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Phase separation in bulk statistical copolymers of styrene and poly(methyl methacrylate)

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Phase separation in solid poly(styrene-*stat*-methyl methacrylate) copolymers (styrene volume fractions 0.1–0.9) was investigated by polarized Rayleigh–Brillouin and Rayleigh light scattering methods. Both these methods showed evidence of microphase separation caused by chemical polydispersity of the copolymers. © 1998 Elsevier Science Ltd. All rights reserved.

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Recently there has been much interest in phase transitions in systems with a quenched disorder. In particular, the behaviour of polydisperse copolymer melts consisting of random[1] or correlated[2–4] sequences of A and B monomer units has been investigated. Mean field theories predict that below critical temperature T_c such systems undergo phase transition to a microstructure. Until recently it was assumed that within the limit of an infinite number of blocks per chain, the free energy would be degenerate with respect to the symmetry of the microstructure, leading to the prediction of so-called disordered microphase (e.g. Ref. 2). However, as first demonstrated in Ref. 3, this assumption is not right, and a microstructure with a definite symmetry is predicted. Further investigations showed that fluctuation corrections might be very important[4,5]. In particular, for the degenerate case of an uncorrelated statistical copolymer melt, large fluctuations might result in destruction of the ordered phase[5], which is related to a special degeneracy of such a system. Therefore, both theoretical and experimental studies of possible phase diagrams for copolymer melts with a considerable structural disorder seem to be of great importance.

In this paper we address this question by using polarized Rayleigh–Brillouin and Rayleigh (static) light scattering methods to examine phase behaviour of solid poly(styrene-*stat*-methyl methacrylate) copolymers with varying volume fraction of styrene; $\Phi_S = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 0.9. The copolymers were selected because they were frequently studied in the past and, therefore, conditions for their preparation and their basic properties are quite well known[6,7].

The copolymers were prepared according to the procedure described elsewhere[7]. Both the styrene (S) and methyl methacrylate (MMA) monomers were freed of the inhibitor and mixed together to obtain the desired initial composition. The reaction mixtures were filtered through PTFE membrane filters with the pore diameter 0.2 μm into light scattering cells, freed of oxygen by the three freeze–thaw cycles and sealed in vacuum. The polymerization was initiated thermally by proceeding at 120°C for 18 h and at 150°C for 8 h. After completion of the polymerization, the ampules were slowly cooled to the room temperature. The conversions exceeded 98%. The copolymers were used for light scattering measurements directly as obtained.

Molecular weights were determined by the GPC method (THF, 25°C) and are shown in *Table 1*. The GPC column was calibrated by using polystyrene standards.

Static light scattering (SLS) measurements were performed with a Sofica instrument equipped with a He–Ne laser (vertically polarized, wavelength $\lambda_o = 632.8$ nm) in the nagular range $\theta = 30°–150°$. The scattered intensity I_S reported in figures of this paper has been normalized by the intensity scattered by benzene at the scattering angle $\theta = 90°$ and corrected for the change in scattering volume with θ; $I_S = I_m \sin\theta$, where I_m is the normalized scattered intensity measured at the scattering angle θ. The light scattering data were fitted to the Ornstein-Zernike (OZ) equation; $I_S(q) = I_S(0)/(1 + \xi^2 q^2)$, where $I_S(q)$ is the scattered intensity at the scattering vector $q = 4\pi n \sin(\theta/2)/\lambda_o$, to extract the correlation length ξ.

Brillouin light scattering (BLS) measurements were made using a Brillouin light scattering apparatus previously described[8]. The light source was an Ar-ion laser (488 nm) (frequency-stabilized Coherent Innova 304). The scattered light was analysed with a piezoelectrically scanned, single-pass Fabry-Perot interferometer (Tropel model 350). The reflectivity and flatness figures defining the mirrors are 99% and λ/200, respectively. The actually realized finess was in excess of 70 and the free spectral range of the Fabry–Perot interferometer 36.61 GHz. Only polarized Rayleigh–Brillouin spectra are examined in this work as a function of copolymer composition at room temperature. The Rayleigh–Brillouin spectra were approximated by a Lorentzian shape and analysed using a non-linear least-squares fitting procedure.

Both the homopolymers (PS and PMMA) and copolymers with volume fraction of styrene, $\Phi_S = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 0.9, were used for the static light scattering study. The scattered light intensity, I_S, at $\theta = 90°$ is strongly dependent on the volume fraction of styrene Φ_S as shown in *Figure 1a*. We found that samples with Φ_S about 0.5 are optically transparent with the value of I_S smaller than that of polystyrene alone. The light scattering increases as the Φ_S deviates from 0.5 indicating the presence

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Table 1 Molecular characteristics of styrene-*stat*-methyl methacrylate copolymers from GPC

Code	Φ_S^a	$M_w \times 10^5$	M_w/M_n
sm1/9	0.1	16.5	3.6
sm2/8	0.2	9.0	3.3
sm3/7	0.3	5.9	3.1
sm4/6	0.4	4.9	2.8
sm5/5	0.5	4.3	2.7
sm6/4	0.6	3.1	2.8
sm7/3	0.7	2.6	3.0
sm8/2	0.8	3.0	3.1
sm9/1	0.9	3.0	3.0

[a] vol. fraction of styrene

of optical inhomogeneities. The light scattering properties are not symmetrical around this composition. Thus, the sample with $\Phi_S = 0.2$ shows higher light scattering than that with 0.8. Further evidence of optical inhomogeneities was obtained from Rayleigh–Brillouin measurements. Particular, the ration of the Rayleigh scattering intensity, I_R, to the Brillouin intensity, $2I_B$, (i.e. the Landau–Placzek (L–P) ratio) is understood as a measure of optical homogeneity of samples[9]. The smaller the $I_R/2I_B$ ratio, the more homogeneous is the sample. The dependence of $I_R/2I_B$ ratio on composition measured at $\theta = 90°$ is given in *Figure 1b*. As expected, the data in *Figure 1b* are very similar to those in *Figure 1a*.

The presence of large optical inhomogeneities was confirmed by angular dependence measurements of I_S shown for samples with a lower content of S in *Figure 2*. The correlation length, ξ, of these inhomogeneities evaluated by the Ornstein–Zernike fit to experimental data are given in *Table 2*. The correlation length increases with decreasing content of S from 21 nm for a sample with $\Phi_S = 0.5$ up to about 500 nm for samples with $\Phi_S = 0.1$ and 0.2. For the samples with $\Phi_S \geq 0.60$ the size of the inhomogeneities is very small ($\approx$ 20 nm) which is at the limit of detection by static light scattering.

The optical inhomogeneities observed in the above experiments may arise from microphase separation of copolymers but may also be caused by density fluctuations frozen-in at the last viscous stages of the polymerization processes. Since the glass transition temperature, T_g, of both the homopolymers and copolymers are practically identical (A. Sikora, personal comm.) ($T_g \approx 110°C$) the effect of the synthesis should be independent of the copolymer composition being the same as with homopolymers, i.e. only small density fluctuations (smaller than 20 nm) are formed. Therefore, the large optical inhomogeneities probably reflect a frozen microphase-separated structure produced during the thermal polymerization at 150°C. This microphase separation is probably driven by the incompatibility of the copolymer molecules due to: (i) chemical; and/or (ii) molecular weight polydispersity. Under the plausible assumption that the refractive index of solid copolymers is only slightly molecular-weight-dependent, the phase-separated domains due to molecular-weight polydispersity should not be optically observable. Thus, the observed microphase separation is most likely related to composition inhomogeneities of copolymers caused by their chemical polydispersity. This interpretation is supported by the fact that both I_S and $I_R/2I_B$ ratio qualitatively follow the composition dependence of chemical heterogeneity[10]. The lowest scattering intensity observed with samples with $\Phi_S = 0.4$–0.6 can be related to the fact that their composition is close to the azeotropic composition of copolymers. Under such conditions, chemical polydispersity of the copolymers is very low and, consequently, the phase separation is negligible. In the case of a non-azeotropic composition of monomer mixtures, the content of the individual constituent units in macromolecules varies with increasing conversion during the copolymerization, so that the copolymers thus arising are chemically heterogenous. There exists a possibility of calculating the variance in the copolymer chemical composition, σ^2, for random copolymers using theoretical results based on copolymerization parameters[11]. Thus, the maximum attainable value of σ^2 for the styrene-methyl methacrylate system ($\sigma^2 = 2 \times 10^{-3}$) was found for initial composition 21.5 and

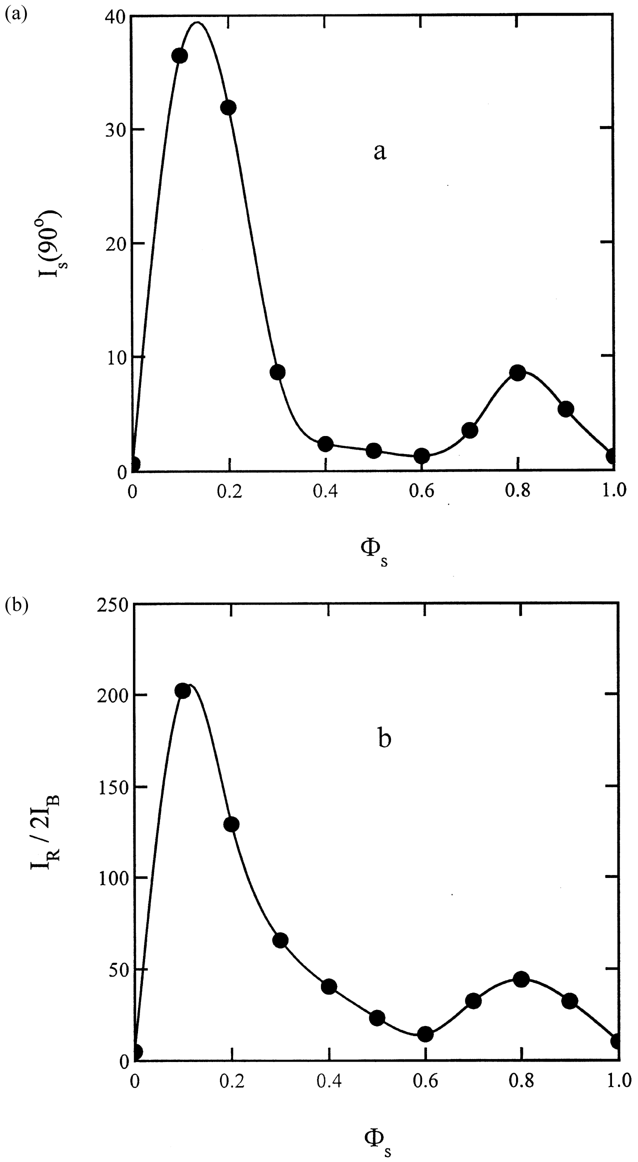

Figure 1 (a) Dependence of the scattered light intensity measured at 90°, $I_S(90°)$, on the volume fraction of styrene, Φ_S, in styrene-*stat*-methyl methacrylate copolymers. (b) Φ_S-dependence of the Landau-Placzek ratio $I_R/2I_B$

Table 2 Correlation length (ξ) and zero angle intensity ($I_S(0)$) of optical inhomogeneities in styrene-*stat*-methyl methacrylate solid copolymers

Code	sm1/9	sm2/8	sm3/7	sm4/6	sm5/5
ξ/nm	480	540	190	180	21
$I_S(0)$	3000	4400	69	13	2.2

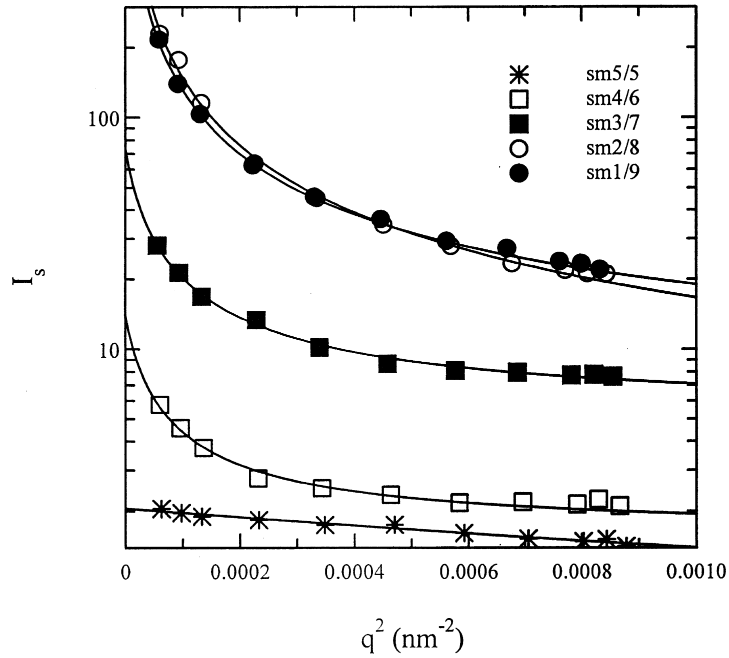

Figure 2 q^2-dependence of the scattered light intensity, I_S, for copolymers as indicated. The full lines are the best least-square fits (OZ equation) to the data

78.5 vol% of styrene at conversion 0.9[10]. This calculation was confirmed by dynamic light scattering experiments on semidilute solutions of S-*stat*-MMA copolymers in benzene[12]. Our investigation of random association of S-*stat*-MMA copolymers in the selective solvent acetone led to conclusion that chemical heterogeneity is not the only parameter controlling this association process[13]. The magnitude of the molecular weight of copolymers can also stimulate the association process. The effect of molecular weight can explain the observation that the maximum of I_S was found for the copolymer with $\Phi_S = 0.1$ instead for that with 0.2 as expected from the calculation of the variance of chemical composition. From *Table 1*, it can be seen that M_w of sample sm1/9 is about 1.8 times higher than that of sm2/8. Also, the asymmetry observed in *Figure 1a* and *b* is probably due to higher molecular weights of copolymers with a lower content of styrene than those of high-styrene copolymers (cf. *Table 1*).

In conclusion, we point out that the microstructure was observed in bulk copolymer samples of S-*ran*-MMA copolymers by light scattering methods. The microstructure seems to be a disordered microphase characterized by the correlation length, ξ, rather than the ordered one.

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