Aggregation of a Poly(ethylene oxide)–Poly(propylene oxide)–Poly(ethylene oxide) Triblock Copolymer in Aqueous Solution Studied Using Rayleigh–Brillouin and Dynamic Light Scattering

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ABSTRACT: Aqueous solutions of a PEO–PPO–PEO copolymer were studied using Rayleigh–Brillouin (R–B) and dynamic light scattering (DLS) over the concentration range 0.1–0.4 g/mL as a function of temperature. The purpose was to investigate associative and aggregation phenomena in the system. Although the R–B spectra were not influenced by the micellar to cubic phase transition, both the sound velocity (v) and spatial attenuation (α) increased with decreasing temperature below the phase transition temperature in the region in which micellar cluster formation is observed using DLS. The observations can be explained in terms of the structure of the solutions. The increase in v and α is shown to be caused by the scattering of sound waves by the clusters.

Introduction

PEO–PPO–PEO block copolymers of low molecular weight are important nonionic surface active agents (referred to variously as pluronics, poloxamers, and synperonics). Micelle formation and phase changes in the aqueous solutions have been studied using a variety of techniques: dynamic light scattering, fluorescence quenching, rheology, neutron scattering, etc. (see, for example, refs 1–9). Micellization appears to be driven by the relatively hydrophobic character of the central PPO block. The core structure corresponds to almost liquid-like PPO with a surrounding shell of water-swollen PEO chains. A transition to a cubic phase occurs in the vicinity of the micellar volume fraction 0.53, suggesting hard-sphere crystallization.[8,9] However, the pronounced elastic properties of the "gelled" phase as determined by dynamic mechanical measurements demonstrate that a significant role is played by interchain entanglements of the PEO moieties, since the viscoelastic behavior extends over a broader temperature range with increasing length of the PEO blocks. Due to the viscoelastic character of the solutions, it was of interest to examine the Rayleigh–Brillouin (R–B) scattering in the system. Scattering in a viscoelastic fluid is known to arise mainly from local density fluctuations. The technique has mostly been used in studies directed to an examination of the influence of temperature on the dynamics of bulk polymers near and above the glass transition temperature, T_g. In the latter investigations, the relaxational properties of the longitudinal modulus and shear viscosity in the GHz frequency range have been measured. In such systems the α- and β-relaxations, which are determined by segmental motions in the chain, dominate the dynamics. This type of study has been reviewed by Patterson.[10] In recent investigations, we have directed our attention to the elucidation of the solution dynamics of polymers over a broad range of concentration extending from volume fraction 0.1 up to the bulk polymer.[11-13] In the present paper we describe the use of a combination of polarized ($I_{VV(\omega)}$) R–B scattering and dynamic light scattering (DLS) techniques on a series of PEO–PPO–PEO triblock copolymer samples in water varying in concentration from 0.1 to 0.4 g/mL. The influence on the R–B light scattering spectra of the associative and aggregation phenomena occurring in the system and the phase transition from the micellar solution to the cubic phase have been examined. It is found that the characteristics of the R–B spectra of concentrated solutions of these block copolymers can be explained in terms of the scattering of sound waves by the aggregates (clusters) which feature in the system below the transition to the cubic phase.[4]

It is interesting to note that ultrasound velocimetry has previously been used[1] to characterize micelle formation in PEO–PPO–PEO copolymer systems. In a recent development,[7] the speed of the ultrasonic wave is measured in the sample and it is shown that the speed of sound decreases when micellization occurs (i.e., it decreases in proportion to the number density of particles).

Experimental Section

Materials. The triblock copolymer (P-85) was obtained from Serva AG Heidelberg, Germany. It was used without further purification. The total molecular weight is 4600: 27 + 27 units of ethylene oxide and 39 units of propylene oxide. Water solutions of P-85 at six concentrations ranging between 0.1 and 0.4 g/mL were prepared individually at 6 °C. They were filtered using 0.22 μm (or 0.45 μm) Millex filters into 10-mL cylindrical ampules and sealed.

Rayleigh–Brillouin light scattering measurements were made using the instrument described in ref 11. Only vertically polarized ($I_{VV}(\omega)$) R–B spectra were taken up. The light source was a frequency-stabilized Coherent Innova 304 Ar-ion laser operated at 488 nm. A fixed scattering angle of 90° was used. A Fabry–Perot interferometer (Tropel Model 350) was used in the single-pass mode with a ramp duration of 10 s. The FSR of the instrumental setup was 19.819 GHz. The reflectivity and flatness of the mirrors were, respectively, 99% and $\lambda/200$. A finesse of >70 was achieved.

The scattering light was detected in the photon-counting regime (Hamamatsu R464). The R–B spectra were recorded over the temperature range 5 to 40 °C by a multichannel analyzer/computer as described previously.[12] The spectra were approx-

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imated by a Lorentzian shape and analyzed using a weighted nonlinear least-squares fit based on the Marquardt algorithm. Poisson statistics were assumed, and the squared residuals were weighted with the reciprocal of the measured value. The Brillouin full-width at half-height (corrected for instrumental broadening by subtraction of the instrumental full width from the observed full-width at half-height), $\Delta\nu_B$, and the corresponding frequency shift, ν_B, were determined. Since the sound velocity, v, and the spatial attenuation, α, of the hypersound which are related directly to the hypersound propagation are more important than the frequency shift and the width of the lines, these parameters were evaluated using the relationships

$$v = 2\pi\nu_B/q \tag{1}$$

and

$$\alpha = 2\pi\Delta\nu_B/\lambda_s\nu_B \tag{2}$$

λ_s is the wavelength of sound in the medium, and q is the scattering vector.

Dynamic light scattering (DLS) measurements were made in the homodyne mode using a 50-mW 633-nm He–Ne laser as the light source. The scattering cells (10-mL cylindrical ampules) were immersed in a large diameter (10 cm) thermostated bath of index-matching liquid (transdecalin) of n = 1.479 at 25 °C. The detector system comprised an ITT FW130 photomultiplier, the output of which was digitized by an ALV amplifier–descriminator. The signal analyzer was an ALV multibit, multisample time autocorrelator (ALV3000) with 191 channels covering approximately 8 decades in delay time. To obtain the distribution of relaxation times ($\tau A(\tau)$ vs log τ) an inverse Laplace transform of the correlograms was made using a constrained regularization algorithm called REPES.[14] The vertical axis in these plots is given as $\tau A(\tau)$ to provide an equal area representation. Correlation functions were also fitted to the sum of two distributions: one is Gaussian in log τ and represents the fast peak in the essentially bimodal correlograms, while the other is a so-called generalized exponential (GEX) distribution representing the total of the slow components. The Gauss-GEX fit has been discussed in some detail in ref 15, where the appropriate forms for the distributions are given.

Results and Discussion

The frequency shift, ν_B, and full-width $\Delta\nu_B$ of the Brillouin lines were measured on six concentrations between 0.1 and 0.4 g/mL of P-85 in water at temperatures in the range 5 to 40 °C. The longitudinal sound (phonon) velocity, v, and the spatial attentuation, α, of the hypersonic waves were calculated using eqs 1 and 2, respectively. While no substantial changes in v and α were found at low concentrations (c < 0.26 g/mL), strong variations of both parameters were observed at high concentrations and low temperatures. The temperature dependences of v and α are shown for concentrations 0.26, 0.31, and 0.42 g/mL in Figure 1a,b. Both quantities were unaffected by the crossovers to the cubic phase which occur, depending on the temperature, at 14 °C (0.42 g/mL), 23 °C (0.31 g/mL), and 29 °C (0.26 g/mL), but these parameters increased, particularly α, with decreasing temperature.

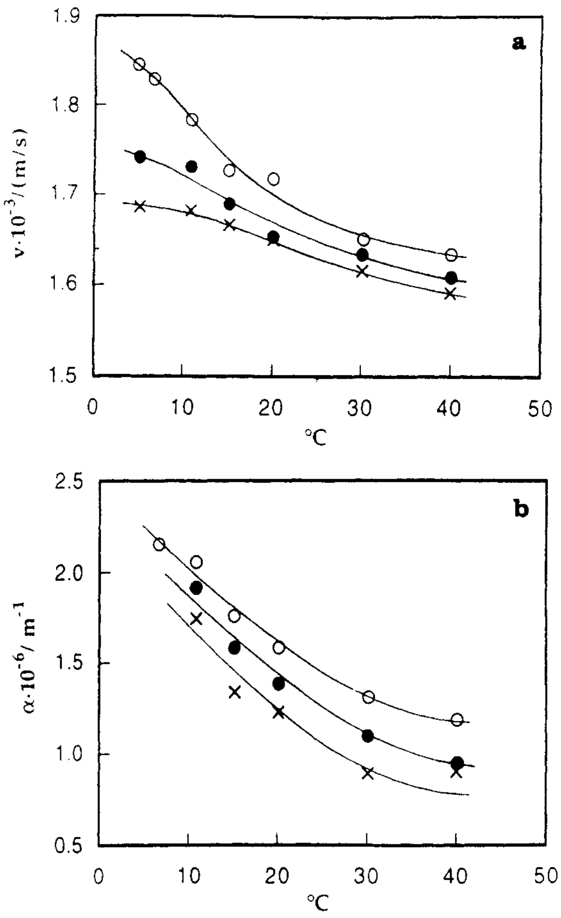

Figure 1. Rayleigh–Brillouin scattering data for the P-85/water system. (a) Longitudinal sound (phonon) velocity, v, as a function of temperature in the solutions with concentrations denoted: 0.26 (×); 0.31 (●); 0.42 (○) g/mL. (b) Spatial attenuation of the hypersonic wave, α, as a function of temperature for the concentrations as in part a.

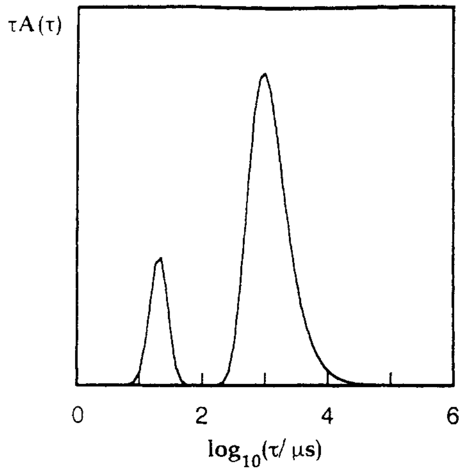

Figure 2. Relaxation time distribution ($\tau A(\tau)$ versus log τ) obtained by Laplace inversion of the dynamic light scattering correlation function for a solution of P-85 at 0.31 g/mL and 10 °C.

In order to obtain independent and complementary information, DLS measurements were made on the same samples. Figure 2 shows relaxation time distributions ($\tau A(\tau)$ versus log τ) for the concentration 0.31 g/mL at 10 °C as obtained by fitting the autocorrelation function to the sum of a Gaussian function and a generalized exponential (GEX).[15] The fast Gaussian mode represents the relaxation of the micelles, and the broad, slow peak describes the diffusion of polydisperse clusters of micelles. The clusters give the dominant contribution to the scattered intensity below the transition to the cubic phase. Since the observed relaxational modes are diffusive (i.e., q^2-dependent), the apparent hydrodynamic radius (R_{app}) can be calculated from the mean decay rate of the slow mode(s) using the Stokes–Einstein relation together with the solvent viscosity. The radius is observed to increase with decreasing temperature (see Table I). This derived radius cannot be understood as a true hydrodynamic radius since DLS data at finite concentrations are used in the calculation. Nevertheless, R_{app} serves for estimation of changes in the cluster size. The ratio of the scattering amplitudes (A_s/A_f) increases with decreasing temperature (Figure 3). This behavior reflects changes in the size (Table

Table I. Temperature Dependence of Cluster Sizes (R_{app})

temp (°C)	R_{app}/nm		
	0.26 g/mL	0.31 g/mL	0.42 g/mL
4.9	105.8	57.0	55.2
6.9	82.6	44.9	42.8
8.0	62.4	38.7	52.7
14.9	37.1	26.9	33.6
19.9	20.4	14.0	25.3
25.0	24.6	18.5	30.6

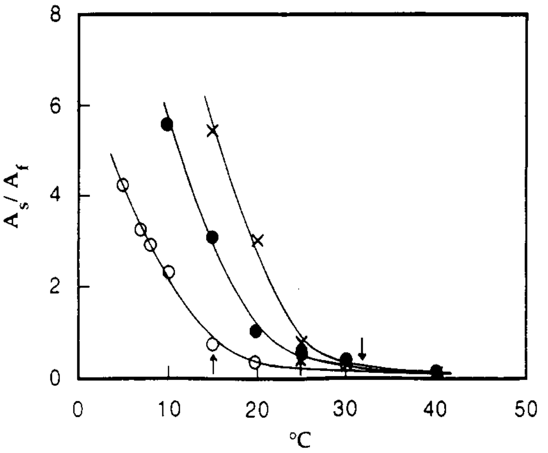

Figure 3. Dynamic light scattering data: relative amplitude ratio of slow to fast components in the bimodal relaxation time distributions as a function of temperature at the concentrations as denoted in Figure 1.

I) and concentration of clusters with decreasing temperature. Cluster formation occurs at temperatures well below the transition to the cubic phase. The latter is shown at each concentration by the arrows in Figure 3. In the case of the Brillouin light scattering data, the behavior of the attenuation, α, cannot be explained by the relaxing viscosity since the solutions are well above the glass transition temperature, T_g. (T_g for PEO is 203K and PPO 198K.[16]) An alternative explanation of the changes, which is substantiated by the independent DLS measurements, is that the phonons (hypersound waves), which have a wavelength similar to the wavelength of the light in the medium, are scattered by the *same* clusters—the concentration and size of which increase with decreasing temperature. Such a scattering interpretation was invoked to describe the Brillouin scattering data for gelatin gels[17] and epoxy resins.[18] Phonon scattering leads to a shortening of the phonon lifetime and manifests itself in an increase of the spatial attenuation, α.

Phonon scattering can be understood, at least qualitatively, using expressions for spherical scatterers. Thus, the attenuation, α, for a mixture containing N spheres of radius a, embedded in a medium having negligible sound attenuation is $\alpha = N\Sigma$, where Σ is the scattering cross-section per sphere given by the relationship[19]

$$\Sigma = (4/9)\pi a^2(ka)^4[(K_n - K_o)/K_o^2 + 1/3(3\rho_n - 3\rho_o)/(2\rho_n - \rho_o)^2] \quad (3)$$

where K_n,ρ_n (K_o,ρ_o) are, respectively, the compressibility and density of the spheres (medium) and the sound wave vector is $k = 2\pi/\lambda_s$, with λ_s the wavelength of the sound in the medium. The scattering model allows us to link the results of both light scattering techniques. The temperature dependences of the attenuation reflect the same cluster concentration and size changes which are responsible for the temperature variations of A_s/A_f.

Like the attenuation, the sound velocity increases slightly (<10%) with decreasing temperature over the range used and is not affected by the transition to the cubic phase (see Figure 1b). Small changes in the sound velocity can be related to changes in the mean compressibility and/or density of the concentrated solutions[19]

$$(\Delta v/v) = (1/2)[(\Delta K/K) - (\Delta\rho/\rho)] \quad (4)$$

assuming $\Delta K/K$ and $\Delta\rho/\rho \ll 1$. For a system of N spheres, radius a, embedded in the medium[11]

$$\Delta K = (4/3)\pi N a^3(K_n - K_o) \quad (5a)$$

and

$$\Delta\rho = (4/3)\pi N a^3(\rho_n - \rho_o) \quad (5b)$$

If we suppose that the observed clusters represent regions with a higher polymer concentration, then clustering should increase the hypersound velocity, v. This is based on the experimental finding that v increases with increasing concentration (Figure 1a). The increase in v with decreasing temperature is thus probably due to a corresponding increase of the cluster radius a and number density N. Unfortunately, the values of K_n and ρ_n are not known and this precludes a quantitative verification of the theory. However, by assuming the extreme situation in which the observed clusters are spherical droplets of the dry polymer, the volume fraction $\Phi_p = (4/3)(\pi N a^3)$ of the clusters can be roughly estimated from eqs 4 and 5. Employing the dry-state values for $K_n \approx 4.44 \times 10^3$ MPa calculated from the extrapolated value of the sound velocity ($v_n \approx 2000$ m/s), $\rho_n = 1.11 \times 10^3$ kg m^{-3}, and $K_o = 2.25 \times 10^3$ MPa, $\rho_o = 1 \times 10^3$ kg m^{-3} for water at 20 °C, we have calculated the value $\Phi_p = 0.12$ to give the observed 5% increase in the Brillouin shift. This value of Φ_p is smaller than the actual concentration of polymer in solution. Supposing that all dissolved polymer is in the form of clusters, we can suppose a rather high swelling ratio for the clusters, e.g., ≈50% for the sample with concentration 0.26 g/mL. Approximating the scattering center as a sphere of radius 40 nm, we can calculate the corresponding change in the sound attenuation, $\Delta\alpha$, from eq 3 using $k = 2.423 \times 10^7$ m^{-1}. This yields a value of $\Delta\alpha = 8.3 \times 10^5$ m^{-1}, giving 1 order of magnitude agreement with the observations. In the above discussion we have used the apparent hydrodynamic radius (Table I) for the clusters since this is considered to be a better approximation for the geometrical radius of the solid-like particles than would be given by the radius of gyration. We emphasize that the effects connected with the phonon scattering are only measurable for high polymer volume fractions, Φ_p, and thus the changes in v and α are not observable at low concentrations in the micellar region.

In conclusion, it would appear that the shapes of the Brillouin spectrum for the concentrated solutions of PEO–PPO–PEO may be explained by the presence of clusters (aggregates) of micelles in the solutions existing in the micellar solution prior to the cubic phase transition. The changes in the low frequency mechanical moduli observed at the cubic phase transition[4] are not reflected in changes in the high frequency (GHz) modulus studied by the R–B scattering technique.

Conclusions

We describe a Rayleigh–Brillouin and dynamic light scattering investigation on micellar solutions of the PEO–PPO–PEO triblock copolymer P-85. Both the sound velocity and attenuation are found to be influenced by micellar cluster formation occurring below the phase transition to the cubic phase, but not by the transition to the cubic phase itself. The results are interpreted in terms of the scattering of sound waves by the micellar clusters existing below the phase transition. The investigation shows that Rayleigh–Brillouin light scattering spectroscopy is a useful and valuable tool for studying phase transitions.

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