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Notes

Molar Mass Dependence of the Correlation Length of Local Composition Fluctuations in Different Polystyrene/Solvent Systems of Critical Composition

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A. Introduction

There is a continuing interest in experimentally determined values of the exponent n characterizing the molar mass dependence of the correlation length ξ of local composition fluctuations in polymer solutions near the critical point.[1−3] In this note, published static light scattering data for polystyrene with a narrow molar mass distribution (typically $M_w/M_n \approx 1.05$; M_n (M_w), number-average (weight-average) molar mass) dissolved in cyclohexane,[4−7] methylcyclohexane,[10] and ethylcyclohexane[11] are reanalyzed to determine the value of n. The value of the exponent n is expected to be system independent (here independent of the solvent). The analysis is based on eq 1.

$$\xi = \xi_0^* N^n t^{-\nu} \qquad (1)$$

ξ_0 ($=\xi^*{}_0 N^n$) is the critical amplitude of the correlation length ξ in a solution of critical composition. N is the number of repeat units forming the polymer chain. The quantities N and M_n characterizing the polymer are related by $N = M_n/M_0$. M_0 is the molar mass of the repeat unit (polystyrene: $M_0 \approx 104$ g mol^{-1}). t is the reduced temperature ($t = (T - T_c)/T_c$; T, thermodynamic temperature; T_c, critical temperature). It is established that the value of the system-independent critical exponent ν is consistent with the predictions of the 3-D Ising model ($\nu = 0.63$).[12−14]

The method of choice to determine the critical amplitude ξ_0 of a polymer solution at the critical composition is to measure the angular dependence of scattered light intensity at different constant temperature differences $(T - T_c)$ in the vicinity of the critical temperature T_c (upper critical temperature). The critical composition is determined using the criterion of equal volumes of coexisting liquid phases approaching the upper critical temperature from below (i.e. $\lim_{T \to T_c^{\rm vis}} V'/V'' = 1$). $T_c^{\rm vis}$ is the visually determined temperature of phase separation of the mixture of critical composition.

The critical temperature and the critical composition are functions of the molar mass and the chemical properties of the polymer and the solvent. To determine ξ as a function of $(T - T_c)$, light scattering and turbidity data are analyzed using the Ornstein−Zernike approximation $g_{OZ}(x)$ of the universal correlation scaling function $g(x)$ (i.e. $I_s(q,t) = At^{-\gamma} g_{OZ}(x)$ with $g_{OZ}(x) = (1 + x^2)^{-1}$ and $x = q\xi$; q is the absolute value of the scattering vector, $q = (4\pi/\lambda)\sin(\theta/2)$; λ, the wavelength of incident radiation within the solution; θ, the scattering angle). $g_{OZ}(x)$ is a good approximation of the universal correlation scaling function for $q\xi < 1$.[8,9]

B. Determination of the Exponent *n*

The value of the critical amplitude ξ_0 of the correlation length in a given polymer solution of critical composition is extracted from the experimental $\xi(T - T_c^{\rm vis})$ data by fitting the power law $\xi = \xi_0 t^{-\nu}$ to the data using fits with three free parameters (T_c, ξ_0, ν) or two free parameters (T_c, ξ_0, $\nu = 0.63$). It turns out that the parameters of the fit are highly correlated. It is usually found that for polymer solutions the value of $T_c^{\rm fit}$ is lower than $T_c^{\rm vis}$ by about 0.1 K.[4−7]

The analysis of the data obtained by Debye et al. is based on a mean field expression for the temperature dependence of the correlation length (i.e. $L = lt^{-\nu^*}$; L, correlation length; l, Debye parameter; $\nu^* = 0.5$; fit with two free parameters l and T_c).[4−6,11,15] Chu, who used data for the system polystyrene/cyclohexane (eight samples)[4−6] to determine the exponent n, reports a value of 0.285.[16]

Engels et al. and Shinozaki et al. analyzed the correlation length data in terms of the power law $\xi = \xi_0 t^{-\nu}$ using a fit with three free parameters (T_c, ξ_0, ν).[7,10] The values of ν obtained in this way vary in the range $0.54 \leq \nu \leq 0.67$.[10]

Published experimental static light scattering data for polystyrene dissolved in the solvents cyclohexane, methylcyclohexane and ethylcyclohexane have been reanalyzed to determine the exponent n using two methods:

(1) The information, taken from the work of Debye et al.,[4−6,11] is used to re-create $L(T - T_c^{\rm fit})$ data sets in a temperature range $(T - T_c^{\rm fit}) < 3$ K based on the known values of l and $T_c^{\rm fit}$ ($L = l\,[(T - T_c^{\rm fit})/T_c^{\rm fit}]^{-0.5}$). The function $L = \hat{l}t^{-0.63}$ is fitted to the re-created $L(T - T_c^{\rm fit})$ data with two free parameters ($\hat{l}$ and again T_c). ξ and L are related by $\xi = 6^{-1/2}\,L$.

(2) Shinozaki et al. obtained ξ_0 values from two-parameter fits of the function $\xi = \xi_0 t^{-0.63}$ to experimental $\xi(T - T_c^{\rm vis})$ data (free parameters ξ_0 and T_c, $\nu = 0.63$).[10] They are presented in a $\ln\xi_0$ versus $\ln M_w$ plot (see Figure 7 of their work). The ξ_0 data are extracted from this plot. The M_w values are converted into M_n values using the information given by the authors.

The results of the two types of analysis comprising 22 polystyrene mixtures of critical compositions in three different solvents (cyclohexane, methylcyclohexane, ethylcyclohexane) were combined. The molar mass of the polystyrene samples covers a range of $8.5 \times 10^3 \leq M_n \leq 2.82 \times 10^6$ g mol^{-1}. The data are shown graphically in Figure 1 in form of a $\ln\xi_0$ versus $\ln N$ plot. The data follow a straight line to a satisfactory approximation. The straight line in Figure 1 represents the function $\ln\xi_0 = n \ln N + \ln\xi_0^*$ with $n = (0.218 \pm 0.026)$ and $\xi_0^* = (0.149 \pm 0.026)$ nm. The parameter values are obtained using a standard least squares fitting procedure (fit of the logarithm of 22 (ξ_0−N) data pairs).[17] No criterion could be found from an experimental point of view to exclude particular data sets from the analysis in terms of eq 1.

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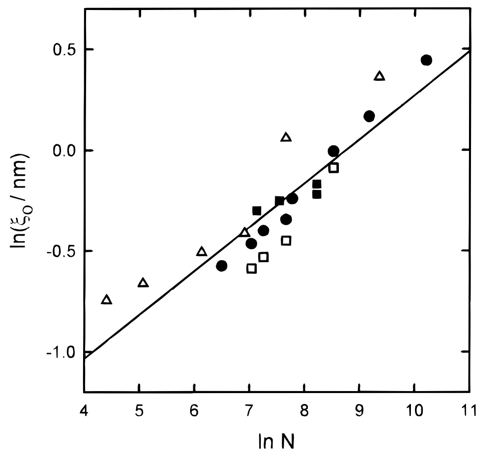

Figure 1. Plot of the natural logarithm of the correlation length ξ_0 as a function of the natural logarithm of the number of repeat units N of polystyrene dissolved in three different solvents. The data refer to critical compositions. The straight line, $\ln\xi_0 = n \ln N + \ln\xi_0^*$ with $n = (0.218 \pm 0.026)$ and $\xi_0^* = (0.149 \pm 0.026)$ nm, represents a linear least squares fit to the data. The data are available as supporting information. (●) Polystyrene/cyclohexane;[4−6] (■), polystyrene/cyclohexane, polystyrene/cyclohexane-d_{12}, polystyrene-*d*/cyclohexane;[7] (△), polystyrene/methylcyclohexane;[10] (□) polystyrene/ethylcyclohexane.[11]

Shinozaki et al. give a value of $n = (0.28 \pm 0.03)$ calculated from the ξ_0 data obtained with six polystyrene samples ($8.5 \times 10^3 \leq M_n \leq 1.20 \times 10^6$ g mol^{-1}) dissolved in methylcyclohexane.[10] These $\xi_0(M_n)$ data are included in Figure 1. From the data reported by Debye et al. and Engels et al., a value of $n = (0.270 \pm 0.018)$ is obtained (12 polystyrene samples PSH and PSD dissolved in cyclohexane; molar mass: $0.69 \times 10^5 \leq M_n \leq 28.20 \times 10^5$ g mol^{-1}).[4−7] This value is consistent with that given by Chu ($n = 0.285$).[16]

Caylor and Law carried out ellipsometric measurements with polystyrene ($0.44 \times 10^5 \leq M \leq 1.971 \times 10^6$ g mol^{-1})/cyclohexane mixtures of critical composition to study critical adsorption.[2] These authors found that their data followed a single curve when plotted as a function of the reduced variable ($n_p\xi/\lambda$) (n_p, refractive index of the polymer solution; ξ, correlation length of density fluctuations, $\xi = \xi_0 t^{-\nu}$; λ, wavelength of incident light intensity in vacuum). They deduce a value of $n = (0.258 \pm 0.017)$ for the molar mass dependence of ξ_0 using five polystyrene samples.

Mean field calculations of n have predicted a value of $n = {}^1/_4$.[18] More recent scaling arguments by de Gennes lead to a value of $n = (1 - \nu)/2 = 0.185$.[19] Other contemporary theories give values of n in the range $0.17 \leq n \leq 0.195$.[3] The values of n given in this note are above the upper limit of the theoretical values.

Supporting Information Available: Tables containing the recalculated values of the critical amplitude ξ_0 of the correlation length of local composition fluctuations for polystyrene dissolved in cyclohexane, methylcyclohexane, and ethylcyclohexane (2 pages). Ordering information is given on any current masthead page.

References and Notes

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(19) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; Chapter VII, p 213 [$\xi \approx R_0[(\theta - T_c)/(T - T_c)]^{\nu}$; $R_0 \sim N^{1/2}$; $T_c \sim N^{1/2}$].

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