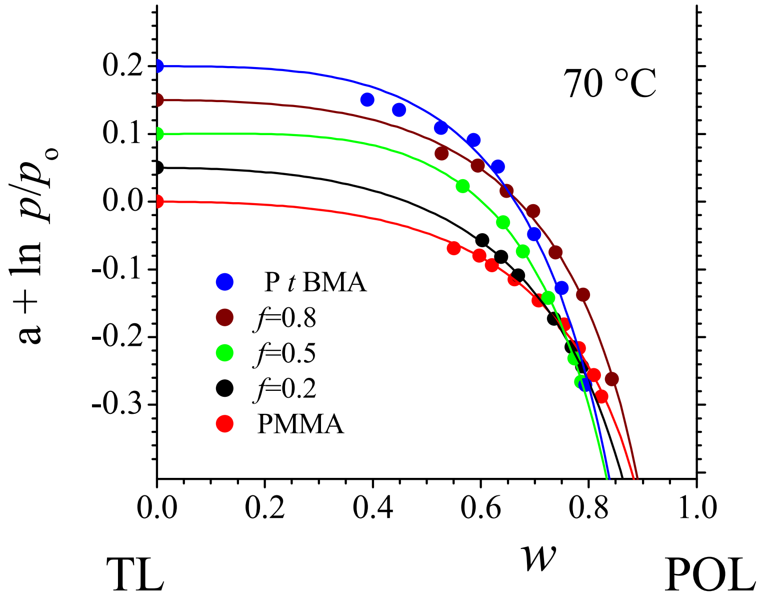

Fig. 1. Reduced vapor pressures of toluene as a function of polymer concentration at 70 °C for the different copolymers. For better visibility the data are shifted on the ordinate by increments of 0.05.

All curves were all calculated by means of eqn (1) and the parameters collected in Table 3. As an example for the dependence of these parameters on the composition of the copolymers they are in Fig. 2 displayed for 30 °C.

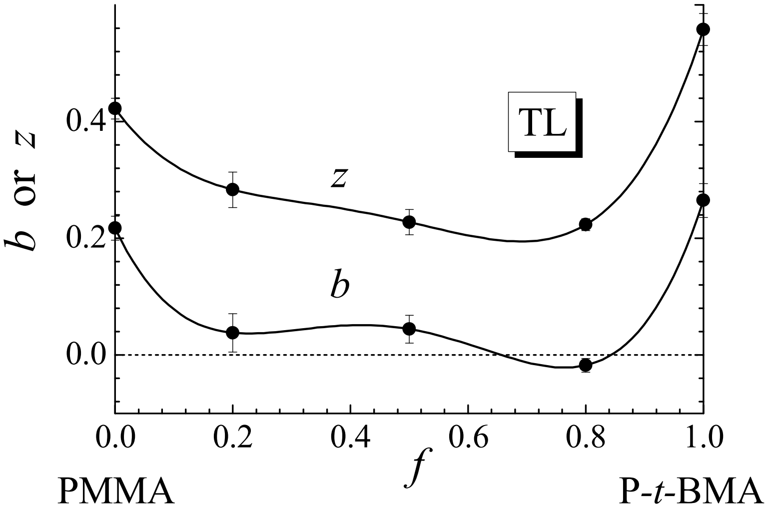

Fig. 2. Example for the dependence of the system specific parameters *b* and *z* on the composition of the copolymer for toluene and 30 °C.

The phenomenological thermodynamic meaning of the two adjusted parameters can be seen from eqn (3): The solvent quality rises as *z* and *k* become larger, where *k* is predefined and inversely proportional to the molar mass of the polymer (eqn (2)). The opposite is the case if the *b* values increase. For *f* =0.8 and 30 °C both contributions are according to Fig. 2 favorable; otherwise they are counteracting.

4.2 Chloroform

In an earlier work[3] we have also studied the solution behavior of the present copolymer in chloroform at 50 °C. These results were modeled and discussed by means of an approach accounting explicitly for chain connectivity and conformational relaxation[17-19]. Here we evaluate these vapor pressure data on the basis of the unified approach[14] as a further check of its generality and for the sake of a comparison of the solvent qualities of toluene and chloroform.

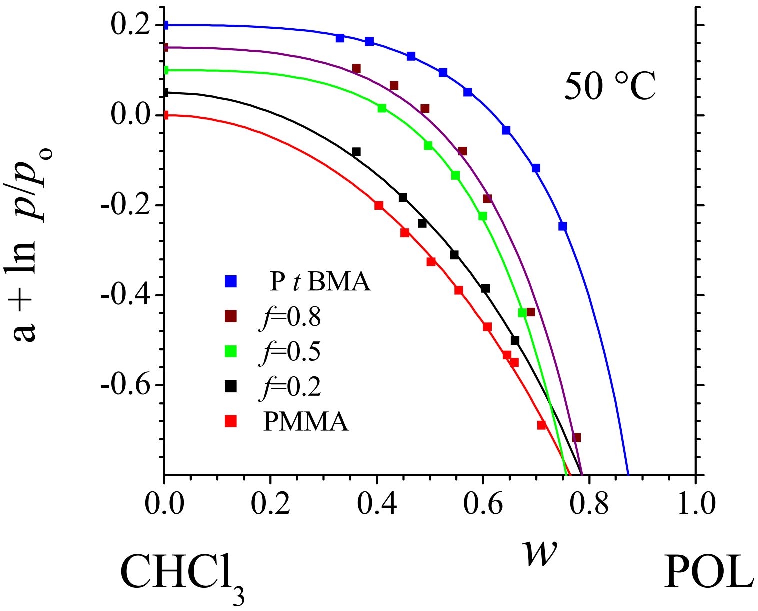

Fig. 3. As **Fig. 1** but for chloroform instead of toluene.

The dependence of the system specific parameters on the composition of the copolymers is shown for chloroform in Fig. 4. The results for the two solvents differ even qualitatively (toluene: cf. Fig. 2) despite the fact that both are good solvents. Chloroform turns out to be uncommonly favorable for PMMA and the PMMA-rich copolymers due to the fact that both parameters, *z* and *b*, are advantageous.

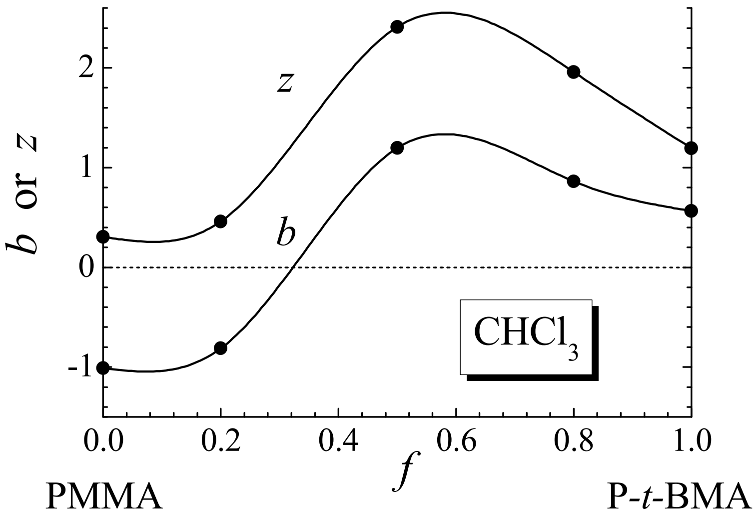

Fig. 4. Dependence of the system specific parameters *b* and *z* on the composition of the copolymer for chloroform and 50 °C

The entire set of parameters obtained from the evaluation of the vapor pressure data according to eqn (1) is collected in Table 3.

Table 3 System specific parameters of eqn (1) and their experimental uncertainties for the solutions of the copolymers in either toluene or chloroform at the different indicated temperatures. The parameter c is not required for the modeling of the present systems and can be set zero.

TL	***f***	***z***	±	***b***	±	$k\ 10^4$
30 °C	0	0.422	0.018	0.218	0.020	9.03
	0.2	0.283	0.030	0.038	0.033	12.10
	0.5	0.228	0.022	0.045	0.024	9.69
	0.8	0.223	0.010	- 0.017	0.012	5.30
	1	0.558	0.027	0.265	0.029	8.63
50 °C	0	0.369	0.010	0.123	0.011	9.03
	0.2	0.409	0.026	0.062	0.030	12.10
	0.5	0.421	0.015	0.116	0.017	9.69
	0.8	0.344	0.048	0.053	0.058	5.30
	1	0.760	0.034	0.393	0.036	8.63
70 °C	0	0.399	0.019	0.124	0.022	9.03
	0.2	0.501	0.011	0.140	0.013	12.10
	0.5	0.917	0.016	0.534	0.018	9.69
	0.8	0.538	0.030	0.192	0.035	5.30
	1	0.954	0.086	0.470	0.092	8.63
$CHCl_3$	***f***	***z***	±	***b***	±	$k\ 10^4$
50 °C	0	0.306	0.116	- 1.010	0.108	13.00
	0.2	0.460	0.177	- 0.812	0.155	17.60
	0.5	2.412	0.069	1.198	0.062	14.10
	0.8	1.957	0.172	0.861	0.176	7.70
	1	1.194	0.034	0.564	0.033	12.50

4.3 Interrelation of parameters

Comparing eqn (3) with the corresponding expression of the Flory-Huggins theory suggests that the parameter *z* should be primarily of entropic nature whereas parameter *b* should be dominated by enthalpy effects. Based on this supposition and the general experience that enthalpy and entropy contribution cannot be changed independently we look in Fig. 5 for an interrelation of *b* and *z* in the case of toluene.

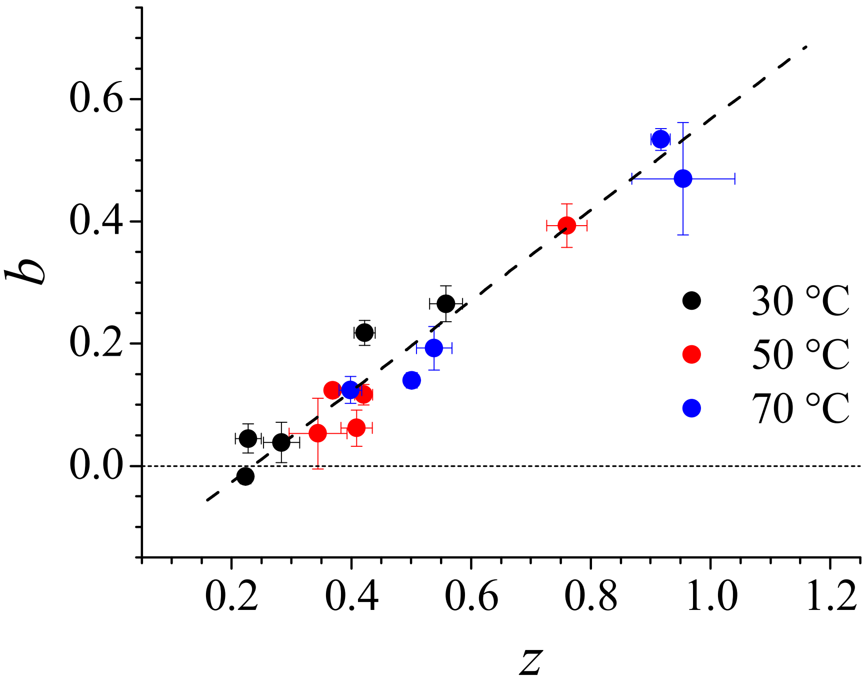

Fig. 5. Interrelation of the system specific parameters for the solutions in toluene. (b= - 0.175+0.742 *z*)

Indeed it is obvious that the system specific parameters are not independent of each other. However, according to information on the solutions in chloroform the interrelation may obviously vary from solvent to solvent. For this solvent only the data for *f* = 0.5, 0.8 and 1.0 (i.e. for sufficiently large content of t-BMA) fall on the same line; for PMMA and PMMA rich copolymers - for which chloroform is an extremely good solvent - the *b* values at low *z* values are on the order of – 1 instead of approximately zero.

5 Normalized parameters

For a comparison of the interactions of different polymers with a given solvent it is necessary to establish a common basis, because the modeling of each binary system yields an individual characteristic *z* value for one and the same solvent depending on the solute. In other words: The number of effective segments ascribed to a solvent will normally not be independent of the solute. This situation also implies that the amount of substance will differ from system to system for one mol of segments.

The way out of the situation consists in the normalization of the parameters as described in eqn (4). Dividing the entire eqn (3) by *z* ensures that the molar mass of the solvent molecule defines the segment in all cases. We can now plot b^* as a function of f and assess the interaction of the different copolymers with toluene by means of this parameter. Although the b^* already contains the most important thermodynamic information, some uncertainties concerning the exact solvent quality remain because of the neglect in the dissimilar molar masses of the different copolymers. According to model calculations by means of data published for the system benzene/PDMS[20] the effects are, however, on the order of the experimental uncertainties only. Because of the just described situation we refrain from the discussion of $b^*(f)$ and refer to Fig. 9, which compares the solvent quality as a function of copolymer composition in terms of the Gibbs energies of mixing.

For the more detailed discussion of the mixing thermodynamics we require the temperature dependencies of the parameters b^* and k^* as formulated in eqn (6) to obtain access to the enthalpies and consequently entropies of mixing. The following two graphs show the experimental results. Interpreting k^* as dominated by entropy and b^* as being primarily of enthalpic nature, the observation that the temperature influences on the two parameters are opposite is not surprising. A more detailed analysis is being given in the next section.

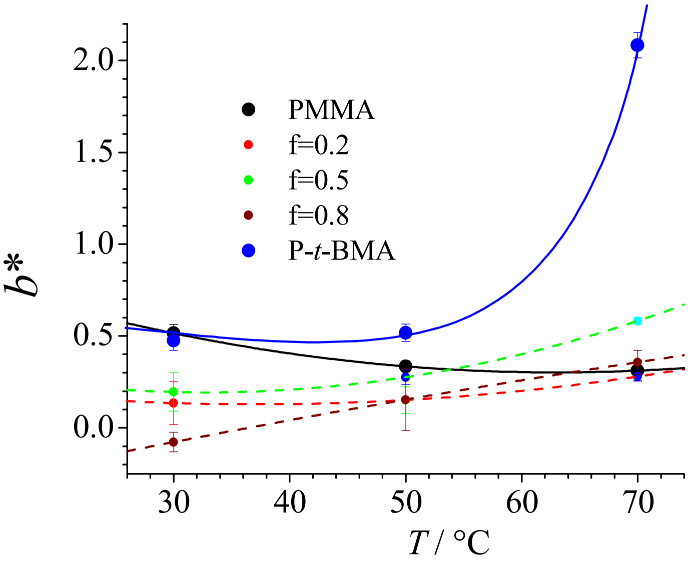

Fig. 6. Temperature dependence of the parameter b^* for the copolymers of the indicated compositions.

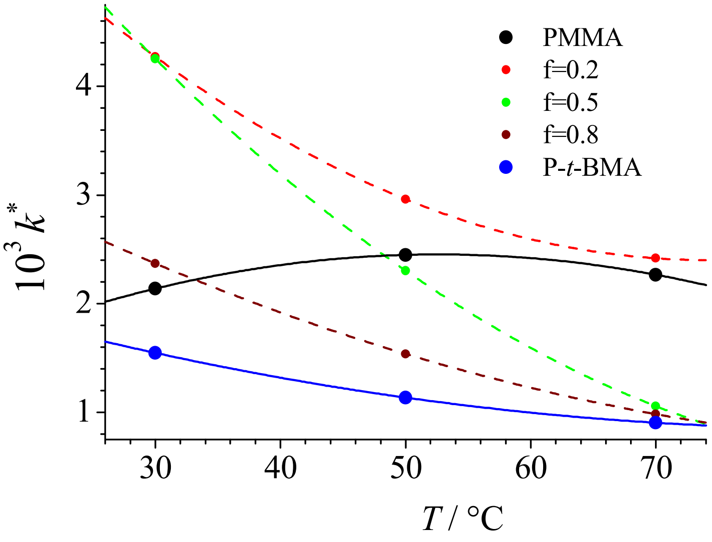

Fig. 7. As Fig. 6 but for the parameter k*

6 Mixing thermodynamics

A central item of the present study concerns the question, how the quality of a given solvent changes with the composition of the copolymers. If the systems under investigation could be described by the Flory-Huggins theory (composition independent interaction parameter χ) the answer would be easy: The lowest χ value would indicate the most favorable interaction. Because this is not the case here we must evade to another criterion; here we are making direct use of the Gibbs energies of mixing. As long as the individual curves for the copolymers of different monomer contents do not intersect, the largest reduction of the Gibbs energy at a given composition of the system signifies the best solvent. An easier to quantify and simpler criterion is the depth of the minimum in the Gibbs energy of mixing.

6.1 Gibbs energies of mixing

Fig. 8 gives an example for the dependence of Gibbs energies of mixing on the weight fraction of the polymers, calculated by means of eqn (4) from the parameters collected in Table 3 for the different polymers.

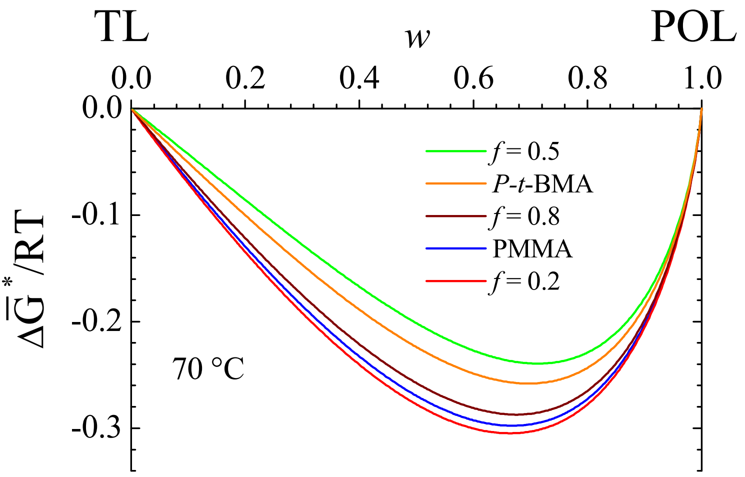

Fig. 8. Example (70 °C) for the Gibbs energy of mixing copolymers of indicated composition with toluene.

For a common validation and comparison of solvent quality the depths of the minima are in Fig. 9 plotted as a function of polymer composition for the indicated temperatures. The most striking features of these dependencies are the observed extrema: They indicate that the interaction of the copolymers with toluene is best if the content of the minor monomer remains moderate, whereas it becomes worst if the fractions of MMA and *t*-BMA are comparable.

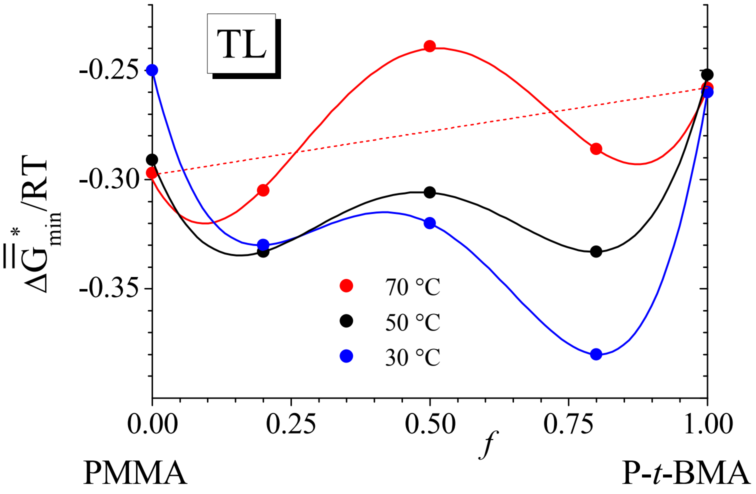

Fig. 9. Minima of the Gibbs energies of mixing as a function of polymer composition for the indicated temperatures

In Fig. 10 we are comparing the solvent powers of toluene and chloroform[3]. The data indicate that $CHCl_3$ is dramatically better for the homopolymer PMMA and for the MMA rich copolymers than TL; only for a predominance of the *t*-BMA units in the copolymer the thermodynamic quality of the solvents becomes comparable. This finding is corroborated by published caloric data[21]: The mixing of $CHCl_3$ and PMMA is approximately twice as exothermal as for TL and PMMA. It is also interesting to note that the dipole moments of the solvents are markedly dissimilar ($CHCl_3$ = 1.15 D; TL = 0.31 D). A more detailed molecular explanation for the present observation has to be sought in two types of dissimilarities of the components: Differences in the fraction of their lyophilic and lyophobic parts (controlling the interaction between them) and in their molecular shapes (causing for instance diverse excess volumes of mixing with all their thermodynamic consequences).

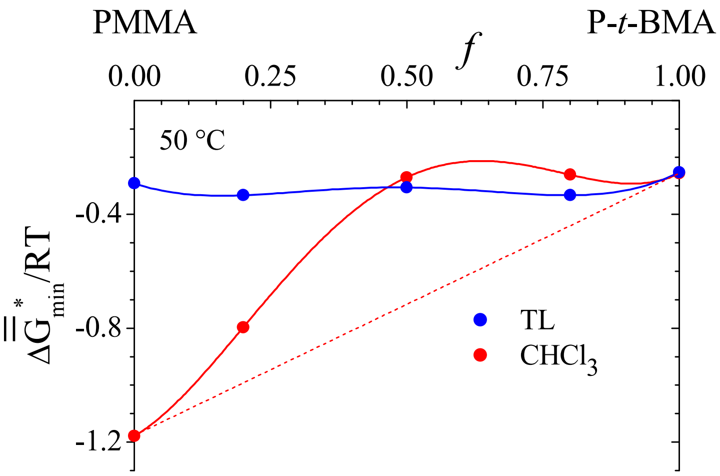

Fig. 10. Comparison of the thermodynamic quality of chloroform with toluene at 50 °C in a diagram like that shown in Fig. 9

The complicated dependence of solvent quality on the composition of the copolymer documented in the last two graphs for both solvents was not anticipated. One would rather expect either a linear variation or only one type of extremum in the depth of the minimum of the Gibbs energy of mixing as a function of f. Experiments yield two minima (in case of $CHCl_3$ the one at low f is shifted to the homopolymer PMMA) and one maximum. The explanation of the minima seems natural: The adverse interaction between the MMA and the t-BMA units favors the insertion of solvent between them, i.e. increases the mixing tendency.

However, if this were the sole effect, only one minimum should be found, namely around $f = 0.5$. What we therefore lack is a reasonable explanation for the minimum in solvent quality (maxima of the curves in Fig. 9 and Fig. 10) for copolymers composed of comparable amounts of both types of monomers. One possibility could lie in Gibbs energetically preferred arrangements between MMA and *t*-BMA units (like special clusters) that can be established under these conditions. This supposition implies a reduction of the mixing tendency of the polymers with the solvent and explains the observed minima of the solvent power. The existence of special ternary interactions of the type toluene/MMA/*t*-BMA could also contribute to the observed behavior.

6.2 Enthalpies and entropies of mixing

In the case of toluene we have studied the influences of temperature on its vapor pressures above the copolymer solutions. By means of the temperature dependence of the system specific parameters and eqn (6) we can therefore calculate the enthalpies of mixing. Fig. 11 shows as an example the results for 50 °C.

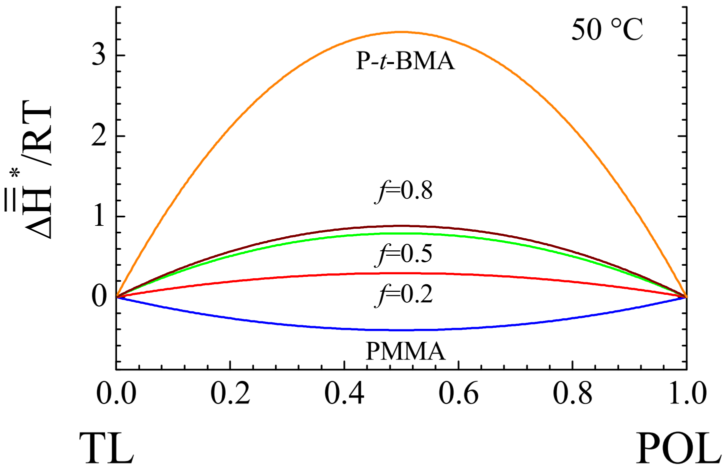

Fig. 11. Example (50 °C) for the enthalpies of mixing copolymers with the indicated composition with toluene

For a joint assessment of all results we plot in Fig. 12 the extrema of the heats of mixing as a function of copolymer composition for the different temperatures, by analogy to Fig. 9. The curves shown in Fig. 12 are guides for the eye only and must not be over interpreted.

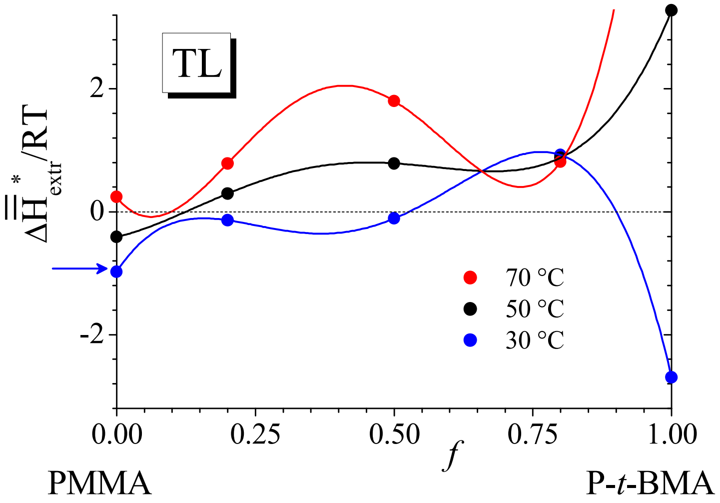

Fig. 12. Extreme values of the enthalpies of mixing the copolymers with toluene as a function of *f* for the indicated temperature. The value for *f* = 1 and 70 °C is 10. The blue arrow indicates the calorimetric results[21] for PMMA at 25 °C.

In order to check the validity of the individual data points we have searched the literature for independent information on the heat effects of the homopolymer solutions. In the case of PMMA we were successful and found a publication studying the heats of mixing of PMMA with a number of solvents[21] among them toluene and chloroform. For the system TL/PMMA and 298 K the authors report a minimum value of – 23.7 J/g, which yields $\Delta\overline{\overline{H}}^{*}/RT = -0.914$. The agreement of the present data stemming from the temperature dependence of vapor pressures with this directly obtained calorimetric value is surprisingly good. This does, however not imply that the accuracy is as high in all cases. Nevertheless some solid conclusions can be drawn from the present results. These are above all the pronounced temperature influences on the heats of mixing in the regions around *f* = 0.4 and *f* = 1. T-effects are obviously less pronounced for small *f* and for *f* around 0.75.

For the sake of completeness of the thermodynamic information Fig. 13 gives - as an example - the composition dependence of the entropy of mixing at 50 °C. This graph shows the entropic predominance of the driving force for establishment of a homogeneous state for all (co)polymers under consideration with the exception of PMMA.

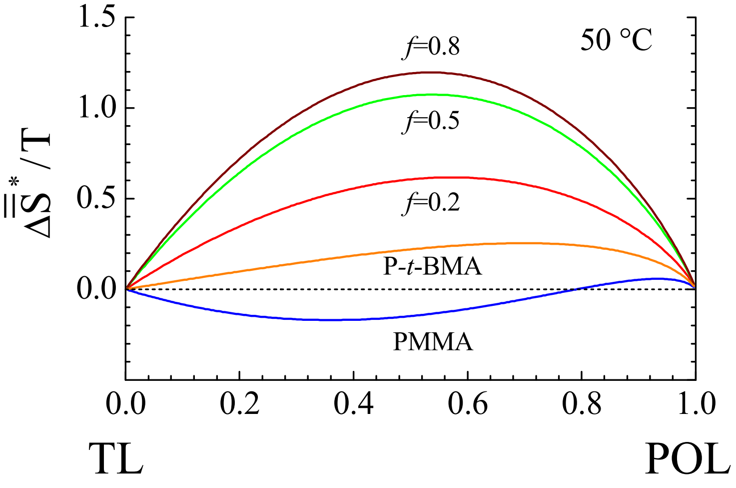

Fig. 13. Example (50 °C) for the entropies of mixing copolymers with the indicated composition with toluene.

7 Conclusions

The present study documents the capability of the unified approach to describe the composition dependence of vapor pressures above solutions of random copolymers quantitatively by means of two parameters. It gives full access to the thermodynamic information on the systems of interest if the measurements are also performed as a function of temperature.

The thermodynamic quality of a given solvent for the present copolymers of variable comonomer content is quantified by the minimum Gibbs energy of mixing as a function of polymer concentration. The present results reveal complex dependencies: With rising *t*-BMA content of the copolymer the solvent quality improves, passes a maximum, which is followed by a minimum, and finally runs through a second maximum again before the curve ends at the homopolymer. This behavior is the same for all temperatures. The occurrence of the minima can be easily rationalized in terms of unfavorable interactions between the two types of monomers. Concerning the reasons for the occurrence of the maximum we can presently only speculate. The two most obvious options are favorable interactions between the comonomers if their concentration in the copolymer is comparable or extra interactions for ternary contacts between the solvent and the two types of monomers.

The influences of the copolymer composition on the heats and on the entropies of mixing are again uncommonly complex. They pass maxima and minima again and turn out to vary strongly with temperature in some cases, above all for P-*t*-BMA. Regrettably the possibility to compare the present results with independent data is limited. We could only find one publication[21] which reports pertinent calorimetrically determined heats of mixing, namely for the system toluene/PMMA. The agreement between the information obtained by independent methods is very promising. An answer to the question, whether the complex thermodynamic behavior observed for the present copolymers is general must presently remain open. It requires directed experiments for more dissimilar comonomers.

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Dependence of Solvent Quality on the Composition of Copolymers: Experiment and Theory for Solutions of P(MMA-ran-*t*-BMA) in Toluene and in Chloroform

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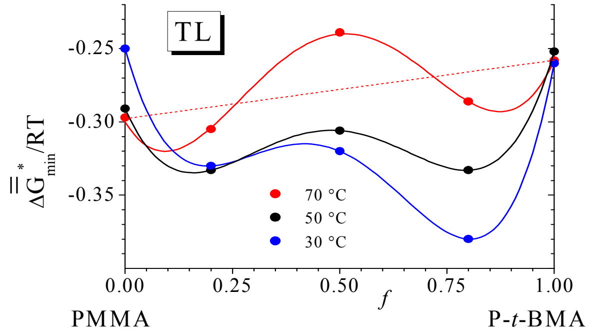

Solvent quality of toluene for P(MMA-*ran*-*t*-BMA) as function of the *t*-BMA content *f,* quantified by the minima in the Gibbs energies of mixing toluene with the individual copolymer.