Interfacial tension of demixed polymer solutions*

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A model is described which permits the estimation of interfacial tensions of demixed polymer solutions from knowledge of the polymer coil size, the intrinsic viscosity and chemical potential data. The latter is most conveniently determined from equilibrium phase diagrams. The model is used for demixed polystyrene in methylcyclohexane solutions, and the results are compared to literature data on interfacial tension. Qualitative agreement is good over a large molecular weight and temperature range.

(Keywords: interfacial tension; polymer solutions; phase separation; phase diagram; demixing)

INTRODUCTION

The interfacial tension of demixed polymer solutions is an important topic because an accurate description of this phenomenon is the first step towards a description of spinodal decomposition in polymer solutions. In fact the thermodynamics of the two phenomena are identical, and therefore any model of spinodal decomposition should be capable also of predicting interfacial tensions. The difference between the two is that spinodal decomposition also requires a description of the solution dynamics in addition to equilibrium thermodynamic information. This is an area of active research; however, most work is limited to polymer melts or to concentrated polymer solutions where a mean-field description is appropriate. Yet, the lower concentration region is important to the study of gelation in semidilute polymer solutions and in the technology of microcellular foams and membranes[1].

de Gennes has argued that the interfacial thickness of demixed polymer solutions equals the correlation length in the most concentrated phase[2]. On shorter length scales, a polymer chain is unaffected by the presence of other polymers in the solution. Hence, a mean-field description of the interface might not be expected to work well. The mean-field theory of Roe[3] predicts interfaces that are broader than the estimated correlation length and subsequently predicts interfacial tensions that are substantially smaller than those observed experimentally[4]. In this paper we attempt to quantify the prediction of de Gennes by use of a simple, but reasonable, model of the interfacial structure and by use of established thermodynamic relationships such as the Gibbs' adsorption isotherm, which relates interfacial tension to polymer adsorption and chemical potentials. Chemical potentials are obtained from empirical fits of the Flory–Huggins theory to equilibrium phase diagrams. The predictions of the model are very easy to make, and based upon the comparisons to experimental data, have an accuracy comparable to available mean-field theory predictions.

MODEL DESCRIPTION

We consider phase diagrams of the type shown schematically in *Figure 1* where the interface occurs between a semidilute polymer solution (α) and a dilute polymer solution (β). We specifically exclude consideration of the near-critical region, as defined by Shinozaki *et al.*[5], in which the interfacial thickness is larger than the polymer coil size. This is only a small temperature region around the critical temperature for the high molecular weights considered here. Our model of the interface assumes that its thickness is equal to the correlation length in phase α which is obtained from[2]:

$$\xi = C\langle r^2\rangle_\theta^{1/2}\frac{\phi_p^*}{\phi_p^\alpha} \tag{1}$$

The rms end-to-end distance at theta conditions is $\langle r^2\rangle_\theta^{1/2}$, and $\phi_p^* = 1/\rho_p[\eta]_\theta$ is the critical polymer volume fraction for coil overlap. $[\eta]_\theta$ is the intrinsic viscosity at theta conditions and ρ_p is the polymer density. The

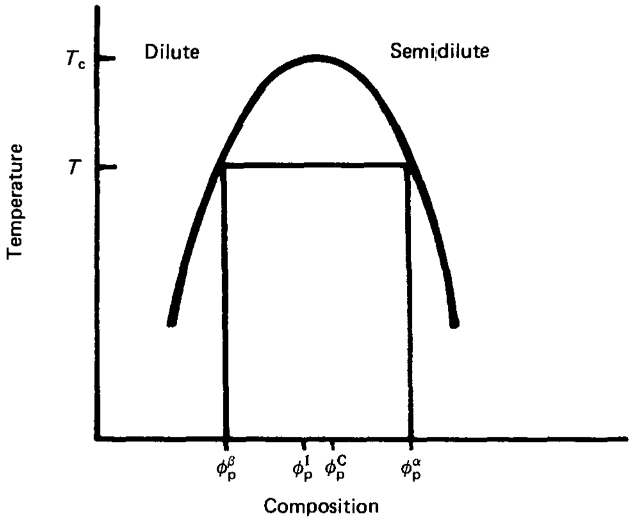

Figure 1 Schematic phase diagram for a polymer solution showing the critical point (T_c,ϕ_p^c) and two equilibrium concentrations ϕ_p^β and ϕ_p^α occurring at temperature T

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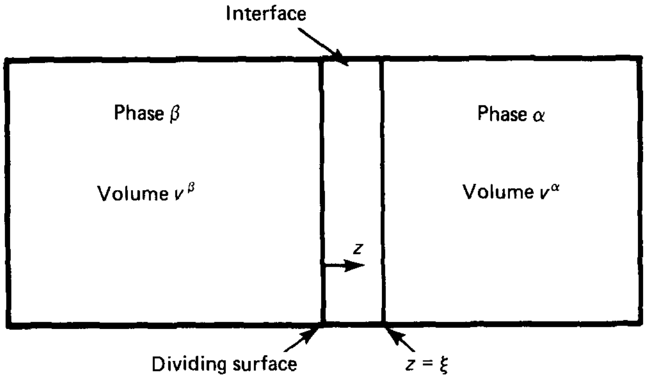

$$\frac{\phi_p^\alpha v^\alpha + \phi_p^\beta v^\beta}{v^\alpha + v^\beta} \approx \phi_p^I = \frac{1}{\xi}\int_0^\xi \phi_p(z)\,dz$$

Figure 2 Interfacial tension is calculated by considering the amount of energy which would be evolved upon the destruction of an interface between a dilute polymer phase β and a semidilute polymer phase α

coefficient C cannot be determined from scaling but should be of the order 1. In our model we assume that it is equal to 1. All of our results are directly proportional to the value of C.

Consider a volume of solution containing both phases α and β and their interface as shown in *Figure 2*. The volumes of phases α and β are chosen such that the average polymer volume fraction is equal to that in the interfacial region, ϕ_p^I. Conceptually the two phases could be isothermally and reversibly homogenized by moving one polymer at a time from phase α to phase β. The free energy change associated with this can be divided into two parts corresponding to bulk fluid mixing and interfacial fluid mixing. The latter is by definition the exact opposite of the interfacial tension and can be calculated from the Gibb's adsorption isotherm[6]:

$$d\sigma = -\Gamma_p d\mu_p - \Gamma_s d\mu_s \tag{2}$$

This equation relates the differential change in interfacial tension, σ, to the polymer and solvent adsorption, Γ_p and Γ_s, and the differential change in the polymer and solvent chemical potentials, μ_p and μ_s. As the phases are homogenized the chemical potentials of both polymer and solvent change as the concentration is changed. Initially the chemical potential of the polymer or the solvent is the same in both phases and within the interface since this is the equilibrium state. In the final state the chemical potentials are those of a homogeneous solution at the average concentration. We have chosen this average concentration to be the average occurring within the original interface. The interfacial tension is obtained from integration of equation (2):

$$\sigma = \int_{\mu_p(\phi_p^\alpha)}^{\mu_p(\phi_p^I)} \Gamma_p d\mu_p + \int_{\mu_s(\phi_s^\alpha)}^{\mu_s(\phi_s^I)} \Gamma_s d\mu_s \tag{3}$$

This equation could be applied to any interface but in general one has no way of knowing the polymer or solvent adsorption and, therefore, the integration cannot be done. By using de Gennes' assertion that the interfacial thickness is equal to the correlation length of phase α, we can calculate the interfacial adsorptions.

The interfacial adsorptions are defined as the interfacial excess concentration of either polymer or solvent with respect to a dividing surface. For convenience we take the dividing surface to be exactly one correlation length into the interface from phase α. Since few, if any, entire polymer molecules are within the interface, the polymer adsorption equals:

$$\begin{aligned}\Gamma_p &= \int_0^\infty (c_p(z) - c_p^\alpha)dz \\ &\simeq -c_p^\alpha \xi = -\xi\phi_p^\alpha \frac{\rho_p N_{av}}{M_p}\end{aligned} \tag{4}$$

where c_p^α is the polymer concentration in phase α, $c_p(z)$ is the corresponding quantity at position z within the interface, and M_p is the molecular weight of the polymer. Since the correlation length in phase α is inversely proportional to c_p^α or $\phi_p{}^\alpha$ (equation (1)), this term conveniently drops out in equation (4) and:

$$\Gamma_p = \frac{-\langle r^2\rangle_\theta^{1/2} N_{av}}{M_p[\eta]_\theta} \tag{5}$$

Note that for polymer solutions the second term in equations (3) is small compared with the first term. In our calculations, the second term is usually about 10% of the first term. In order to calculate the second term our model requires one additional piece of information on the interfacial structure, which is the ratio of the average polymer volume fraction within the interface to that within phase α, (ϕ_p^I/ϕ_p^α). Our model assumes that this ratio is 0.5. The justification for this is easy to visualize. Because the interfacial region has a thickness much smaller than the polymer coil size (consistent with deep quenches), this region contains few, if any, entire polymers or polymer centres-of-mass. The segments located there are donated by the polymers in phases α and β. The average segment density within the interface is nearly the average within phases α and β, and since phase β is almost void of polymer this is equivalent to one-half the segment density in phase α. This assumption of the model could be eliminated with a detailed structural model of the interface. However, that would be unwarranted for the simple model presented here. Since, the second term of equation (3) is a relatively small correction to the interfacial tension an improvement of this approximation would have very little effect on the calculation. With the assumption that ϕ_p^I/ϕ_p^α is equal to 0.5, the solvent interfacial adsorption can be similarly calculated to be:

$$\Gamma_s = \frac{\rho_s \langle r^2\rangle_\theta^{1/2} N_{av}}{2\rho_p M_s[\eta]_\theta} \tag{6}$$

Using these expressions for the polymer and solvent interfacial adsorptions enables equation (3) to be integrated directly, which results in the following expression for the interfacial tension:

$$\begin{aligned}\sigma &= \frac{-\langle r^2\rangle_\theta^{1/2} N_{av}}{M_p[\eta]_\theta}[\mu_p(\phi_p^I) - \mu_p(\phi_p^\alpha)] \\ &\quad + \frac{\rho_s\langle r^2\rangle_\theta^{1/2} N_{av}}{2\rho_p M_s[\eta]_\theta}[\mu_s(\phi_s^I) - \mu_s(\phi_s^\alpha)]\end{aligned} \tag{7}$$

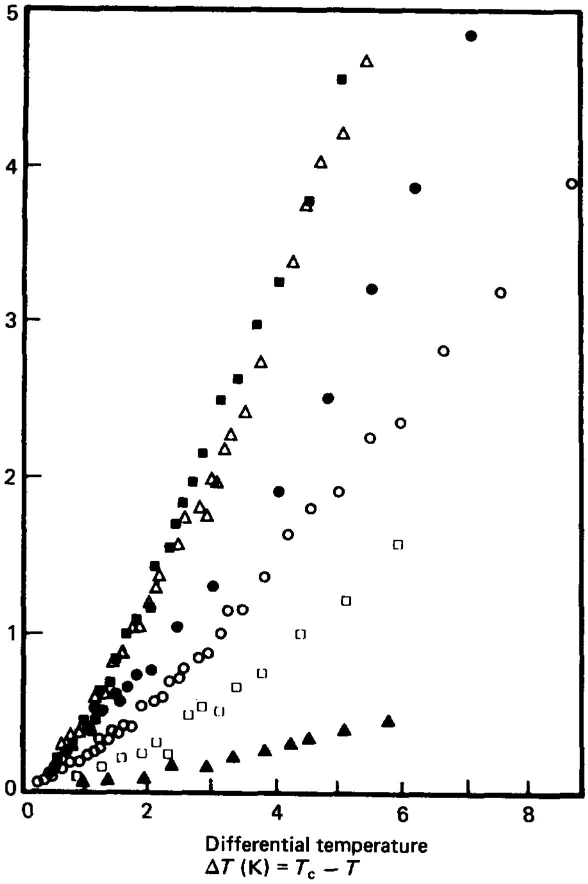

Figure 3 Experimental data obtained by Shinozaki *et al.*[4] on the interfacial tension of demixed polystyrene–methylcyclohexane solutions. M_w: ■, 9000; △, 17500; ●, 37000; ○, 110000; □, 233000; ▲, 1260000

This expression can be used to calculate interfacial tensions if one knows the rms end-to-end distance and intrinsic viscosity at theta conditions, if one knows the phase diagram and has an espression relating this to the chemical potentials, and if one knows the average interfacial volume fraction, ϕ_p^I. The latter is estimated to be $0.5\phi_p^\alpha$ in our model. We will comment on the sensitivity of this approximation below. This expression requires very little computational effort. Despite the relative simplicity, however, good qualitative predictions appear to be possible.

COMPARISON WITH EXPERIMENT

Although many theoretical investigations have been done on the interfacial tension of demixed polymer solutions, only a small number of experimental investigations have been undertaken[4,5,7,8]. The most frequently studied system has been that of polystyrene in methylcyclohexane[4], which has allowed the molecular weight dependence of the polymer to be systematically studied. *Figure 3* shows some experimental data obtained by Shinozaki *et al.*[4] on the interfacial tension of demixed polystyrene–methylcyclohexane solutions. For this system, equilibrium phase diagrams have also been experimentally determined by Dobashi *et al.*[9,10]. This information is necessary because in order to test our model we require phase diagram data for the same polymer–solvent system whose interfacial tension has been determined. The results have been fitted to the Flory–Huggins theory by developing the following empirical expression for the interaction parameter:

$$g(\phi_p,T) = -0.1091 + \frac{\left(-0.5832 + \frac{278.6}{T} + 1.695\times10^{-3}T\right)}{(1-0.2481\,\phi_p)} \qquad (8)$$

Because $g(\phi_p,T)$ was allowed to vary with both temperature and polymer volume fraction, the equilibrium phase diagrams were reproduced well by the Flory–Huggins theory for large molecular weights and within about 5 K of the critical point. *Figure 4* shows the fit of this empirical interaction parameter for the Flory–Huggins theory to actual phase diagrams determined experimentally by Dobashi *et al.*

In the Flory–Huggins theory the polymer and solvent chemical potentials are:

$$\begin{aligned}\frac{(\mu_p-\mu_p^0)}{kT} &= -x\phi_s + \ln\phi_p + x\left(g+\phi_p\frac{\partial g}{\partial\phi_p}\right)\phi_s^2 \\ \frac{(\mu_s-\mu_s^0)}{kT} &= \ln\phi_s + \left(1-\frac{1}{x}\right)\phi_p + \left(g-\phi_s\frac{\partial g}{\partial\phi_p}\right)\phi_p^2\end{aligned} \qquad (9)$$

where x is the ratio of polymer to solvent molar volumes and for polystyrene–methylcyclohexane solutions is $M_p/146$ (ref. 4). Equations (7), (8) and (9) together with the experimental phase diagram data of Dobashi *et al.* were used to calculate interfacial tensions for various molecular weights and undercoolings below the critical point. The required polymer properties were obtained from the 'Polymer Handbook'[11].

Figure 5 shows comparisons of experimentally determined interfacial tensions[4] with those calculated from our model as a function of the polymer molecular weight and the undercooling below the critical point. The experimentally determined interfacial tensions were generally determined for molecular weights that differed from those for which phase equilibria were established. Therefore, a direct comparison could only be made for

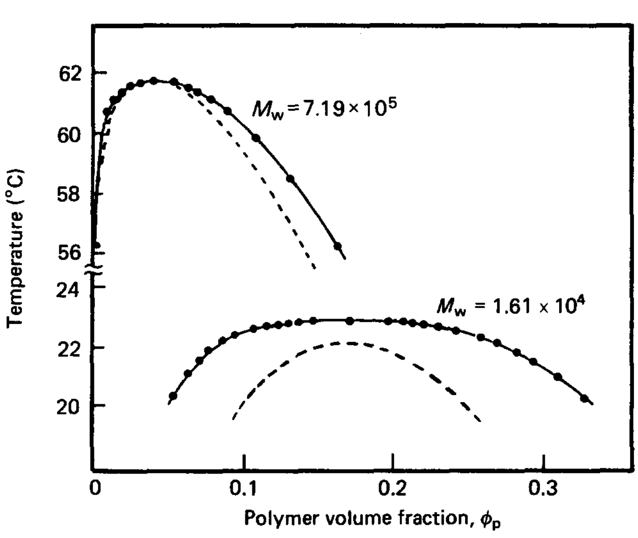

Figure 4 Empirical fit (– – –) by Dobashi *et al.*[9,10] of the Flory–Huggins theory to experimental phase diagrams of polystyrene–methylcyclohexane (●). The fit works well only for high molecular weights

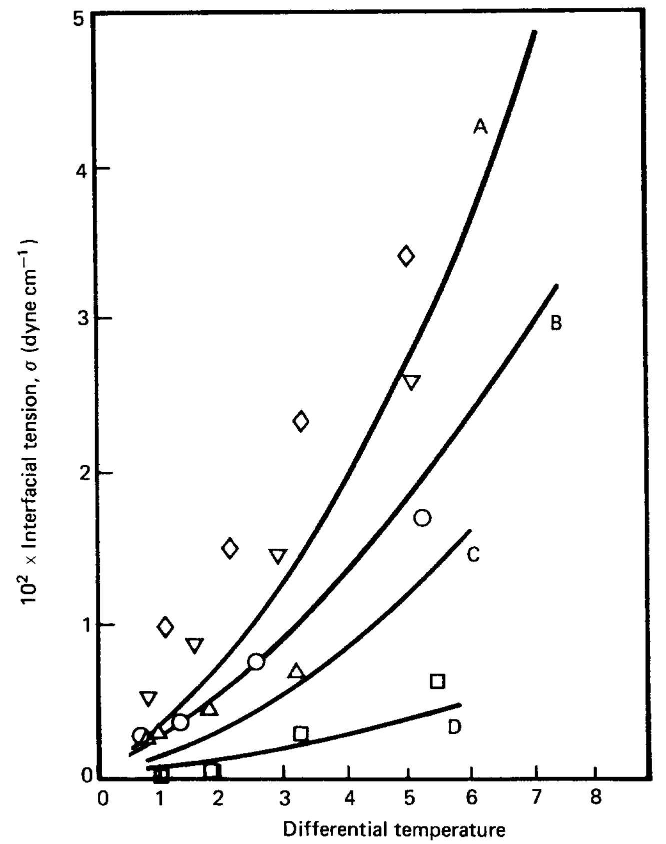

Figure 5 Comparison of predicted and experimentally determined values of interfacial tension as a function of the undercooling below the critical point and polymer molecular weight. Solid lines are smoothed experimental data of Shinozaki *et al.*[4] for molecular weights, M_w: A, 3.70×10^4; B, 1.10×10^5; C, 2.33×10^5; D, 1.26×10^6. Points are calculated for molecular weight, M_w: ◇, 3.49×10^4; ▽, 4.64×10^4; ○, 1.09×10^5; △, 1.81×10^5; □, 7.19×10^5

molecular weight 1.09×10^5. With our stated assumptions (in particular our choice of the coefficient in the scaling relation of equation (1)), the agreement for this molecular weight was good. The maximum deviation occurred at 5 K undercooling but was less than 15%.

Figure 5 shows that the interfacial tension for other molecular weights follows the correct molecular weight sequence. For example, the calculated interfacial tensions for $M = 7.19 \times 10^5$ fall below the experimental data for $M = 2.33 \times 10^5$, 1.10×10^5 and 3.7×10^4, but in general fall above the experimental data for $M = 1.26 \times 10^6$. The calculated interfacial tensions for $M = 1.81 \times 10^5$ fall below the experimental data for $M = 3.7 \times 10^4$, above the experimental data for $M = 2.33 \times 10^5$ and 1.26×10^6 and overlap the experimental data for $M = 1.10 \times 10^5$. The model predictions for $M = 4.64 \times 10^4$ fall above all of the experimental data for the higher molecular weights, as they should, and are scattered about the experimental data for $M = 3.70 \times 10^4$. Finally, the model predictions for $M = 3.49 \times 10^4$ lie above all of the experimental data for the higher molecular weights, as expected. Additionally, the curvature apparent in the experimental data is also mimicked.

A close comparison can be made between measurements for $M = 3.70 \times 10^4$ and model calculations for $M = 3.49 \times 10^4$. In this case the agreement is worse. The model appears to overpredict interfacial tension by about 20% at 5 K undercooling to over 60% at 2 K undercooling. A large part of this discrepancy could be due to the failure of the empirical free energy expression accurately to reproduce the phase diagram for this lower molecular weight (*Figure 4*).

In order to accomplish the integration in equation (7), we estimated the average polymer volume fraction in the interfacial region. Our estimate was that ϕ_p^I/ϕ_p^α was 0.5. This estimate was justified only in a crude way; however, our calculations are very insensitive to this approximation. Consider the model predictions for $M = 1.09 \times 10^5$ and a temperature 3 K below the critical point. The measured interfacial tension was 0.92×10^{-2} dyne cm^{-1} (ref. 4). Assuming that ϕ_p^I/ϕ_p^α is 0.5, our model gives 0.97×10^{-2} dyne cm^{-1}, which is 5.4% higher than the experimental value. If we assume instead that the ratio is only 0.3, then our model predicts that the interfacial tension is 0.84×10^{-2} dyne cm^{-1}, which is 8.5% lower than the experimental value. If we assume that the ratio is 0.7, then our model predicts that the interfacial tension is 1.04×10^{-2} dyne cm^{-1}, which is 13% higher than the experimental value. This range of predicted values of the interfacial tension is certainly within the experimental scatter and certainly minimal compared to other assumptions of this model.

We have compared our model calculations of interfacial tension to an additional prediction of de Gennes that the quantity $kT/\sigma\xi^2$ should be constant[2]. As was also found for the experimental data[4], this quantity does show systematic variation with the interfacial tension (*Figure 6*). This is not really surprising because strict compliance with this rule would necessitate that the free energy function go exactly at kT/ξ^3. The Flory–Huggins theory does not conform to this[2] and neither does a recent free-energy expression developed for semidilute polymer solutions by Muthukumar and Edwards[12].

CONCLUSIONS

The model described here is qualitatively able to predict interfacial tensions of demixed polymer solutions with a

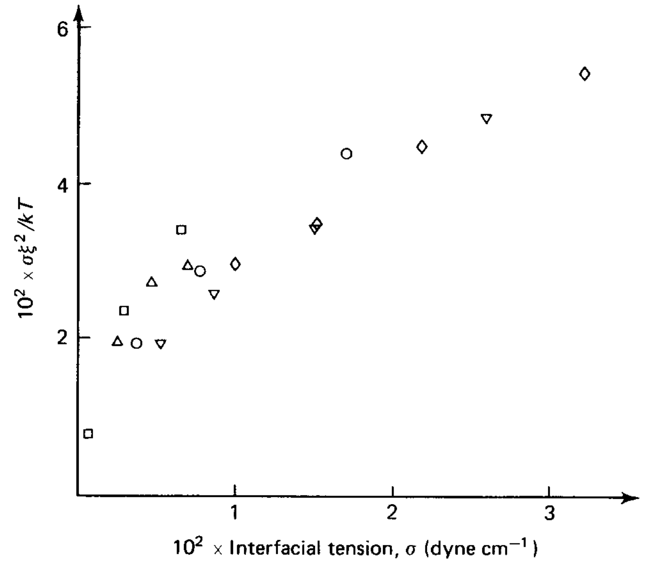

Figure 6 Test of de Gennes' scaling prediction[2], that σ goes as kT/ξ^2, shows that this is not followed exactly for the experimental data[4] and for the predictions of this model. M_w: ◇, 3.49×10^4; ▽, 4.64×10^4; ○, 1.09×10^5; △, 1.81×10^5; □, 7.19×10^5

minimum amount of effort. Under the stated assumptions, the predictions appear to be comparable to those obtained from mean-field theory predictions. The good qualitative agreement between the predictions and experiments is evidence that de Gennes' assertion that the interfacial thickness scales as the correlation length of the concentrated phase is accurate. This evidence should influence any theory of spinodal decomposition in the low concentration regime. The model could be made quantitative with a determination of the coefficient in the scaling relationship in equation (1).

REFERENCES

1 Aubert, J. H. and Clough, R. L. *Polymer* 1985, **26**, 2047

2 de Gennes, P.-G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979

3 Roe, R.-J. *J. Chem. Phys.* 1975, **62**, 490

4 Shinozaki, K., Van Tan, T., Saito, Y. and Nose, T. *Polymer* 1982, **23**, 728

5 Shinozaki, K., Abe, M. and Nose, T. *Polymer* 1982, **23**, 722

6 Moore, W. J. 'Physical Chemistry', 4th Edn., Prentice-Hall, Englewood Cliffs, 1972

7 Langhammer, G. and Nestler, L. *Makromol. Chem.* 1965, **88**, 179

8 Nose, T. and Van Tan, T. *J. Polym. Sci., Polym. Lett. Edn.* 1976, **14**, 705

9 Dobashi, T., Nakata, M. and Kaneko, M. *J. Chem. Phys.* 1980, **72**, 6685

10 Dobashi, T., Nakata, M. and Keneko, M. *J. Chem. Phys.* 1980, **72**, 6692

11 Brandrup, J. and Immergut, E. H. (Eds.), 'Polymer Handbook', 2nd Edn., John Wiley and Sons, New York, 1975

12 Muthukumar, M. and Edwards, S. F. *J. Chem. Phys.* 1982, **76**, 2720