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Islands of Immiscibility for Solutions of Compatible Polymers in a Common Solvent: Experiment and Theory

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ABSTRACT: Experimentally obtained islands of immiscibility are reported for the systems PS/PVME/THF at 20 °C and for PS/PVME/CH at 55 °C (PS: polystyrene, PVME: poly(vinyl methyl ether), THF: tetrahydrofuran, CH: cyclohexane). THF is a good solvent and CH is a marginal solvent for both polymers. In the case of THF, information on the Flory–Huggins interaction parameters of the three binary subsystems suffices for a qualitative prediction of the phase behavior of the ternary system. Quantitative agreement can be achieved by means of composition-independent ternary interaction parameters. For the marginal solvent CH, the exclusive use of binary interaction parameters wrongly predicts complete miscibility of all three components. In this case, one ternary interaction parameter must be treated as a function of composition in order to match experiment and theory. On the basis of the present results, it can be concluded that the preparation of homogeneous mixtures with arbitrary composition from a pair of compatible polymers and a common solvent is only possible on rare occasions.

1. Introduction

The simplest method to mix two chemically different polymers thoroughly uses solvents that are thermodynamically favorable for both components and evaporates the volatiles once the homogeneous state is reached. According to recent model calculations, the phase state of the thus obtained materials requires careful examination because the blend may be two-phase even if the polymers are compatible. The first reports concerning such phenomena date back to the 70s of the last century.^{1,2} Recent model calculations³ generally predict large islands of immiscibility for such ternary systems. For the above process, they mean that the demixed state passed during blend preparation may be preserved due to the high viscosity of the mixture if the drying takes place too rapidly.

By means of this investigation, we wanted to answer two questions: (i) Are the predicted islands of immiscibility for ternary systems polymer 1/polymer 2/common solvent really as widespread as anticipated? So far there do exist several indications concerning such phenomena^{1,2,4,5} but they might be not representative. The second question (ii) reads: Is it possible to predict such islands from thermodynamic information concerning the corresponding binary subsystems and – if not – how can one model the experimental results?

For the present study, we have chosen joint solutions of polystyrene (PS) and poly(vinyl methyl ether) (PVME) in either tetrahydrofuran (THF), that is in a solvent which is favorable for both polymers, or in cyclohexane (CH), which is marginal for both polymers; the corresponding endothermal theta temperatures are:⁶ 34–35 °C for PS and 51 °C for PVME. We have chosen these two ternary systems because the thermodynamic information concerning the binary subsystems required for the modeling was already available.^{7–9} Section 2 presents the results of cloud point measurements and section 3 starts with a brief recapitulation of the thermodynamic relations used for the quantitative description of the two component mixtures and extends them to ternary systems. In the conclusion of this

part, we describe how the phase diagrams measured for PS/PVME/THF and PS/PVMA/CH can be modeled.

2. Experimental Section

2.1. Materials and Procedures. The polymers used for present measurements and their characteristic data are specified in Table 1. The low molecular weight PS was kindly synthesized anionically by Prof. A. Böker, now University of Aachen; the high molecular weight sample is an industrial product (Vestayron) of the former Hüls AG and PVME was fractionated¹⁰ from an industrial product, (Lutonal M 40) obtained from BASF, by means of the large-scale method of continuous polymer fractionation. The solvents were of p.a. quality and were purchased from Fluka. All cloud and clear points were determined visually; the exact establishment of these conditions was no problem because of the large differences in the refractive indices of the coexisting solutions.

PS 6/PVME 87/THF.

Most of the cloud points were for this ternary mixture determined by preparing homogeneous solutions with a total polymer content of approximately 12 wt % and slowly evaporating the solvent (during several days) until the liquid becomes turbid. The corresponding concentrations were calculated from the known weights of the polymers and the weight of the turbid mixture. The removal of solvent was then carried on until the mixtures become clear again and the clearing compositions were determined analogously. This second set of data for high polymer contents coincides with the cloud points obtained as highly concentrated homogeneous mixtures are diluted by slowly adding solvent via the gas phase in rotating vials. For that reason, we do in the following not distinguish between cloud points and clear points.

PS 240/PVME 87/CH.

Two different types of demixing experiments were performed for this system, depending on polymer concentration. For sufficiently low total polymer concentrations, PS solutions in CH were titrated with solutions of PVME in the same solvent until turbidity becomes visibly and vice versa. In the region of high polymer concentrations, we have prepared inhomogeneous mixtures (located

Table 1. Molar Masses of the Polymer Samples

polymer	M_w	M_n
PS 6	5970	5800
PS 240	240 000	133 000
PVME 87	87 000	64 000

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Table 2. System Specific Parameters (Eq 4) for the Binary Subsystems^{7,8} of PS/PVME/THF at 20 °C; the Subscripts at the Abbreviations of the Polymers State the (Weight Average) Numbers of Segments in Terms of the Molar Volume of THF

system	α	ν	ζ	λ	r
THF/PS ₆₉	1.679	0.324	2.520	0.5	
THF/PVME ₁₀₁₈	1.134	0.257	1.320	0.5	
PS ₆₉ /PVME ₁₀₁₈	-0.0125 ^a	-0.600 ^a	0.0015 ^a	1.5 ^a	1.233

^a These parameters, characterizing the polymer blend, were taken from the literature;⁷ they refer to 100 mL/segment and 20 °C.

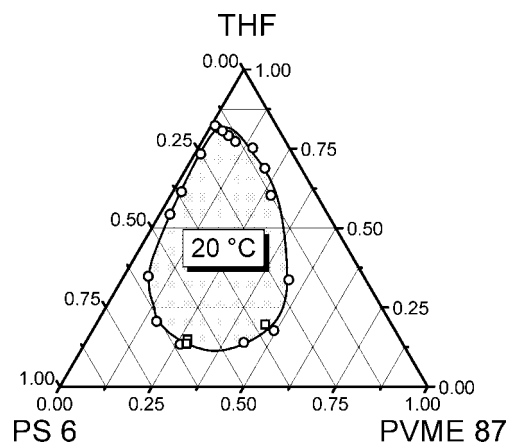


Figure 1. Cloud point curve for the system PS/PVME/THF at 20 °C. ○: resulting from the evaporation of the solvent, □: resulting from the solvent uptake of polymer-rich homogeneous solutions. This curve and all following curves are guides for the eye only.

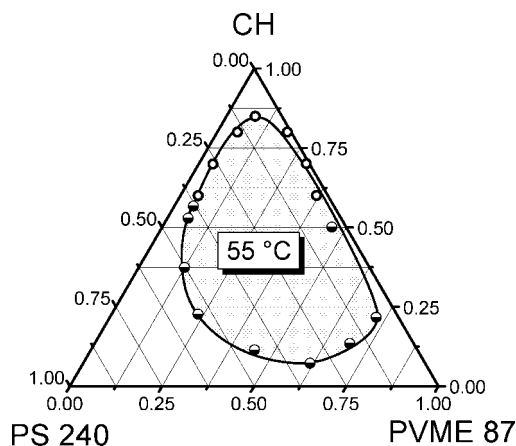


Figure 2. Demixing curve for the system PS/PVME/CH at 55 °C. ○: cloud points obtained by titration, ⊙: clear points reached from the inhomogeneous region.

inside the island of immiscibility) and have slowly (during several days) evaporated the solvent under continuous stirring until the mixture becomes clear.

2.2. Results. Figures 1 and 2 depict the demixing curves obtained for the two different solvents of the compatible polymer blend as described in the last section. With THF and with CH, one observes an extended island of immiscibility. The location of the two-phase area within the Gibbs triangle reflects the differences in the thermodynamic quality of the solvent for the two polymers. THF is interacting more favorably with PS than with PVME (as expected from the low molar mass of PS and the thermodynamic parameters collected in Table 2). This fact obviously means that the addition of very little of PVME to moderately concentrated solutions of PS in THF suffices to cause demixing as shown in Figure 1.

The solvent quality of CH is at 55 °C marginal for both polymers, as documented by the proximity of this temperature to the

corresponding theta temperatures.⁶ The island of immiscibility is in this case located close to the PVME/CH edge of the phase triangle, which implies that the addition of very small amounts of PS to solutions of PVME in CH induces the segregation of a second phase.

3. Theoretical Part

3.1. Background. The most convenient and still very common way for the thermodynamic characterization of polymer/solvent systems starts from the subdivision of the reduced segment molar Gibbs energy of mixing, $\Delta\bar{G}/RT$, into a combinatorial part, $\Delta\bar{G}^{\text{comb}}/RT$ and into a residual (or noncombinatorial) part $\Delta\bar{G}^R/RT$

$$\frac{\Delta\bar{G}}{RT} = \frac{\Delta\bar{G}^{\text{comb}}}{RT} + \frac{\Delta\bar{G}^R}{RT} \quad (1)$$

In the case of binary systems the first term reads

$$\frac{\Delta\bar{G}^{\text{comb}}}{RT} = \frac{(1 - \varphi)}{N_s} \ln(1 - \varphi) + \frac{\varphi}{N_p} \ln \varphi \quad (2)$$

where φ is the segmental molar fraction of the polymer, made up of N_p segments, and N_s is the number of segments of which the solvent consists. In most cases, the size of a segment is defined in terms of the molar volume of solvent; in these cases N_s becomes unity. All thermodynamic characteristics of real systems are incorporated into the second term of eq 1, the residual, reduced segment molar Gibbs energy of mixing,

$$\frac{\Delta\bar{G}^R}{RT} = g\varphi(1 - \varphi) \quad (3)$$

and quantified by the *integral* Flory–Huggins interaction parameter g . This g is not identical with the experimentally accessible differential interaction parameters (usually denoted as χ) because of the experimentally well established composition dependence of interaction parameters.

The main reasons for the influences of composition on the thermodynamic interaction between the components lie in two effects the original Flory–Huggins theory¹¹ did not account for. These are the inability of polymer segments to spread out over the entire volume of a system (chain connectivity) and the capability of chain molecules to respond to changes in their molecular neighborhood (conformational relaxation) to attain the state of minimum Gibbs energy. These two effects were incorporated by conceptually subdividing the mixing process into two clearly separable steps. In this manner, we have established the following expression for the integral interaction parameter⁹

$$g = \frac{\alpha}{(1 - \nu)(1 - \nu\varphi)} - \zeta(1 + (1 - \lambda)\varphi) \quad (4)$$

The four parameters of this relation have the following meaning, where both additionally considered contributions are contained in the second term; α accounts for the effect of contact formation between the two types of segments, keeping the conformation of components unchanged, and ν corrects for the differences in the molecular surfaces of these segments¹² (of equal volume). The contribution of conformational relaxation, bringing the system into equilibrium, is quantified by the parameter ζ (which becomes zero under theta conditions) and λ corrects for chain connectivity. At first sight, eq 2 appears rather useless because of too many parameters. However, at least an estimate of ν can normally be obtained from tabulated data for the surfaces and volumes of the components and λ is for polymer solutions always very close to 0.5 so that the deviations from this value are usually negligible. This leaves us with the two leading parameters of eq 4, namely α and ζ . From the molecular picture briefly outlined above, it is furthermore obvious that these two

parameters cannot be independent of each other; the more preferred contact formation is, the less conformational rearrangement will be able to contribute to the minimization of the Gibbs energy. According to experimental evidence, there exists a clear-cut interrelation between α and ζ within a given class of systems, for instance solutions of linear vinyl polymers in low molecular weight liquids. This means that the knowledge of only one of these two parameters often suffices to describe such binary systems.

Eqs 2, 3, and 4 give access to the quantitative modeling of phase diagrams for the binary system by the direct minimization of the Gibbs energy.^{13,14} The method uses test tie lines to determine the curvatures of the Gibbs energy function. In this manner, one obtains the spinodal conditions from the change in curvature and the compositions of coexisting phases via the maximum reduction of G obtained from the segregation of a second phase.

The composition dependence of the reduced segment-molar Gibbs energy required for the description of the ternary mixtures of present interest reads

$$\frac{\Delta \bar{G}}{RT} = \frac{\varphi_i}{N_i} \ln \varphi_i + \frac{\varphi_j}{N_j} \ln \varphi_j + \frac{\varphi_k}{N_k} \ln \varphi_k + g_{ij} \varphi_i \varphi_j + g_{ik} \varphi_i \varphi_k + g_{jk} \varphi_j \varphi_k \quad (5)$$

where the components are designated as i , j , and k . For the practical application of this relation, it is important to keep in mind that all g values must refer to the same size of a segment.

For the present purpose, we select \bar{V}_s , the molar volume of the solvent, to fix the size of a segment. This choice allows the direct use of the interaction parameters published for the four polymer/solvent subsystems of interest (as the solvent sets the segment). On the other hand, the corresponding data for the mixture of the high molecular weight components need to be adequately converted because this information is usually reported for 100 mL/segment. To make this difference easier visible, we mark data not referring to \bar{V}_s by asterisks. Because of the just described situation, the binary interaction parameters for the blend must be converted. For that purpose, we need to calculate how many segments r of volume \bar{V}_s we obtain from one-polymer segment comprising 100 mL/segment

$$r = \frac{100}{\bar{V}_s} \quad (6)$$

and divide the corresponding summand of eq 5 by r .

This adaptation of the noncombinatorial part of the Gibbs energy to the present problem is still incomplete due to the fact that eq 5 was established for composition independent interaction parameters and does not account for the fact that different amounts of the third component must in the case of $g(\varphi)$ yield different contributions of a certain binary contact to the Gibbs energy of the ternary mixture. The individual g_{ij} contributions must be weighted³ by the factor $(1 - \varphi_k)$ to obtain their correct contribution to the total Gibbs energy of the system as formulated in eq 7.

In view of the usual graphical representation of the present phase diagrams, which places the two polymers on the edges of the baseline and the solvent on the top of the triangle, we have assigned index 1 to PS, index 2 to PVME, and index 3 to the solvent (either THF or CH). Using this nomenclature, the relation, extending eqs 3 and 4 to ternary mixtures, reads

$$\begin{aligned} \frac{\Delta \bar{G}^R}{RT} = & \left[\frac{\alpha_{12}^*}{(1 - \nu_{12}^*)(1 - \nu_{12}^* \varphi_2 (1 - \varphi_3))} - \zeta_{12}^* (1 + (1 - \lambda_{12}^*) \varphi_2 (1 - \varphi_3)) \right] \frac{\varphi_1 \varphi_2}{r} + \\ & \left[\frac{\alpha_{32}}{(1 - \nu_{32})(1 - \nu_{32} \varphi_2 (1 - \varphi_1))} - \zeta_{32} (1 + (1 - \lambda_{32}) \varphi_2 (1 - \varphi_1)) \right] \varphi_3 \varphi_2 + \\ & \left[\frac{\alpha_{31}}{(1 - \nu_{31})(1 - \nu_{31} \varphi_1 (1 - \varphi_2))} - \zeta_{31} (1 + (1 - \lambda_{31}) \varphi_1 (1 - \varphi_2)) \right] \varphi_3 \varphi_1 \quad (7) \end{aligned}$$

In this relation, the sequence of the indices is important and is determined by the choice of the independent composition variable for the description of the binary subsystem; for instance, g_{32} means that the composition dependence for the subsystem solvent/PVME is expressed in terms of the volume fraction of PVME.

Model calculations on the basis of eq 7 – using exclusively binary interaction parameters – have shown³ that all typical phenomena observed with polymer containing ternary mixtures are well reproduced, without the need to account for ternary interactions. For this reason, we want to check first, to which extent it is possible to model the results of the present measurements by the mere experimental information concerning the corresponding binary interaction parameters, that is without any adjustable parameters.

In case of mismatch between experiment and theory, we want to follow the common practice to introduce ternary interaction parameters accounting for special effects associated with triple contacts between the three components. This extra term to be added on the right-hand side of eq 7 reads

$$\frac{\Delta \bar{G}_t^R}{RT} = -t \varphi_1 \varphi_2 \varphi_3 \quad (8)$$

where we call t an *unspecific* ternary interaction parameter because its value does not depend on the further molecular environment of such triple contacts. The negative sign in the above relation was chosen in view of molecular considerations specified in the next section.

The parameters of eq 4 for the polymer solutions of present interest have already been reported^{8,9} and they stem primarily from vapor pressure and light scattering measurements. The corresponding information for the polymer blend was obtained by a theoretical analysis of the dependence of the critical phase separation conditions on the molar masses of the components.⁷ That evaluation has led – depending on two different theoretical assumptions – to two different sets of parameters of eq 4, which can both model the experimental findings with the same accuracy. The present calculations have been performed with both versions and yield practically identical results. They differ most pronouncedly in the value of λ , which is for polymer blends no longer close to 0.5 as for polymer solutions because both components are now high molecular weight in nature. In view of the fact that the variant with $\lambda = 1.5$ is closer to the theoretical expectation of approximately unity,³ we present only the results for this version. The entire set of binary interaction parameters is presented in Table 2 for the common solvent THF and in Table 3 for CH.

3.2. Results and Discussion. Binary Interaction Parameters and Unspecific Ternary Parameters.

PS 6/PVME 87/THF.

This solvent is good for both blend components, PS, and

Table 3. System-Specific Parameters^{7,9} (Eq 4) for the Binary Subsystems of PS/PVME/CH at 55 °C; the Subscripts at the Abbreviations of the Polymers State the (Weight Average) Numbers of Segments in Terms of the Molar Volume of CH

system	α	ν	ζ	λ	r
CH/PS ₂₀₂₃	0.520	0.258	0.150	0.5	
CH/PVME ₇₉₇	1.239	0.342	1.514	0.5	
PS ₂₀₂₃ /PVME ₇₉₇	-0.0062 ^a	-0.600 ^a	0.001 ^a	1.5 ^a	0.887

^a These parameters, characterizing the polymer blend, were taken from the literature;⁷ they refer to 100 mL/segment and 55 °C.

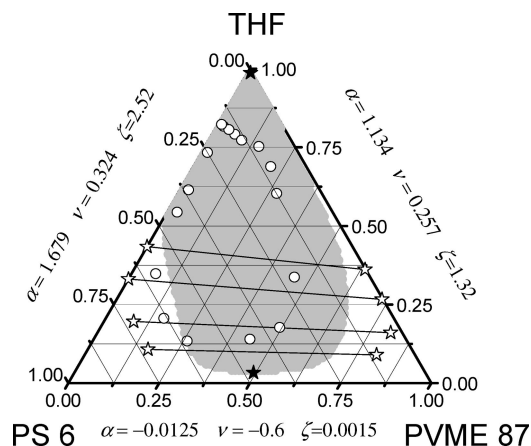


Figure 3. Measured and calculated phase diagram for the system PS/PVME/THF at 20 °C. ○: measured cloud points. The modeling was performed by means of the eqs 4 and 7 using the parameters of Table 2. The calculated spinodal area is shaded; ☆: composition of the coexisting phases, ★: critical points.

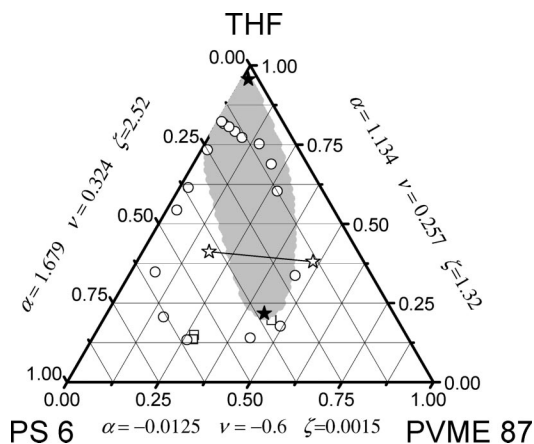


Figure 4. Reduction of the extension of the calculated island of immiscibility, as compared with that of Figure 3, resulting from an unspecific ternary interaction parameter $t = 0.5$ (eq 8).

PVME. Using eq 7 in combination with the parameters collected in Table 2 yields the phase diagram depicted in Figure 3.

In agreement with the experimental observation, the modeling on the basis of binary interaction parameters only, that is without any adjustable, predicts an island of immiscibility. However, its extension is by far too large. It expands into the solvent edge almost up to pure THF. This finding is a clear indication for the necessity of ternary interaction parameters. Hence, we repeat the calculation, extending eq 7 by adding the term formulated in eq 8. The result is shown in Figure 4.

Positive ternary interaction parameters reduce the extension of the island as expected. However, these changes are unselective and do not prove satisfactory, irrespective of the values of

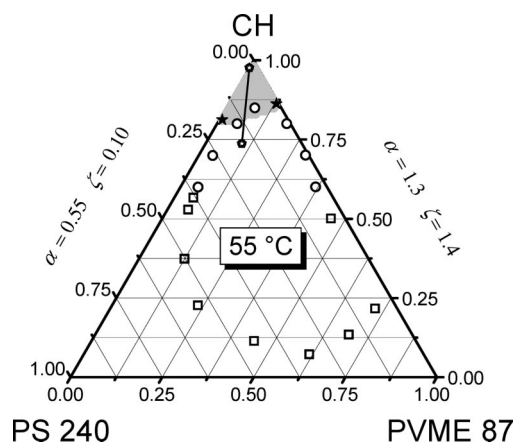


Figure 5. Calculated and measured phase diagram for the system PS/PVME/CH and 55 °C. The modeling was performed by means of eqs 4 and 7, changing some of the parameters of Table 3 to the values indicated in the graph such that the homogeneity of the binary subsystems is maintained. The calculated spinodal area is shaded; ☆: composition of the coexisting phases, ★: critical points. ○ and □: measured cloud points.

the ternary interaction parameter t .

PS 240/PVME 87/CH.

This solvent is in contrast to THF very poor for both polymers. The calculations on the basis of eq 7 in combination with the parameters collected in Table 3 do not yield any two phase areas; according to this result the three components should be completely miscible at all ratios. However, a slight reduction in the solvent power of CH for PS and for PVME with respect to that quantified by the parameters of Table 3 (keeping the corresponding binary subsystems still homogeneous) produces an island of immiscibility as shown in Figure 5. This demonstrates the proximity of the ternary system as modeled by eq 7 and the parameters of Table 3 to phase separation; in terms of the composition dependence of the Gibbs energy this signifies an extremely flat surface. Under such circumstances, the slightest unfavorable contribution may locally induce a negative curvature and consequently lead to phase separation.

A rigorous discussion of the importance of polydispersity for the comparison of measured and calculated phase diagrams is presently impossible because it would require directed experiments or/and the extension of the approach to multicomponent systems. Some plausible considerations can, however, nevertheless be made. An augmentation of the molecular nonuniformity leads – according to general experience – to a shortening of the tie lines but leaves their position within the Gibbs phase diagram practically unchanged. For the present case, this means that the mismatch of the measured phase diagram and that calculated by means of binary interaction parameters only is very probably not caused by polydispersity; the predicted tie lines are approximately perpendicular to all other, realistically calculated tie lines. However, it may well be that the necessity of introducing a composition-dependent ternary interaction parameter (cf. the results shown in Figure 10) represents an outcome of polydispersity.

By analogy to the procedure employed for the common solvent THF, we complement the binary parameter (collected in Table 3 and not leading to phase separation) by a ternary interaction parameter, which has to be negative, to produce an island of immiscibility. An example for these calculations is presented in Figure 6.

The introduction of an unspecific ternary interaction parameter of $t = -0.5$ yields an extended island of immiscibility as shown in Figure 6. However, the effect is unspecific, like in the case

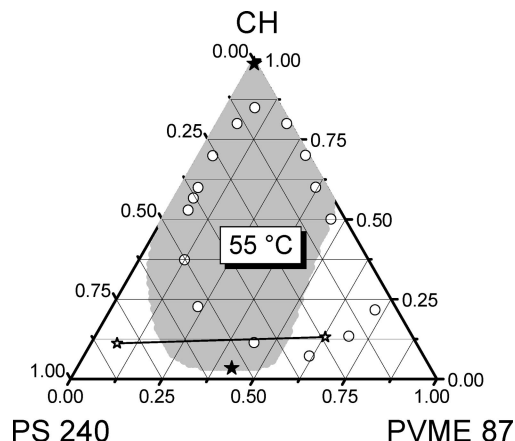


Figure 6. Calculated and measured phase diagram for the system PS/PVME/CH and 55 °C. The modeling was performed by means of the parameters of Table 3 and makes allowance for extra effects of ternary intersegmental contacts (eq 7 in combination with eq 8) by setting $t = -0.5$.

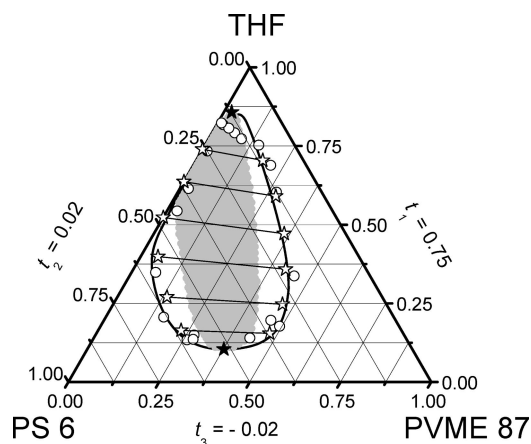


Figure 7. Phase diagram of the system PS/PVME/THF at 20 °C. O: Measured cloud points, ★: calculated critical points, ☆: calculated tie lines. The values of the *specific* ternary interaction parameters (eq 9) are indicated on the edges the binary interaction parameters and collected in Table 2.

of THF, where positive t values made the islands shrink but did not improve the quantitative agreement between experiment and theory. Worth commenting on is the change in the direction

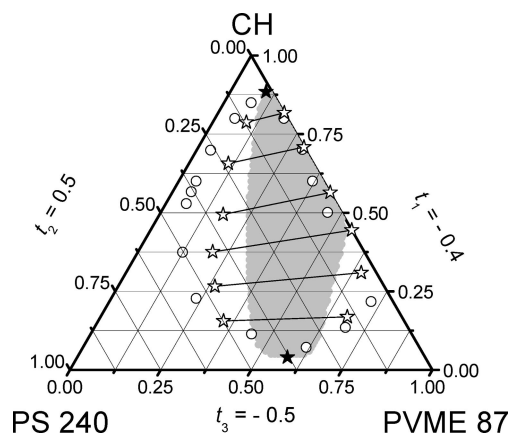


Figure 8. Modeling of the phase diagram by analogy to that shown in Figure 7. The parameters of eq 9 – indicated on the edges of the triangle – were chosen to reproduce the experimentally observed phase separation behavior on the PVME-rich side of the blend.

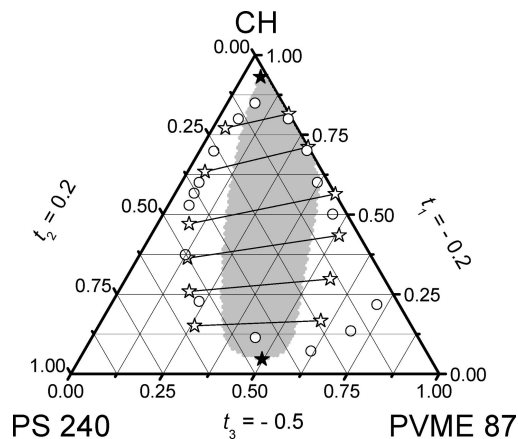


Figure 9. As in Figure 8 but modeling of the PS-rich side of the phase diagram.

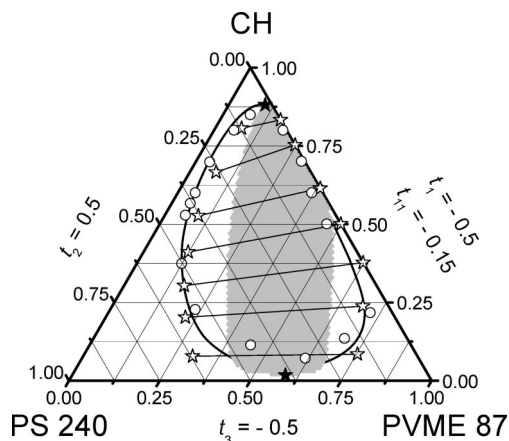


Figure 10. Like Figure 8 and Figure 9 but introducing a composition dependence for the specific ternary interaction parameter t_1 as formulated in eq 10.

of the tie lines by 90° caused by t (Figure 5 and Figure 6). In view of the shortcomings of the unspecific ternary interaction parameter, we are in the next section examining whether the general practice to account for ternary interactions as formulated in eq 8 is physically meaningful at all.

Binary Interaction Parameters and Specific Ternary Interaction Parameters. In this context, it is helpful to keep in mind that eq 8 has been established on the basis of eq 5 under the assumption that the binary interaction parameters do not depend on composition. This premise implies that the contribution of the formation of triples of segments i, j , and k to the total Gibbs energy of the system is a constant for a given system and for given conditions. With composition-dependent interaction parameters this is no longer true. For instance, in the light of the present approach it means that the formation of an $i-j-k$ triple by adding a segment k to an $i-j$ contact may lead to a different change in the Gibbs energy (for instance via the conformational relaxation of the components) than in the cases $i-k+j$ or $j-k+i$. This supposition results in the necessity to introduce three different ternary interaction parameters. Furthermore, it requires a weighting of these contribution to account for the fact that they must be largest in the limit of the first addition of the third component k (highest fraction of $i-j$ contacts) and die out as component k becomes dominant (vanishing fraction of $i-j$ contacts). The simplest possibility to account for these considerations is formulated in eq 9, where the negative sign was chosen by analogy to the second term of eq 4 quantifying the effects of chain connectivity and conformational relaxation.

$$\frac{\Delta \bar{G}_{t_i}^R}{RT} = -[t_1(1 - \varphi_1) + t_2(1 - \varphi_2) + t_3(1 - \varphi_3)]\varphi_1\varphi_2\varphi_3 \quad (9)$$

t_1 corrects for the changes in the residual Gibbs energy associated with the formation of a ternary contact 1–2–3 out of a binary contact between the component 2–3 by contacting it with a segment of component 1. The meaning of t_2 and t_3 is analogous. The aptitude of the residual Gibbs energies, as formulated in eq 9 and combined with eq 7, for the modeling of the observed phase behavior is in the following examined. The specific ternary interaction parameters used for that purpose are assembled in Table 4.

PS 6/PVME 87/THF.

In this case, where the common solvent THF is very favorable for both polymers, the measured phase diagram can be modeled quantitatively by means of the specific ternary interaction parameters as shown in Figure 7.

According to this result, the interaction between THF and PVME is considerably improved ($t_1 > 0$) by the vicinity of PS, whereas that between THF and PS is only slightly improved by the vicinity to PVME and that between PS and PVME is only little deteriorated by THF.

PS 240/PVME 87/CH.

The solvent quality of cyclohexane is marginal for both polymers. This feature is probably the reason for the difficulties encountered with the calculation of the phase diagram and the observation that the binary interaction parameters do not even qualitatively predict the real behavior. Even by means of eq 9, it is only possible to model either the PVME-rich side of the island of immiscibility realistically (Figure 8) or the PS-rich side (Figure 9) but not both branches at the same time.

It is highly probable that the difficulties with the quantitative modeling of the phase diagram encountered with this system are caused by the fact that both polymer solutions are close to the pseudo-ideal behavior prevailing at the corresponding theta temperatures. According to both variants of modeling, the formation of triple contacts PS/PVME/CH by adding CH to PS/PVME is very adverse and in both cases t_1 is as unfavorable as t_2 is favorable. In molecular terms, this means that PVME segments in the neighborhood of PS/CH contacts turn out to be particularly advantageous, irrespective of whether the right-hand side or the left-hand side of the island of immiscibility is modeled realistically.

The present findings indicate that the thermodynamic preferences for certain binary contacts may become so large that it is no longer permissible to use composition-independent specific ternary interaction parameters. In other words, under these particular circumstances it may make an important difference, whether the coordination sphere of a certain binary contact contains one or more segments of the third component. To check whether this idea is useful for a quantitative modeling, we assume that the specific ternary interaction parameters may in the general case depend on the composition as formulated in eq 10.

Composition-Dependent Specific Ternary Interaction Parameters. The extension of eq 9 to composition-dependent ternary interaction parameters can be written as follows

$$\frac{\Delta \bar{G}_{t_i(\varphi)}^R}{RT} = -[(t_1 + t_{11}\varphi_1)(1 - \varphi_1) + (t_2 + t_{22}\varphi_2)(1 - \varphi_2) + (t_3 + t_{33}\varphi_3)(1 - \varphi_3)]\varphi_1\varphi_2\varphi_3 \quad (10)$$

This relation contains six adjustable parameters in total, a number that is definitely unsuitable for practical purposes, even if – as in the present cases – all information concerning the binary subsystems is already available. Fortunately, one may expect that the t_{ii} parameters are not required for good solvents like THF. In the case of the marginal solvent CH, we are subsequently checking, whether it suffices to treat only one of the specific ternary interaction parameters as composition dependent. According to the modeling shown in Figure 8 and in Figure 9, an augmentation of the number of styrene segments in the vicinity of the PVME/CH contact appears to be particularly disadvantageous. We therefore adjust t_{11} only and set $t_{22} = t_{33} = 0$ for the refined modeling; the t_2 and t_3 values remain the same as that used for the calculations of the phase diagram shown in Figure 8. All data required for the modeling are collected in Table 4.

The results shown in Figure 10 demonstrate that it indeed suffices to treat only one of the ternary interaction parameters as composition dependent. The finding that both, t_1 and t_{11} , are negative signifies that the formation of the first encounter of a binary contact between CH and a segment of PVME with a segment of PS is already considerably unfavorable and that the addition of further PS segments still worsens the interaction. According to the results presented in Figure 10, the agreement between experiment and theory could still be improved by introducing a slight composition dependence of the effect of CH for the interaction between PS and PVME. However, because of the molecular nonuniformity of the polymers (mismatch of cloud point curve and coexistence curve) and in view of the finite accuracy of measurements we have refrained from that option.

4. Conclusions

The present experimental results and their modeling indicate that a blend of compatible polymers is normally only incompletely miscible with a common solvent, irrespective of whether this solvent is favorable or only marginal for the two high molecular weight components. Extended islands of immiscibility are observed with THF (good solvent) as well as with CH (marginal solvent) in combination with PS and PVME. There are, however, remarkable differences in the details of modeling on the basis of the present approach accounting for chain connectivity and conformational relaxation. In the case of THF, the occurrence of a closed miscibility gap is already predicted from the mere knowledge of the binary interaction parameters for the three subsystems, even if its extension is considerably overestimated. Conformity between theory and experiment can be reached by introducing composition-independent ternary interaction parameters. With CH, on the other hand, the binary interaction parameters predict complete miscibility of all three components, in contrast with reality. In this case, at least one of the ternary interaction parameters must be treated as composition-dependent to model the phase behavior quantitatively. These differences in the complexity of the thermodynamic description are most probably due to the closeness of the polymer solutions to the corresponding theta conditions, where the unfavorable enthalpic mixing effects are compensated by favorable residual entropies of mixing. This situation obviously makes the system particularly vulnerable to effects that are too small to become operative with good solvents.

When the first closed miscibility gaps of the present type were observed,² they were explained in terms of the so-called $\Delta\chi$ effect, that is as a consequence of a pronounced selectivity of

Table 4. Specific Ternary Interaction Parameters (Eqs 9 and 10)

system		t_1	t_{11}	t_2	t_3
PS ₆₉ /PVME ₁₀₁₈ /THF	Figure 7	0.75		0.02	−0.02
PS ₂₀₂₃ /PVME ₇₉₇ /CH	Figure 9	−0.20		0.20	−0.50
	Figure 8	−0.40		0.50	−0.50
	Figure 10	−0.50	−0.15	0.50	−0.50

the solvent. In the light of the current findings, this interpretation appears problematic. Islands are observed even if the solvent quality is very similar for both blend components, irrespective of whether it is high or low, as demonstrated here. The reason for phase separation of the solutions of polymer blends in a common solvent lies — according to the present modeling — in the pronounced lowering of the Gibbs energy that can be achieved by separating the homogeneous ternary mixtures into two phases: one containing preferentially one blend component and the coexisting phase containing preferentially the other blend component. The resulting tie lines, which are only marginally tilted out of parallelism to the baseline of the phase diagrams also speaks against the $\Delta\chi$ effect. According to the present findings, it must be concluded that solutions of a pair of compatible polymers in a common solvent will in almost all cases exhibit a closed miscibility gap, irrespective of the preferences of the solvent for one of the polymer components. The absence of islands of immiscibility should only be expected in particular cases, where uncommon interactions overrule the typical behavior.

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