

# Phase dissolution in polymer blends at different quench depths

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Isothermal phase dissolution of phase-separated structures at different quench depths to one single temperature below the lower critical solution temperature was studied by the light scattering technique for different polymer blends. During the process of phase dissolution the light scattering intensity decays exponentially with time at a rate depending on an effective diffusion coefficient for the centre-of-mass motion of the chain molecules in the melt. The apparent diffusion coefficient varies as a function of the quench depth  $\Delta T$  which indicates that the diffusion coefficient is directed by the thermodynamic driving force. With increasing  $\Delta T$  the diffusion coefficient also increases initially. However, further increase of  $\Delta T$  leads to a decrease of the diffusion coefficient. This is interpreted in terms of the interfacial free energy which contributes to the thermodynamic driving force.

(Keywords: blends; copolymers; phase dissolution; diffusion coefficient; miscibility; light scattering)

## INTRODUCTION

In a previous paper we studied the isothermal phase dissolution of phase-separated structures after a rapid temperature jump from the two-phase into the one-phase region below the lower critical solution temperature (LCST) by the light scattering technique<sup>1</sup>. In the last stage of phase dissolution the light scattering intensity decays exponentially with time at a rate depending on an effective diffusion coefficient for the centre-of-mass motion of the chain molecules in the melt. In the one-phase region the phase-separated structures are dissolved by a continuous descent of the thermodynamic driving force responsible for the phase separation. Hence, the phase dissolution is the reverse phenomenon to phase separation, and the theory of phase separation can also be used to discuss phase dissolution.

In the context of Cahn's linearized theory of spinodal decomposition the apparent diffusion coefficient is given by<sup>2</sup>

$$D_{\text{app}} = M \frac{\partial^2 G}{\partial \phi^2} \quad (1)$$

where  $G$  is the Gibbs free energy of the mixture in which the concentration of one component is given by a constant value  $\phi$  and  $M$  is the mobility constant which is positive. As can be seen from equation (1) the apparent diffusion coefficient is directed by the mobility as well as by the thermodynamic driving force. In a previous paper<sup>1</sup> we studied chiefly the influence of mobility on the diffusion coefficient. In the present paper we focus our attention on the influence of the thermodynamic driving force.

Recently, it was shown that poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-acrylonitrile) (P(S-*co*-

AN))<sup>3</sup> as well as poly(vinyl chloride) (PVC) blended either with PMMA, poly(butyl methacrylate) (PBMA), or poly(methyl methacrylate-*co*-butyl methacrylate) (P(MMA-*co*-BMA)) form homogeneous systems<sup>4</sup>. The blends exhibit miscibility and LCST behaviour. For these systems we investigated the dependence of the apparent diffusion coefficient on the thermodynamic driving force.

## EXPERIMENTAL

Systems used in this study were 50/50 mixtures (by weight) of PMMA/P(S-*co*-AN), PVC/PMMA, PVC/PBMA, and PVC/P(MMA-*co*-BMA) where statistical copolymers of 31.5 wt% AN units and 50 and 30 wt% MMA units, respectively, were used. The PMMA sample ( $M_w = 43\,000 \text{ g mol}^{-1}$ ;  $M_w/M_n = 1.72$ ) was prepared at 60°C in butanone-2 using  $0.02 \text{ mol l}^{-1}$  AIBN as initiator and a monomer concentration of  $8 \text{ mol l}^{-1}$ . All the other components are commercial polymers with weight-average molecular weights of about  $2 \times 10^5$  for P(S-*co*-AN) and  $1 \times 10^5$  for the remaining polymers.

As described previously<sup>1,3</sup> mixing of the respective polymers in a common solvent followed by evaporation was used in the preparation of the polymer blends. Two equal amounts (by weight) of both polymers were dissolved to a total of 5 wt% in 1,2-dichloroethane (for PMMA/P(S-*co*-AN)) and dimethylformamide for blends containing PVC as one of the components. The blend specimens were prepared by casting the solutions onto cover glasses and evaporating the solvent at room temperature until constant weight was obtained. The as-cast films were transparent.

Light scattering has been employed for monitoring the kinetics of phase dissolution. Details of the apparatus used are described elsewhere<sup>1,3</sup> and will not be repeated here. The experiments were carried out as shown schematically in Figure 1. The film specimens underwent rapid temperature jumps from room temperature to different temperatures set isothermally above LCST to

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reach phase separation. The blend of PMMA and P(S-co-AN) was annealed under nitrogen at the respective temperatures for 5 min. Owing to the relatively high temperatures of phase separation ( $>200^{\circ}\text{C}$ ) the samples containing PVC were annealed only for a few

seconds ( $\sim 15$  s) to avoid extended thermal degradation. After that the films were cooled rapidly to room temperature. The cloudy samples were then heated quickly by placing the cover glasses onto a hot plate preheated at  $150^{\circ}\text{C}$  (corresponding to  $T_0$  in Figure 1) and  $190^{\circ}\text{C}$  (for PMMA/P(S-co-AN)), respectively, in a thermostatically controlled chamber. It should be noted that the time  $t$  always refers to the time 30 s after insertion of the sample into the chamber. The procedure corresponds to temperature jumps from different temperatures in the two-phase region to one single temperature in the one-phase region below LCST.

Thus, the variation of the light scattering intensity was detected as a function of time during isothermal annealing at 190 and  $150^{\circ}\text{C}$ , respectively. Finally, the samples were heated again up to a temperature just below LCST for estimating the reference intensity caused by the fully transparent film. For the light scattering intensity at any time of the experiment we used the difference in the instantaneous value and the base line which we assumed to be equal to the scattering intensity upon heating the film specimens somewhat below the LCST.

The diffusion coefficients submitted below are in most cases the averages of two measurements.

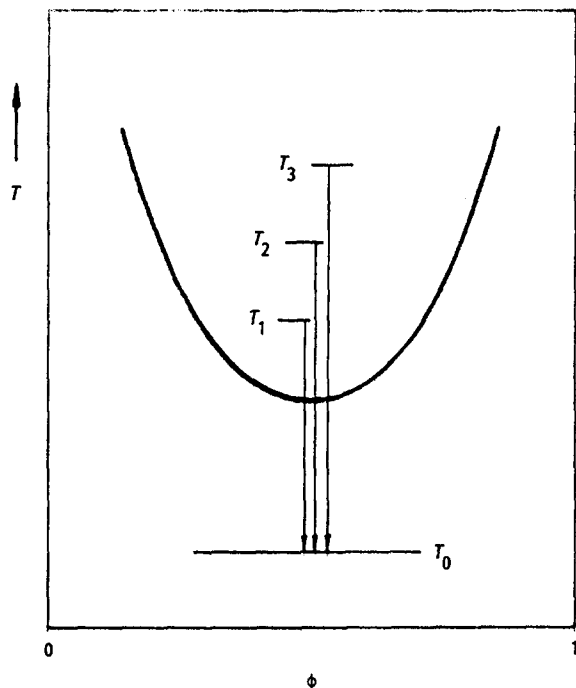


Figure 1 The course of the experimental procedure

### RESULTS AND DISCUSSION

The cloud point curve of the blend PMMA/P(S-co-AN)-31.5 is presented in reference 3. For 50/50 blends phase separation occurs at  $200^{\circ}\text{C}$ . The

Table 1 LCSTs of different blends with PVC

	PMMA	P(MMA-co-BMA)-30	P(MMA-co-BMA)-50	PBMA
$\theta$ ( $^{\circ}\text{C}$ )	208	232	240	190

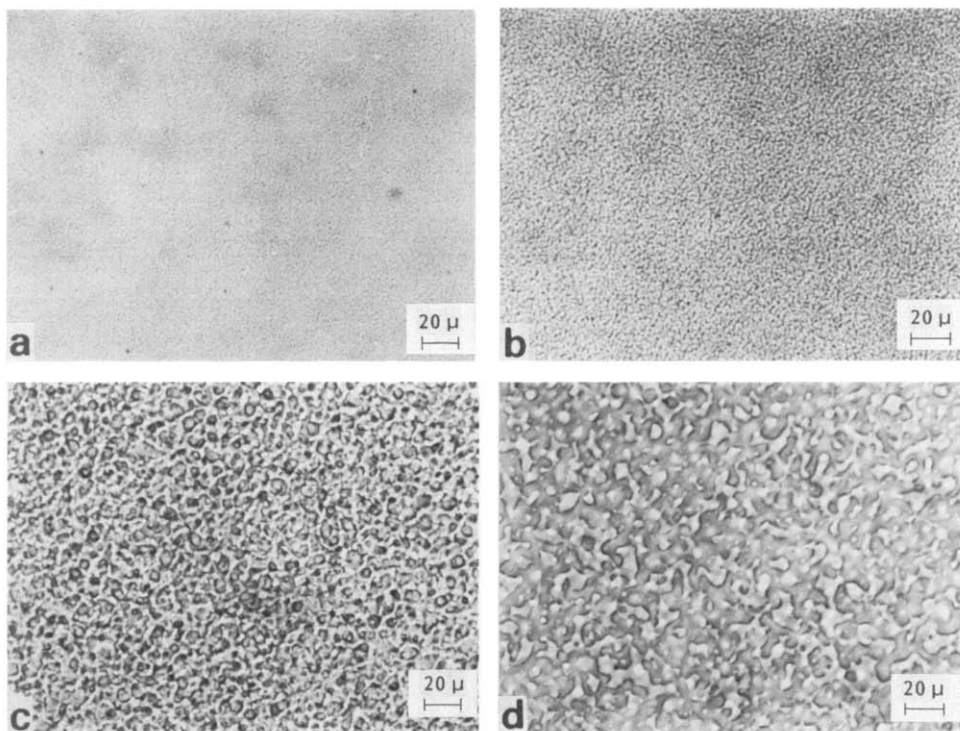
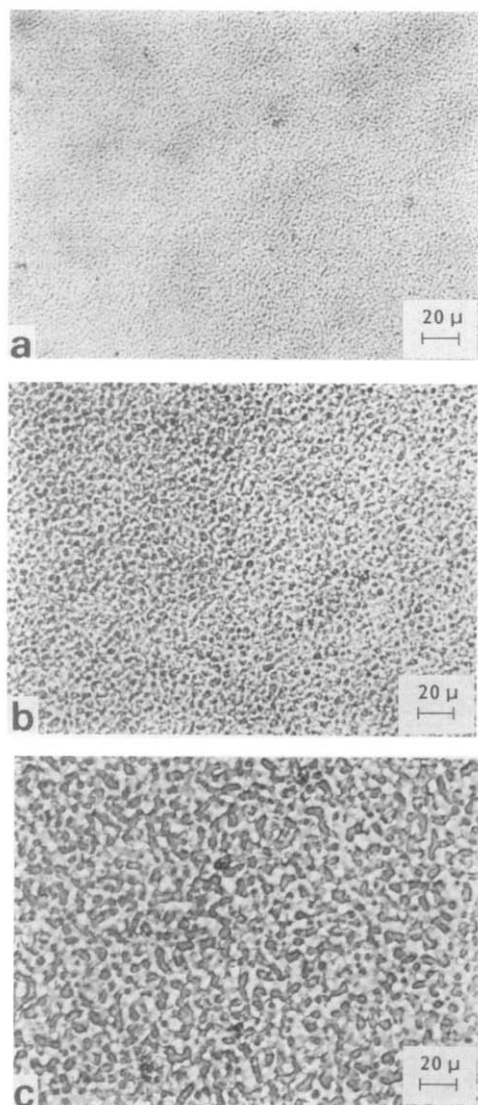


Figure 2 Phase-separated structures of a 50/50 PVC/PBMA blend at different temperatures above the LCST: (a) 215; (b) 225; (c) 245; (d) 265 $^{\circ}\text{C}$



**Figure 3** Phase-separated structures of a 50/50 PVC/P(MMA-co-BMA)-30 blend at different temperatures above the LCST: (a) 245; (b) 265; (c) 300°C

LCSTs of the other 50/50 blends studied in this paper are listed in *Table 1*.

As reported previously, various polymer blends display just above the LCST a very regular, highly interconnected two-phase morphology<sup>3,5,6</sup>. This was also found for the blends studied here. Typical examples are shown in *Figures 2* and *3* for 50/50 blends of PVC with PBMA and P(MMA-co-BMA)-30, respectively. Above a certain temperature the regular two-phase morphology decays rapidly into an irregular two-phase structure.

After the temperature jump from the two-phase region into the one-phase region below LCST the phase dissolution starts leading finally to a homogeneous system. Therefore, below LCST the scattering intensity ( $I$ ) decreases as the phase dissolution progresses with the time of annealing. The intensity decay reflects the phase dissolution. In the context of Cahn's linearized theory the intensity descends exponentially with time<sup>7</sup>

$$\ln\left(\frac{I}{I_0}\right) = -2D_{\text{app}}q^2t \quad (2)$$

where  $t$  is the annealing time after the temperature jump and  $I_0$  the scattered intensity at annealing time zero. The

quantity  $q$  is the scattering vector and equals  $4\pi/\lambda \times (\sin \frac{\theta}{2})$  where  $\lambda$  is the wavelength of radiation which is used to study the phase dissolution and  $\theta$  is the scattering angle.

For all the blends studied in this paper the intensity decayed according to equation (2) at least in the late stage ( $t \geq 10$  min) of phase dissolution. Therefore, the rate of intensity decrease is proportional to the quantity  $D_{\text{app}}$ . All the experiments were carried out at  $q = 1.37 \times 10^5 \text{ cm}^{-1}$ .

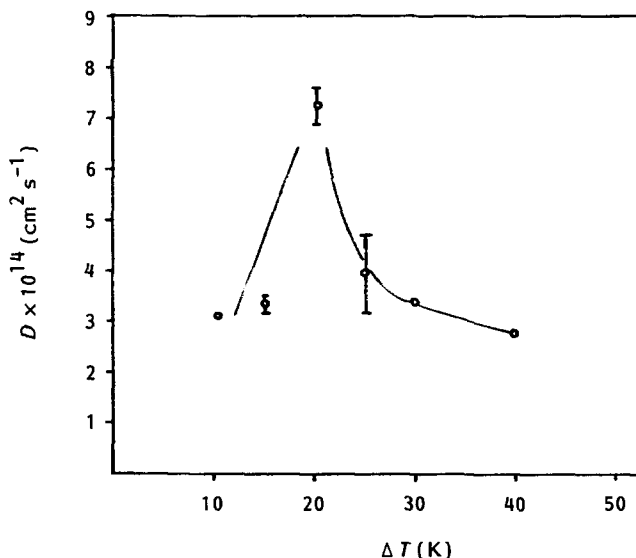
The variation of the apparent diffusion coefficient as a function of quench depth  $\Delta T \equiv T - T_s$ , where  $T_s$  is the spinodal point, is presented in *Figures 4* and *5* for different blends. In the first instance, the apparent diffusivity increases with increasing quench depth  $\Delta T$ . However, when the quench depth is further raised the apparent diffusion coefficient starts to decrease with  $\Delta T$ . Comparison with *Figures 2* and *3* suggests that the change occurs when the temperature approaches the stability limit of the regular two-phase morphology. For the blend PVC/PMMA the regular two-phase morphology could be observed over the whole range of temperatures studied here. Therefore, no decrease in the diffusivity could be detected.

#### ANALYSIS BASED ON THE LINEARIZED THEORY OF SPINODAL DECOMPOSITION

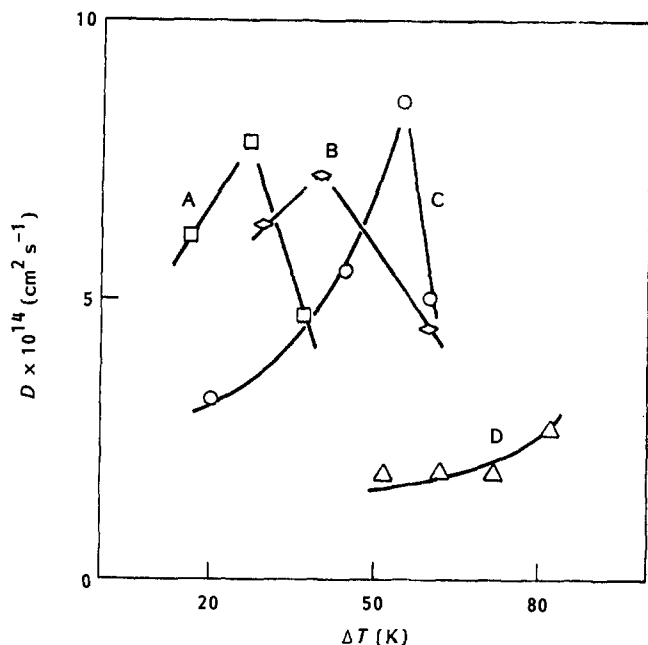
The variation of the apparent diffusion coefficient of phase dissolution as a function of quench depth reflects the influence of the thermodynamic driving force on the kinetics of phase dissolution. Obviously, the thermodynamic driving force, in turn, depends on the dispersal of the phases in the two-phase region, i.e., the interfacial energy has to be taken into consideration. The difference in the Gibbs free energies of the dispersed and the bulk system might be expressed as

$$\Delta G(d) - \Delta G(\infty) = \phi(1-\phi)A\delta K \quad (3)$$

where  $d$  = length characterizing the size of the dispersed phase,  $A$  = molar interfacial area,  $\delta$  = interfacial tension, and  $K$  = equilibrium constant characterizing the degree



**Figure 4** Apparent diffusivity as a function of quench depth for a 50/50 blend of PMMA/P(S-co-AN)-31.5



**Figure 5** Apparent diffusivity as a function of quench depth for 50/50 blends of PVC/P(MMA-co-BMA)-30 (A), PVC/P(MMA-co-BMA)-50 (B), PVC/PBMA (C) and PVC/PMMA (D)

of dispersion. For  $K$  it follows

$$K = \exp(-A\delta/RT)$$

Applying for  $\Delta G(\infty)$  the Flory-Huggins expression we arrive at

$$\frac{\partial^2 \Delta G(d)}{\partial \phi^2} = -2RT(\chi - \chi_s) - 2A\delta \exp(-A\delta/RT) \quad (4)$$

where  $\chi_s$  is the interaction parameter  $\chi$  between the constituent polymers at the spinodal point  $T_s$ . In equation (4) terms in  $A(\partial\delta/\partial\phi)_T$  can be neglected and therefore, have been omitted. We are interested chiefly in the variation of  $\partial^2 \Delta G(d)/\partial \phi^2$  as a function of the quench depth  $\Delta T$ . In the case of miscible polymers displaying LCST behaviour the interaction parameter can be approximated by  $\chi = a - b/T$ . It follows that  $\chi - \chi_s = b \frac{\Delta T}{TT_s}$ . According to Cahn's linearized theory a

particular Fourier component of concentration fluctuations with wave number  $q_m$  has a maximum growth rate. Therefore, we assume the molar interfacial area to be  $A \sim q_m^{-2}$ . In the context of the mean-field approximation for the spinodal decomposition one obtains

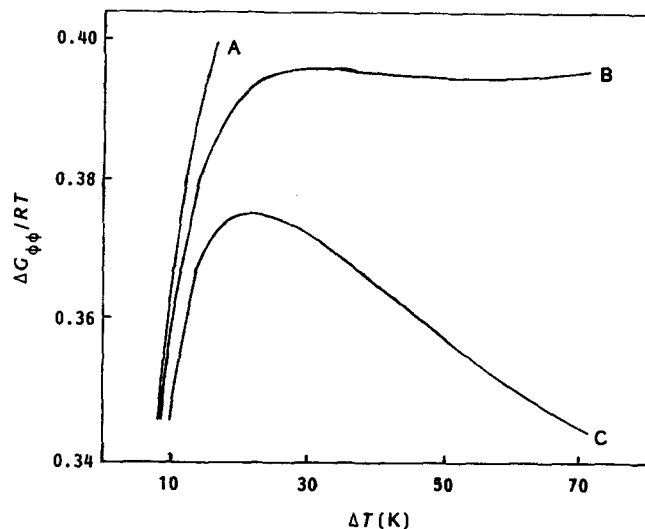
$$q_m^2 \sim (\chi - \chi_s)/\chi_s$$

Furthermore, it has been shown<sup>8,9</sup> that the interfacial tension between two polymers is

$$\delta \sim RT(\chi - \chi_s)^{1/2}$$

Hence, we get for the variation of  $\partial^2 \Delta G(d)/\partial \phi^2$  (equation (4)) as a function of  $\Delta T$

$$\frac{1}{RT} \left| \frac{\partial^2 \Delta G(d)}{\partial \phi^2} \right| = \frac{\alpha}{Y^2} + \beta Y e^{-\beta Y} \quad (5)$$



**Figure 6** Thermodynamic driving force according to equation (5) for  $\beta=0.2$  and  $\alpha=1$  (A), 0.6 (B), and 0.2 (C);  $T_s=473$  K

where

$$Y \equiv \left( \frac{1}{\Delta T/T_s} + 1 \right)^{1/2}$$

and  $\alpha$ ,  $\beta$  are considered as adjustable parameters representing the magnitude of the bulk and interfacial contribution, respectively, to the thermodynamic driving force. For  $\Delta T/T_s \ll 1$ , equation (5) changes linearly with  $\Delta T/T_s$ :

$$\frac{1}{RT} \frac{\partial^2 \Delta G}{\partial \phi^2} \sim \frac{\Delta T}{T_s}$$

Figure 6 shows the thermodynamic driving force as a function of quench depth  $\Delta T$  for different ratios  $\alpha/\beta$ . According to equation (5) the variation observed for the apparent diffusivity only occurs for  $\alpha \approx \beta$ ; with increasing  $\alpha/\beta$  ratio the effect lessens more and more and finally disappears. We may conclude, that equation (5) gives, at least qualitatively, an explanation for the change of the apparent diffusivity with quench depth  $\Delta T$ .

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