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Light Scattering Characterization of an Alternating Copolymer of Ethylene and Tetrafluoroethylene

The molecular weight of poly(tetrafluoroethylene), $-(CF_2CF_2)_x-$, commercially known as Teflon (registered trademark of Du Pont), is not really known because the polymer is essentially insoluble in any solvent and has an extremely high melt viscosity even though Teflon was invented more than 40 years ago. Tracer studies of oxidation–reduction polymerization using radioactive sulfur in bisulfite and persulfate initiator components have been used to determine end groups and molecular weights of some poly(tetrafluoroethylene) samples under a variety of conditions.[1] The results were based on a number of assumptions and yielded number-average molecular weights on specially prepared poly(tetrafluoroethylene) samples that were believed to have considerably lower molecular weights than those speculated for the commercial forms of Teflon. While in search of a solvent for Teflon, we have succeeded in characterizing a Teflon copolymer, an alternating copolymer of ethylene and tetrafluoroethylene (PETFE), $-(CF_2CF_2CH_2CH_2)_y-$. It represents one more step toward the eventual light scattering characterization of Teflon. In this Communication, we briefly report the development of necessary procedures required in using light scattering to characterize such a speciality polymer, leaving the details to two subsequent works on (i) the static and dynamic properties of and (ii) the molecular weight distribution of PETFE.

The essential steps in using laser light scattering as an absolute technique to characterize any homopolymer (including alternating copolymer) in solution can be summarized as follows: (1) prepare a dust-free polymer solution; (2) perform light scattering measurements; and (3) analyze data based on sound mathematical and physical principles. The three steps are not so easy to realize for speciality polymers because of the unique properties of the polymers. For example, the experimental difficulties encountered in the light scattering characterization of linear polyethylene[2] are quite different from those of poly(1,4-phenyleneterephthalamide)[3-5] (or PPTA), commercially known as Kevlar (Du Pont). In the case of polyethylene, we were concerned mainly with the preparation and clarification of polyethylene in 1,2,4-trichlorobenzene at high temperatures. For PPTA, the problems were much more complex[3] because PPTA fluoresces at $\lambda_0 = 488$ nm, has a reddish tint denoting absorption in the visible region, is a rodlike anisotropic polyelectrolyte that aggregates easily, and requires the addition of electrolytes to form a mixed solvent. Yet, we have been able to overcome all such experimental difficulties in order to characterize PPTA. The present experimental procedure is an extension of our light scattering studies of speciality polymers[2-5] and copolymers.[6]

1. Preparation and Clarification of PETFE in Diisobutyl Adipate.[7] PETFE has very few known solvents. In diisobutyl adipate, it was necessary to dissolve the polymer at elevated temperatures (~250 °C), near the solvent boiling point. Consequently, the polymer (PETFE) and the solvent (diisobutyl adipate) had to be placed in a closed system, and as a precautionary measure, under an inert atmosphere (N_2). The polymer solution was then filtered at 250 °C in the same closed apparatus without exposure to the atmosphere. It should be noted that as PETFE is not soluble in common solvents, we also had to develop a procedure to clean the entire dissolution and filtration apparatus after use. Otherwise, the instrument could be used only once. We have successfully developed such an apparatus for high-temperature polymer solution preparation and clarification.

2. Light Scattering Measurements. A normal commercial light scattering spectrometer is often capable of high-temperature work up to ~100 °C. In our polyethylene studies,[2] a high-temperature chamber was developed for temperature control of ±0.02 °C to ~150 °C. The refractive index matching of optical scattering cells by immersing them in oil, which also acts as the thermostat fluid, is no longer feasible at ~250 °C. Thus, a new light scattering spectrometer capable of light scattering measurements up to ~500 °C was developed. Light scattering measurements at fixed scattering angles and elevated temperatures (~240 °C) have been reported.[8] However, in the new light scattering instrument we have capabilities to measure the angular distribution of the absolute scattered intensity as well as its spectral distribution, to the same order of precision as state-of-the-art spectrometers at room temperatures. With these features, we could then be able to obtain a detailed characterization of the PETFE copolymer.

3. Time Correlation Function Data Analysis. In photon correlation spectroscopy, the measured intensity–time correlation function $G^{(2)}(K,\tau)$ is related to the normalized first-order electric-field correlation function $|g^{(1)}(K,\tau)|$ by the relation

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

where A is the base line and b is a spatial coherence factor depending upon experimental conditions and is usually taken as an unknown parameter in the data-fitting procedure. $K = (4\pi/\lambda) \sin(\theta/2)$, with λ and θ being the wavelength of light in the scattering medium and the scattering angle, respectively. τ is the delay time. For a monodisperse polymer in dilute solution and in the absence of internal motions, $|g^{(1)}(K,\tau)| = e^{-\Gamma(K)\tau}$, with $\Gamma = DK^2$ and D being the translational diffusion coefficient. For a polydisperse polymer in solution

$$g^{(1)}(K,\tau) = \int_0^\infty G(K,\Gamma) e^{-\Gamma(K)\tau}\, d\Gamma \qquad (2)$$

where $G(K,\tau)$ is the normalized characteristic line-width distribution function. The main objective to our time correlation function data analysis is to perform a Laplace inversion of eq 2 in order to obtain an approximate $G(K,\Gamma)$ without an a priori assumption on the form of $G(\Gamma)$, especially when we have no knowledge on the magnitude of polydispersity for our PETFE polymer whatsoever. As the inversion of eq 2 is an ill-conditioned problem because of unavoidable noise in the experimental data and the necessary bandwidth limitation of our instrumentation, we have used three separate algorithms to estimate $G(K,\Gamma)$.

(a) Multiexponential Singular Value Decomposition[9] (MSVD). The technique is a modification of the eigen-

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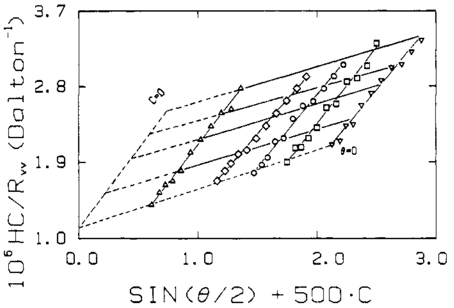

Figure 1. Zimm plot of PETFE in diisobutyl adipate at 240 °C. Hollow triangles denote 1.22×10^{-3} g/mL; hollow diamonds, 2.32×10^{-3} g/mL; hollow circles, 2.94×10^{-3} g/mL; hollow squares, 3.50×10^{-3} g/mL; and inverted hollow triangles, 4.25×10^{-3} g/mL. $M_w \simeq 9.0 \times 10^5$.

value approach developed by McWhirter and Pike.[10,11] It differs from our earlier histogram method,[12] which is nonlinear. MSVD has been tested by using simulated time correlation functions and experiments involving dilute solutions of polystyrene, poly(methyl methacrylate),[13] and polyethylene.[2]

(b) Method of Regularization Based on Tikhonov and Miller As Used by Abbiss et al.[14] The regularization technique considered the ill-posed problem carefully and was shown to yield results comparable to those from MSVD for unimodal distribution functions under realistic experimental conditions. In particular, we compared the two Laplace inversion approaches (a) and (b) in our studies of PPTA in concentrated sulfuric acid[5] and PMMA in methyl methacrylate.[15]

(c) CONTIN. This regularization algorithm was kindly provided by Provencher,[16] who introduced Fisher's statistic test for determining the optimum solution in the inversion procedure. CONTIN has the ability to resolve multimodal $G(\Gamma)$ under favorable conditions.

Laplace inversion of the time correlation function must be handled with a great deal of caution because of its ill-posed nature. We tried to accomplish this step (3) using three different tested schemes: the singular value decomposition technique with discrete multiexponentials to approximate $G(\Gamma)$, a method of regularization whereby a linearized smoothing operator was used, and CONTIN, which had been distributed widely by Provencher throughout the world. It was gratifying to confirm that the three schemes yielded comparable results for $G(\Gamma)$ in our data analysis, with the variance agreeing to within 10%.

For a PETFE polymer in diisobutyl adipate, we were able to dissolve the polymer, clarify the solution, and perform the dilution at 250 °C under nitrogen. Static and dynamic light scattering measurements as well as differential refractometry measurements were performed at 240 (±0.02) °C and λ_0 = 488 nm using an argon ion laser (Spectra Physics Model 2020-03) operating at ~100 mW. Figure 1 shows a Zimm plot whereby we determined the weight-average molecular weight $M_w = 9.0 \times 10^5$. By combining static and dynamic properties with the Laplace inversion of $|g^{(1)}(\tau)|$, we were able to determine, for the first time, an estimate of the molecular weight distribution (MWD) of an alternating copolymer of ethylene and tetrafluoroethylene, as shown in Figure 2. The molecular weight distribution was surprisingly narrow, as $G(\Gamma)$ yielded a variance $\mu_2/\bar{\Gamma}^2$ of only ~0.10, where $\bar{\Gamma} = \int \Gamma G(\Gamma)\, d\Gamma$ and $\mu_2 = \int (\Gamma - \bar{\Gamma})^2 G(\Gamma)\, d\Gamma$. In the transform from $G(\Gamma)$ to MWD, we determined the scaling relation between the translational diffusion coefficient and the molecular weight using polymers of different molecular weights, each individually characterized. A detailed characterization is under way.

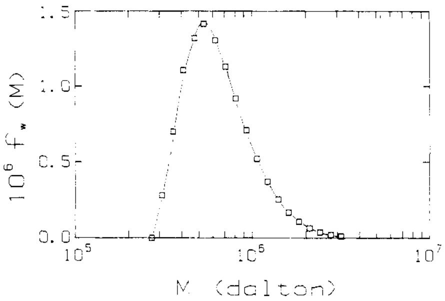

Figure 2. Molecular weight distribution $f(M)$ of a PETFE sample. $M_w = 9.0 \times 10^5$, $M_w/M_n \approx 1.35$.

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Registry No. PETFE, 25038-71-5.

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A Comment on the Stability of Orientational Order in Homopolymer Melts[1]

It is now widely known that rigidly rodlike chain molecules will spontaneously adopt a nematic order whenever sufficiently concentrated. Theory[2,3] indicates that attractive interchain forces are not necessary for support of

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