

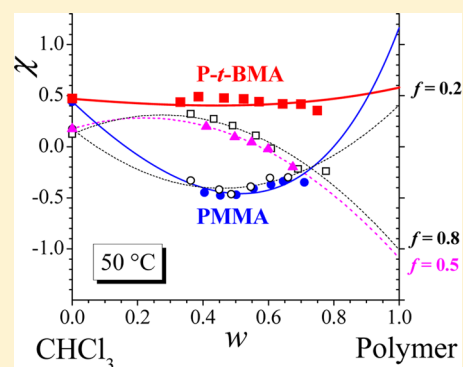
# Thermodynamics of Copolymer Solutions: How the Pair Interactions Contribute to the Overall Effect

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**ABSTRACT:** Vapor pressure measurements were performed for solutions of poly(methyl methacrylate-*ran-tert*-butyl methacrylate) with different weight fractions of *tert*-butyl methacrylate units, and their parental homopolymers in chloroform at 323 K, over a large domain of concentrations. The Flory–Huggins interaction parameters obtained from these experimental investigations show complex dependences of the Flory–Huggins interaction parameter on concentration and copolymer composition. This behavior can be modeled by taking into account an approach which considers the ability of the polymers to rearrange in a response to changes in their molecular surroundings [*Adv. Polym. Sci.* **2011**, 238, 1–66]. According to this concept, the mixing process is subdivided into two clearly separable steps and accounts for the specific interactions between the solvent and copolymer segments.



## INTRODUCTION

Numerous attempts have been made to extend or to modify the Flory–Huggins theory in order to obtain an adequate expression which illustrates as well as possible the thermodynamic behavior in agreement with the experimental observations. Recently<sup>1</sup> it was shown in detail for different types of polymeric structures that the deficiencies of the original Flory–Huggins theory can be eliminated by taking into account the hitherto ignored consequences of chain connectivity and considering the ability of macromolecules to rearrange after mixing with the solvent in such a manner that the Gibbs energy of the system is minimum. In this context, many efforts have been undertaken over the past decade to examine the interactions exhibited in polymer solutions,<sup>2–8</sup> homopolymer mixtures,<sup>9</sup> and random<sup>10</sup> and block<sup>11</sup> copolymers, driven both by the fundamental interest and by the potential technological applications of these materials. The investigation of thermodynamic properties for copolymer solutions may have a special contribution in understanding the behavior of polymer blends and also may have a potential interest for a variety of applications including the recovery of organic vapors using polymeric membranes, packaging and coating materials, drug-delivery systems, biocompatible materials, and so on. Because interactions between the monomer units of a copolymer influence the solution properties of copolymers, theoretical and experimental studies<sup>1,10–14</sup> were undertaken for a better understanding of molecular interactions in multicomponent systems. Some copolymer or polymer mixtures are miscible although their corresponding homopolymers are not miscible; for example, over a range of acrylonitrile content, styrene/acrylonitrile copolymers are miscible with poly(methyl methacrylate) but neither polystyrene nor polyacrylonitrile is miscible with poly(methyl methacrylate). Similarly, over a

composition range, butadiene/acrylonitrile copolymers are miscible with poly(vinyl chloride) while none of the binary combinations of the homopolymers [polybutadiene, polyacrylonitrile, and poly(vinyl chloride)] are miscible. This behavior has been attributed to “intramolecular repulsion” between unlike copolymer segments.<sup>14</sup> An opposite effect has been observed for poly(styrene-*ran*-methyl methacrylate) in different solvents. The combined effects of polar MMA segments and polar solvent interactions on the motion of the aromatic rings cause a loss in the entropy of the copolymer, resulting in a decrease in acetone and methyl acetate absorption.<sup>10</sup>

This contribution aims to improve the understanding of the thermodynamic behavior of random copolymers in solution. The effects of changes in the copolymer composition on their interaction with a given solvent (chloroform in the present study) were investigated for the first time for poly(methyl methacrylate-*ran-tert*-butyl methacrylate) of different compositions. For the theoretical interpretation, it used a new approach<sup>1–4</sup> which is able to describe complex composition dependences of Flory–Huggins interaction parameters of random copolymers if the behavior of their homopolymers is known.

## EXPERIMENTAL SECTION

Three poly(methyl methacrylate-*ran-tert*-butyl methacrylate) [P(MMA-*ran-t*-BMA)] samples with weight fraction of *tert*-butyl methacrylate (*f*) in the sample of 0.2, 0.5, and 0.8, as well as poly(*tert*-butyl methacrylate) (P-*t*-BMA) and poly(methyl methacrylate) (PMMA) samples, were commercial products

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**Table 1.** Molecular Weights, Polydispersities,  $A_2$  and  $\chi_o$  of (Co)polymer Samples as a Function of Weight Fraction of *tert*-Butyl Methacrylate ( $f$ ) in the Sample

$f$	$M_w$ (kg mol <sup>-1</sup> )	$M_n$ (kg mol <sup>-1</sup> )	$M_w/M_n$	$10^4 \times A_2$ (mol mL g <sup>-2</sup> )	$\chi_o$
0.0 (PMMA)	99.4	92.1	1.08	5.1733	0.441
0.2	164	67.8	2.43	25.8848	0.215
0.5	196	84.7	2.32	32.1179	0.174
0.8	329	155	2.12	18.9743	0.323
1.0 (P- <i>t</i> -BMA)	101	95.1	1.06	2.5913	0.477

purchased from Polymer Standard Service, Germany. The samples were dried at 313 K in a vacuum oven for 3 days before use. Chloroform (CHCl<sub>3</sub>) was of p.a. grade and purchased from Fluka.

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<sup>-1</sup> to 2 g dL<sup>-1</sup> were prepared 1 day in advance and kept at 323 K in an oven. Prior to measurements, they were filtered through a 0.45 μm membrane filter (Milipore) directly into the thoroughly cleaned optical cells (Helma, Müllheim, Germany) and thermostated in the light scattering apparatus for 15 min. The characteristics of homo- and copolymer samples, determined by light scattering measurements at 323 K, are given in Table 1.

Vapor pressure measurements were carried out as described in the literature<sup>4–8</sup> by means of an apparatus consisting of the headspace-sampler Dani HSS 3950, Milano (Italy) and a normal gas chromatograph Shimadzu GC 14B Kyoto (Japan). This procedure gives access to the amount of 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, we have prepared samples with weight fractions of the polymer ranging from 0.32 to 0.80 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 323 K for 2 weeks, agitated 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%.

## RESULTS AND DISCUSSION

Vapor pressure measurements constitute the main source of information concerning the interaction of chloroform with the homopolymers PMMA and P-*t*-BMA and with different random copolymers made up of the two types of monomeric units. Figure 1 shows the primary data in terms of the reduced vapor pressures ( $p/p_o$ , where  $p$  and  $p_o$  represent the vapor pressure of the polymer solution and pure solvent, respectively) as a function of  $w$ , the weight fraction of the polymers.

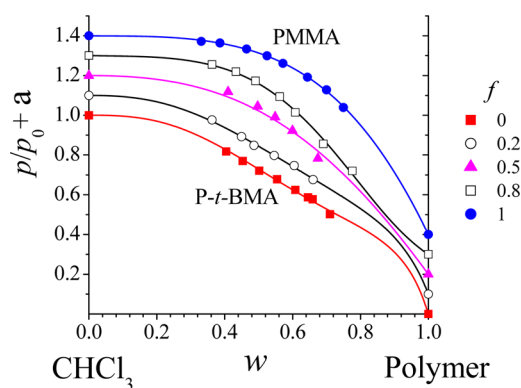
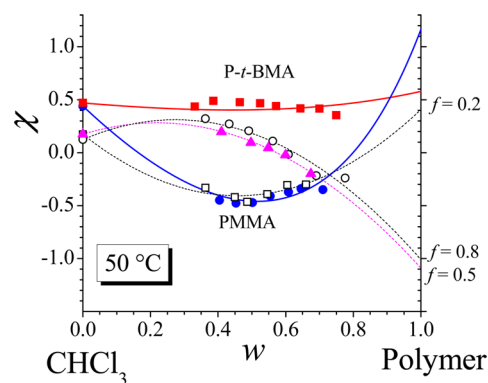
**Figure 1.** Composition dependence of the reduced vapor pressures measured above solutions of PMMA, P-*t*-BMA, and different random copolymers of MMA and *t*-BMA at 323 K;  $f$  is the weight fraction of *t*-BMA in the copolymer. For better visibility, the individual curves are displaced by 0.1.**Figure 2.** Dependence of the Flory–Huggins interaction parameters  $\chi$  on the weight fraction  $w$  of the polymers for solutions of the different polymers in chloroform; the weight fraction of *t*-BMA units in the copolymer is denoted as  $f$ .

Figure 2 collects the comprehensive thermodynamics of these systems in terms of Flory–Huggins interaction parameters,  $\chi$ . For highly dilute solutions the information was obtained via light scattering, and the rest stems from the vapor pressure measurements. The curves connecting the data are modeled by means of eq 3. The most striking feature of this graph is the observation that the copolymer containing 20 wt % of *t*-BMA units deviates only moderately from the behavior of PMMA, whereas the incorporation of 20 wt % MMA units into P-*t*-BMA has dramatic consequences.

The limiting value of the Flory–Huggins interaction parameter  $\chi_o$  shown in Figure 2 was calculated from the second osmotic virial coefficient  $A_2$  according to

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

where  $\bar{V}_1$  is the molar volume of the solvent and  $\rho_2$  is the density of the polymer. The  $\chi$  values at finite polymer concentrations were calculated from the vapor pressure of the solvent by means of the following relation:

$$\chi = \frac{\ln(p/p_0) - \ln(1-w) - (1-1/N)w}{w^2} \quad (2)$$

$p_0$  is the vapor pressure of the pure solvent, and  $N$  is the number of polymer segments calculated from the ratio of the molar masses of the polymer and of the solvent, respectively.

The following relation has proven to describe the thermodynamic properties of chain molecules quantitatively:<sup>1</sup>

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

This approach is based on a conceptual subdivision of the dilution process into two steps: (i) contact formation, keeping the conformations of the components unchanged, characterized by the parameter  $\alpha$ , and (ii) relaxation into the equilibrium state by molecular rearrangements, characterized by the composed parameter  $\zeta\lambda$ . The parameter  $\nu$  is required to account for dissimilar effective surfaces of the solvent molecules and of the polymer segments;  $\varpi$  is only needed for systems exhibiting special interactions between the components, like hydrogen bonds. Equation 2 attains its simplest form for theta systems ( $\zeta\lambda = 0$ ), equal effective segmental surfaces of the components ( $\nu = 0$ ), and the absence of specific interactions ( $\varpi = 0$ ). Under these conditions the original Flory–Huggins expression (composition independent interaction parameter, here  $\alpha$ ) is retained. Equation 3 yields the following expression for limiting value of  $\chi$  for infinite dilution:

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

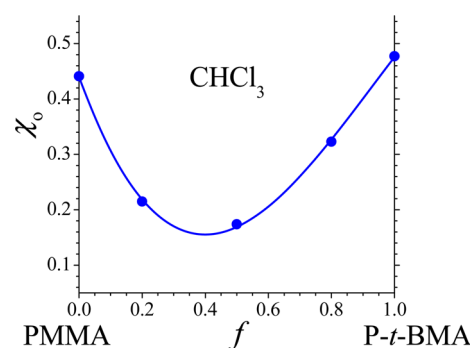
The numerical values of the parameters of the present approach were obtained by means of eq 5 resulting upon the insertion of  $\alpha$  from eq 4 into eq 3:

$$\chi = \frac{\chi_o + \zeta\lambda}{(1-\nu w)^2} - \zeta\lambda(1+2w) + \varpi w(3w-2) \quad (5)$$

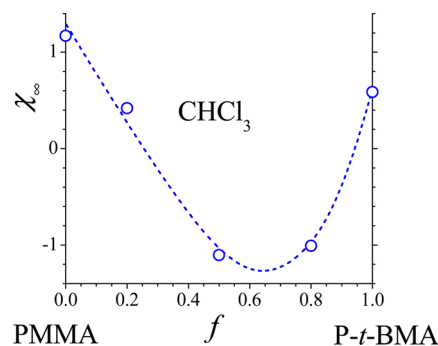
For the fitting  $\chi_o$  is prescribed because of its high accuracy. Thus, the thermodynamic behavior of copolymers in solution can be evaluated by means of the relation 5, adjusting three parameters, namely  $\zeta\lambda$ ,  $\nu$ , and  $\varpi$ . The parameter  $\chi$  is experimentally determined via light scattering experiments, osmosis, or vapor pressure measurements.<sup>2,4–11,15,16</sup> In the following, we are discussing the different system specific parameters separately.

Figure 3 shows how  $\chi_o$  changes with the composition of the copolymer; for the sake of completeness the complementary information, i.e., the interaction parameter in the limit of vanishing solvent content ( $\chi_\infty$ ), is also depicted (Figure 4).

The uncertainty in  $\chi_\infty(f)$  is necessarily much higher than that of  $\chi_o(f)$  due to the required extrapolation procedure (according to Figure 2). Nevertheless the essential finding of both dependencies is the same, namely, that the dilution tendency is largest (smallest  $\chi$  values) for copolymers containing comparable amounts of both monomer types. This finding can be easily rationalized if one assumes that PMMA and P-*t*-BMA are highly incompatible in the pure state. This situation signifies that the insertion of solvent molecules between contacting segments belonging to different polymer chains is



**Figure 3.** Dependence of  $\chi_o$ , the limiting value of the Flory–Huggins interaction parameter for infinite dilution, on the weight fraction  $f$ , of *t*-BMA in the copolymer.



**Figure 4.** Dependence of  $\chi_\infty$ , the interaction parameter in the limit of vanishing solvent content, on copolymer composition.

particularly advantageous if they separate very unfavorably interacting MMA and *t*-BMA units.

In an attempt to understand the totally different outcome of incorporating small amounts of the second monomer type into the respective homopolymer addressed earlier, we are now comparing all parameters required for the modeling of the curves shown in Figure 2. For that purpose we use the *integral* segment molar Gibbs energy of mixing:

$$\frac{\Delta \bar{G}}{RT} = gw(1-w) \quad (6)$$

where  $g$ , the *integral* interaction parameter, is given by<sup>1</sup>

$$g = \frac{\chi_o + \zeta\lambda}{(1-\nu)(1-\nu w)} - \zeta\lambda(2+w) + \varpi w^2 \quad (7)$$

The first challenge lies in the rationalization of the dissimilar solution behavior of PMMA and P-*t*-BMA; the only agreement lies in the observation that  $\varpi = 0$  for both of them. The reason must therefore be sought in the (interrelated<sup>1</sup>) parameters  $\alpha$  and  $\zeta\lambda$ , the leading terms of the first two contributions of eq 3. Figure 5 shows how  $\alpha$  varies with copolymer composition, and Figure 6 gives this information for  $\zeta\lambda$ .

The parameter  $\alpha$  as well as  $\zeta\lambda$  are for the homopolymers considerably larger than for all copolymers and pass a pronounced minimum; furthermore, they are eight to nine times larger for PMMA than for P-*t*-BMA. The latter finding can be interpreted in terms of Gibbs energetically much more favorable contacts between the monomer units of PMMA as compared with P-*t*-BMA. One possible cause for this behavior may lie in the formation of PMMA associates; this reasoning is consistent with literature reports<sup>17,18</sup> concerning the association

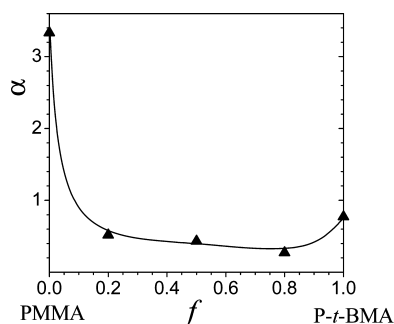


Figure 5. Dependence of the parameter  $\alpha$  (eq 3) on the composition of the copolymer.

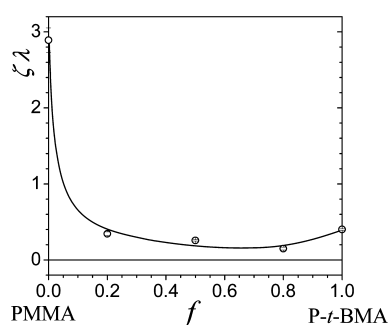


Figure 6. Dependence of the parameter  $\zeta\lambda$  (eq 3) on the composition of the copolymer.

tendency of this polymer. It signifies that the separation of intersegmental contacts by the insertion of a solvent molecule is for PMMA much more costly (larger  $\alpha$ ) than for P-*t*-BMA; the relaxation into the equilibrium state of the system after contact formation is conversely much more favorable (larger  $\zeta\lambda$ ).

We are now dealing with the surprising observation that the parameter  $\varpi$  is required for the description of the thermodynamic properties of the copolymer solutions, but not for the corresponding homopolymers, as demonstrated in Figure 7.

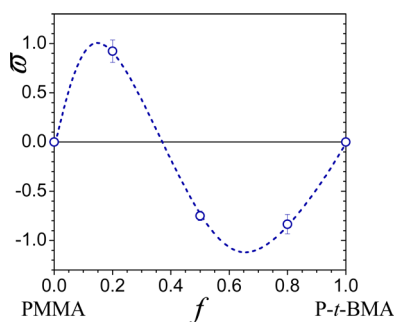


Figure 7. Dependence of the parameter  $\varpi$  (eq 3) on the composition of the copolymer.

At least some tentative explanation can be offered; it is again based on the differences in the association behavior of the homopolymers. On the PMMA side of the composition range, intersegmental contacts between the individual MMA segments are abundant and so stable (the presence of *t*-BMA segments “forces” them together) that their destruction involves considerable Gibbs energies, i.e., large positive  $\varpi$  values are required to model their separation. On the P-*t*-BMA side of the composition range multiple *t*-BMA contacts dominate. From

the observation of  $\varpi < 0$  one may conclude that chloroform is able to mediate the formation of stable clusters between them, probably via favorable interaction with the *tert*-butyl methacrylate groups. In this case the formation of advantageous structures yields a strong driving force toward mixing, i.e., negative  $\varpi$  values. Approximately in the middle of the composition range the contributions of MMA/MMA clusters and of *t*-BMA/ $\text{CHCl}_3$  cluster should compensate so that  $\varpi$  becomes zero. The explanations set out above are plausible but require additional evidence.

Still to be discussed is the composition dependence of the parameter  $\nu$ . Due to the fact that the monomers are chemically bound to each other this parameter is typically on the order of 0.3–0.4 for homopolymers, as in the present case. Molecularly it means that the homopolymer segments (identical in their volume with that of the solvent) expose about 30–40% less surface for interaction with other components.

Figure 8 evidences that the  $\nu$  value changes fundamentally upon the incorporation of comonomer units into the

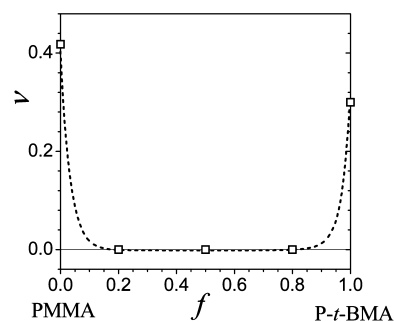


Figure 8. Dependence of the parameter  $\nu$  (eq 3) on the composition of the copolymer.

homopolymers: only about 20 wt % of the second monomer type is required to reach  $\nu \approx 0$ . This behavior corresponds to the pronounced minimum in  $\alpha$  (Figure 5). It is tentatively attributed to the higher effective accessibility of the different monomer units (larger interacting surfaces) as a result of the destruction of local orders prevailing in the homopolymers.

The dependence of parameters  $\alpha$ ,  $\zeta\lambda$ ,  $\nu$ , and  $\varpi$  of the present approach on the composition of the copolymers was in some way or other attributed to the pronounced incompatibility of PMMA and P-*t*-BMA. An attempt is therefore made to obtain information on the interaction between the two homopolymers from the behavior of the copolymers. To that end we modify the so-called single liquid approximation of Scott.<sup>19</sup> This concept was developed for the modeling of ternary systems composed of a mixed solvent (indices 1 and 2) and a homopolymer A. In the present terminology the expression for the interaction of the mixed solvent  $\langle 12 \rangle$  with the polymer A reads:<sup>20–22</sup>

$$g_{\langle 12 \rangle A} = w_1 g_{1A} + w_2 g_{2A} - w_1 w_2 g_{12} \quad (8)$$

where  $w_1$  and  $w_2$  are the weight fractions of the solvent components in the mixed solvent;  $g_{iA}$  represent the corresponding polymer/solvent interaction parameters. If the interaction between the low molecular weight components,  $g_{12}$ , and the interaction of the polymer with the single solvents are known, it is possible to calculate  $g_{\langle 12 \rangle A}$ , i.e. to estimate the behavior of A in the mixed solvent.

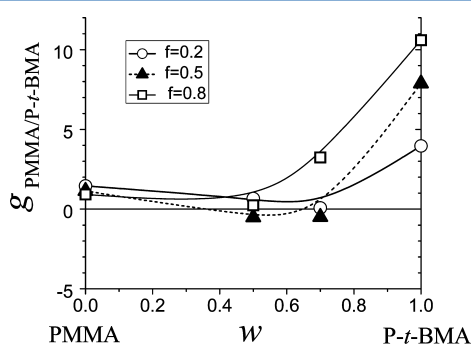


For the present task we adapt eq 8 to describe solutions of random copolymers in a single solvent. Denoting the polymer segments as A and B we can write

$$g_{AB} = \frac{g_{A1}^{f=0}(1-f) + g_{B1}^{f=1}f - g_{AB,1\text{measured}}^f}{f(1-f)} \quad (9)$$

The left-hand side of the above relation represents the interaction parameter between the two homopolymers. It can be calculated from  $g_{AB,1\text{measured}}^f$ , the measured interaction parameter of the copolymer of composition  $f$  with the solvent of interest, if information on the corresponding homopolymers is available. If eq 9 is quantitatively correct, neither the composition  $f$  of the copolymer nor its weight fraction in solution should influence the value calculated for  $g_{AB}$ .

Figure 9 demonstrates that this is expectedly not the case. The observation that each polymer concentration yields a



**Figure 9.** Composition dependence of the interaction parameter between the homopolymers calculated by means of eq 9 from the solution behavior of different copolymers.

different  $g_{AB}$  parameter is in accord with the general experience that interaction parameters vary considerably with composition in most cases. This feature can also explain the comparatively large  $g_{AB}$  values as compared with estimations based on constant interaction parameters. The much less pronounced influence of  $f$  can probably be attributed to the dissimilar distribution of the monomeric units along the polymer chain. Despite these complications and the approximate nature of eq 9 the results are plausible: except for comparable weight fractions of the two monomer types in the copolymer one calculates extremely unfavorable  $g_{AB}$  values. Unfortunately it is impossible to compare the data with independent measurements because of the lack of independent information.

## CONCLUSIONS

The reported results demonstrate how the thermodynamic behavior of random copolymers in solution can be described quantitatively by accounting for the effects of chain connectivity and for the ability of polymer coils to change their spatial extension in response to alterations in their molecular environment.

The question how the behavior of the solutions of random copolymers can be estimated knowing the interaction parameters of the solvent with the corresponding homopolymers cannot be answered in a simple and straightforward manner. This difficulty is above all a consequence of the fact that the individual interaction parameters do normally vary considerably with composition. There is, however, a way out of this dilemma by breaking the gross interaction parameters

down into composition independent contributions, characterizing the features of interaction in more detail. In this work the disassembling is performed in terms of the system specific parameters of eq 7.

The prime quantities of this approach are the leading parameters  $\alpha$  and  $\zeta\lambda$  of the homopolymers. The values obtained for PMMA and for P-*t*-BMA differ pronouncedly and constitute the main reason for the incompatibility of the homopolymers in the blend. With respect to the copolymer solutions this situation leads to Gibbs energetically very favorable clusters. On the PMMA rich side of the copolymer composition the solute tends to form very stable MMA associates, whereas P-*t*-BMA rich copolymers form comparably stable solvent mediated clusters because of the preference of the solvent for the *t*-BMA units.

In the described manner it is possible to rationalize the observation (cf. Figure 2) that the incorporation of small amounts of a comonomer into a homopolymer not only may change its interaction with a given solvent as compared with that of the parent homopolymer dramatically but may even invert the composition dependence of  $\chi$ . Although the present approach is not predictive in actual stage of development, it helps the rationalization of experimental data. Furthermore, it enables orienting considerations concerning the solution properties of random copolymers if the behavior of the parent polymers is known in sufficient detail.

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### Notes

The authors declare no competing financial interest.

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