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Communications to the Editor

Transition of Polystyrene in Cyclohexane from the Θ to the Collapsed State

The coil-to-globule transition has been a fascinating and fundamental problem in dilute polymer solution physics and can be classified as one of the experimental challenges in light-scattering spectroscopy. We have worked on this problem starting in the late 1970s and our experiments have encountered different stages of development.[1-5] Now, we have finally achieved our aim in reaching the globule state of polystyrene in cyclohexane based on the hydrodynamic radius. The essential experimental findings are presented in this paper, leaving the details to a later article.

The challenge can be subdivided into several standard experimental procedures: materials, solution preparation, and instrumentation as well as information on the thermodynamic state of the polymer solution under investigation. We often consider polystyrene (PS) as one of the best characterized model polymer coils with an accessible narrow molecular weight distribution (MWD), and high molecular weight PS samples are available commercially on the market (e.g., sources such as Toyo Soda, Polyscience, Pressure Chemical). What we need is an ultrahigh molecular weight PS polymer with $M_w > 10^7$ g/mol and $M_w/M_n \leq 1.03$. None of the commercial sources could satisfy our requirements. We obtained the last of the 44 million PS sample prepared by L. Fetters, and through courtesy of H. Fujita, PS samples from the Japan Synthetic Rubber Co. The special PS samples also showed possible degradation or revealed polydispersities beyond the acceptable range for our experiment. Finally, an IK-3000 PS sample from the Japan Synthetic Rubber Co. was fractionated by Professor Ju Zuo over a period of close to 1 year. The fractionation had to be performed extremely slowly in order to be effective. With final fractions recovering only microgram quantities of high molecular weight PS samples. It should be interesting to note that although our starting material had $M_w = 2.3 \times 10^7$ g/mol with $M_w/M_n \approx 1.2$ as reported by the manufacturer, we characterized the same PS polymer and found $M_w = 2.35 \times 10^7$ g/mol with $M_w/M_n \approx 2.1$. The final fractions we used had $M_w = 4.83 \times 10^7$ g/mol and were fractionated from the IK-3000 PS sample.

Ultrahigh molecular weight PS polymers are subject to shear and thermal degradation. Oxygen had been excluded from the fractionation and solution preparation steps. The temperature was maintained only slightly above the Θ temperature during dissolution. The polymer solution was never filtered for fear of shear degradation. Cyclohexane was filtered and made dust free directly in the light-scattering cell, which was a component of an integrated filtration circuit.[6] Small-angle light-scattering experiments could not have succeeded without such a closed filtration/dilution circulation system for solvent/solution clarification. We tried to prepare the stock polymer solution as clean as possible before its dilution by a factor of 10^3–10^4 in the filtration circuit containing dust-free cyclohexane. The excess dilution was another factor in achieving the preparation of a dust-free ultrahigh molecular weight polymer solution. To avoid shear degradation, the introduction of the polymer solution in the filtration circuit (but bypassing the filters) took a few hours.

With the ultrahigh molecular weight polymer solution, measurements of the angular distribution of solution scattered intensity and the corresponding Rayleigh line width need to be performed at small scattering angles satisfying the condition $KR_g \leq 1$. This requirement cannot be met by commercial light-scattering spectrometers and translates into the need to construct a new small-angle light-scattering instrument which was perceived in the late 1970s. Furthermore, we were interested in designing an efficient spectrometer with high beating efficiency and the light-scattering cell should require only a small volume of fluid as we anticipated in advance that ultrahigh molecular weight PS samples were going to be precious and difficult to come by. After an initial demonstration,[7,8] we have now succeeded in adapting the prism light-scattering spectrometer[6] to perform light-scattering measurements for polystyrene in cyclohexane in the collapsed regime. It is sufficient to mention here that the spectrometer has a scattering angular range of $2° \leq \theta \leq 120°$ and a beating efficiency (b) of 0.9 at small scattering angles, with the theoretical limit being $b = 1$. The intensity–intensity time correlation function $G^{(2)}(K,\tau)$ has the form

$$G^{(2)}(K,\tau) = A(1 + b|g^{(1)}(K,\tau)|^2) \tag{1}$$

where A is the base line, b is the coherence factor and represents a measure of beating efficiency, and $|g^{(1)}(K,\tau)|$ is the normalized electric field correlation function with $b|g^{(1)}(K,\tau)|^2$ $[\equiv G^{(2)}(K,\tau)/A - 1]$ being the net intensity correlation function.

Figure 1 shows a plot of $G^{(2)}(K,\tau)/A - 1$ versus τ for a fractionated PS in cyclohexane measured at 35 °C and $K^2 = 4.9 \times 10^8$ cm^{-2}. The solid line denotes $G^{(2)}(K,\tau)/A - 1 = 0.0028 \exp(-17.4\tau)$ with the delay time τ expressed in seconds. In Figure 1, we have noted three significant features. (1) The net intensity time correlation function can be fitted by using a single-exponential function, revealing that our PS fraction has a polydispersity index beyond the resolution of the dynamic light-scattering spectrometer. If we were to use a cumulants fit, $\mu_2/\bar{\Gamma}^2 \approx 0.006 \pm 0.004$ with $\mu_2 = \int G(\Gamma)(\Gamma - \bar{\Gamma})^2 \, d\Gamma$ and $\bar{\Gamma} = \int \Gamma G(\Gamma) \, d\Gamma$, $G(\Gamma)$ being the normalized characteristic line-width distribution. Such a PS fraction with $M_w = 4.83 \times 10^7$ g/mol represents the highest narrow MWD sample ever prepared. (2) With $b \approx 0.86$, an intercept of 0.0028 represents that the ratio of PS scattering to the solution scattering is about 0.057. Measurements of polymer solution with an excess scattering intensity of 6% of the

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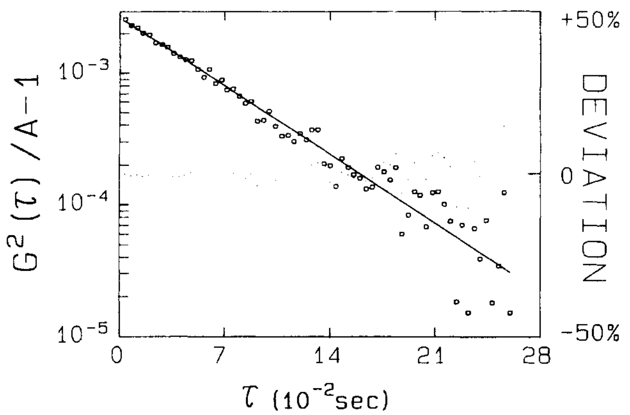

Figure 1. Plot of $G^{(2)}(K,\tau)/A - 1$ and percent deviation versus τ. Hollow circles denote measured data at 35 °C; solid line denotes $G^{(2)}(K,\tau)/A - 1 = 0.0028 \exp(-17.4\tau)$ with τ expressed in seconds. $\theta = 6.9°$; $C \approx 3 \times 10^{-8}$ g/mL for PS polymer with $M_w = 4.83 \times 10^7$ g/mol. DEVIATION = 1 − log $(G^{(2)}_{\text{calcd}}(K,\tau)/A - 1)$/log $(G^{(2)}_{\text{measd}}(K,\tau)/A - 1)$.

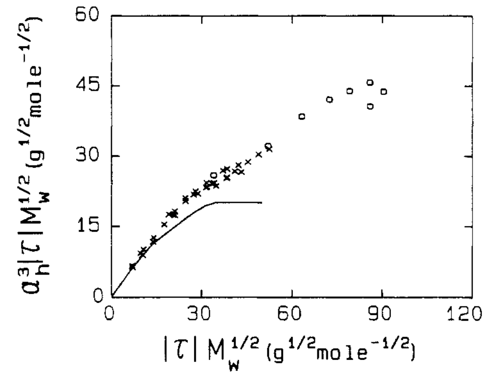

Figure 2. Plot of $\alpha_h^3|\tau|M_w^{1/2}$ versus $|\tau|M_w^{1/2}$. Solid line denotes $\alpha_s^3|\tau|M_w^{1/2}$. Crosses denote earlier results[2] using lower molecular weight PS polymers at higher concentrations; hollow circles denote this work using a PS sample with $M_w = 4.83 \times 10^7$ g/mol, $M_w/M_n \leq 1.03$, $C \approx 3 \times 10^{-8}$ g/mL, and measured at small scattering angles ($KR_g \leq 1$).

solvent due to polymer solute scattering represent, to our knowledge, light-scattering experiments in the most dilute solution and small-angle scattering limits ever performed. (3) The agreement between the measured and computed base line is typically $A_{\text{meas}} = 8.65633 \times 10^6$, $A_{\text{compt}} = 8.65610 \times 10^6$, i.e., one part in 3.8×10^4. This means that our system including polymer solution clarification has achieved an extremely high operating efficiency.

Figure 2 shows a plot of scaled expansion factor of hydrodynamic size $\alpha_h^3|\tau|M_w^{1/2}$ ($g^{1/2}$ mol$^{-1/2}$) versus scaled reduced temperature $|\tau|M_w^{1/2}$ ($g^{1/2}$ mol$^{-1/2}$) where $\alpha_h = R_h(T)/R_h(\Theta)$ with R_h and Θ being the hydrodynamic radius and the Θ temperature, respectively. By using a $M_w = 4.83 \times 10^7$ g/mol, PS polymer of extremely narrow MWD ($M_w/M_n \leq 1.03$), and a concentration of 3×10^{-8} g/mL, we have reached the collapsed state for polystyrene in cyclohexane based on the hydrodynamic size. The crosses represent our earlier results[2] and circles denote the present work. The solid line denotes a plot of $\alpha_s^3|\tau|M_w^{1/2}$ versus $|\tau|M_w^{1/2}$ with $\alpha_s = R_g(T)/R_g(\Theta)$, R_g being the root-mean-square z-average radius of gyration. The ratio of the plateau values for $\alpha_h^3/\alpha_s^3 = (43.2 \pm 2.0)/(20.2 \pm 0.8) = 2.14 \pm 0.19$, in reasonable agreement with a value of 2.08, based on the blob theory.[9] A more detailed analysis and further measurements are under way.

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Registry No. PS, 9003-53-6; cyclohexane, 110-82-7.

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Polymerization of Monomers Containing Functional Silyl Groups. 5. Synthesis of New Porous Membranes with Functional Groups

Microporous membranes are commercially produced from polymers by using phase-separation process.[1] In this paper, a new attempt is described to make microporous membranes from the film of a block copolymer with well-defined chain structure which is prepared by anionic living polymerization. This method involves casting a block copolymer film with a microphase-separated lamellar structure, fixation of one microdomain by cross-linking between the polymer chains, oxidative decomposition of the other microdomain, and leaching out the degraded low molecular weight compounds from the inside of micropores formed by oxidation. The lamellar structure of the original block copolymer film was found to be directly reflected in the shape and size of the micropores produced by these steps. Thus, the microstructure of the porous membrane can be controlled through these procedures chiefly by the morphology of the segregated microphase depending on architecture of block copolymer and casting conditions of the film. Regulated pore size of the membrane may control the permeability of a fluid. Furthermore, it is observed that the resulting membrane contains carbonyl groups by oxidative cleavage of the polymer chain, which will enable some functions such as enzymes and metal complexes to be linked in the micropores.

Experimental Section. Block Copolymerization. The anionic living polymer of isoprene (20.4 mmol) was prepared with oligo(α-methylstyryl)dipotassium (0.05 mmol) in dry THF (26 mL) at −78 °C for 3 h in a sealed glass tube equipped with breakable seals. For the characterization of homopolyisoprene, an aliquot of the reaction mixture (12 mL) was withdrawn. (4-Vinylphenyl)dimethyl-2-propoxysilane (**1**) (5.63 mmol) in 5.5 mL of THF was added to the residual THF solution (15 mL) of anionic living polyisoprene at −78 °C and was kept at the same temperature for 5 min to give a triblock copolymer, **2**, as shown in Scheme I. The living polyisoprene and block copolymer were quenched with methanol. The polymers