Laser Light Scattering Characterization of a Novel Polymer Nanofiber

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Introduction

It is well-known that a diblock copolymer may form a microphase separation in the bulk state due to the self-assembling of each block. Depending on the segment ratio of each block, the morphology could be spherical, cylindrical or lamellar.[1] When dissolved in a selective solvent, which is a good solvent for one block, but poor for the other, diblock copolymers may form a core−shell micelle with the insoluble block as the core and the soluble block as the shell.[2] If a solid substrate is in contact with this polymer solution, diblock copolymers may deposit on it to form a polymer brush when the solid/insoluble block interaction is favorable.[3] Recently, Liu et al.[4] prepared a novel type of nanofiber by photocrosslinking the PCEMA blocks in the self-assembled cylindrical phase of a polystyrene and polystyrene-*b*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA) diblock copolymer blend. The TEM graph showed that the nanofibers are ∼25 nm in diameter and ∼10³ nm in length. In this study, a combination of static and dynamic laser light scattering (LLS) was used to determine the mass and composition of such novel nanofibers as well as their conformation in solution.

Experimental Section

Sample Preparation. The polystyrene and poly(2-cinnamoylethyl methacrylate) blocks in the diblock copolymer, respectively, have 125 and 158 repeating units. The details of the copolymer synthesis and the nanofiber preparation were reported before.[4,5] Here, we only outline the nanofiber formation. A 1-mm thick copolymer film was prepared, in which PS-*b*-PCEMA formed a cylindrical phase. The film was irradiated half an hour on each side to cross-link the PCEMA blocks in the center of the cylindrical phase. The dissolution of polystyrene matrix in tetrahydrofuran (THF) led to a nanofiber suspension which contains soluble and insoluble portions. The TEM graph showed that both portions consisted of the nanofibers. In the insoluble portion, the nanofibers were longer and more entangled. In this study, only the soluble portion was investigated. The nanofiber concentration used was so dilute (10^{-5}–10^{-6} g/mL) that the overlapping of the nanofibers in the solution was avoided. The solutions were clarified by a 1 μm pore size PTFE filter to remove dust before LLS measurements. There was no obvious flagging of the filter during the clarification and no obvious concentration change after the clarification.

Laser Light Scattering. A modified commercial LLS spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-τ

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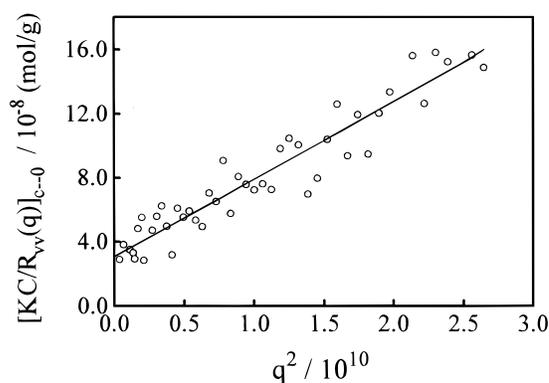
Figure 1. Angular dependence of the excess Rayleigh ratio $KC/R_{vv}(\theta)$ of the nanofibers in infinite dilution.

digital time correlator and a solid-state laser (ADLAS DPY 425II, output power ≈ 400 mW at λ_o = 532 nm) as the light source was used. The primary beam is vertically polarized with respect to the scattering plane. The instrument was calibrated with toluene to make sure that the scattering intensity has no angular dependence in the angular range 6−154°. The small angle range (6−21°) is particularly useful in this study because the nanofibers are quite long. The detail of the LLS instrumentation and theory can be found elsewhere.[6,7] All the LLS measurements were done in toluene at 25.0 ± 0.1 °C.

In static LLS, the angular dependence of the excess absolute time-averaged scattered intensity $R_{vv}(q)$, known as the excess Rayleigh ratio, was measured. For a dilute polymer solution measured at a low scattering angle, $R_{vv}(q)$ can be related to the weight-average molar mass M_w, the second virial coefficient A_2, and root-mean-square z-average radius of gyration $\langle R_g^2 \rangle_z^{1/2}$ (or written as $\langle R_g \rangle$) by[8]

$$\frac{KC}{R_{vv}(q)} \approx \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g^2 \rangle_z q^2\right) + 2A_2C \tag{1}$$

where $K = 4\pi^2 n^2 (\mathrm{d}n/\mathrm{d}C)^2/(N_A\lambda_0^4)$ and $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with N_A, $\mathrm{d}n/\mathrm{d}C$, n, and λ_o being Avogadro's number, the specific refractive index increment, the solvent refractive index, and the wavelength of light in a vacuum, respectively. The value of $\mathrm{d}n/\mathrm{d}C$ was 0.11 mL/g.[5] In dynamic LLS, a precise intensity−intensity time correlation function $G^{(2)}(t,q)$ in the self-beating mode was measured. The Laplace inversion of $G^{(2)}(t,q)$ can lead to a line width distribution ($G(\Gamma)$).[6]

Results and Discussion

Figure 1 shows the angular dependence of the excess Rayleigh ratio of the nanofibers in infinite dilution. The values of M_w, R_g and A_2 calculated on the basis of eq 1 are 3.3 × 10⁷ g/mol, 2200 nm, and ∼7 × 10⁻⁴ mol·cm³/g², respectively. Considering that individual diblock copolymer chains have a molar mass of ∼1.5 × 10⁵ g/mol, we were able to estimate that each nanofiber consists of ∼220 diblock copolymer chains. Our results showed that the depolarization ratio ($\rho_V = (R_{vh}(\theta)/R_{vv}(\theta))$) in dilute solution was quite small, less than 5 × 10⁻³, where $R_{vh}(\theta)$ and $R_{vv}(\theta)$ are the excess Rayleigh ratios measured by respectively putting a horizontal and a vertical polarizer in front of the detector. The ratio is related to the chain anisotropy δ by $\rho_V = 3\delta^2/(5 + 4\delta^2)$. Nagai stated that all the measured LLS parameters have to be corrected;[9] namely, $M_w = M_{w, \text{mead}}/\gamma$, $R_g = \gamma^{1/2}R_{g, \text{mead}}$, and $A_2 = \gamma^2 A_{2, \text{mead}}$ with $\gamma = (1 + 4\delta^2/$
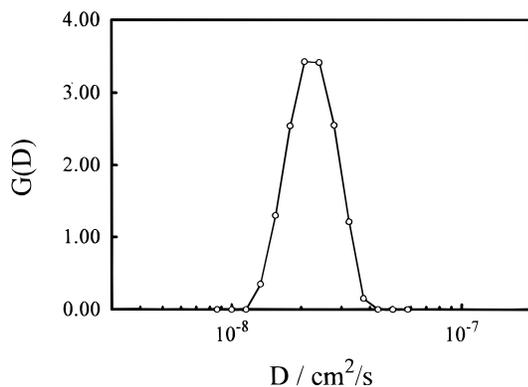
Figure 2. Typical translational diffusion coefficient distribution of the nanofiber in toluene, where the nanofiber concentration is 6×10^{-6} g/mL and the scattering angle is 6°.
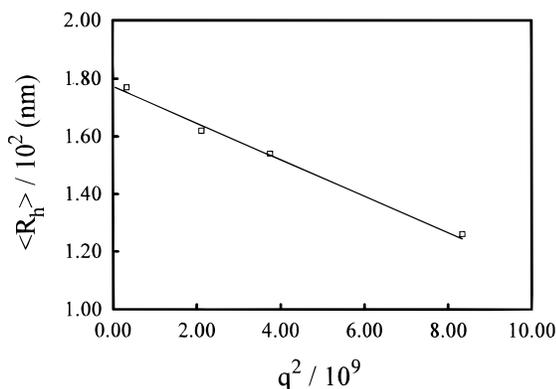
Figure 3. Angular dependence of the average hydrodynamic radius $\langle R_h \rangle$ of the nanofibers in THF, where the nanofiber concentration is 6×10^{-6} g/mL.

5). It can be seen that the corrections in this case are insignificant.

At a very small angle, i.e., $qR_g \ll 1$, the translational diffusion is decoupled from both rotational diffusion and internal motions of the nanofibers in dynamic LLS. In this way, the line width Γ is only related to the translational diffusion coefficient D by $\Gamma = Dq^2$. Figure 2 shows a typical translational diffusion coefficient distribution of the nanofibers in toluene at 6°. Further, D can be converted to the hydrodynamic radius R_h by the Stokes–Einstein equation: $R_h = k_B T/6\pi\eta D$ where k_B, η, and T are the Boltzman content, the solvent viscosity, and the absolute temperature, respectively.[10] Figure 3 shows that at $\theta = 6°$ (the left-most point), $\langle R_h \rangle$ is essentially the same as $\langle R_h \rangle_{q \to 0}$. In infinite dilution, $\langle R_h \rangle = 178$ nm. It should be noted that such obtained $\langle R_h \rangle$ is an apparent one since the shape of the nanofibers are not spheric. The ratio of $\langle R_g \rangle/\langle R_h \rangle \sim 1.22$ indicates that the nanofibers do not have an extended thin-rod conformation, which is different from what we expected.

Next, let us estimate the composition of the nanofibers on the basis of our LLS results. Considering the nanofibers as a rigid rod, we estimated its length (L) to be $\sim$750 nm from its radius of gyration, i.e., from $\langle R_g^2 \rangle \sim L^2/12$. On the other hand, we know that for a rigid
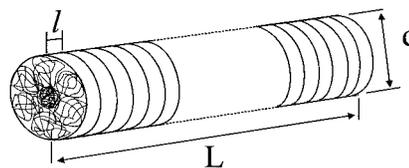
Figure 4. Schematic composition of the nanofiber in toluene.

rod with a diameter of d and a length of L, $D = (k_o T/3\eta L) \ln(L/d)$, i.e., $L = 2R_h \ln(L/d)$, so that $L/d \sim 8$ or $d \sim 91$ nm. Therefore, the nanofibers have a thick rod conformation in solution, which also explains why $\langle R_g \rangle/\langle R_h \rangle$ is very low. Transmission electron microscopy graph showed that the cylindrical phase is hexagonal and the nanofiber has a diameter of $\sim$25 nm in its dried state. Further, considering that, in the hexagonal cylindrical phase,[4] each layer consists of six copolymer chains, as shown in Figure 4, we estimated that each nanofiber, on average, is made of $\sim$36 layers and each layer has a thickness (l) of $\sim$21 nm because each fiber contains $\sim$220 copolymer chains. The values of d and l reasonably agree with those estimated from the polystyrene chains with a similar molar mass in toluene. The fact that $d/l \sim 4.5$ indicates that the PS blocks are highly stretched in toluene, which is expected because toluene is a good solvent for polystyrene. Further, the average density of the nanofibers estimated from its average mass and hydrodynamic radius is $\sim$2.8 $\times 10^{-2}$ g/cm^3 which is slightly higher than that for the polystyrene chains free in toluene because here only the PS blocks can swell, but not the cross-linked PCEMA blocks.

References and Notes

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MA9800663