Polymer Blends

Phase dissolution in polymer blends
Estimation of diffusion coefficients and the associated activation energy

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Summary

Isothermal phase dissolution of regularly phase–separated structures at deep quench depths below the lower critical solution temperature was studied by light scattering technique for the blend of poly(styrene–co–acrylonitrile) and poly(methylmethacrylate). The phase dissolution studied in this work was that in the diffusion–controlled regime. 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 center–of–mass motion of the chain molecules in the melt. The diffusion coefficient and the associated activation energy were estimated to be in the order of 10^{-14} cm^2/s and 50 kJ/mol, respectively.

Introduction

Miscible polymers tend to phase separation at elevated temperatures. It is well–known, that the phase–separation kinetics for liquid mixtures of polymers in the thermodynamically unstable region can be described in the early stage by CAHN's theory of spinodal decomposition (1). The spinodal decomposition of a polyblend above the lower critical solution temperature (LCST) involves mutual diffusion of the entangled chain molecules presumably by a process of reptation (2). The reverse phenomenon occurs when phase–separated structures are dissolved by switching off the thermodynamic driving force responsible for the phase separation. Of course, the diffusion coefficient associated with the dynamics of phase dissolution is positive unlike the case of phase separation. The small diffusion coefficients D and the large thermal correlation lengths ξ of chain molecules in the molten state make characteristic times for the phase transition $\tau \equiv \xi^2/D$ sufficiently large. In other words, the demixing and dissolution process, respectively, is over a sufficiently extended period of time primarily diffusion controlled. This provides an approach for estimating the diffusion coefficient accompanying the phase separation or phase dissolution.

The translational diffusion coefficients have been determined for various polymeric systems by different

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techniques such as radioactive (3-5) and infrared labeling (6), by pulsed NMR (7-9) and light scattering technique (10,11).

Here, we employ the light scattering technique to study the translational diffusion of chain molecules accompanied with phase dissolution after a temperature-jump from the two-phase region into the single-phase region below LCST.

Experimental

Materials

The polymers used were poly(styrene-co-acrylonitrile) (SAN) (VEB Chemisches Kombinat BUNA) containing 31.5 wt% of AN, which showed an $\overline{M_w}$ of 2.25×10^5 g/mol and $\overline{M_w}/\overline{M_n}$ of 1.82 by g.p.c. and poly(methylmethacrylate) (PMMA) prepared in our laboratory by solution polymerization in butanone-2 at 60°C using 0.02 mol/l AIBN as initiator. PMMA showed $\overline{M_w} = 4.3 \times 10^4$ g/mol and $\overline{M_w}/\overline{M_n} = 1.72$.

Preparation of blends

Mixing in a common solvent followed by evaporation was used in the preparation of blends. Two equal amounts by weight of both polymers were dissolved in 1,2-dichloroethane. The solution concentration was about 5 wt%. Then the blend specimens were prepared by casting the solutions onto cover glasses and evaporating the solvent at room temperature and finally in a vacuum oven at 90°C until constant weight was obtained. Due to miscibility of both components the cast films were transparent.

Light scattering

Phase behavior has been examined by measuring the light scattered from the sample. The blend film on the cover glass was inserted into a sample holder located in a thermostatically controlled chamber. The Kr^+/Ar^+ ion laser beam (150 mW) of 647 nm wavelength was focused onto the sample and the intensity of the light scattered at 90° was measured using a Raman spectrometer (12). Before the light scattering studies were carried out, the films were heated at 3°C/min up to 210°C to reach phase separation and development of a highly interconnected two-phase morphology (12). After that the films were rapidly cooled. The cloudy samples were then heated up to three different constant temperatures (180, 160 and 140°C). Thus, the change of the light scattering intensity was detected during the isothermal annealing. Finally, the samples were heated again for estimating the reference intensity caused by the fully transparent film. As light scattering intensity at any time of 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 of the film specimen somewhat below the LCST.

Results and Discussion

The LCST of PMMA/SAN blends has been submitted in (12).
The film specimen with the regular two-phase structure above
LCST underwent rapid temperature-jumps to room temperature
and then to various higher temperatures set isothermally be-
low the LCST. This corresponds to a temperature-jump from the
two-phase region into the single-phase region below LCST.
Below LCST the scattering intensity I decreased with time of
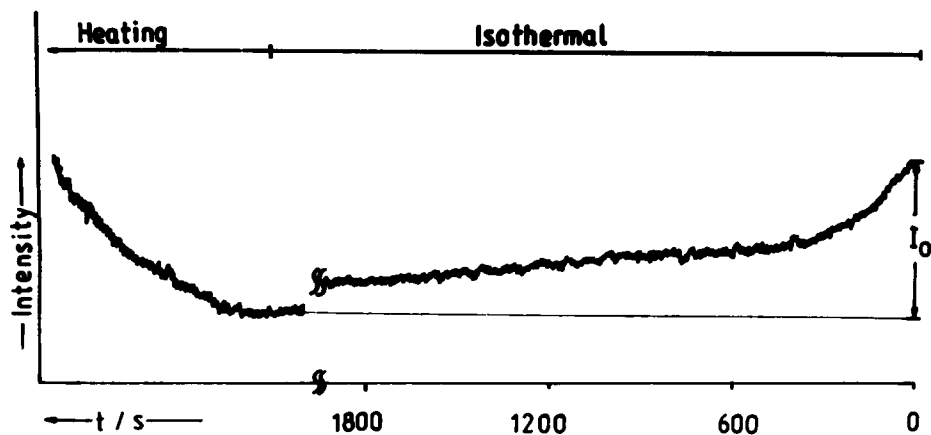annealing. A typical example is presented in Fig.1.

Fig.1: Change of light scattering intensity during an-
nealing at 160°C and then heating with 3°C/min

The intensity decay reflects the phase dissolution of the
two-phase structure after the temperature-jump into the one-
phase region below LCST leading to an almost homogeneous
system. In Fig.2 $\ln(I/I_0)$ is plotted versus annealing time
after the temperature-jump, where I_0 is the intensity at
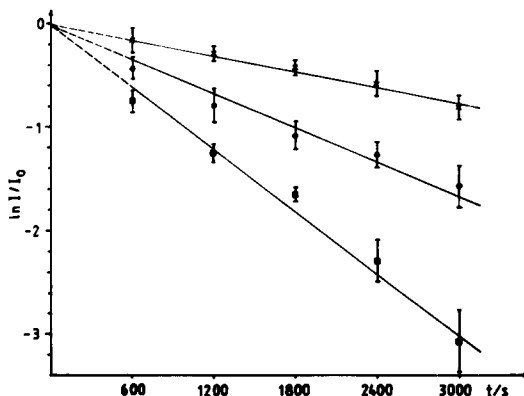annealing time zero.

Fig.2: Change of relative scattering intensity
$\ln(I/I_0)$ during annealing at various tempera-
tures ■ 180°C, ● 160°C, × 140°C

As can be seen, after a certain time (of around 10 min) the intensity decreases exponentially in the later stage. The linear change of $\ln(I/I_0)$ with time is in accord with theoretical predictions concerning the kinetics of phase dissolution (13) :

$$\ln\left(\frac{I}{I_0}\right) = -2D \left[\frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)\right]^2 t \qquad /1/$$

where λ, θ, t are the wavelength of the light, the scattering angle and the time, respectively; D represents the effective diffusion coefficient for the center-of-mass of the components having nearly equal diffusion coefficients. Applying Eq./1/ the slope of the plot in Fig.2 yields the effective diffusion coefficient accompanying the dissolution of the two phase morphology. The diffusion coefficients thus estimated at different temperatures below LCST are listed in Tab.1.

Table 1: Diffusion coefficients for the PMMA/SAN blend at different temperatures below LCST

ϑ / $^{\circ}C$	140	160	180
D /$10^{-14}cm^2$/s	0.9	1.6	3.1

The experimental error of the data reported in Tab.1 is less than 10%. The diffusion coefficients are in the same order of magnitude (apart from the sign) as those submitted in (9) for the kinetics of spinodal decomposition.

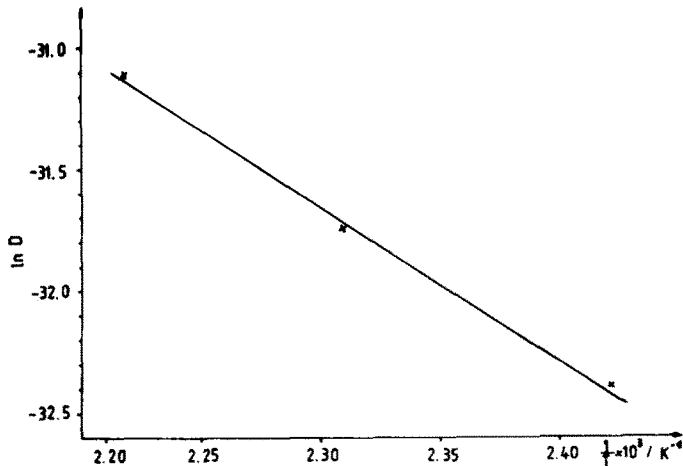Fig.3 shows a ln D versus 1/T plot.

Fig.3: Arrhenius plot of the effective diffusion coefficient

The linear relationship suggests that the diffusion obeys an Arrhenius type equation. Therefrom, an activation energy of

~50 kJ/mol is obtained. Fig.3 demonstrates that the effective diffusion coefficient associated with the phase dissolution increases with increasing temperature. This indicates that the dissolution occured in the diffusion-controlled regime. The effective diffusion coefficient in Eq./1/ consists of two factors: the translational mobility coefficient i.e., an energy-driven diffusion coefficient, and the thermodynamic driving force for dissolution. The dissolution process has been studied in this work at sufficiently deep quenches. Therefore, the dissolution process is primarily governed by the mobility coefficient rather than the thermodynamic driving force and the temperature dependence of the effective diffusion coefficient is chiefly controlled by the mobility constant. When the temperature is further raised and approaches the binodal the thermodynamic driving force will outweigh the mobility constant resulting in a linear decrease of the effective diffusion coefficient with temperature in a region very near the binodal.

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