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Interfacial Tension between Poly(isobutylene) and Poly(dimethylsiloxane): Influence of Chain Length, Temperature, and Solvents

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ABSTRACT: The interfacial tension σ was determined by means of spinning-drop and sessile-drop measurements for binary mixtures of low molecular weight and comparatively uniform fractions of poly(isobutylene) (PIB: 1.5, 3.3, and 5.0 kg/mol) plus poly(dimethylsiloxane) (PDMS: 11.3 and 19.6 kg/mol) as a function of temperature (20–80 °C). All values lie in the range between 2.5 and 4.0 mN/m. For PIB-1.5/PDMS-11.3 σ increases with T, for PIB-3.3/PDMS-11.3 it passes a maximum, and for PIB-5.0/PDMS-11.3 it decreases; these observations are interpreted in terms of closed miscibility gaps. At 25 °C it was also investigated how the addition of solvents of different thermodynamic quality changes the interfacial tension between PIB and PDMS. With toluene, a good solvent for both polymers, σ reduces monotonously to zero. With methyl ethyl ketone, which is a marginal solvent for PIB and a good solvent for PDMS, σ passes a distinct minimum; this finding indicates cosolvency. None of the different existing theories can predict the experimental observations satisfactorily.

Introduction

The interfacial tension σ between an "incompatible" pair of macromolecules is presently of great theoretical[1–5] and practical[6–8] interest. On the practical side the incentives lie primarily in the desire of plastics manufacturers to produce inexpensive materials with good properties by the coextrusion of commodity polymers in the presence of "compatibilizers". On the theoretical side there exists a considerable lack of understanding; the qualitatively obvious interrelation between σ on one hand and the thermodynamic interaction parameter χ on the other still cannot be cast into reliable and experimentally verified theoretical equations; in particular, none of the existing theoretical approaches takes account of the fact that χ normally depends on composition.

In the present study it was—by means of polymer samples with comparatively narrow molecular weight distributions—measured for different representatives of the system poly(isobutylene)/poly(dimethylsiloxane) (PIB/PDMS) how σ depends on molecular weight and temperature; furthermore, it was investigated how σ changes upon the addition of solvents of different thermodynamic quality. Toluene (TL) was chosen as an example for a solvent which is good for both polymers, and methyl ethyl ketone (MEK) was selected as a representative of a liquid which is completely miscible with only one of the two higher molecular weight components (here with PDMS).

Experimental Section

Materials. The poly(isobutylene) samples PIB-1.5 and PIB-3.3 were obtained through discontinuous fractionation (of Oppanol from BASF Ludwigshafen, Germany) using toluene as the solvent and methanol as the nonsolvent. PIB-5.0 has already been fractionated by means of the CPF (continuous polymer fractionation) earlier.[9] The numbers in the abbreviations of the polymers give their (weight average) molar masses in kg mol^{-1}; the molecular nonuniformities $U = (M_w/M_n) - 1$ of the PIB samples lie between 0.21 and 0.38. The poly(dimethylsiloxane)s were products from Wacker (Munich, Germany) with $U = 0.66$ and 0.82, respectively. The solvents toluene (TL) (content > 99.7 wt %) and methyl ethyl ketone (MEK) (p.a. > 99.5 wt %) were purchased from Merck (Darmstadt, Germany).

Table I. Densities of the Coexisting Phases (25 °C) of the System TL/PIB-3.3/PDMS-11.3 as a Function of w_{TL}, the Overall Weight Fraction of Toluene in the Ternary Mixture, for Different Constant Values of w^*_{PIB}, the Overall Weight Fraction of PIB in the Binary Polymer Blend

$w^*_{PIB} = m_{PIB}/(m_{PIB} + m_{PDMS})$	density of the PIB-rich phase at 25 °C (kg m^{-3})	density of the PDMS-rich phase at 25 °C (kg m^{-3})
0.10	$\rho = 902.0 - 40.5w_{TL}$	$\rho = 965.5 - 109.3w_{TL}$
0.46	$\rho = 903.1 - 40.0w_{TL}$	$\rho = 965.3 - 104.8w_{TL}$
0.71	$\rho = 903.3 - 41.2w_{TL}$	$\rho = 966.6 - 103.9w_{TL}$

Densities. The densities ρ (in kg m^{-3}) of the pure polymers, measured in conventional pycnometers, obey the following relations in the range from 20 to 80 °C (ϑ in °C):

$$\rho_{PIB-1.5} = 909.9 - 0.6\vartheta$$

$$\rho_{PIB-3.3} = 920.2 - 0.6\vartheta$$

$$\rho_{PIB-5.0} = 925.9 - 0.6\vartheta$$

$$\rho_{PDMS-11.3} = 986.6 - 0.9\vartheta$$

$$\rho_{PDMS-19.6} = 990.3 - 0.9\vartheta$$

The densities of the pure solvents, taken from the literature,[10,11] are (in kg m^{-3}, 25 °C) $\rho_{MEK} = 802.0$ and $\rho_{TL} = 862.0$. The densities of the coexisting phases of the ternary system TL/PIB-3.3/PDMS-11.3 (also measured by means of conventional pycnometers at 25 °C) can be represented by the relations given in Table I. These data are within experimental error identical with those calculated from the densities of the pure substances for negligible volumes of mixing. For the densities of the solutions of PDMS-11.3 in MEK one obtains the following relation:

$$\rho/(\text{kg m}^{-3}) = 961.7 - 165.0\frac{m_{MEK}}{m_{MEK} + m_{PDMS}}$$

where the m_i are the masses of the components.

Preparation of the Coexisting Phases. For the system TL/PIB-3.3/PDMS-11.3, different amounts of toluene were added to blends of PIB and PDMS (constant ratio of the polymers as indicated in Figure 3 by a, b, and c). The mixtures were then stirred in a closed cell for a minimum of 24 h, keeping the temperature higher than the corresponding demixing temperature; after that, the samples were cooled to 25 °C and kept at

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this temperature for 1–14 days, until the phases became clear and could be separated.

With the system MEK/PIB-3.3/PDMS-11.3 the procedure had to be changed, since this system cannot be homogenized by variation of temperature. Therefore different mixtures of MEK and PDMS-11.3 were prepared at compositions from $w_{\mathrm{MEK}} = 0.1$ to 0.8 in 0.1 intervals. The interfacial tensions measured upon the addition of a droplet of PIB to these solutions demonstrate that the equilibrium states are quickly reached. The two completely miscible components MEK and PDMS are highly enriched in one of the coexisting phases and PIB in the other.

Cloud Point Curves and Tie Lines. The phase diagrams of the binary system MEK/PIB-3.3 and of the ternary system TL/PIB-3.3/PDMS-11.3 were determined visually. The tie lines reported for the latter system stem from gravimetric measurements (separation of the coexisting phases by means of syringe, evaporation of the solvent and weighing, analysis of the polymer mixture). Due to the pronounced incompatibility of PIB and PDMS, the coexisting phases contain only one kind of polymer as long as the weight fraction of TL remains below ca. 0.6.

Interfacial Tension. Most measurements were carried out on a spinning-drop apparatus from Krüss (Hamburg, Germany). Because of the high viscosity of the samples, it can be filled best if two glass syringes are connected by means of a small Teflon tube to the inlet and outlet of the capillary, respectively. In the actual case one glass syringe contained ca. 3 mL of the PDMS-rich phase (heavier) and a droplet of the PIB-rich phase (lighter). The other syringe simply served to take up the overflow of the matrix phase. The remainder of the procedure is described elsewhere.[8]

As long as the ratio of the length and the radius r of the droplet exceeds a value of 8, the following relation can be used:[12]

$$\sigma = 0.25\omega^2 r^3 \Delta\rho \qquad (1)$$

where $\Delta\rho$ is the difference in the densities of the two phases and ω is the velocity with which the capillary is rotated.

The procedure with the sessile-drop measurements is described in the literature;[8,13] σ was calculated by means of Porter's equation.[14] This relation is only valid if the ratio of the height of the droplet (from its center to the apex) and half its maximum diameter remains below 0.5.

The main experimental errors of the spinning- and sessile-drop measurements stem from the determination of the dimensions of the droplet and $\Delta\rho$. For the binary system PIB/PDMS the errors are ca. ±1.5%. For the ternary system TL/PIB/PDMS they increase from ±4.2% for $w_{\mathrm{TL}} = 0.1$ up to ±10% for $w_{\mathrm{TL}} = 0.5$ because of the evaporation of the solvent. The smaller the values of r (i.e., σ), the greater the errors become. For the ternary system MEK/PIB/PDMS and spinning-drop measurements they lie between ± 3 and ± 18%. For $m_{\mathrm{MEK}}/(m_{\mathrm{MEK}} + m_{\mathrm{PDMS}}) \approx 0.34$ (cf. Figure 7), $\Delta\rho$ passes zero; this means that very large droplets would be required to obtain h/r ratios that are less than 0.5 in that range of compositions. This, however, is not possible with the present apparatus of fixed size. For this reason the measurements are rather uncertain for this composition.

Results and Discussion

A. Binary Systems. The variation of the interfacial tension σ with temperature is shown in Figure 1a for mixtures of PDMS-11.3 with PIBs of different molar masses and in Figure 1b for mixtures of PIB-3.3 with different PDMSs.

Since the interfacial tension and the thermodynamic interaction parameter χ vary in the same direction, it is possible to obtain some qualitative information concerning the phase diagrams of the different representatives of the system PIB/PDMS. Although this idea is neat at hand, it has—to the knowledge of the authors—not been checked against directly measured phase diagrams.

The fact that maxima in $\sigma(T)$ are observed for some combinations of chain lengths indicates the existence of closed miscibility gaps. On the basis of the entire experimental information shown in Figure 1 the scheme presented in Figure 2 can be drawn. According to orienting turbidimetric titrations in the temperature range between 20 to 170 °C, the mutual solubility of the components is in this graph highly exaggerated.

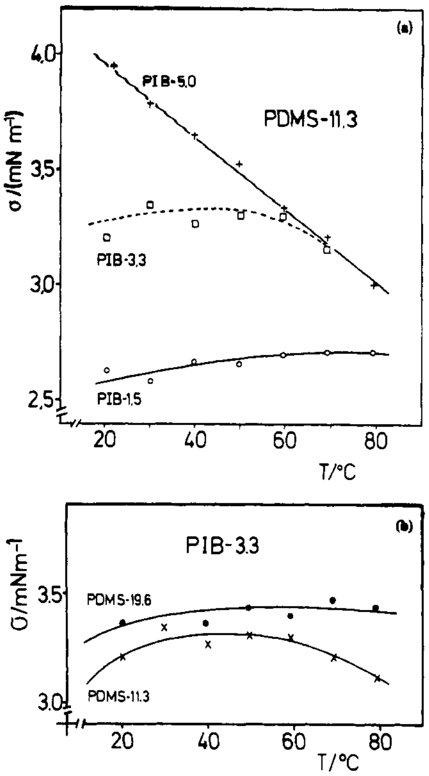

Figure 1. Interfacial tension σ as a function of temperature for different representatives of the system poly(isobutylene)/poly(dimethylsiloxane) (PIB/PDMS): (a) mixtures of PDMS-11.3 with different samples of PIB; (b) mixtures of PIB-3.3 with different samples of PDMS. The numbers after the abbreviations of the polymers signify their molecular masses in kg/mol.

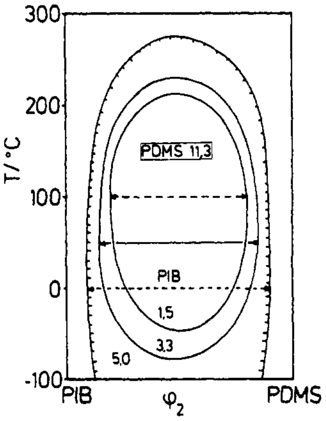

Figure 2. Schematic phase diagrams for different representatives of the system poly(isobutylene)/poly(dimethylsiloxane) (PIB/PDMS) resulting from the temperature dependence of the interfacial tension shown in Figure 1a (φ_2 is the volume fraction of PDMS); the two-phase area is located inside the closed miscibility gaps. The solid arrow indicates the temperature of highest immiscibility (maximum in σ) observed with the PIB sample of intermediate mass; the broken arrows show where this T is expected for the other PIB samples according to the results of Figure 1a.

A quantitative theoretical discussion of the molecular weight and temperature influences on σ is difficult for at least three reasons: First, although a comparatively large number of theoretical relations have been proposed to correlate σ and χ, all of them refer to infinite molar mass of the polymers and it has not yet been checked which of these relations describes reality best. Second, the χ values that would be required to assess this validity normally cannot be measured. For this reason another set of theoretical equations has to be used to calculate χ from data of the pure substances, and—according to experience—most of them are rather unreliable. Finally, none of the theoretical relations accounts for the fact that χ normally varies considerably with the composition of the system.

Notwithstanding this situation in the following some attempts are made to see whether predictions[1,2,4] of σ and its temperature dependence are at least qualitatively correct for the largest M values. Furthermore, it is investigated whether the semiempirical "harmonic-mean" relation[7,15-17] turns out to be useful.

According to Helfand and Tagami[2] σ for infinitely long chains (σ_∞) should be proportional to $\chi^{0.5}$ as formulated in eq 2

$$\sigma_\infty = b\rho_0 kT\left(\frac{\chi_{AB}}{6}\right)^{0.5} \tag{2}$$

where

$$\chi_{AB} = \frac{(\delta_A - \delta_B)^2}{\rho_0 kT} \tag{3}$$

$$b = M_0^{0.5}\frac{r_0}{M^{0.5}} \tag{4}$$

$$\rho_0 = \frac{N_L(\rho_A\rho_B)^{1/2}}{M_0} \tag{5}$$

M_0 is the relative molecular weight of a monomer unit, M is that of the polymer, r_0 is the unperturbed mean-square end-to-end distance, and $r_0/M^{0.5}$ is the characteristic ratio; ρ_A and ρ_B are the densities and δ_A and δ_B are the solubility parameters of the components.

Calculation for PIB-3.3/PDMS-11.3 on the basis of tabulated[18] data yields σ values for 25 °C which lie in the range from 0.53 to 3.14 mN/m (in comparison to σ = 3.9 mN/m, measured for the highest molecular weight mixture); the large uncertainty in the prediction results primarily from the different values[18,19] that can be chosen for the solubility parameters of the components. From the temperature dependence of the solubility parameters and the other factors of eq 2, one predicts an augmentation of σ as T is raised, in contrast to the actual measurements for the highest molecular weight mixtures.

Vrij[4] reported the following theoretical relation for $\sigma(T)$:

$$\sigma = \left(\frac{s^2}{6}\right)^{0.5}\Omega\sigma_r \tag{6}$$

with

$$\Omega = 2(\delta_A - \delta_B)^2 \tag{7}$$

$$\sigma_r = \left(\frac{\pi}{32^{0.5}}\right) - 0.426\left(\frac{T}{T_c}\right) \tag{8}$$

where $(s^2)^{0.5}$ is the geometric mean of the radii of gyration. Equation 6 contains the interaction parameter implicitly (the exponent of χ being unity, as compared with the 0.5 of Helfand and Tagami) and the critical temperature T_c of the system explicitly.

To check whether eq 6 is at least qualitatively correct, the T_c value of the system PIB$_\infty$/PDMS$_\infty$ was estimated by extrapolating the straight line given in Figure 1a for PIB-5.0/PDMS-11.3 toward σ = 0. On the basis of this T_c (262 °C) and tabulated δ values,[18] the calculated σ ranges from 0.15 to 3.17 mN/m at 30 °C (again because of the uncertainty in δ). This means that the quality of the prediction is similar to the previous one. Due to the temperature dependence of the reduced interfacial tension σ_r, the forecast temperature effects are this time in qualitative accord with the actual measurements.

The Cahn–Hilliard theory, as modified by Koberstein[19] et al., was not applied to the present problem since no experimental data of the interaction parameter for the pair of incompatible polymers were available, and the results would for that reason be as uncertain as the above ones.

The already-mentioned semiempirical "harmonic-mean" relation reads[7,15-17]

$$\sigma_{AB} = \gamma_A + \gamma_B - \frac{4\gamma_A{}^d\gamma_B{}^d}{\gamma_A{}^d + \gamma_B{}^d} - \frac{4\gamma_A{}^p\gamma_B{}^p}{\gamma_A{}^p + \gamma_B{}^p} \tag{9}$$

where γ_i is the surface tension of component i, $\gamma_i{}^d$ is its dispersion component, and $\gamma_i{}^p$ is its polar component. The γ^d value of PDMS is reported in the literature[16] to be 96.0% of the total γ at T = 20–200 °C; for PIB the dispersion and polar components were obtained by means of the three-dimensional solubility parameter[20,21]

$$\delta^2 = \delta_d{}^2 + \delta_p{}^2 \tag{10}$$

and the polarity e^p

$$e^p = (\delta_p/\delta)^2 \tag{11}$$

according to eq 12

$$\gamma^p/\gamma = e^p = 1 - e^d \tag{12}$$

The molecular weight influences on γ were taken into account by the following equations, which turned out to yield practically identical results:

$$\gamma^{-1/4} = \gamma_\infty{}^{-1/4} + k_s/M_n \tag{13}$$

$$\gamma = \gamma_\infty - \frac{k_e}{M_n{}^{2/3}} \tag{14}$$

M_n is the number-average molecular weight of the sample, γ_∞ is the surface tension for infinitely long chains, and k_s and k_e are tabulated[7] constants. The following γ and γ^p values resulted: 20.9 and 0.8 mN/m for PDMS and 33.4 and 0.4 for PIB.

The "harmonic-mean" equation turned out to be suited best for an estimation of the interfacial tensions. This is probably so since relation 9 does not require an interaction parameter. Furthermore, the uncertainty associated with solubility parameters has only little effect on the results, since these data are only required to split the surface tension of the pure polymers into a polar and an apolar part. Calculations on the basis of eqs 9–14 for the system PIB-3.3/PDMS-11.3 and 24 °C yielded for instance a σ value of 3.04 mN/m as compared with 3.27 mN/m in the actual measurements.

B. Ternary Systems. Toluene. As can be seen from the position of the tie lines in the phase diagram of Figure 3, TL is a thermodynamically good solvent for both polymers. Due to the incompatibility of PIB and PDMS, which is already very pronounced even for the short chains of present interest, the coexisting phases do practically contain one kind of polymer only, as soon as the weight fraction of solvent falls below 0.6. It should be noted that the "bimodal" cloud-point curve and the position of the critical point on it are likely due to the nonnegligible molecular nonuniformities[22] of PDMS.

Interfacial tensions were measured at 25 °C for the ternary system and the different starting ratios of the polymers indicated in Figure 3 by arrows. Figure 4 shows these results as function of w_{TL}, the weight fraction of toluene in the entire mixture. The data obtained for a different mixing ratio of PIB and PDMS should coincide

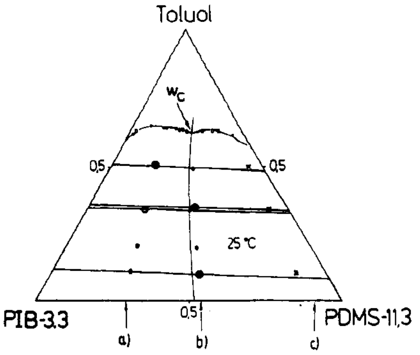

Figure 3. Phase diagram of the system toluene/poly(isobutylene)/poly(dimethylsiloxane) at 25 °C; the numbers after the abbreviations of the polymers signify their molar masses in kg/mol. In addition to the cloud-point curve (tiny open circles), this graph also gives some tie lines. The solid curve drawn to connect their middle position should extrapolate to the critical point w_{cr} of the ternary system. The arrows at a, b, and c indicate w^*_{PIB} [$=m_{PIB}/(m_{PIB} + m_{PDMS})$], the composition of the binary polymer blends to which increasing amounts of solvent were added: (a) 0.71; (b) 0.46; (c) 0.10. Interfacial tension measurements were performed at the indicated compositions; the compositions for which tie lines were determined are encircled.

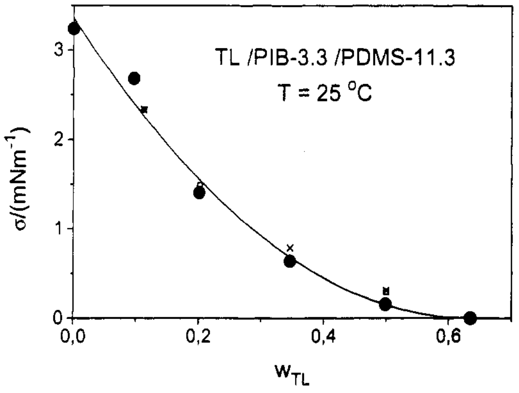

Figure 4. Interfacial tension σ for the system toluene/poly(isobutylene)/poly(dimethylsiloxane) at 25 °C as a function of w_{TL}, the weight fraction of toluene in the mixture. The different symbols represent a constant composition of the starting polymer blend and have the same meaning as in Figure 3. The curve shown in the present graph is drawn for $w^*_{PIB} = 0.46$ (full circles) according to the evaluation of Figure 5; for this composition the interfacial tension extrapolates smoothly to the critical value of the system, where σ approaches zero.

only if the tie lines are parallel to the base of the Gibbs phase triangle, and only in case of the critical ratio can they be followed down to zero interfacial tensions.

The line connecting the data points in this graph is based on the measurements indicated in Figure 3 by (b) since these experiments are most likely performed closest to the critical compositions of the mixture. By analogy with the usual determination of the critical exponents of the interfacial tension, σ was plotted as a function of the relative difference in the weight fraction of toluene in a given mixture to its critical value according to $\ln \sigma = \ln \sigma_0 + a \ln[(w_{cr} - w_{TL})/w_{cr}]$, where σ_0 is the interfacial tension of the polymer blend in the absence of solvent. As can be seen from Figure 5, one obtains indeed a straight line (slope 2.0), despite the fact that the distance to the critical condition is still rather large. In view of the fact that both polymers are molecularly nonuniform and different slopes (ranging between 1.5 and 2.0) therefore result for the different sets of experiments a–c of Figure 3, the above result is not discussed theoretically.

In view of the difficulties in the theory of binary systems, it cannot be expected that a realistic description is possible for the present ternary ones,[2,3] except for special cases where justified simplifications can be made. One of these approaches is due to Leibler and Broseta,[5] who discuss systems of the present type, where the solvent is good for both polymers.

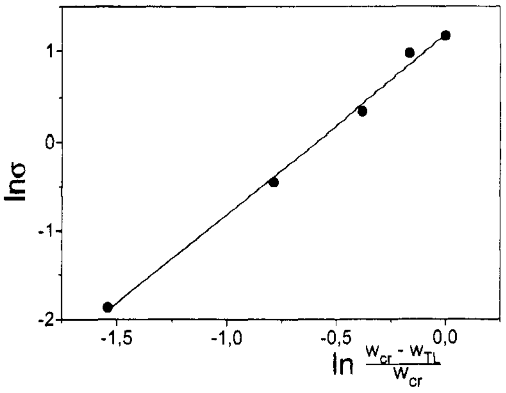

Figure 5. Linearization of the σ data shown in Figure 4 by analogy to the usual determination of critical exponents; w_{TL} is the weight fraction of toluene, and w_{cr} is its critical value.

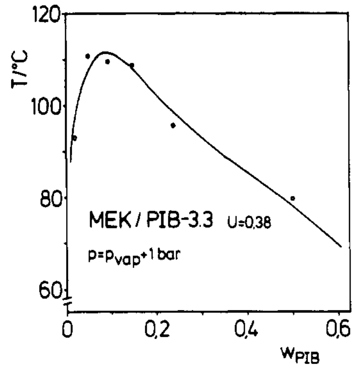

Figure 6. Cloud-point curve for the binary subsystem methyl ethyl ketone/poly(isobutylene) (MEK/PIB-3.3) demonstrating that PIB becomes completely miscible with MEK as one raises the temperature above the boiling point of the solvent (80 °C).

They reported the following equation

$$\sigma = \sigma_\infty\left(1 - \frac{1.64}{\omega} - 1.67\chi\right) \qquad (15)$$

in which the interfacial tension is a function of σ_∞, the interfacial tension for infinitely large chains, the incompatibility degree ω, and the thermodynamic interaction parameter χ; σ_∞ can be calculated as[5]

$$\sigma_\infty = \left(\frac{kT}{\xi^2}\right)\left(\frac{\omega}{6}\right)^{0.5} \qquad (16)$$

from the correlation length ξ, which itself is obtained from the geometric mean of the radii of gyration. On the basis of the equations[5] reported by the authors, orienting calculations were performed for an incompatibility degree ω of 7.5, taking the radii for the calculation of the correlation lengths ξ from ref 18. For 25 °C one obtains 2.31 mN/m (measured: 2.33) at $w_{TL} = 0.113$, 1.23 mN/m (0.79) at $w_{TL} = 0.339$, and 0.83 mN/m (0.29) at $w_{TL} = 0.500$. Most likely, the overall agreement could be improved by assuming ω to vary with the solvent content of the system.

Methyl Ethyl Ketone. This solvent mixes completely only with PDMS, whereas it constitutes a marginal solvent for PIB, as demonstrated by the phase diagram shown in Figure 6. The system MEK/PIB is highly endothermal and exhibits an UCST above the (atmospheric) boiling of the solvent.

As was already mentioned in the Experimental Section, with MEK the droplets required for the measurements of σ had to be prepared differently as compared with TL, since it is impossible to realize a homogeneous state for

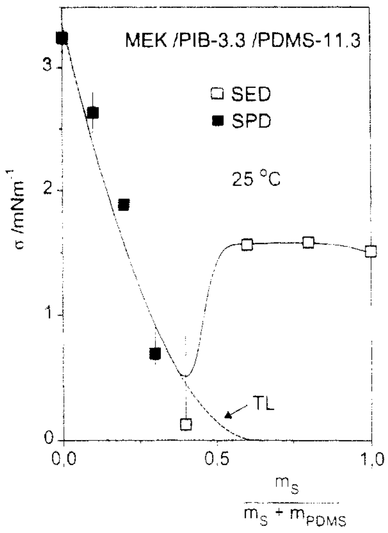

Figure 7. Interfacial tension σ for the system methyl ethyl ketone/poly(isobutylene)/poly(dimethylsiloxane) at 25 °C as a function of $m_s/(m_s + m_{PDMS})$, the weight fraction of the solvent in the binary mixture of solvent and PDMS. This variable for the abscissa was chosen to be able to compare the results for MEK with those for toluene (broken line). In both cases the σ data refer to the first experimentally accessible two-phase situation that arises as PIB is added. The full squares in the region of low concentration of MEK correspond to measurements with the spinning-drop (SPD) method; at high contents reliable data could only be obtained with the sessile-drop (SED) method due to problems with insufficient differences in the densities of the coexisting phases. Some typical error bars are indicated.

the ternary system by changing T. Adding a small amount of pure PIB to homogeneous mixtures of PDMS and MEK turned out to be the best procedure. The σ data presented in Figure 7 were obtained in this manner; according to experimental experience the minimum of σ with respect to composition cannot be attributed to the change from the spinning-drop to the sessile-drop method.

To be able to compare the results for the solvents MEK and TL, $m_s/(m_s + m_{PDMS}) = w_s^*$, the composition of the homogeneous binary subsystem solvent (S) and PDMS, was chosen as the variable for the abscissa. In both cases the σ data refer to the first experimentally accessible two-phase situation that arises as PIB is added. In the region of low w_s^* values, the dependence obtained from Figure 5 was drawn for both systems; it is interesting to note that this relation can also describe the effects of MEK as long as the solvent concentration remains small. In contrast to expectation, σ is not decreasing monotonously from the large value of PDMS/PIB to the lower value of MEK/PIB but shows a distinct minimum when MEK and PDMS are present in the ternary system in comparable concentration.

The information on the phase behavior of the binary subsystems (cloud-point curve of Figure 6 for MEK/PIB, incompatibility of PIB and PDMS, and complete miscibility of MEK and PDMS) plus the variation of σ with the solvent content of the ternary system can be used to construct a qualitative phase diagram; the result of these considerations is shown in Figure 8. According to orienting turbidimetric titrations, the solubility of PIB in mixtures of this polymer with MEK is so low that it could hardly be seen in a phase diagram drawn to scale.

The minimum in σ translates into a considerable shortening of the tie lines within the range of intermediate w_{MEK}^* values; in other words, the present system shows cosolvency (i.e., mixtures of MEK and PDMS are better solvents for PIB than MEK or PDMS alone). From the observation that already minute amounts of PIB added to mixtures of MEK and PDMS lead to demixing, one has to conclude that the tie lines withdraw from the PIB corner of the Gibbs phase triangle. Diagrams of the type shown in Figure 8 have already been observed for instance for the system methanol/isooctane/nitrobenzene.[23]

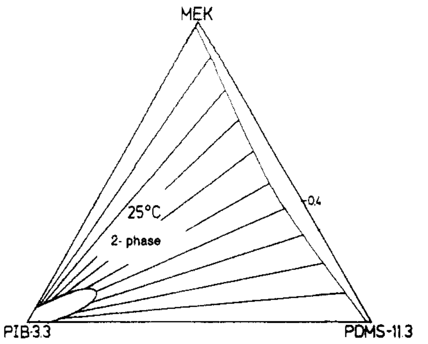

Figure 8. Schematic phase diagram of the system methyl ethyl ketone/poly(isobutylene)/poly(dimethylsiloxane) at 25 °C resulting from the dependence of σ on the composition of the mixture (cf. Figure 7) and from the knowledge of the miscibility of the components of the binary subsystems.

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References and Notes

(1) Helfand, E. *Polymer Compatibility and Incompatibility, Principles and Practices*; Šolc, K., Ed.; MMI Press: Chur, 1987.
(2) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1972**, *56*, 3592.
(3) Hong, K.; Noolandi, J. *Macromolecules* **1980**, *13*, 964. Hong, K.; Noolandi, J. *Macromolecules* **1981**, *14*, 763.
(4) Vrij, A. *J. Polym. Sci.; Part A* **1968**, *6*, 1919.
(5) Broseta, D.; Leibler, L. *J. Chem. Phys.* **1987**, *87*, 7248.
(6) Wu, S. *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 1, Chapter 6.
(7) Wu, S. *J. Macromol. Sci., Rev. Macromol. Chem., C* **1974**, *10* (19), 1.
(8) Heinrich, M.; Wolf, B. A. *Polymer* **1992**, *33*, 1926.
(9) Geerissen, H.; Roos, J.; Schützeichel, P.; Wolf, B. A. *J. Appl. Polym. Sci.* **1987**, *34*, 271. Geerissen, H.; Schützeichel, P.; Wolf, B. A. *J. Appl. Polym. Sci.* **1987**, *34*, 287.
(10) D'Ans-Lax *Taschenbuch für Chemiker und Physiker*; Springer-Verlag: Berlin, 1967.
(11) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 66th ed.; CRC Press, Inc.: Boca Raton, FL, 1985.
(12) Miller, C. A.; Neogi, P. *Interfacial Phenomena, Equilibrium and Dynamic Effects*; Marcel Dekker Inc.: New York, 1985.
(13) Shinozaki, K.; van Tan, T.; Saito, T.; Nose, T. *Polymer* **1983**, *23*, 728.
(14) Porter, A. W. *Philos. Mag.* **1923**, *15*, 163.
(15) Wu, S. *J. Phys. Chem.* **1970**, *74*, 632.
(16) Wu, S. *J. Polym. Sci., Part C* **1971**, *34*, 19.
(17) Wu, S. *J. Colloid Interface Sci.* **1969**, *31*, 153.
(18) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Interscience Publishers: New York, 1989.
(19) Anastasiadis, S. H.; Gancarz, I.; Koberstein, J. T. *Macromolecules* **1988**, *21*, 2980.
(20) Gnamm, H.; Fuchs, O. *Lösungsmittel und Weichmachungsmittel*, Wissenschafliche; Verlagsgesellschaft mbH: Stuttgart, 1980; Vol. 1.
(21) Koberstein, J. T. *Encyclopedia of Polymer Science and Engineering*; John Wiley and Son, Inc.: New York, 1987; Vol. 8, pp 237–279.
(22) Koningsveld, R.; Kleintjens, L. A. *Polymer Blends and Mixtures*; Walsh, D. J., Higgins, J. S., Maconnachie, A., Eds.; Martinus Nijhoff Publishers: Dordrecht, 1985.
(23) Francis, A. W. *J. Am. Chem. Soc.* **1954**, *76*, 393.