

- (18) Hassner, A.; Alexanian, V. *Tetrahedron Lett.* 1978, 4475.
- (19) Archer, W. I.; Armstrong, R. D. *The Application of A.C. Impedance Methods to Solid Electrolytes*, Electrochemistry Specialist Periodical Report; The Chemical Society: London, 1981.
- (20) Vogel, H. *Phys. Z.* 1921, 22, 645. Tamman, G.; Hesse, W. Z. *Anorg. Allg. Chem.* 1926, 156, 245. Fulcher, G. S. *J. Am. Ceram. Soc.* 1925, 8, 339.
- (21) Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J. Electrochem. Soc.* 1982, 129, 1694.
- (22) Ratner, M. In *Polymer Electrolyte Reviews-1*, MacCallum, J. R.; Vincent, C. A., Ed.; Elsevier Applied Science: London, 1987.
- (23) Allporte, D. C.; Janes, W. H. *Block Copolymers*, Appl. Sci. Publ. Ltd: Barking, 1973.
- (24) Kelly, I.; Owen, J. R.; Steele, B. C. H. *J. Electroanal. Chem.* 1984, 168, 467.
- (25) Kelly, I. E.; Owen, J. R.; Steele, B. C. H. *J. Power Sources* 1985, 14, 13.
- (26) Gray, F. M. In *Polymer Electrolyte Reviews-1*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science: London, 1987.

Light-Scattering Characterization of Poly(tetrafluoroethylene)

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ABSTRACT: Laser light scattering including angular dependence of absolute integrated scattered intensity and of the spectral distribution has been used successfully, for the first time, to characterize a tetrafluoroethylene polymer $[-(\text{CF}_2\text{CF}_2)_x]$, PTFE in oligomers of poly(chlorotrifluoroethylene) at 340 °C. In order to carry out the experiments at high temperatures, i.e., at 340 °C instead of 240 °C which was the temperature needed for the light scattering characterization of an alternating copolymer of ethylene and tetrafluoroethylene $-(\text{C}_2\text{F}_4\text{C}_2\text{H}_4)_y-$, we modified a high-temperature light-scattering spectrometer and developed a new all-glass dissolution/filtration apparatus, capable of dissolving, transferring, and clarifying the polymer solution at elevated temperatures under an inert gas without moving components except for the stopcock. For the PTFE polymer sample, we determined the weight-average molecular weight M_w [$= 2.8 \times 10^5 \pm 10\%$ g/mol], the z -average radius of gyration R_g [$= 18.0 \pm 10\%$ nm], the second virial coefficient A_2 [$= 6.5 \times 10^{-5} \pm 20\%$ mol $\text{cm}^3 \text{g}^{-2}$], the z -average translational diffusion coefficient at infinite dilution D_0 [$= 3.26 \times 10^{-7} \pm 2\%$ cm^2/s], and the variance μ_2/\bar{T}^2 [$= 0.2 \pm 10\%$]. Precise measurements of the intensity-intensity time correlation function permit us to make a Laplace inversion using a variety of techniques including a multiexponential singular value decomposition (MSVD), regularized inversion of Laplace integral equation (RILIE), and the CONTIN algorithm developed by Provencher. We were able to obtain an estimate of the normalized characteristic line-width distribution which could be reduced to a distribution of translation diffusion coefficient at infinite dilution, independent of the method used in the Laplace inversion. By assuming a scaling exponent of ~ 0.5 between D_0° and M_w , i.e., $D_0^\circ \sim M_w^{-0.5}$, we could estimate the molecular weight distribution (MWD) of the PTFE polymer with $M_z/M_n: M_w/M_n \sim 2.9:1.9$.

1. Introduction

Laser light scattering (LLS) has been used successfully to characterize a range of relatively intractable polymers, such as polyethylene (denoted as PE) in 1,2,4-trichlorobenzene,^{1,2} poly(ethylene terephthalate) (denoted as PET) in hexafluoro-2-propanol,³ poly(1,4-phenylene terephthalamide) (denoted as PPTA) in concentrated sulfuric acid,⁴⁻⁸ and an alternating copolymer of ethylene and tetrafluoroethylene (denoted as PETFE) in diisobutyl adipate.⁹⁻¹¹ An absolute determination of the molecular weight of polytetrafluoroethylene (denoted as PTFE), $-(\text{CF}_2\text{CF}_2)_x-$, commercially known as "Teflon" TFE fluorocarbon resin (a registered trademark of Du Pont) by means of laser light scattering represents another advance in the development of LLS as an analytical technique for polymer characterizations.¹² In this paper, we present details of our light scattering studies on PTFE solution

properties above the melting point of PTFE (~ 330 °C). Although "Teflon" was invented more than 40 years ago, an absolute determination of the molecular weight represents an interesting challenge by any analytical techniques. To date, no solvents that are suitable for Teflon have been found. Thus, in our approach to create a Teflon solution, we used oligomers of Teflon-like polymers, e.g., oligomers of poly(chlorotrifluoroethylene), with the following criteria: (a) a boiling point sufficiently high so that the oligomer melt forms a liquid at temperatures greater than 330 °C, (b) a refractive index sufficiently different from that of the Teflon polymer so that a reasonable refractive index increment exists, and (c) the oligomer molecular weights sufficiently low so that the characteristic decay times are distinctly different from those of Teflon. The same approach could be applicable to other difficult to dissolve polymers.

Oligomers of poly(chlorotrifluoroethylene) appear to be poor solvents for Teflon. We were able to study only a low molecular weight Teflon polymer in detail. As a delicate balance exists among the three criteria above, higher molecular weight Teflon polymers can be expected to dissolve in higher molecular weight fractions of polyperfluorocarbons. Nevertheless, the present study demonstrates our new approach to light-scattering characteriza-

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tions of such intractable polymers. It should also be noted that we are aware of the effects associated with the presence of multicomponent solvents.¹³ However, as the refractive index difference among oligomers within a narrow boiling-point range must necessarily be fairly small, corrections for preferential interactions between different solvent components and the polymer are relatively small. Furthermore, the oligomers are chemically similar, which could provide another reason to consider such a "solvent" as a pseudo one-component fluid in light-scattering studies. We shall show the validity of this approximation by using two different boiling-point fractions of the oligomer as solvents. Our approach to Teflon solution characterization is also influenced by the high melting point (T_m) exhibited by Teflon. With $T_m \sim 330^\circ\text{C}$, our instrumentation must have capabilities of high-temperature ($\sim 350^\circ\text{C}$) operation, not only for the light-scattering spectrometer but also for all aspects of solution preparation, transfer, and clarification. The success of our study depends essentially on experimental developments in being able to achieve high-temperature operations at all levels. In this paper we shall be concerned with the refinements for high-temperature operations and show that our results are independent of the multicomponent nature of the oligomers used as well as the methods of data analysis.

2. Experimental Methods

2.1. Preparation of Solvent. The solvent used in this work was a mixture of oligomers of chlorotrifluoroethylene made by Hooker Industrial & Specialty Chemicals Division of Occidental Chemical Corp. The specific grade used was "Fluorolube" LG-160. Prior to use the "Fluorolube" was distilled at a pressure of 0.01 mmHg. The fraction boiling between 169 and 179 $^\circ\text{C}$ (56% of the mixture) was used for the majority of the light-scattering work. This fraction had an atmospheric pressure boiling temperature of about 345 $^\circ\text{C}$. Vapor-phase chromatography of this material (6 ft \times 1.4 in. column, 20% OV-210 on "Chromosorb" PAW/DMCS, 150–240 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$, then isothermal at 240 $^\circ\text{C}$, thermal conductivity detector) showed 85 area % to be present as three triplet peaks with retention times centered at 6.3, 9.6, and 13.9 min.

In order to assess thermal stability of the "Fluorolube" solvent, a sample of the distilled solvent was sealed under vacuum in a heavy-walled glass tube and then placed in a circulating air oven at 340 $^\circ\text{C}$ for 24 h. After this heat treatment, the solvent had changed from water clear to yellow. Vapor-phase chromatography of this material showed a complex mixture with a large increase in the amount of low elution time components. Mass spectroscopic analysis of several of the peaks showed them to be chlorofluorocarbon residues from solvent degradation. Thus, the solvent degrades slowly at this temperature, possibly due to end-group instability.

2.2. Preparation of Solutions. Two distilled fractions of Fluorolube with boiling points ~ 350 and $>350^\circ\text{C}$ and indices of refraction 1.320 and 1.325 at 488 nm and 340 $^\circ\text{C}$, respectively, were used as solvents for a sample of the Teflon polymer. Solutions at different concentrations were prepared individually by dissolving known amounts of Teflon in the fractionally distilled oligomer solvents at $340 \pm 2^\circ\text{C}$. Particular care should be taken to consider polymer dissolution at only a few degrees centigrade below the solvent boiling point. Over periods of hours at elevated temperatures, the oligomers may degrade or decompose to form lower boiling-point fluids resulting in a pressure increase which could cause a mild explosion destroying the dissolution/filtration apparatus originally designed for PETFE characterization.¹⁰ Thus, we modified the dissolution/filtration apparatus¹² as shown schematically in Figure 1. The dissolution/filtration procedure has been described elsewhere.¹² In the figure caption we have also outlined some of the details associated with the functions of various components in the dissolution/filtration apparatus. The important point is to be able to dissolve a polymer and to filter the polymer solution under an inert atmosphere at elevated temperatures without moving components as all glass stopcocks

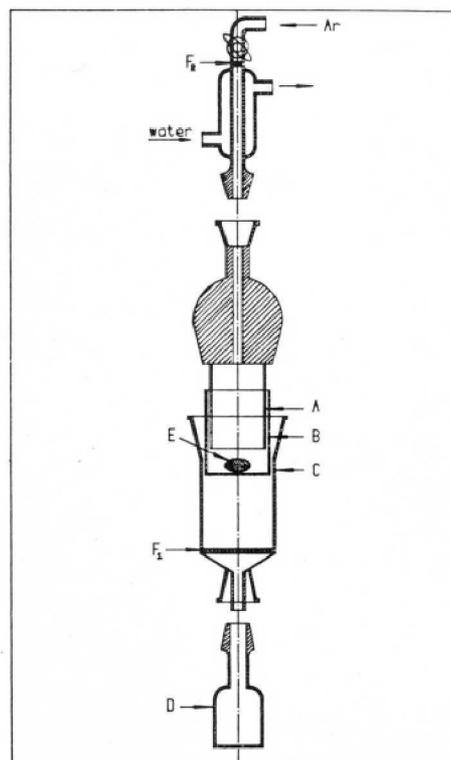


Figure 1. Separate components of a high-temperature dissolution/filtration apparatus. The assembled apparatus, as shown in Figure 1 of ref 12 (with the exception of the water-cooled condenser at the top), can be placed in a high-temperature oven controlled at $340 \pm 2^\circ\text{C}$: A, cylindrical insert (without bottom) with a diameter ~ 2 mm less than that of the solution vessel B; C, filtration section with fine-grade sintered-glass filter (F_1) and ground-glass joints to light-scattering cell (D) and ground-glass joint adapter for the water-cooled condenser which is located outside of the temperature-controlled oven; E, magnetic stirring bar. Shaded areas denote volume reduction so that the volume accessible by vapor phase is no more than a few times the fluid phase. The miniature water-cooled condenser has a coarse-grade sintered-glass filter (F_2) so that the entire system is always isolated from external dusty environment. The greaseless stopcock above F_2 is for operating the apparatus as a closed system, for introduction of low vacuum in order to degas the solvent before dissolution, for filling the apparatus with inert gas, such as argon, in order to alleviate chemical decomposition, and for releasing possible pressure buildup if chemical decomposition does take place. The entire apparatus is portable and can be inserted into the high-temperature light-scattering spectrometer with the light-scattering cell (D) and part of the filtration component (C) controlled at 340 $^\circ\text{C}$. On occasion, a ground-glass joint stopper with a pressure relief stopcock is used to replace A and B.

or joints tend to lock themselves at very high temperatures. We must also provide a pressure release mechanism but without permitting the low vapor pressure oligomers to escape. Thus, the miniature water-cooled condenser was introduced. The all glass dissolution filtration apparatus can be cleaned by pyrolysis so that it can be used repeatedly without degradation of performance.

2.3. Methods of Measurements. The high-temperature light-scattering spectrometer originally constructed for the PETFE characterization⁹⁻¹¹ was further modified. Figure 2 shows schematic top and side views on the essential features of the modified high-temperature, multiple-detector light-scattering spectrometer. The glass vacuum jacket was replaced by a stainless-steel shield to thermally isolate and decouple, at least partially, the temperature environment of the inner light-scattering chamber (5) from the outside chamber (3). This modification was made to accommodate light-scattering cells which can be accessed externally, e.g., for pressure release. At 340 $^\circ\text{C}$, temperature gradient becomes a more critical factor. The platinum resistance thermometer (16 in Figure 2) is located very close to the polymer solution. Figure 3 shows a typical tracing of the temperatures

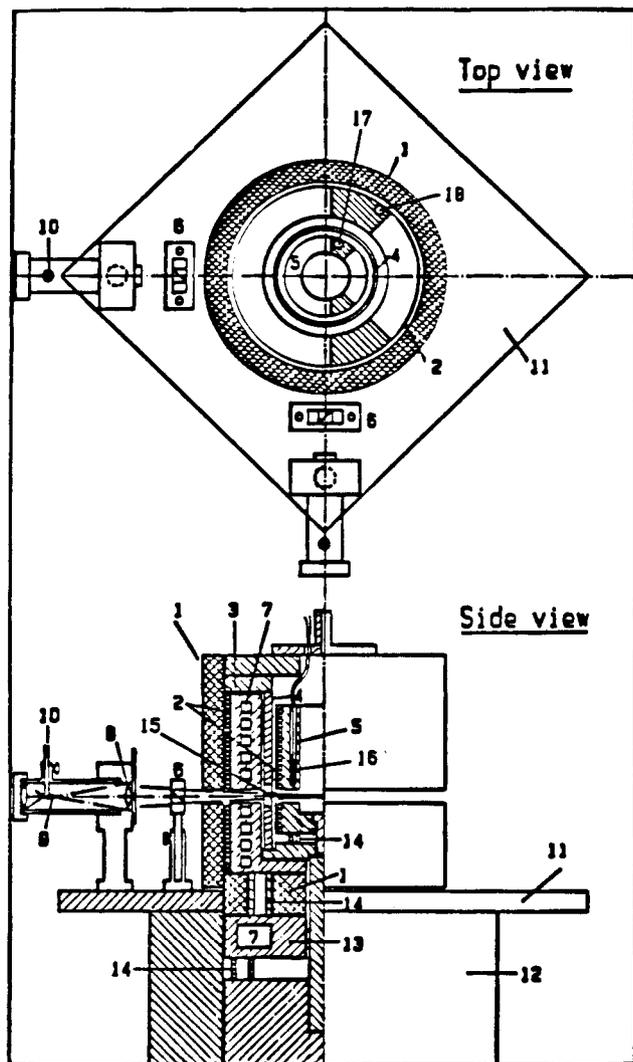


Figure 2. Schematic top and side view of the high-temperature multiple detector light-scattering spectrometer. Numbers 1–3 and 5–14 have the same notation as Figure 2 of ref 10. The modifications are as follows: 4, Stainless-steel temperature shield (instead of a glass jacket made of precision polished glass of 2.25 in o.d.) with precision polished glass windows of 2.25 in o.d. (15) for light beams entering and exiting the light scattering cell located in the inner brass thermostat (5); 16, location of platinum resistance thermometer; 17, location of temperature sensor for temperature control of the inner thermostat (5); 18, Location of temperature sensor for temperature control of the outer brass thermostat (3).

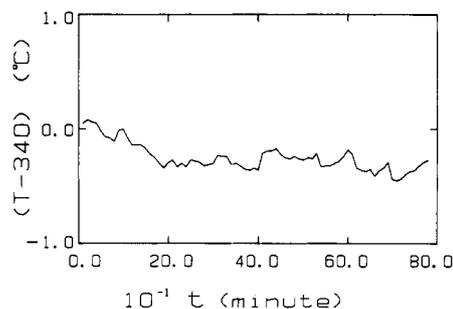


Figure 3. Typical temperature fluctuations of the inner thermostat (5 in Figure 2) at 340 °C. Intermediate-term (1 h) temperature fluctuations were ± 0.1 °C. Long-term (10 h) temperature fluctuations were ± 0.5 °C.

monitored by the platinum resistance thermometer (16 in Figure 2) located near the light-scattering cell in the inner thermostat (5 in Figure 2). Intermediate term (1 h) control of ± 0.1 °C and long term (10 h) control of ± 0.5 °C could be achieved at 340 °C.

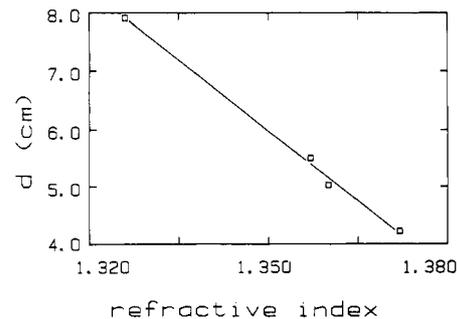


Figure 4. Calibration of a distorted light-scattering cell for refractive index determinations using organic solvents of known refractive index at $\lambda_0 = 488$ nm and 25 °C. d denotes the laser beam displacement as measured by a micrometer. $(\partial d/\partial n)_T = -80.12$ cm with a resolution of ± 0.001 mm.

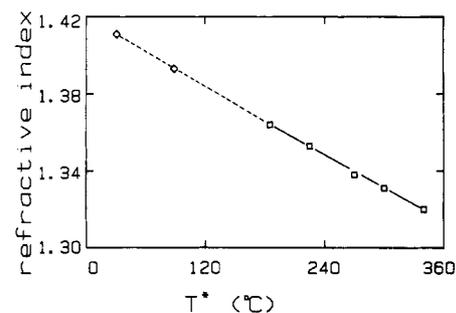


Figure 5. Refractive index (n_0) of the lower boiling fraction (bp ~ 350 °C) oligomers of poly(chlorotrifluoroethylene) as a function of temperature at $\lambda_0 = 488$ nm. $n_0 = 1.364 - 2.86 \times 10^{-4} (T^* - 185)$ with T^* expressed in °C and the expression valid over a temperature range from 185 to 340 °C. At 340 °C and $\lambda_0 = 488$ nm, $n_0 = 1.320$. The absolute refractive index of the oligomers was also measured by using a standard refractometer as shown by the two diamond symbols at lower temperatures.

Long-term temperature control depends partially on room-temperature fluctuations even in the presence of an outer thermostat (3 in Figure 2) and stainless-steel shielding (4 in Figure 2) between the two thermostats (3 and 5 in Figure 2). All preparations and measurements were usually completed within a 6–8-h period. During the course of solution preparation and measurements we would release any pressure developed by opening the stopcock on top of the water-cooled condenser in the dissolution/filtration apparatus.

Intensity and line-width measurements were performed in a similar manner as described elsewhere.¹⁰

3. Results and Discussion

3.1. Refractive Index and Refractive Index Increment. We again used a deformed cylindrical light-scattering cell so that the solution/glass/air interface was not perpendicular to the incident laser beam at the exit side of the light-scattering sample chamber. Refraction could be measured and calibrated by using organic solvents of known refractive index, as shown in Figure 4. Figure 5 shows a plot of refractive index of the lower boiling fraction (bp ~ 350 °C) oligomers of poly(chlorotrifluoroethylene) as a function of temperature. We obtained $n_0 = 1.364 - 2.86 \times 10^{-4} (T^* - 185)$ with T^* expressed in °C. At 340 °C and $\lambda_0 = 488$ nm, the two boiling fractions have $n_0 = 1.320$ and 1.325, respectively. Figure 6 shows a plot of displacement, d , as a function of PTFE polymer concentration. We obtained $(\partial n/\partial C)_T = (\partial d/\partial C)_T/(\partial d/\partial n)_T = -4.25$ cm g^{-1} mL/ -80.12 cm = 0.053 mL g^{-1} at 340 °C and $\lambda_0 = 488$ nm for the lower boiling fraction oligomers and $(\partial n/\partial C)_T = 0.047$ mL g^{-1} for the high boiling fraction oligomers ($n_0 = 1.325$).

3.2. Light-Scattering Intensity Measurements. The excess absolute integrated scattered intensity of light

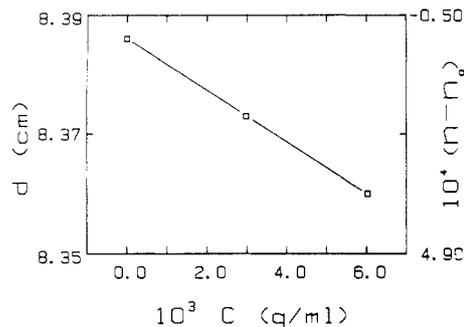


Figure 6. Plot of displacement d as a function of PTFE polymer concentration in oligomers of poly(chlorotrifluoroethylene). $(\partial d/\partial C)_T = -4.25 \text{ cm mL g}^{-1}$ and $(\partial n/\partial C)_T = 0.053 \text{ mL g}^{-1}$ at 340°C and $\lambda_0 = 488 \text{ nm}$. n and n_0 are refractive index of polymer solution and that of solvent, respectively.

scattered by a dilute polymer solution at concentration C (g/cm^3) and scattering angle θ has the approximate form:

$$\frac{HC}{R_{\text{vv}}(K)} \cong M_w^{-1}(1 + K^2 R_g^2/3) + 2A_2 C \quad (1)$$

where H (in units of $\text{mol cm}^2 \text{g}^{-2}$) is equal to $4\pi^2 n_0^2 (\partial n/\partial C)_T^2 / (N_A \lambda_0^4)$ with N_A , λ_0 , and $(\partial n/\partial C)_T$ being, respectively, Avogadro's number, the wavelength of light in vacuo, and the refractive index increment. R is the excess Rayleigh ratio, and the subscript vv denotes vertically polarized incident and scattered light. A_2 (in units of $\text{mol cm}^3 \text{g}^{-2}$) is the second virial coefficient, and $K = (4\pi n/\lambda_0) \sin(\theta/2)$. From a Zimm plot, we can determine the weight-average molecular weight M_w , A_2 , and the root-mean-square z -average radius of gyration R_g . Figure 7 shows Zimm plots of a Teflon polymer in two different boiling fractions of poly(chlorotrifluoroethylene) oligomers. We recognize that oligomers within a narrow boiling point range still represent a multicomponent fluid. However, in light-scattering studies, some of the essential characteristics can be approximated as those of a single component. For example, the effect due to preferential absorption among oligomers should be weak. As refractive indices of oligomers are similar, the preferential absorption effect becomes less important in the molecular weight determination by light-scattering intensity measurements. We also made dynamic light-scattering measurements and could measure time correlation function in the delay time range of interest to Teflon characterization. Parts a and b of Figure 7 yield $M_w \approx 2.84 \times 10^5$ and $2.78 \times 10^5 \text{ g/mol}$, $A_2 \approx -6.7 \times 10^{-5}$ and $-6.2 \times 10^{-5} \text{ mol cm}^3 \text{g}^{-2}$, and $R_g \approx 17.8$ and 18.3 nm for the two oligomer fractions. From the two independent determinations, we could get $M_w \approx 2.8 \times 10^5 \text{ g/mol}$, $A_2 \approx -6.5 \times 10^{-5} \text{ mol cm}^3 \text{g}^{-2}$, and $R_g \approx 18.0 \text{ nm}$. Estimated errors are about 10% for M_w and R_g values and 20% for A_2 . The agreement appears to be better than expected. If we took the results from Figure 7b and used the refractive index (1.320 instead of 1.325) and refractive index increment (0.047 instead of 0.053 mL g^{-1}) values for the lower boiling point fraction oligomer as in Figure 7a to compute the molecular weight, $M_w \approx 2.2 \times 10^5 \text{ g/mol}$, which would be incorrect and thus confirm the self-consistency of our molecular weight determination. For the higher boiling point fraction oligomer, the lower $A_2 \approx -6.2 \times 10^{-5} \text{ mol cm}^3 \text{g}^{-2}$ value might be in the right direction as higher molecular weight fractions of the oligomer of poly(chlorotrifluoroethylene) could be slightly better solvents for Teflon. We tried to dissolve another Teflon sample estimated to have a much higher molecular weight. The polymer solution appeared to have some insoluble suspensions. Higher boiling-point fractions ($>350^\circ\text{C}$) of

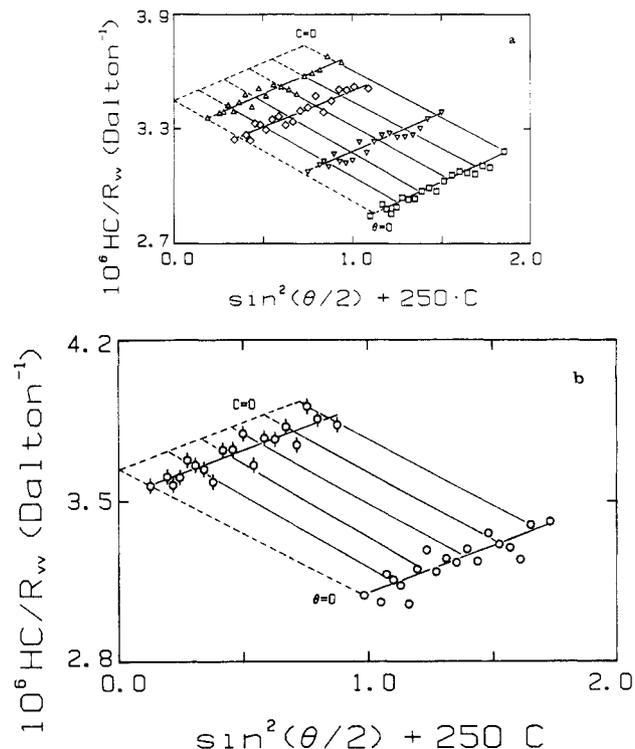


Figure 7. (a) Zimm plot of Teflon in oligomer with $n_0 = 1.320$ and $(\partial n/\partial C)_T = 5.3 \times 10^{-2} \text{ mL g}^{-1}$. The results have been published in ref 12. The plot is reproduced here for comparison with Figure 7b. (b) Zimm plot of Teflon in oligomer with $n_0 = 1.325$ and $(\partial n/\partial C)_T = 4.7 \times 10^{-2} \text{ mL g}^{-1}$; ϕ , $C = 5.17 \times 10^{-4} \text{ g/mL}$; \circ , $C = 3.93 \times 10^{-3} \text{ g/mL}$; $M_w \approx 2.78 \times 10^5 \text{ g/mol}$; $A_2 \approx -6.2 \times 10^{-5} \text{ mol cm}^3 \text{g}^{-2}$; $R_g \approx 18.3 \text{ nm}$.

oligomers need to be prepared, and further studies on the chemical decomposition of oligomers at high temperatures ($>350^\circ\text{C}$) should be performed before we could obtain the constants k_D and α_D in the scaling relation $\bar{D}_0^0 = k_D M_w^{-\alpha_D}$ where \bar{D}_0^0 is the z -average translational diffusion coefficient extrapolated to infinite dilution.

3.3. Light-Scattering Line-Width Measurements. The measured intensity-intensity time correlation function $G^{(2)}(K, \tau)$ in the self-beating mode has the form:

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

where A is the background and b is a parameter depending on the detection optics. In our correlation function measurements, we do not use A as an adjustable parameter and insist on having A and $\lim_{\tau \rightarrow \infty} G^{(2)}(K, \tau)$ agree to within 0.1%. For polydisperse polymers, the measured first-order electric field correlation function $b|g^{(1)}(K, \tau)|$ is related to the normalized characteristic line-width distribution $G(\Gamma)$:

$$g^{(1)}(K, \tau) = \int_0^\infty G(\Gamma) e^{-\Gamma(K)\tau} d\Gamma \quad (3)$$

We shall continue to use four different established methods of correlation function profile analysis: (i) Cumulants expansion¹⁴

$$\ln |g^{(1)}(K, \tau)| = -\bar{\Gamma}(K)\tau + \frac{1}{2}\mu_2(K)\tau^2 + \dots \quad (4)$$

where $\bar{\Gamma} = \int_0^\infty \Gamma G(\Gamma) d\Gamma$ and $\mu_2 = \int_0^\infty (\Gamma - \bar{\Gamma})^2 G(\Gamma) d\Gamma$ with $\text{VAR} = \mu_2/\bar{\Gamma}^2$. The cumulants method is applicable for $G(\Gamma)$ distributions which are not too broad ($\mu_2/\bar{\Gamma}^2 < 0.4$).

(ii) Multiexponential singular value decomposition (MSVD)^{8,15,16}

$$G(\Gamma) \approx \sum_j P_j \delta(\Gamma - \Gamma_j) \quad (5)$$

such that $g^{(1)}(\tau_i) = \sum_j P_j \exp(-\Gamma_j \tau_i)$ with P_j being the in-

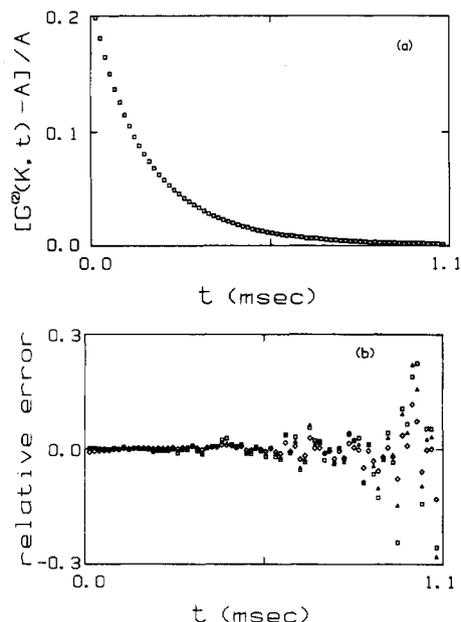


Figure 8. (a) Plot of $b[g^{(1)}(K,t)]^2$ versus t for PTFE in oligomers of poly(chlorotrifluoroethylene) at $C = 7.51 \times 10^{-4}$ g/mL, $\theta = 30^\circ$, and 340° C (same as Figure 3 of ref 12). (b) Relative errors in fitting the measured net intensity-intensity time correlation function of Figure 8a: squares, CONTIN; diamonds, RILIE; triangles, MSVD.

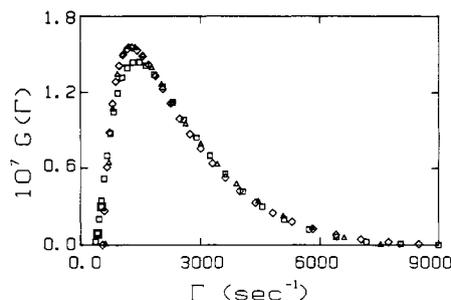


Figure 9. Plots of $G(\Gamma)$ versus Γ for 7.5×10^{-4} g/mL PTFE ($M_w = 2.8 \times 10^5$ g/mol) in oligomers of poly(chlorotrifluoroethylene) at 340° C using three different methods of Laplace inversion: squares, CONTIN; diamonds, RILIE; triangles, MSVD.

tensity weighting factor of the j th representative fraction. The MSVD technique can be used to fit $G^{(2)}(\tau)$ exhibiting fairly broad unimodal characteristic line-width distributions. With $\mu_2/\bar{\Gamma}^2 \gtrsim 0.5$, the cumulants method becomes difficult to use.

(iii) Regularized inversion of Laplace integral equation (RILIE).¹⁶ A modified version of the method developed by Abbiss et al. was used and is described in detail elsewhere.¹⁶ RILIE, like MSVD, is applicable for unimodal $G(\Gamma)$ but has a slightly faster algorithm.

(iv) CONTIN:^{18,19} kindly furnished by S. W. Provencher. In the Communication,¹² we determined $\text{VAR} \sim 0.21$ by using a third-order cumulant fit for a typical time correlation function measured at $\theta = 30^\circ$ and $C = 7.51 \times 10^{-4}$ g/mL as shown in Figure 8a. The same correlation function is now analyzed by using methods (ii), (iii), and (iv) with $G(\Gamma)$ vs Γ shown in Figure 9 and relative errors of the three fits shown in Figure 8b. The inversion results clearly show that estimates of $G(\Gamma)$ using different methods of Laplace inversion agree for the Teflon solution. The same procedure has been tested by a variety of approaches, such as use of simulated data and polymers of known polydispersity. Thus, we are quite confident in our present estimate for $G(\Gamma)$, especially when $\mu_2/\bar{\Gamma}^2 \sim 0.2$. Figures 10 and 11 show the K and concentration dependence of

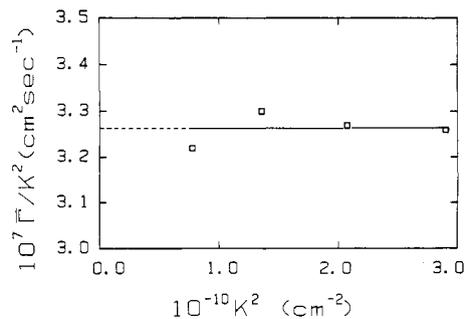


Figure 10. Plot of $\bar{\Gamma}/K^2$ versus K^2 for PTFE in oligomers of poly(chlorotrifluoroethylene) at 340° C and $C = 7.51 \times 10^{-4}$ g/mL. $\bar{\Gamma}/K^2$ is essentially independent of K .

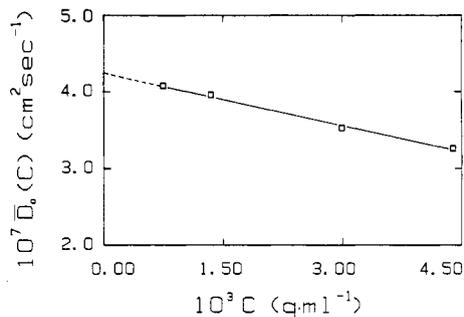


Figure 11. Plot of \bar{D}_0 versus C . $\bar{D}_0 = \lim_{K \rightarrow 0} \bar{\Gamma}/K^2$; $\bar{D}_0^0 = \lim_{C \rightarrow 0} \bar{D}_0$. $\bar{D}_0 = \bar{D}_0^0 (1 + k_d C)$ with $\bar{D}_0^0 = 4.26 \times 10^{-7}$ cm²/s and $k_d = -53.4$ mL/g for Teflon ($M_w = 2.8 \times 10^5$ g/mol) in oligomers of poly(chlorotrifluoroethylene) at 340° C.

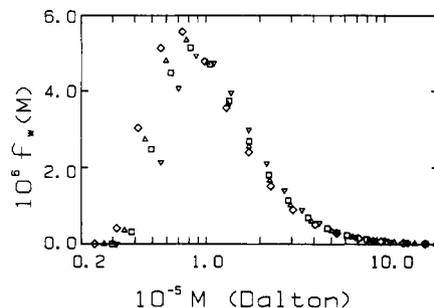


Figure 12. Molecular weight distribution of PTFE from $G(\Gamma)$, $M_w \sim 2.8 \times 10^5$ g/mol, and assumed α_D values of 0.5, 0.45, 0.425, and 0.40 symbol, equation, $M_z/M_n:M_w/M_n$: inverted triangles, $\bar{D}_0^0 = 2.34 \times 10^{-4} M^{-0.50}$, 2.88:1.84; squares, $\bar{D}_0^0 = 1.29 \times 10^{-4} M^{-0.45}$, 3.70:2.05; triangles, $\bar{D}_0^0 = 9.53 \times 10^{-5} M^{-0.425}$, 4.32:2.17; diamonds, $\bar{D}_0^0 = 7.05 \times 10^{-5} M^{-0.40}$, 5.18:2.32.

$\bar{\Gamma}/K^2$. By extrapolating $\bar{\Gamma}/K^2$ to zero K , we obtain the z -average translational diffusion coefficient \bar{D}_0 ($\equiv \lim_{K \rightarrow 0} \bar{\Gamma}/K^2$). As the Teflon polymer sample has a relatively low molecular weight with $M_w \approx 2.8 \times 10^5$ g/mol, it is not surprising to find $\bar{\Gamma}/K^2$ to be essentially independent of K , as shown in Figure 10. In Figure 11, we obtained

$$\bar{D}_0 = \bar{D}_0^0 (1 + k_d C) \quad (6)$$

with \bar{D}_0^0 ($= \lim_{K \rightarrow 0, C \rightarrow 0} \bar{\Gamma}/K^2$) = 4.26×10^{-7} cm²/s and the diffusion second virial coefficient $k_d = -53.4$ mL/g. With only one Teflon polymer characterized at this time, we could not determine the scaling relation $\bar{D}_0^0 = k_D M_w^{-\alpha_d}$. Nevertheless, as A_2 is slightly negative, we can make molecular weight distribution (MWD) estimates by assuming $\sigma_D < 0.5$. Figure 12 shows MWD estimates using $M_w = 2.8 \times 10^5$ g/mol and α_D values of 0.5, 0.45, 0.425, and 0.40. If we take $\alpha_D \sim 0.45$, $M_w/M_n \sim 2$ which could be considered a reasonable estimate under the present restriction.

Figure 13 shows a log-log plot of R_z versus M_w for different polymer solutions. As A_2 for PTFE is negative, the

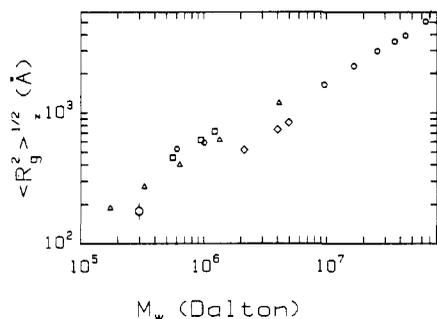


Figure 13. log-log plot of $\langle R_g^2 \rangle^{1/2}$ versus M_w for different polymer solutions (same as Figure 9 of ref 10): Δ and \circ , polystyrene in benzene; \diamond , polymethyl methacrylate in methyl methacrylate; \circ , polyethylene in 1,2,4-trichlorobenzene; \square , PETFE in diisobutyl adipate; \odot , PTFE in oligomers of poly(chlorotrifluoroethylene).

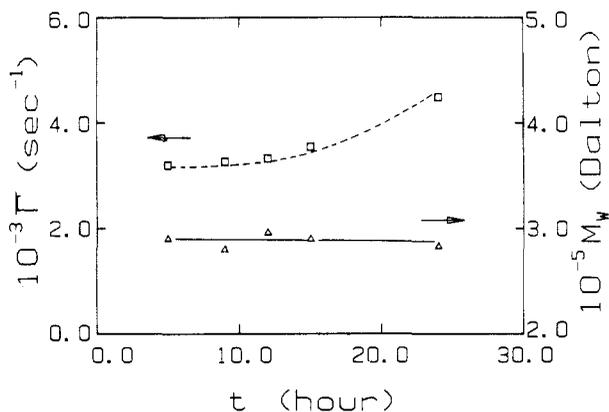


Figure 14. Stability of PTFE solution at 340 °C in terms of M_w and Γ : triangles, M_w ; squares, Γ at $\theta = 30^\circ$.

Teflon coil appears to be substantially contracted, in agreement with our present perception that PTFE coils are similar to those of polyethylene (PE) or PETFE. There could be subtle differences on the configuration of such polymer coils (PE, PETFE, PTFE) because of size differences between H and F. However, once in their respective solvents at whichever temperatures, the statistical configurations are essentially the same. Finally, we also made a time study on the stability of Teflon solution at 340 °C, as shown in Figure 14. M_w remains

constant for over a 24-h period while $\bar{\Gamma}$ ($\theta = 30^\circ$) appears to change after ~ 10 h. All our measurements were performed immediately after solution preparation within an 8-h period.

In summary, we have developed laser light scattering as a noninvasive analytical technique, especially suitable for intractable polymers such as PPTA (or "Kevlar", a registered trademark of Du Pont), PETFE (or "Tefzel", a registered trademark of Du Pont), and Teflon. With information on M_w and MWD as well as R_g and second virial coefficients, further improvements on polymerization and processing could be considered.

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Registry No. PTFE, 9002-84-0.

References and Notes

- (1) Chu, B.; Onclin, M.; Ford, J. R. *J. Phys. Chem.* **1984**, *88*, 6566.
- (2) Pope, J. W.; Chu, B. *Macromolecules* **1984**, *17*, 2633.
- (3) Naoki, M.; Park, I.-H.; Chu, B. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 2567.
- (4) Chu, B.; Ying, Q.-C.; Wu, C.; Ford, J. R.; Dhadwal, H.; Qian, R.; Bao, J.; Zhang, J.; Xu, C. *Polym. Commun.* **1984**, *25*, 211.
- (5) Ying, Q.-C.; Chu, B. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 785.
- (6) Chu, B.; Wu, C.; Ford, J. R. *J. Colloid Interface Sci.* **1985**, *105*, 473.
- (7) Ying, Q.-C.; Chu, B.; Qian, R.; Bao, J.; Zhang, J.; Xu, C. *Polymer* **1985**, *26*, 1401.
- (8) Chu, B.; Ying, Q.-C.; Wu, C.; Ford, J. R.; Dhadwal, H. S. *Polymer* **1985**, *26*, 1408.
- (9) Chu, B.; Wu, C. *Macromolecules* **1986**, *19*, 1285.
- (10) Chu, B.; Wu, C. *Macromolecules* **1987**, *20*, 93.
- (11) Wu, C.; Buck, W.; Chu, B. *Macromolecules* **1987**, *20*, 98.
- (12) Chu, B.; Wu, C.; Zuo, J. *Macromolecules* **1987**, *20*, 700.
- (13) Chu, B.; Lee, D.-C. *Macromolecules* **1986**, *19*, 1592.
- (14) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
- (15) Ford, J. R.; Chu, B. In *Proceedings of the 5th International Conference on Photon Correlation Techniques in Fluid Mechanics*; Schulz-DuBois, E. O., Ed.; Springer-Verlag: New York, 1983; pp 303-314.
- (16) Chu, B.; Ford, J. R.; Dhadwal, H. S. *Methods Enzymology*; Colowick, S. P., Kaplan, N. O., Eds.; Academic: Orlando, FL, 1985; pp 256-297.
- (17) Abbiss, J. B.; Demol, C.; Dhadwal, H. S. *Opt. Acta* **1983**, *30*, 107.
- (18) Provencher, S. W. *Biophys. J.* **1976**, *16*, 27; *J. Chem. Phys.* **1976**, *64*, 2772; *Makromol. Chem.* **1979**, *180*, 201.
- (19) Version 2, March 1984. Courtesy of S. W. Provencher.

Light Scattering Study of Ionomers in Solution. 2. Low-Angle Scattering from Sulfonated Polystyrene Ionomers

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ABSTRACT: Low-angle light scattering studies were conducted for partially sulfonated polystyrene ionomers in a polar and a low-polarity solvent. In the low-polarity solvent tetrahydrofuran (THF), aggregation of ionomers due to the attraction of ion pairs was seen in changes of molecular weight and interaction parameter (second virial coefficient) with ion content. At high ion content, negative interaction parameters were observed. In the polar solvent dimethylformamide (DMF), typical polyelectrolyte behavior was observed in light scattering data. Effective diameters of macroions (ionomers) were used to discuss the effect of counterion and ion content on the structural change of ionomers.

Introduction

Ionomers are a class of ion-containing polymers, which have ionic groups in concentration up to 10-15 mol %, distributed in nonionic backbone chains.¹⁻³ Since the development of Surlin resin by Du Pont in 1966,⁴ ionomers

have caught the attention of people in both industry and academia. This is based on the fact that the incorporation of ions into solid polymers frequently leads to profound changes in properties, such as glass transition temperature and melt viscosity. Consequently, much work has been