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Light Scattering and Image Analysis Studies in Polymer Blends

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SUMMARY: Various optical techniques have been investigated as potential candidates for characterization of multiphase polymeric materials. The model calculations and corresponding experiments (time-resolved light scattering and image analysis) have been conducted to investigate the kinetics of phase dissolution of polymer blends. The blends studied were polystyrene/poly (methyl methacrylate) mixtures with diblock copolymer composed of the corresponding homopolymers. The time evolution of the spinodal peak position $q_m(t,T)$ and the scattered intensity maximum $I_m(t,T)$ at q_m have been compared with theoretically predicted values of exponents for distinct time scales of the phase dissolution in various temperature regimes.

Introduction

For design of new materials by polymer blending one needs a basic understanding of the phase behaviour: phase equilibrium, kinetics of phase separation and kinetics of phase dissolution in polymer blends.

Time-resolved light scattering experiments and image analysis have been conducted to investigate the kinetics of phase dissolution and morphology development of polymer blends. The blends studied were polystyrene/poly(methyl methacrylate)(PS/PMMA) mixtures with admixed diblock copolymer composed of the corresponding homopolymer blocks. Time-resolved light scattering (which probes the q range from 0.2 to 30 μm^{-1}, where q is the wavenumber of fluctuations) has been widely used to examine the phase separation kinetics in polymer blends and solutions(1). The value of peak position $q_m(t,T)$ is related to the average or predominant phase-separated domain size d by $d = 2\pi/q_m$.

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Theoretical

The theory of dissolution[2,3] predicts the power-law dependence of $q_m(t,T)$ on time t. Hence

$$q_m(t,T) \cong t^{-1/2} \qquad (1)$$

and the peak intensity I_m should decrease exponentially as a function of time.

Investigations of the dissolution process are very limited and the kinetics of q_m changes during annealing has been studied very scarcely[2-4].

Experimental and Materials

The experimental set-up for time-resolved light scattering measurements is illustrated in Fig. 1a,b. We used as detection systems a conical lens with a photodiode, and a CCD camera. PS (M_w 8.9 × 10^4 g/mol, Polyscience), PMMA (M_w 7.4 × 10^4g/mol, Pressure Chem.) and PS-*b*-PMMA copolymer (M_w 8.0 × 10^4 g/mol) were used. The glass temperatures T_g are: T_g(PS) = 99 °C, T_g(PMMA) = 105 °C.

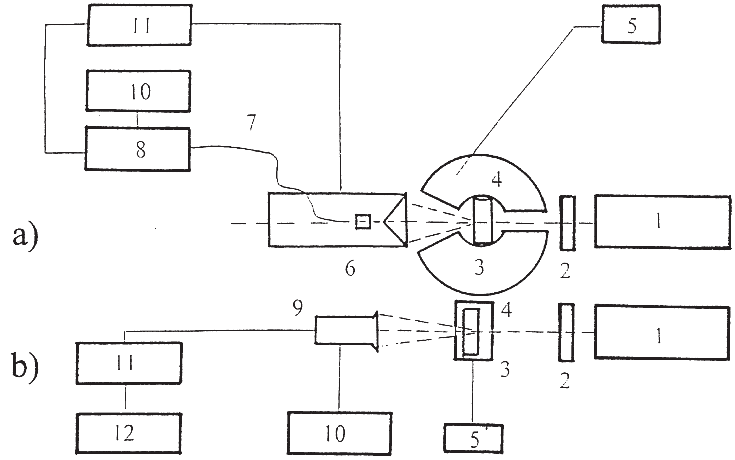

Fig. 1. Optical and block scheme of the time-resolved small-angle light scattering set-up: (a) detector-photodiode (upper part), (b) detector-CCD camera (lower part), 1 laser, 2 density filter, 3 temperature cell, 4 sample, 5 temperature controller, 6 linear scanner, 7 optical fibre, 8 photodiode detector, 9 CCD camera, 10 voltage supply, 11 PC, 12 videorecorder.

Results and Discussion

PS/PMMA blends

We present here the results for two systems: PS/PMMA (30/70) with 2 % diblock copolymer and PS/PMMA(30/70) mixture . The size scale of the morphology observed by comparing the corresponding q_m for samples with and without the copolymer (cf. Fig. 2a and Fig. 4), was found to decrease with added diblock copolymer. The relative intensity plots with values q_m and $I(q_m)$ for samples with a copolymer are tures T = 130, 160 and 180 °C. Thirty time scans at $\Delta t = 90$ s are presented for each temperature. Even if the exact localization of the copolymer is difficult, the phase contrast microscopy and comparable intensities $I(q_m)$ for samples without and with a copolymer testify to the co-continuous starting morphology in the two phase region with the most copolymer at the interphase.

The interplay between thermodynamic driving force of decreasing concentration fluctuations during annealing and of the slowing down of the interdiffusion process due to the influence of the glass transition is most below the spinodal temperature (T_{sp} is approx. apparent. At T = 130 °C, where the system is 155 °C), the prevailing change in morphology is associated with the growing size of domains. The time evolution of the $I(q_m)$

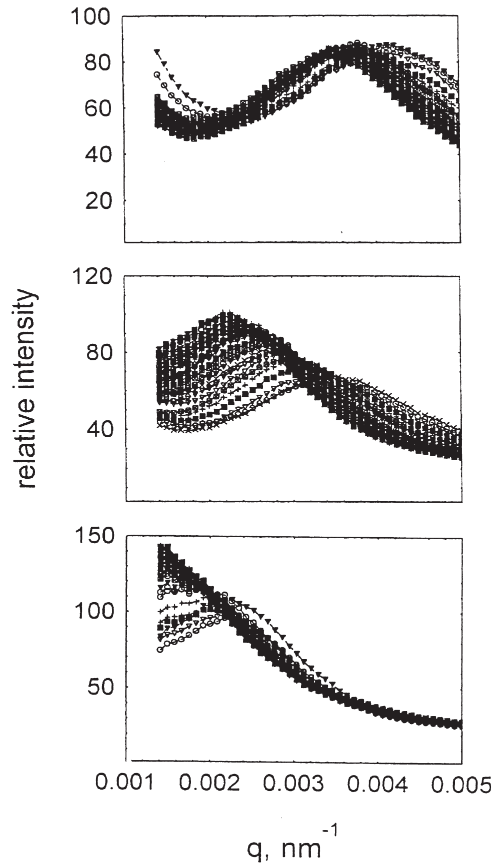

Fig. 2a,b,c. Experimental time evolution of intensity profiles for PS30/PMMA70 blend with 2% of copolymer. 30 scans at given temperature with time delay between scans $\Delta t = 90$ sec. Experimental set-up as in Fig. 1a. (a) T = 130 °C, (b) T = 160 °C, (c) T = 180 °C.

is not so significant. The kinetics of coarsening and dissolution processes are different. This is because growth occurring during the phase-separation coarsening process is influenced by a competition for material between the evolving phases, while the growth during the dissolution (annealing) involves the rate of bulk interdiffusion of the dissolving species. In our study, the dimensions of the phase-separated domains grow gradually during the annealing. The time evolution of q_m at T=160 °C is presented in Fig. 3. The q_m values decrease almost exponentially with time rather than according to the power law (cf. Eq.(1)). Especially for the higher annealing temperatures is the exponential fit substantially better then the power law fit. The power law exponent obtained from the fit in Fig. 2b gives 0.06, almost an order of magnitude different from the theoretically predicted value 0.5. This low value might be influenced by the proximity of the T_g temperatures of both homopolymers, but the further

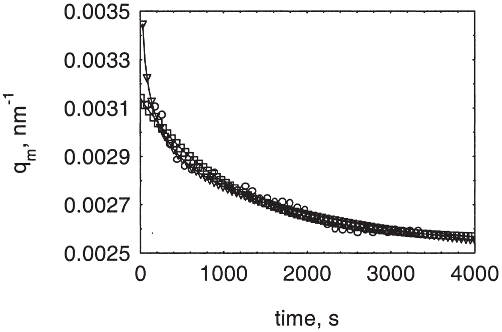

Fig. 3. Time evolution of q_m for PS30/PMMA70 blend with 2 % of copolymer, T = 160 °C (see Fig. 2b). The exponential (□) and power law (∇) fits are illustrated.

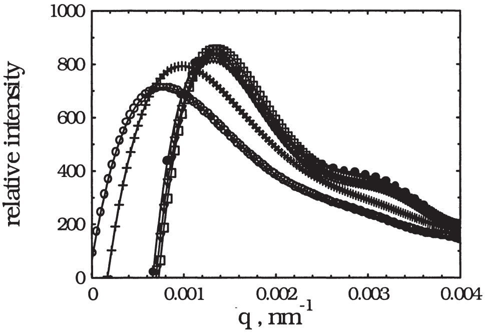

Fig. 4. Experimental time evolution of intensity profiles for PS30/PMMA70 blend. Temperature scans from T = 130 °C to T = 170 °C, with time delay Δt = 3 min between temperature jumps ΔT = 10 °C. Experimental set-up as in Fig. 1b. T = 140 °C (□), T = 150 °C (∇), T = 160 °C (●), T = 170 °C (+), T = 180°C (o).

tests of this hypothesis are necessary. The same results are obtained from the power law fit in Fig. 2c. The decrease in I(q_m) with time has not been observed for T=130 °C. For higher temperatures of annealing, deviations from the exponential decay are observed especially during the initial time period. Use of experimental set-up presented in Fig.1a is illustrated in Fig.4. The blends without the copolymer display larger starting domain sizes in comparison with the blends with the copolymer (cf. Fig. 2a and Fig. 4) and the theoretically predicted evolution of I(q_m) with time is partly followed in the given temperature regime.

Conclusions

(a) The dissolution process for the studied system cannot be reasonably modelled by a power-law decrease in the scattered vector q_m and an exponential decrease in I(q_m) with growing dissolution time for the samples with an added copolymer

(b) The prevailing effect of phase dissolution for the PS/PMMA/PS-*b*-PMMA system in the studied temperature regimes is the growing size of separated domains. A non-exponential decrease in I(q_m) is observed in the initial time period.

(c) The samples without the copolymer display larger starting domain sizes and the theoretically predicted I(q_m) versus time behaviour is approximately followed in the given temperature regime.

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References

1. T. Sato, C.C. Han, *J. Chem. Phys.* **88,** 2057 (1988)
2. A. Z. Akcasu, R. Klein, *Macromolecules* **26,** 1429 (1993)
3. A. Z. Akcasu, I. Bahar, B. Erman, Y. Feng, C. C. Han, *J. Chem. Phys.* **97,** 5782 (1992)
4. M. Best, H. Sillescu, *Polymer* **33**, 5249 (1992)