Interfacial tension between solutions of polystyrenes: establishment of a useful master curve

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(Received 16 April 1991; accepted 17 June 1991)

The interfacial tension σ between the coexisting phases of the systems methylcyclohexane/polystyrene and cyclohexane/polystyrene was measured by means of the spinning drop and sessile drop methods as a function of $(T_c - T)/T_c = \tau$, the reduced distance from the critical temperature, for different relative molar masses M of the polymer (17500–175000). The minimum τ value that could be realized amounted to 1.7×10^{-3} and the corresponding σ value to 0.0007 mN m^{-1}. The results were evaluated according to the relations (1) $\ln \sigma = A - \zeta_\mu \ln M + \mu \ln \tau$ and (2) $\ln \Delta\varphi = B - \zeta_\beta \ln M + \beta \ln \tau$ in which $\Delta\varphi$ is the difference in the volume fraction of the polymer in the coexisting phases, A and B are constants for a given solvent, and ζ_μ, ζ_β, μ and β are the critical exponents. With increasing M the exponent μ is found to fall from values which are close to that predicted by the mean-field theory (1.50) to those resulting from the Ising model (1.26); β equals 0.35 in the entire region of M (mean-field: 0.50, Ising: 0.31). In contrast to the critical exponents, A and B are not universal constants but vary from solvent to solvent, i.e. the above relations are of little use for the prediction of σ. This deficiency can, however, be overcome by substituting τ from (2) into (1) and replacing M by N, the number of monomeric units. The different parameters of the resulting relation (3) $\ln \sigma = D + \delta \ln N + (\mu/\beta) \ln \Delta\varphi$ no longer depend on the particular chemical nature of the system. It therefore constitutes a useful master curve to obtain σ from knowledge of the composition of the coexisting phases. The evaluation of the present measurements together with unpublished material yields $D = \ln[0.153(\mathrm{mN\,m^{-1}})]$, $\delta = (\zeta_\beta \mu/\beta) - \zeta_\mu = 0.50$ (identical with the mean-field value) and $\mu/\beta = 3.85$ (mean-field: 3.00, Ising: 4.00).

(Keywords: interfacial tension; polystyrene; master curve)

INTRODUCTION

For many practical purposes the knowledge of the interfacial tension σ between two liquid phases containing polymers is of essential importance. One example for this situation concerns the newly developed method for a continuous polymer fractionation[1] in which the short chains of the original sample are removed from solution by a counter current extraction. For the optimization of this process it is mandatory to know how σ varies with the distance from the critical point. So far, however, those data can only be obtained from measurements; it is not even certain which of the different theoretically derived relations[2,3] apply.

The present experimental study was performed to obtain this information for solvent/polymer systems in terms of critical exponents and to compare the results with theoretical predictions. Particular attention is given to the role of M, the molar mass of the polymer, and to the changes in the interfacial behaviour induced by an alteration of the chemical nature of the θ solvent. In particular a 'master curve' was sought for the prediction of σ from knowledge of only phase separation data. Furthermore, it is intended to use the present results for another study dealing with the interdependence of σ and the thermodynamic interaction parameter.

EXPERIMENTAL

Materials

The polystyrene samples PS 17.5, PS 42.5, PS 86.3 and PS 175.0 were purchased from Polymer Standards System (Mainz, Germany). Their numbers are identical to 10^{-3} times the (weight average) relative molar mass M (or, equivalently, the actual molar mass in kg mol^{-1}); the molecular non-uniformity $U = (M_w/M_n) - 1$ lies in all cases between 0.02 and 0.05. The solvents were products from Merck (Darmstadt, Germany). Methylcyclohexane (MeCH) was used for synthesis and cyclohexane (CH) was of Uvasol grade. Both liquids were purified by fractional distillation and dried over molecular sieves before use.

Methods

Phase diagrams. For the narrowly distributed PS samples of interest, the cloud point curve and the coexistence curve deviate negligibly from each other, as was ascertained by test experiments. For this reason the transition from the homogeneous to the two-phase regime was determined visually with an accuracy of approximately ±0.1 K. This means that the average error in the critical temperature T_c is of the same order of magnitude.

Densities. The densities ρ of the coexisting phases required for the evaluation of all primary data were taken

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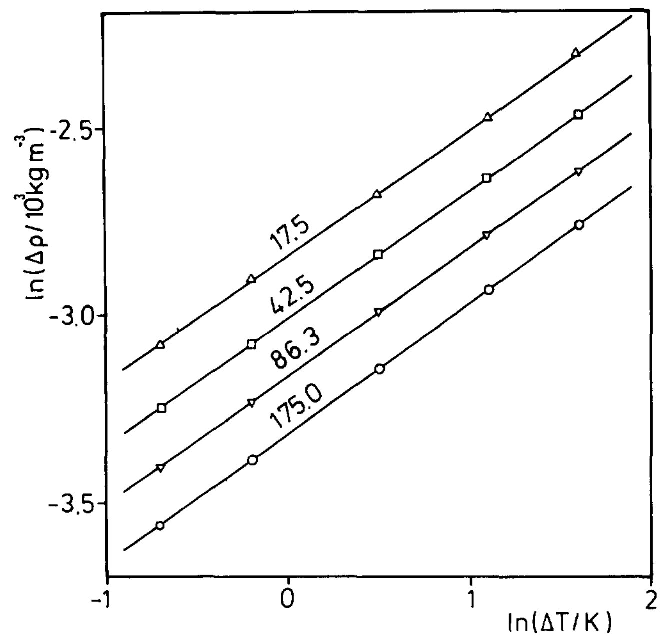

Figure 1 Density difference $\Delta\rho$ of the coexisting phases as a function of the temperature distance to the critical temperature T_c (cf. *Table 1*) for different representatives of the system MeCH/PS. The numbers given to identify the polymer samples are 10^{-3} times the (weight average) relative molar mass M (or, equivalently, the actual molar mass in kg mol^{-1})

from the literature[4–6]. The published volume fractions of PS in the coexisting phases were converted into densities (assuming additivity of the volumes of the components) and $\Delta\rho$ calculated therefrom. Plotting $\ln \Delta\rho$ as a function of $\ln \Delta T$ (where $\Delta T = T_c - T$) yields a straight line for each molecular weight. By means of this graph one can obtain another set of linear dependences plotting $\ln \Delta\rho$ for different constant ΔT values as a function of $\ln M_w$. From these relations it is possible to read the $\Delta\rho$ data for the molecular weights of interest at the chosen ΔT values. The results obtained for the system MeCH/PS (data from ref. 4) are shown in *Figure 1* in terms of a plot of $\ln \Delta\rho$ *versus* $\ln \Delta T$. The results for CH/PS (data from refs 5 and 6) look similar. In order to check the validity of this theoretically justified linear interpolation procedure, some densities were measured using conventional pycnometers for high polymer concentrations (>15 wt%) and a Kratky apparatus (Fa. Paar, Graz, Austria) for the less viscous solutions. The densities of the coexisting phases resulting from the two procedures scatter within an interval of ±0.5%.

Interfacial tension. Most of the measurements were performed with the spinning drop (SPD) method on an apparatus from Fa. Krüss (Hamburg, Germany). The normal operation (i.e. the filling of the tube with the matrix phase first and then introducing a droplet of the less dense phase by means of a syringe) does not work with the present systems, due to the high viscosities of the polymer-rich phase. For this reason two procedures were applied for all determinations of σ. In one type of experiment the solution was introduced at higher T where the system is still one phase and subsequently cooled to the equilibrium temperature, in the other variant two coexisting phases were jointly put into the tube at the temperature of interest. In both cases it is essential to choose a total composition such that the droplet of the less dense phase assumes the required size. The coalescence of the initially disperse suspended phase into a single drop is reached by spinning the tube and tilting it alternately from one side to the other.

The dimensions of the droplet at a given angular velocity ω are then measured using a micrometer eyepiece and evaluated with respect to σ. In order to check whether the results refer to gyrostatic equilibria, measurements were performed for different ω values and only used if they led to σ values which are identical within experimental error. As long as the ratio of length and radius r of the droplet exceeds a value of eight the following relation[7] (cylinder approximation) was used:

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

where $\Delta\rho$ is the difference in the densities of the coexisting phases. In the few cases in which the dimensions of the droplet did not fulfil the above inequality, the evaluation was performed as described in the literature[8,9]. The σ values obtained with the two different filling procedures described above coincide within ~5%.

To check the reliability of the SPD data, additional measurements were performed with the sessile drop (SED) method. To this end an optical cell with plane windows that can be well thermostatted (±0.01 K) was constructed. Phase separation was achieved within the cell and the droplets of the denser coexisting phase were allowed to settle on a Teflon block. Their equilibrium shape was measured by means of a travelling microscope and σ calculated from the obtained dimensions by means of Porter's equation[10].

In the case of the SPD measurements the experimental errors stem from two main sources, the product $\omega^2 r^3$ and $\Delta\rho$. The reproducibility of the former quantity is ±3% and that of the latter increases from 5% for high values of $\Delta\rho$ up to 20% for the lowest. These data yield a total estimated error of σ which rises from ±0.0002 to ±0.004 as σ increases from 0.0007 to 0.048 mN m^{-1}. According to similar calculations the precision of the SED measurements is normally somewhat less than that of the SPD, except for very low σ values where it becomes considerably worse.

RESULTS AND DISCUSSION

Phase diagrams

Figure 2 gives an example of the cloud point curves obtained with the different polymer samples in the two solvents of interest. The resulting T_cs are collected in *Table 1.* The fact that these values agree very well with published material, as demonstrated in *Figure 3*, justifies the determination of the critical conditions via cloud point measurements.

In *Figure 3* the data are evaluated according to the proportionality[2]

$$\ln[(\theta - T_c)/\theta] \sim -\zeta_T \ln M \qquad (2)$$

in which ζ_T should, according to theory[2], equal 0.5. The θ temperatures of the systems MeCH/PS (342.9 K) and CH/PS (307.65 K) were taken from the literature[11]. The ζ_T values of 0.47 (MeCH) and 0.48 (CH) resulting from this material lie close to the predicted values.

Temperature and molecular weight influences

All experimental data concerning the σ between the coexisting phases as a function of ΔT (the depth of penetration into the two-phase regime) and as a function

Table 1 Critical temperature T_c of the different solvent/polymer systems

System	M_w	T_c (K)
MeCH/PS	17 500	296.05
	42 500	311.55
	86 300	320.05
	175 000	326.85
CH/PS	42 500	287.97
	175 000	297.35

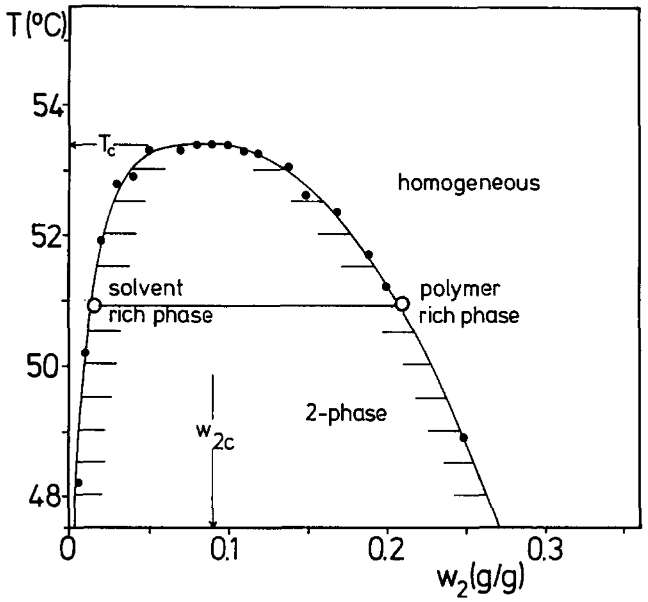

Figure 2 Cloud point curve and one tie line of the system MeCH/PS 175; the critical conditions are indicated

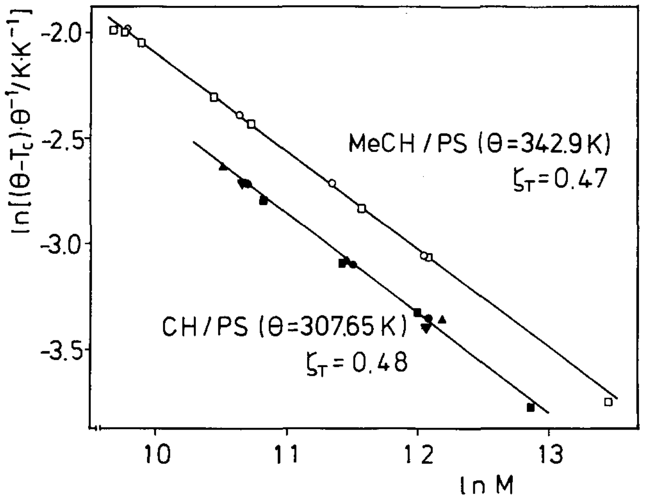

Figure 3 Reduced temperature distance $(\theta - T_c)/\theta$ of the critical temperature T_c from the θ temperature as a function of the molecular mass of the polymer for the systems MeCH/PS and CH/PS: (□) reference 4; (○) present work; (▲) references 12–14; (●) reference 6; (■) reference 15; (▼) present work

of molar mass of the polymer samples are graphically represented in *Figures 4a* and *b*. The former contains only the results for MeCH whereas the latter not only shows the data for the two polymer samples measured in CH but also the corresponding results for MeCH to enable an assessment of the influence of the particular nature of the solvent on σ at constant ΔT.

In both solvents σ decreases with increasing molecular weight as expected. *Figure 4b* reveals that σ differs substantially for the solutions of a polymer of given molar mass in two different solvents, if compared at the same ΔT values.

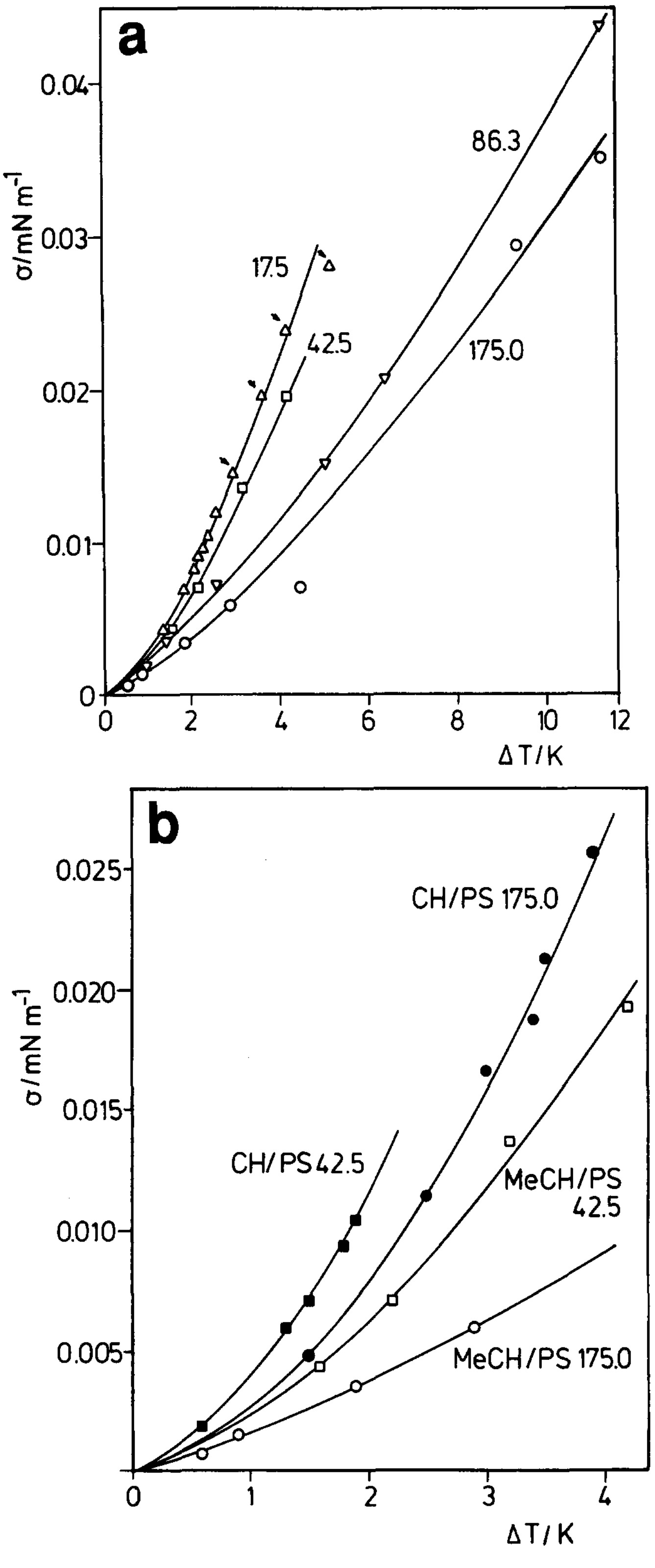

Figure 4 Variation of the interfacial tension σ of solutions of PS with $T-T_c$, the distance to the corresponding critical temperature T_c. All σ values were determined by means of spinning drops except for those marked by an arrow, which stem from sessile drops. (a) Results for MeCH and the indicated samples of PS; (b) shows this dependence for CH and the two polymer samples investigated in this liquid together with the corresponding data for MeCH from (a)

For a theoretical discussion of the results it is essential to know whether the measurements were performed within a region sufficiently close to the critical conditions, for which the results of the non-classical treatments apply, or outside the region, where mean-field approximations are permissible. Equations derived on the basis of the latter approach[2,16–19] have demonstrated that σ should vary with M and $\tau = \Delta T/T_c$ in the following way

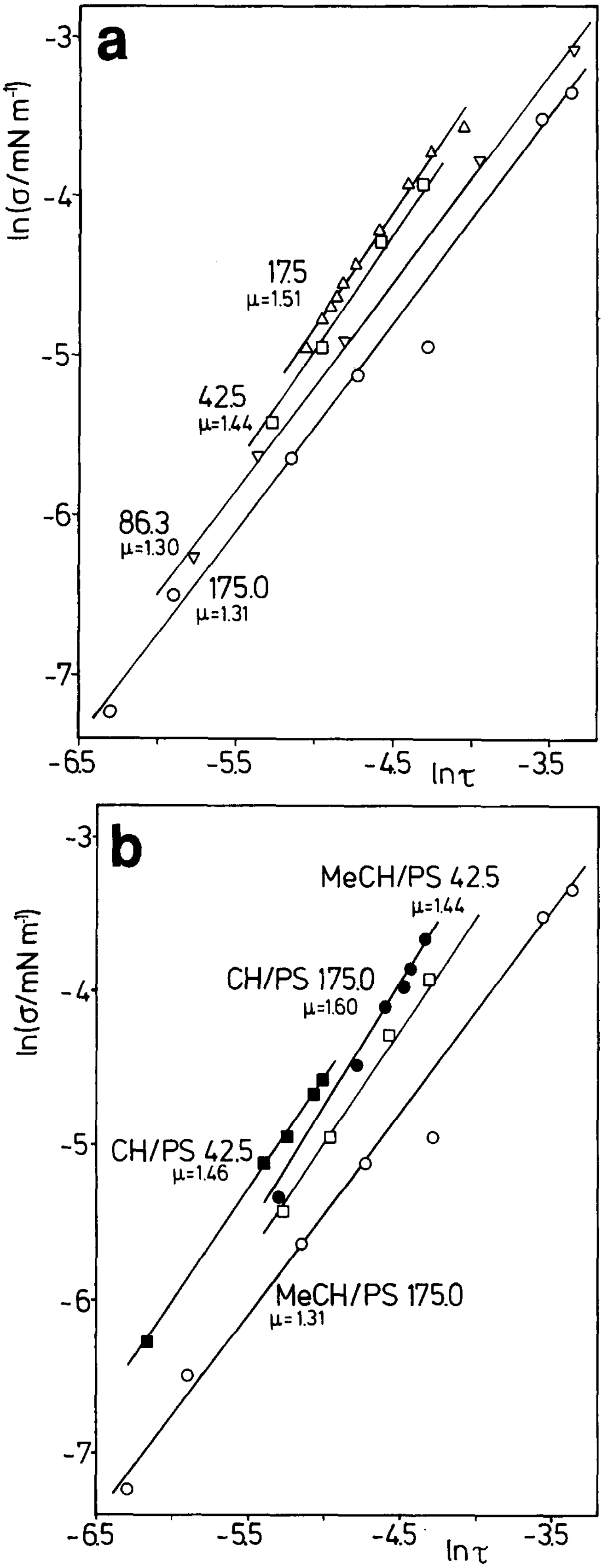

Figure 5 (a, b) Evaluation of the data shown in *Figures 4a* and *b*, respectively, in terms of τ, the reduced distance of the measuring temperature from T_c, according to proportionality (3); the molar masses and critical exponents μ are shown

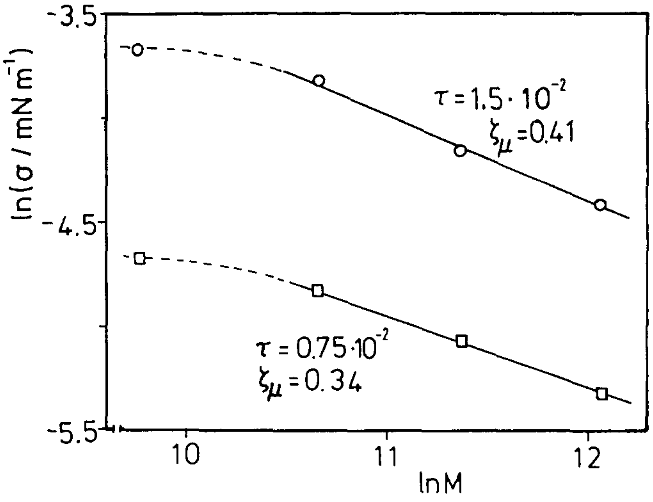

Figure 6 Evaluation of the data shown in *Figures 4a* and *b* in terms of proportionality (3); the τ values (reduced distance of the measuring temperature from T_c), at which these data were read from *Figure 5a*, and the critical exponents ζ_μ are shown

$$\ln \sigma = A - \zeta_\mu \ln M + \mu \ln \tau \qquad (3)$$

where $\zeta_\mu = 0.25$ and $\mu = 1.5$ are the so-called classical critical exponents and A is a constant for a given solvent. According to calculations on the basis of the Ising model, μ should be less, namely 1.26, close to the critical point[3].

The variation of the constant A, resulting from an exchange of one solvent for another, can be rationalized if one takes into account that σ directly reflects the thermodynamic interaction parameter g, whereas a given value of τ will correspond to markedly different interaction parameters for solvents of different heats of mixing. In other words, even if τ is constant, g can vary and consequently σ too.

In order to decide which of the above theoretical treatments has to be applied to our measurements, the Ginzburg criterion[20] is used. It states that the classical approach is permissible as long as

$$T_c - T > \theta N^{-0.5} \qquad (4)$$

where N is the number of monomeric units of the polymer, or written in terms of the interaction parameters g alternatively[21] as long as

$$[(g/g_c) - 1] > 9(3/4\pi)^{4/3} N^{-1} \qquad (5)$$

Equation (4) reveals that the overwhelming majority of the present measurements lie well within the classical region so that we need not discuss non-mean-field critical behaviour.

Figures 5a and *b* show the evaluation of the data given in *Figures 4a* and *b* according to equation (3) with respect to μ. *Figure 6* gives the evaluation of the results for MeCH with respect to ζ_μ. Due to the logarithmic scale the errors increase considerably as τ becomes smaller; for that reason only data are given for which $\Delta T > 0.6$ K. From the former graphs it becomes obvious that the critical exponents μ vary, in contrast to the theoretical prediction, with the molar mass of the polymer. For the discussion of molecular weight influences (*Figure 6*) this result implies that ζ_μ depends on τ.

The deviations of μ from the classical exponent 1.5

become more pronounced as M increases. For the highest molar masses μ lies close to 1.26, the value predicted from the Ising model for non-classical behaviour. This trend is in accord with previous reports[3] but disagrees with the inequalities (4) and (5) which state that the probability of finding mean-field behaviour should increase with rising M. This fact implies that the M dependence of σ should not be due to contributions caused by fluctuations, but rather result from inadequacies in the classical treatment. One source of error could lie in the neglect of concentration-dependent interaction parameters. The discrepancies could also stem from the inapplicability of proportionality (3) for the relatively large τ values realized experimentally; it can then no longer be excluded that μ depends on M and ζ_μ on τ. *Figure 5b* also suggests solvent-dependent μ values; however, this observation requires further confirmation in view of the limited number of measurements and the experimental uncertainties.

Figure 6 reveals that the molecular mass dependence of σ is more pronounced than predicted by the mean-field theory[2,19], which yields $\zeta_\mu = 0.25$. This deviation ($\zeta_\mu = 0.41$ for $\tau = 0.015$ and 0.34 for $\tau = 0.0075$) becomes more pronounced the larger the distance from T_c. Furthermore it can be noticed that ζ_μ is only independent of molar mass for $M > 40$ kg mol^{-1} and becomes smaller below this value.

Master curve with respect to the concentration differences

The σ value measured for a given sample of PS in CH at a constant reduced distance from T_c is up to twice as large as that resulting for MeCH at an identical τ value. In view of the Cahn–Hilliard theory[16] it appeared interesting to evaluate the interfacial data with respect to the differences in the volume fractions φ of the polymer contained in the coexisting phases (signified by φ' and φ''),

$$\Delta\varphi = (\varphi'' - \varphi') \qquad (6)$$

instead of τ, to check whether solvent influences are also discernible in this quantity.

For that purpose it is necessary to transform τ into $\Delta\varphi$. By analogy to the power-law formulated in equation (3) one can write

$$\ln \Delta\varphi = B - \zeta_\beta \ln M + \beta \ln \tau \qquad (7)$$

where the mean-field theory yields the critical exponents $\zeta_\beta = 0.25$ and $\beta = 0.5$; the experimentally determined values of $\zeta_\beta = 0.22$ and $\beta = 0.35$, reported in the literature[4], are in good agreement with the present results. B [like A of equation (3)] varies from solvent to solvent; the reasons for this are identical with those already discussed for A. *Figure 7* shows for two samples of PS a comparison of the evaluation according to equation (7) for CH and MeCH. Again one can see a shift in the positions of the lines which give the results for the two solvents, similar to that observed in *Figure 5b*.

On the basis of this observation it appeared interesting to investigate whether a generally valid correlation between σ and $\Delta\varphi$ can be obtained by inserting $\ln \tau$ from equation (7) into equation (3). This operation yields

$$\ln \sigma = C + \delta \ln M + (\mu/\beta) \ln \Delta\varphi \qquad (8)$$

where the new critical exponent δ is related to the existing ones by

$$\delta = (\zeta_\beta \mu/\beta) - \zeta_\mu \qquad (9)$$

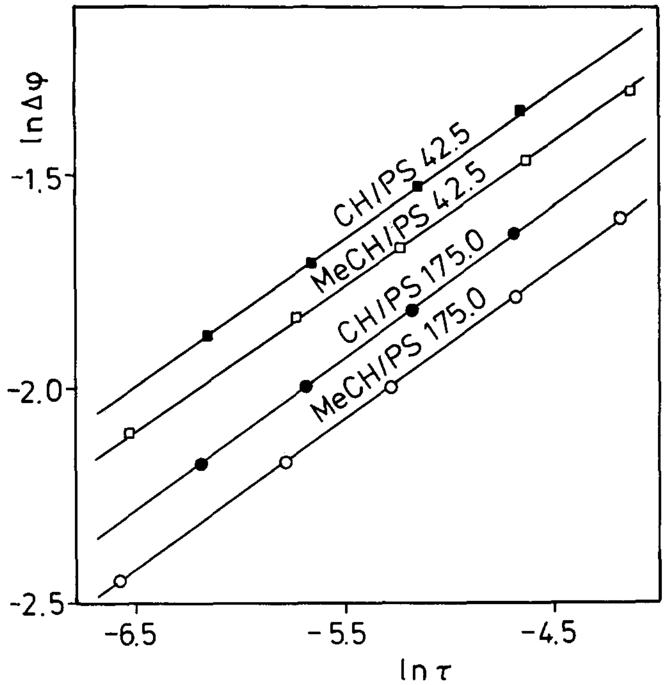

Figure 7 Inter-relation between the difference in the polymer volume fraction $\Delta\varphi$ in the coexisting phases and τ, the reduced distance of the measuring temperature from T_c, for two samples of PS and the solvents CH and MeCH plotted according to equation (7)

According to the mean-field theory δ should be 0.50; inserting the experimentally determined critical exponents into equation (9) yields $\delta = 0.48$. For μ/β, the critical exponent of $\Delta\varphi$, the corresponding theoretical values are 3.00 (mean-field) and 4.00 (Ising) in comparison with the experimental result of 3.86. C is again a constant which, however, should be independent of the chemical nature of the solvent in case the above considerations turn out to be correct. This means that a plot of $\ln(\sigma/M^{0.5})$ *versus* $\ln \Delta\varphi$ should yield one single line for all solutions under investigation with the calculated slope.

Indeed, as demonstrated in *Figure 8*, this is the case. All experimental data fall on one common line, irrespective of the solvent and of the molecular weight of the polymer; linear regression yields a slope of 3.85 and an intercept of -4.2. This means that the master curve formulated in equation (10) should generally hold true for PSs:

$$\sigma\ (\mathrm{mN\ m^{-1}}) = 0.015 M^{0.5} \Delta\varphi^{3.85} \qquad (10)$$

First experiments performed with poly[isobutene]s instead of PS, to check the influence of the nature of the polymer, have demonstrated that the critical exponents are identical with those of the above relation. The numerical value of the factor, on the other hand, turned out to depend on the particular nature of the macromolecules. However, this difference can be eliminated by converting the relative molar mass M into N, the number of monomeric units. The generalized equation then reads

$$\sigma = 0.153 N^{0.5} \Delta\varphi^{3.85} \qquad (11)$$

Naturally the most reliable numerical value of the factor and the precise critical exponents μ/β and δ of the above relation have still to be substantiated by further experiments.

Nevertheless this result is already now of practical and

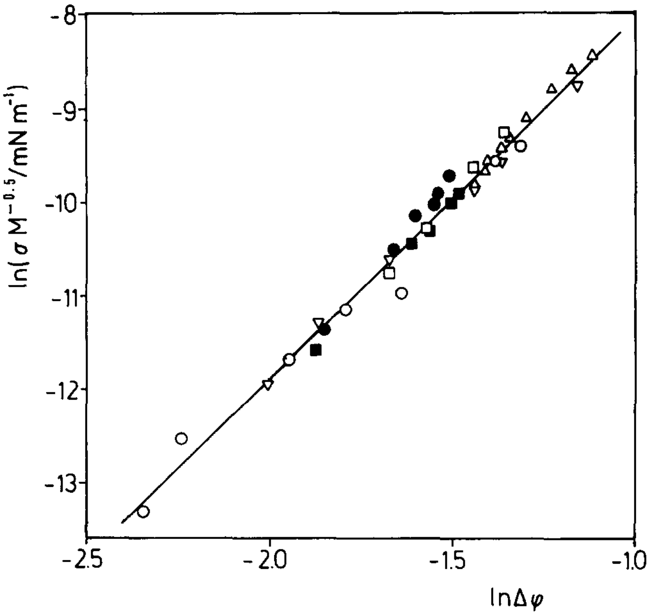

Figure 8 Master curve for the concentration dependence of the interfacial tension of solutions of PS according to equation (9), i.e. plot of $\ln(\sigma/M^{0.5})$ *versus* $\ln\Delta\varphi$, the difference in the polymer volume fraction $\Delta\varphi$ in the coexisting phases: (△) MeCH/PS 17.5; (□) MeCH/PS 42.5; (▽) MeCH/PS 86.3; (○) MeCH/PS 175.0; (■) CH/PS 42.5; (●) CH/PS 175.0

also theoretical importance, since it means that the knowledge of the chain length of the polymer and of the polymer content in the two coexisting phases suffices to predict the σ between them, at least for typical vinyl polymers. It is neither necessary to know the T_c or the θ temperature of the system, nor the equilibrium temperature itself.

Particularly the fact that equation (10) does not contain T explicitly appears surprising at first glance. In a formal way this is however easily conceivable by the elimination of τ [equations (3) and (7)]. Intuitively it can also be rationalized in the following way: if one rewrites equation (10) as $\sigma/N^{0.5} \sim \Delta\varphi^{\mu/\beta}$ (taking $\delta = 0.50$) and converts $N^{0.5}$ into R_θ, the radius of gyration under θ conditions, one ends up with the proportionality

$$\sigma/R_\theta \sim \Delta\varphi^{\mu/\beta} \qquad (12)$$

This relation states that the difference in the composition of the coexisting phases fixes the reduced interfacial tension σ/R_θ unequivocally. σ and R_θ depend both on M and T; however, according to the present findings these influences obviously cancel in the ratio σ/R_θ. Another way to look at the above relation is to interpret σ/R_θ as an energy density which is proportional to the average interfacial energy density of the entire interfacial layer. This approach would mean that the dissimilarity in the composition of the coexisting phases and the average interfacial energy density are related in a very elementary manner. At least qualitatively this conclusion appears plausible.

CONCLUSIONS

From the present results it is obvious that the relation between σ and $\Delta\varphi$, the difference in the volume fraction of the polymer in the coexisting phases, is much more universal than the corresponding dependence of σ on τ, the relative distance to T_c. The reason is that σ like $\Delta\varphi$ depends on the Gibbs energy of mixing only, whereas the τ values which correspond to a given σ also depend on the heat of mixing. A further generalization which eliminates the influences of the particular nature of linear vinyl polymers can be reached by normalizing σ to $N^{0.5}$.

To obtain quick access to interfacial data for new solvent/polymer systems knowing only their phase separation behaviour, equation (11) should prove very useful. As mentioned in the Introduction, this information appears particularly important in the context of mass transport from one liquid phase into another. Conversely the established relation might also be of help in the analysis of systems for which it is more difficult to measure $\Delta\varphi$ than σ. In addition to these practical consequences of the present findings, they should also be helpful in the discussion of the dependence of σ on the thermodynamic interaction parameter.

ACKNOWLEDGEMENT

The authors thank the 'Max-Buchner-Forschungsstiftung' for the stipend granted to MH.

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