Macromolecules **1992,** *25,* 3817–3819

Interfacial Tension between Demixed Solutions of Molecularly Nonuniform Polymers

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Received January 23, 1992
Revised Manuscript Received March 27, 1992

Introduction

How the interfacial tension σ increases with the distance from the critical conditions (for which this quantity vanishes) is studied in great detail theoretically[1,2] and experimentally.[3,4] However, polydispersity effects were so far only discussed for polymer blends,[5,6] where σ is influenced due to the accumulation of small chains at the interface. To the best of our knowledge no attention has so far been payed to the special effects resulting from polymolecularity in the case of polymer solutions, in spite of the fact that this question appears of considerable interest for (i) the comparison of experimental data (which are all based on more or less nonuniform samples) with the predictions of scaling theories and (ii) for the optimization of a large-scale continuous countercurrent extraction method[7,8] (CPF: continuous polymer fractionation) for which it has turned out that its efficiency reaches a maximum for intermediate σ values, i.e. at some optimum distance of the working point from the thermodynamical critical conditions.

For the polymer solutions of present interest and isothermal conditions, the composition of the coexisting phases and $\Delta\varphi$, the difference in the volume fraction of polymer in the more concentrated and in the less concentrated phase, are no longer constant, but depend distinctly on $w_2{}^{\circ}$, the overall polymer concentration.[9] In view of the recent finding[4] that a master-curve relates σ and $\Delta\varphi$, this implies that the interfacial tension should also depend on $w_2{}^{\circ}$.

Theoretical Background

According to the mean-field theory[1] the interfacial tension σ varies with M, the molar mass of the polymer, and $\tau = \Delta T/T_c$, the reduced distance to the thermodynamical critical temperature, in the following way

$$\ln \sigma = A - \zeta_\mu \ln M + \mu \ln \tau \qquad (1)$$

where A is the so-called amplitude and ζ_μ and μ are critical exponents. The corresponding equation for $\Delta\varphi(M,\tau)$ reads

$$\ln \Delta\varphi = B - \zeta_\beta \ln M + \beta \ln \tau \qquad (2)$$

Substitution of τ in eqs 1 and 2, leads to[4]

$$\ln \sigma = C + \delta \ln M + (\mu/\beta) \ln \Delta\varphi \qquad (3)$$

where δ is related with the already introduced critical exponents by

$$\delta = (\zeta_\beta \mu/\beta) - \zeta_\mu \qquad (4)$$

From spinning drop measurements with polystyrenes of different M in various solvents[4] one obtains $\delta = 0.50$ in good agreement with the theoretical prediction; μ/β, on the other hand, is larger (3.85) than expected theoretically (3.0). The comparison of the amplitudes A, B, and C resulting for a given type of polymer but different solvents demonstrates that only eq 3 is generally valid; i.e. only this relation constitutes a master-curve. For polystyrenes (σ given in mN m^{-1}) $C = 0.015$.

If eq 3 were applicable with constant C not only for different solvents but also for different molecular weight distributions, it should be possible to calculate very easily how the overall concentration changes σ, knowing how $w_2{}^{\circ}$ changes $\Delta\varphi$. The experiments reported in the following were performed to check this consideration against the actual interfacial behavior of molecularly nonuniform polymer samples.

Experimental Section

Substances. Poly(styrene) (PS) was kindly supplied by BASF (Ludwigshafen, Germany); according to light scattering and GPC measurements $M_w = 320$ kg mol^{-1} and $M_w/M_n = 2.5$. Cyclohexane (CH), UVASOL grade, was dried over molecular sieves and used without further purification.

Phase Equilibria. The coexisting phase of lower polymer concentration was quantitatively removed using a syringe. Both phases were then diluted with toluene, and the polymer was precipitated by pouring these solutions into a surplus of methanol. The cloud-point curve was determined visually, and the critical point from phase volume ratios.[10] More experimental details can be obtained from a previous work.[11]

Interfacial Tensions. Spinning drop measurements were performed on an apparatus from Fa. Krüss (Hamburg, Germany). The two coexisting phases are conjointly filled into the tube in a suitable volume ratio approximately 2–3 K above the envisaged mesauring temperature. After equilibration, the experiments can then be conducted[4] and evaluated[12] in the usual manner. All data were reproduced at least four times.

Results and Discussion

Phase Equilibria. The composition of the coexisting phases as a function of temperature is shown in Figure 1 for one sub- and one supercritical polymer concentration.

The coexistence curves do not coincide with the cloud-point curve due to the polymolecularity of the sample;[9] furthermore, they are not closed: One branch starts from the cloud-point curve and the other from the so-called shadow curve.[10] Only if $w_2{}^{\circ}$ is identical with w_{2c}, the critical composition, is the coexistence curve closed (with its extremum at w_{2c}). Another very obvious outcome of polymolecularity is the fact that w_{2c} occurs much higher than the position of the extremum of the cloud-point curve (in the present case by a factor of approximately four); correspondingly T_c is found markedly lower than the precipitation threshold temperatue T_{pth} (here approximately 1.2 K).

Interfacial Tension. The results of the present measurements are collected in Table I. Three different $w_2{}^{\circ}$ values were chosen: One sub- and one supercritical value plus $w_2{}^{\circ} = w_{2c}$; the latter case was studied in more detail for different ΔT. Table I also contains the results of the calculation of σ by means of the measured $\Delta\varphi$ values (cf. Figure 1) and from the master-curve given by eq 3, taking M_w of the original polymer as M. It is obvious, as can also be seen from Figure 2, that this relation remains applicable for temperatures higher than T_c where τ becomes negative and eqs 1 and 2 become meaningless.

It has still to be explained (i) why one can take the molecular weight of the *starting* material in the above calculations and (ii) why one can use the *weight* average value. (i) Due to the transient nature of the interfacial layer, the molecular weight distribution of the polymer contained in it should (in contrast to the situation with the bulk phases) be similar to that of the starting material. (ii) Only some preliminary statements can be made concerning the appropriate average of M; out of the different common averages, only M_w—when inserted into eq 3—turned out to give good agreement with the actually

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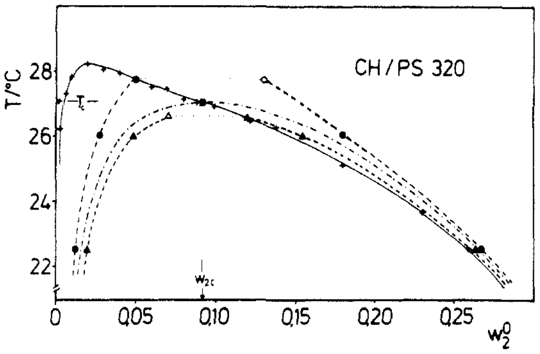

Figure 1. Phase diagram for the system cyclohexane/poly(styrene), M_w = 320 kg mol^{-1} and M_w/M_n = 2.5. The crosses give the visually determined cloud-points, and the broken lines denote the coexistence curves measured for different values of $w_2{}^o$, the overall weight fraction of the polymer. The critical composition is indicated by a filled square. $w_2{}^o$ = 0.050 (●), $w_{2c}{}^o$ = 0.092 (– · –), and $w_2{}^o$ = 0.120 (▲).

Table I
Calculated (Equation 3) and Measured (Spinning Drop) Interfacial Tensions σ for the System Cyclohexane/Poly(styrene) 320 at a Constant Distance $\Delta T = T_c - T$ = 1 °C from the Critical Temperature (T_c = 27.0 °C) for Different Weight Fractions $w_2{}^o$ of the Polymer in the Starting Solution[a]

$w_2{}^o$	w_2'	w_2''	$\Delta\rho$, g cm^{-3}	$\Delta\varphi$	$10^3\sigma_{calc}$, mN m^{-1}	$10^3\sigma_{meas}$, mN m^{-1}
0.050	0.028	0.179	0.034	0.116	2.12	2.10
0.092	0.043	0.167	0.026	0.096	1.01	1.35
0.120	0.049	0.156	0.024	0.082	0.55	0.53

[a] This table also contains the following quantities required in the calculation: the polymer concentrations of the coexisting phases, w_2' and w_2'', the density differences $\Delta\rho$ of these phases, and $\Delta\varphi$, the differences in the volume fraction of the polymer they contain.

measured interfacial tensions, and from simple theoretical considerations one can argue that long and short chains contribute to σ differently and therefore exclude M_n.

The above collection of data demonstrates that there is indeed a pronounced influence of the overall polymer concentration on the interfacial tension of the solutions of phase-separated polymolecular samples (in the present examples it varies by a factor of approximately four). Furthermore, it can be seen that the predictions by means of the master-curve agree surprisingly well with the actually measured σ values, which in hindsight justifies the choice of the weight average value of M in these calculations.

Extensive measurements concerning the dependence of σ on the overall polymer concentration in the case of molecularly nonuniform samples have already been performed earlier with the system phenetol/poly(isobutene). These results were qualitatively identical with that presented above. They could, however, not be evaluated on the basis of eq 3, because of lacking data concerning the composition of the coexisting phases, in contrast to the situation with CH/PS were this information was already available.[11]

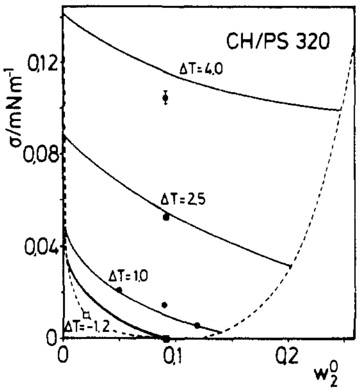

Figure 2. Interfacial tension (solid lines) σ as a function of $w_2{}^o$, the overall weight fraction of polymer, calculated by means of the composition of the coexisting phases (Figure 1) and eq 3 for the system cyclohexane/poly(styrene), M_w = 320 kg mol^{-1} and M_w/M_n = 2.5 keeping the indicated temperature distances $\Delta T = T_c - T$ (T_c: critical temperature) constant. The dependence for ΔT = 0 is given prominence by a thicker line. The σ value at the precipitation threshold is indicated by an open square; the critical composition is given by a filled square. The solid circles are experimental data obtained by means of the spinning drop method.

On the basis of the present results, the curves in Figure 2, describing the variation of σ with the overall polymer concentration $w_2{}^o$, can be calculated for different constant temperatures. All isotherms start and end at the broken line, which is in its abscissa values given by the cloud-point curve and in its ordinate values by the interfacial tension at the verge of phase separation, where the phase volume ratio approaches infinity or zero. On this curve the precipitation threshold constitutes an outstanding point, since $T = T_{pth}$ does not intersect the cloud-point curve twice but degenerates into a tangent. Unlike the situation with uniform polymers where the phases become identical at $T_{pth} = T_c$ and σ = 0, these two temperatures no longer coincide for polymolecular samples and a concentrated solution is segregated from a dilute one at T_{pth}; i.e. σ remains finite.

From Fig. 2 it can be seen that the influence of polymolecularity is most pronounced in the vicinity of the precipitation threshold, where ΔT is negative. As one penetrates into the two-phase region (i.e. increases ΔT and reduces the solvent power), these effects gradually die out. This result simply reflects the fact that the coexistence curves shown in Figure 1 for different overall concentrations approach each other for lower temperatures. In other words, if the solubility of the polymer becomes negligibly small, independent of its chain length, the effects associated with polymolecularity become vanishingly small, since the entire solute is in one phase only.

Conclusions

Two main inferences can be made on the basis of the present study. (i) If narrow fractions of a polymer are unavailable, one should measure the interfacial tension as a function of ΔT for the critical value for the overall polymer concentration. Under these conditions the influences of polymolecularity are lowest. (ii) The other conclusion concerns the fact that a quick access to σ values via the difference $\Delta\varphi$ of the volume fractions of polymer in the coexisting phases is also possible for broadly distributed samples, if the molar mass M is substituted by M_w in the master-curve of eq 3 (established for polystyrene and similar vinyl polymers). The first item should be of some importance for the comparison of theoretical predictions with experimental data. The second finding supplies a useful analytical description of the interfacial behavior of polymolecular systems. Continuous polymer fractionation constitutes one example where such relations are required in order to model the method. The efficiency of this countercurrent extraction process depends markedly on σ, which changes throughout the column as the fractionation proceeds.

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Registry No. PS, 9003-53-6.