Spinodal Decomposition in a Polystyren/ Cyclohexane Solution of Critical Composition

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Results of experiments are reported demonstrating spinoidal decomposition in a critical mixture of polystyrene and cyclohexane. If time and length are properly scaled using data obtained from static and dynamic light scattering experiments, the time evolution of the "spinodal ring" is represented to a good approximation by an empirical equation proposed by Snyder and Meakin which describes spinodal decomposition for various types of systems.

Keywords: Phase transition, spinodal decomposition, critical phenomena, polymer solution.

1. Introduction

We report on experiments demonstrating spinodal decomposition of a solution of macromolecules in a solvent of low molecular weight. The experiments are carried out with critical mixtures of polystyrene in cyclohexane. It is observed that in the early stages of the liquid/liquid phase separation process in the instable region of the phase diagram the critical mixtures produce a scattering pattern under small scattering angles which is characteristic for spinodal decomposition, forming a bright ring. Its intensity increases and its diameter decreases with time.

If time and length are properly scaled using experimental data obtained by independent experiments, the data characterizing spinodal decomposition in the system polystyrene/cyclohexane can be represented to a good approximation by an empirical equation proposed by Snyder and Meakin [1]. This equation may be regarded as manifestation of the superposition of phase separation data from metalic alloys, inorganic glasses, systems of small molecules (e.g. isobutyric acid/water), polymer blends, and also from the system polystyrene/cyclohexane.

2. Experimental Section and Results

Polystyrene (molar mass $M_w = 3 \cdot 10^5\,\mathrm{g \cdot mol^{-1}}$; $M_w/M_n < 1.04$) as supplied by VENTRON (Karlsruhe) and cyclohexane (MERCK, Darmstadt) of "pro analysis" quality (water content $< 0.01\%$) were used without further purification. The critical composition determined on the basis of the equal volume criterium of coexisting liquid phases had a value of $\Phi_c = 0.0512$ (volume fraction of polystyrene). The corresponding mass fraction of polystyrene had a value of $y_c = 0.07$. The visually determined temperature of phase separation was $T_c = 26.36\,°\mathrm{C}$.

A homogeneous solution of polystyrene in cyclohexane with critical composition was filled into a rectangular glass cuvette which had an optical path length of 5 mm. The sample was flame sealed and placed into a double jacket thermostate equipped with optical windows to pass a beam of laser light (Helium-Neon laser, 6 mW, $\lambda_0 = 632.8$ nm, Type 120 S, Spectra Physics) through the cell.

The index of refraction of the solution had a value of $n = 1.43$ at a wave length of $\lambda_0 = 632.8$ nm. The thermostating fluid of the internal thermostate was silicon oil. The temperature of the external thermostate was maintained constant by thermostated water. The internal thermostate was separated from the external thermostate by a layer of air (thickness: 1.0 cm). The temperature of the external thermostate was maintained 10 K below that of the internal thermostate. The angular dependence of light scattered by the sample at low angles ($1° < \Theta < 10°$) was photographed from an opaque screen using a motor driven camera (Type Hasselblad EL/M equipped with a condensor of focus 135 mm; film material: Ilford FP4, 22 DIN; exposure time: 0.25 s; diaphragm: 5.6).

The screen was positioned perpendicular to the light beam at a distance of 90 cm from the center of the cuvette. A small circular platelet fixed to the screen was used to reflect the primary beam. The photographs were analyzed by digitalisation (video camera SONY) in combination with an image processing system (SIGNUM/μVAX). The scattering angle was calculated from the relation $\Theta = \arctan\,(r/L)$ (r: distance from the center of the scattering pattern; L: distance of the screen from the center of the cuvette). The scattering angle was determined to an accuracy of $\pm\,2\%$.

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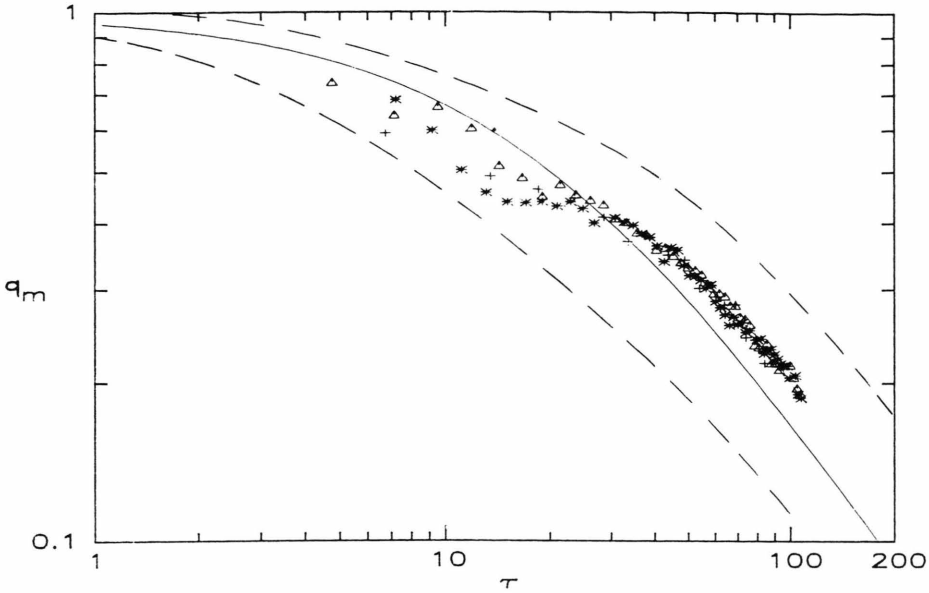

Fig. 1. Scaled representation of the time evolution of the radius of maximal scattered intensity from the system polystyrene/cyclohexane undergoing spinodal decomposition. The variables q_m and τ are given by (1) and (2). The full curve represents the equation $q_m = \tau^{-\alpha} = [\ln(1 + a\tau)/\ln\tau]$ and $a = 0.05$. The dashed curves indicate the range of data of the various systems considered in the paper of Snyder and Meakin.

The cuvette containing a homogeneous solution of polystyrene in cyclohexane of critical composition was inserted into the thermostate. The temperature of the internal thermostate was adjusted to $T_I = T_c + 1.5$ K. After thermal equilibration the following electronically controlled temperature-time program was started:
(a) Change of temperature $T_I \rightarrow T_{II} = T_c + 60$ mK, cooling rate: 0.6 mK/s; (b) establishment of thermal equilibrium, temperature T_{II} maintained for 800 s; (c) change of temperature $T_{II} \rightarrow T_i = T_c + 10$ mK, cooling rate: $2 \cdot 10^{-2}$ mK/s; (d) establishment of thermal equilibrium, temperature T_i maintained for 300 s; (e) temperature quench to temperature T_f (final temperature with $(T_c - T_f)$: 8 mK, 6 mK, and 5 mK, respectively, applied in our experiments). In independent experiments with an oil filled cuvette containing a calibrated thermistor, time response of the cell after small temperature changes ($-15\,\text{mK} < \delta T < +18\,\text{mK}$) was measured. A temperature relaxation time $\tau_T = 10$ s was found.

3. Data Analysis

For the analysis of the scattering patterns attention is focused on the time evolution of the "ring radius" after each quench. The experimental data are expressed in terms of the dimensionless variables [1]

$$q_m = k_m \xi \tag{1}$$

with

$$k_m = (4\pi n/\lambda_0) \sin \Theta_m/2,$$
$$\tau = (D/\xi^2)\, t. \tag{2}$$

ξ: correlation length of local concentration fluctuations ($\xi = \xi_0 \varepsilon^{-\nu}$; $\varepsilon = (T_c - T_f)/T_c$; ξ_0: critical amplitude; ν: critical exponent); n: refractive index; Θ_m: scattering angle corresponding to maximal intensity of the spinodal ring; D: mutual diffusion coefficient ($D = D_0 \varepsilon^{\nu^x}$; D_0: critical amplitude; ν^x: critical exponent; t: time). The origin of the time axis ($t = 0$) of the spinodal decomposition was set at $3\tau_T$, i.e. 30 s after starting the temperature quench.

The values of the critical amplitudes and critical exponents of the system polystyrene ($M_w = 3 \cdot 10^5$ g/mol)/cyclohexane used in the scaling equations (1) and (2) are known from static and dynamic light scattering experiments ($\xi_0 = 0.657$ nm; $D_0 = 1.09 \cdot 10^{-6}$ cm^2/s; $\nu = 0.63$; $\nu^x = 0.746$) [2].

Figure 1 shows the evolution of the radius of peak scattering intensity from the sample of polystyrene/cyclohexane undergoing spinodal decomposition studied in our experiments The $(q_m \cdot \tau)$ data are derived from the results of three runs of different quench depths ($T_c - T_f$): 5 mK, 6 mK, 8 mK. The full curve represents the empirical equation $q_m = \tau^{-\alpha}$ with $\alpha = [\ln(1 + a\,\tau)/\ln \tau]$ and $a = 0.05$ proposed by Snyder and Meaking [1] to fit the data of metallic alloys, inorganic glasses, small molecule systems, and polymer blends. The data of these systems are actually spread over a range indicated by the dashed lines in Figure 1. The data of our experiments are falling well within this range; the S-shaped curvature below $\tau = 20$ may be caused by uncertainties of the point of time at which spinodal decomposition began in our experiments. With this restriction in mind Fig. 1 shows that the scaled phase separation data of polystyrene/cyclohexane superpose those of metallic alloys, inorganic glasses, small molecule systems, and polymer blends within the experimental accuracy and within the range of experimental data so far reported in literature. Thus the results of our experiments support the idea of universal behaviour of phase separation dynamics.

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