monomer formation[3-5] could arise instead from secondary reactions of the initial products, reactions minimized under our conditions. Future experiments include collisionally activated dissociation[24] of the fragment ions to characterize them further, and testing the mechanism with poly(perdeuterio-1-butene sulfone) and other poly(olefin sulfones).

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Light-Scattering Characterization of Poly(tetrafluoroethylene)

We have, for the first time, succeeded in determining the weight-average molecular weight M_w of a poly(tetrafluoroethylene) (PTFE) polymer, $-(CF_2CF_2)_x-$, commercially known as Teflon (a registered trademark of Du Pont), which was invented more than 40 years ago. Furthermore, we have succeeded in determining the z-average root-mean-square radius of gyration (R_g) and the second virial coefficient (A_2) for the PTFE polymer in a high-boiling-point solvent, made up mainly of poly(fluoroethylene/chloroethylene) oligomers, by means of light-scattering intensity measurements and in estimating the molecular weight distribution (MWD) by means of a time correlation function cumulants analysis. In this Communication, we briefly report our development of the light-scattering characterization of Teflon, leaving the details to a subsequent article that will be coauthored with W. Buck at Du Pont.

One of the ultimate challenges in determining the fundamental macromolecular parameters of polymers in solution is to be able to characterize Teflon, an important specialty polymer that has essentially defied an absolute determination of molecular weight over all these years. Radioactive tracers have been used to determine end groups and number-average molecular weights of several specially prepared PTFE polymers.[1] An obvious answer to this challenge is to find a solvent for Teflon, although it is not a trivial extension of any physical technique even if a solvent for Teflon does become available. In our search for a solvent for Teflon, we prefer to investigate the PTFE solution properties above the melting point of PTFE ($\sim$330 °C). Thus, we need a solvent that boils above 330 °C and high-temperature instrumentation.

From recent investigations on polymer probe dynamics[2] using a quaternary system consisting of a semidilute isorefractive polystyrene (PS) in a mixed solvent of α-chloronaphthalene and toluene with dilute poly(methylmethacrylate) (PMMA) as the optical probe, we found that we could characterize the PMMA polymer even in multicomponent solvents with complex structures.[2-4] Oligomers of PTFE could be a solvent for PTFE like alkanes could be solvents for polyethylene at high temperatures. Additional requirements for the PTFE solvent are that we need oligomers of sufficiently high molecular weight in order to achieve the high boiling point and with reasonable refractive index difference from the PTFE polymer in order to yield measurable scattered intensities for such a PTFE solution at dilute concentrations. The fractionally distilled solvents are oligomers of poly(chlorotrifluoroethylene) (to be denoted by MO as mixed oligomers and courtesy of W. Buck). The solvent has a boiling point of $\sim$350 °C and a refractive index of $\sim$1.32 at 340 °C and should suffice for the present demonstration. After completion of the present study, we note that the solvent quality could perhaps be improved by using oligomers of perfluoro polymers.

We have been able to overcome many of the difficulties encountered in the light-scattering characterization of specialty polymers[5-10] such as poly(1,4-phenyleneterephthalamide)[6-9] and an alternating copolymer of ethylene and tetrafluoroethylene (PETFE), commercially known as Kevlar (a trademark of Du Pont) and Tefzel (a trademark of Du Pont), respectively. In the light scattering characterization of Tefzel,[10,11] we constructed a dissolution/filtration apparatus capable of dissolving PETFE in diisobutyl adipate at 250 °C and subsequently filtering the PETFE solution in the same closed apparatus (under an
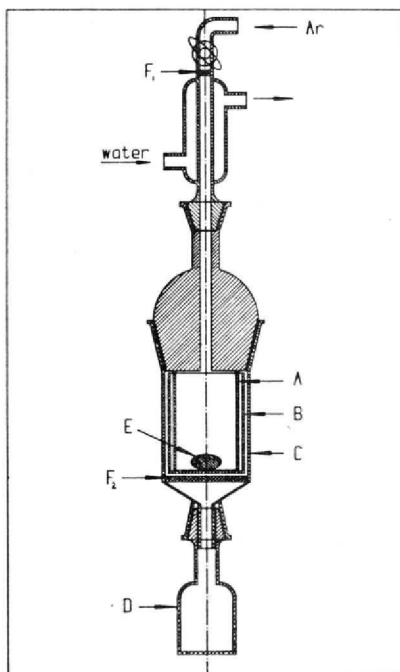
Figure 1. Dissolution/filtration apparatus (see text for description).

Figure 2. Zimm plot of PTFE in MO at 340 °C. Squares, $C = 4.39 \times 10^{-3}$ g/mL; inverted triangles, $C = 2.99 \times 10^{-3}$ g/mL; diamonds, $C = 1.35 \times 10^{-3}$ g/mL; triangles, $C = 7.51 \times 10^{-4}$ g/mL. $M_w = (2.9 \bullet 0.2) \times 10^5$ dalton; $A_2 \sim -(6.7 \pm 1.3) \times 10^{-5}$ g^{-1} dalton^{-1} mL; $R_g \simeq 17.8 \pm 2.4$ nm.

Figure 3. Net intensity–intensity time correlation function $[G^{(2)}(K,t) - A]/A = b|g^{(1)}(t)|^2$ as a function of delay time t at 340 °C. A is the background, b is a coherence factor, and $|g^{(1)}(t)|$ is the normalized electric field time correlation function. $\theta = 30°$; $C = 7.51 \times 10^{-4}$ g/mL; $\lambda_0 = 488$ nm. Solid line denotes third-order cumfits fit: $[G^{(2)}(K,t) - A]/A = b \exp\{-\bar{\Gamma}t + {}^1/_2(\mu_2/\bar{\Gamma}^2)(\bar{\Gamma}t)^2 - {}^1/_6(\mu_3/\bar{\Gamma}^3)(\bar{\Gamma}t)^3\}$ with $\mu_i = \int_0^\infty G(\Gamma)(\Gamma - \bar{\Gamma})^i \, d\Gamma$, $b = 0.218$, $\bar{\Gamma} = 3.17 \times 10^3$ (s^{-1}), $\mu_2/\bar{\Gamma}^2 = 0.21$, $\mu_3/\bar{\Gamma}^3 = 0.046$, and $\bar{D} = \bar{\Gamma}/K^2 = 4.10 \times 10^{-7}$ cm^2/s. Dashed line denotes second-order cumfits fit: $[G^{(2)}(K,t) - A]/A = b \exp\{-\bar{\Gamma}t + {}^1/_2(\mu_2/\bar{\Gamma}^2)(\bar{\Gamma}t)^2\}$ with $b = 0.216$, $\bar{\Gamma} = 3.08 \times 10^3$ (s^{-1}) and $\mu_2/\bar{\Gamma}^2 = 0.15$. If we take $\mu_2/\bar{\Gamma}^2 \sim 0.21$, $M_z/M_w \sim 1 + 4\mu_2/\bar{\Gamma}^2 \sim 1.8$.[13]

inert atmosphere) directly into the light-scattering cell at 250 °C. We also built a high-temperature light-scattering spectrometer capable of measuring the angular distribution of absolute scattered intensity as well as its spectral distribution, to the same order of precision as state-of-the-art spectrometers at room temperatures.[11] It appears that if MO is a suitable solvent for PTFE, we have the essential instrumentation for the preparation and clarification of PTFE in MO and the high-temperature spectrometer to perform the light-scattering experiments. The first attempts at 340 °C resulted in three explosions, destroying several dissolution/filtration apparatus of the original design. Fortunately, the use of explosion shields prevented serious body injuries.

In this work, we modified both the dissolution/filtration apparatus and the high-temperature light-scattering spectrometer. The clear-seal glass joint (J in Figure 1 of ref 11, paper 1) tended to lock itself at high temperatures (>300 °C). Furthermore, our experience with the unexpected explosions requires the use of a pressure-release mechanism. Figure 1 shows a modified dissolution/filtration apparatus. Sleeve A (without a bottom) is joined to the shaded stopper, which is connected to a reflux condenser by means of a greaseless glass joint. Cup B, with magnetic stirrer E, sits on top of the lower (fine grade) sintered glass filter F_2 and is used for polymer solution clarification. The procedure is as follows. Add solvent and polymer to B of the argon-filled apparatus with the dust-free light-scattering cell D already attached. Insert the reflux condenser, which has been flushed with argon, making sure that the apparatus with PTFE and MO is under an inert atmosphere at room temperature. Raise temperature to 340 ± 2 °C. With gentle stirring, complete dissolution should take a few hours. Apply argon pressure through the coarse-grade sintered glass filter F_1 to move the polymer solution from B to C, which has the fine-grade sintered glass (bottom) filter F_2. The additional pressure difference plus gravity will filter the polymer solution directly to the dust-free light-scattering cell D. After the filtration process is completed, the additional argon pressure is released. The stopcock above the upper filter
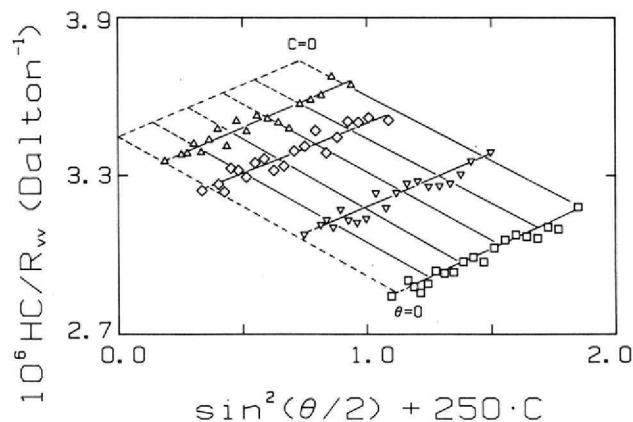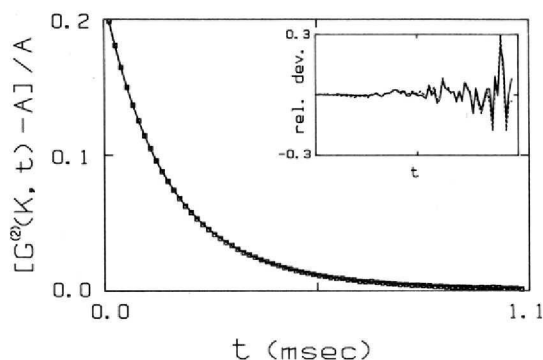
F_1 could be closed for short times during light-scattering experiments. The high-temperature scattering chamber in the light-scattering spectrometer accepts the entire light-scattering cell. The high-temperature thermostats could be controlled to ±0.1 °C at 340 °C over a region of ~1 cm where the polymer solution was located. Temperature could be controlled to ±0.1 °C over a 1-h period.

In a dilute polymer solution at finite concentrations C (g/cm^3), the excess Rayleigh ratio R_{vv} (cm^{-1}) has the approximate form

$$\frac{HC}{R_{vv}} = \left(\frac{1}{M_w}\right)\left(1 + \frac{K^2 R_g^2}{3}\right) + 2A_2 C \qquad (1)$$

where H (mol cm^2 g^{-2}) $= 4\pi^2 n^2 (dn/dC)_T^2/(N_A \lambda_0^4)$ with n, N_A, λ_0, and $(dn/dC)_T$ being respectively the refractive index, Avogadro's number, the wavelength of light in vacuo, and the refractive index increment. Subscript vv denotes vertically polarized incident and scattered light, A_2 (mol cm^3 g^{-2}) is the second virial coefficient, K [$= (4\pi/\lambda) \sin(\theta/2)$] is the scattering vector with $\lambda = \lambda_0/n$ and θ, the scattering angle. Equation 1 is valid for a polymer solution

containing a single solvent. For a mixture of oligomers with small differences in chlorine end groups, but very similar boiling points and molecular weights, the affinities for the PTFE polymer as well as the refractive index of those oligomers could be comparable. We used two different boiling fractions of the MO solvent and obtained essentially the same molecular weight. Figure 2 shows a typical Zimm plot with $M_w = (2.9 \pm 0.2) \times 10^5$ g/mol (or dalton), $A_2 = -(6.7 \pm 1.3) \times 10^{-5}$ mol cm^3 g^{-2}, and $R_g \approx 17.8 \pm 2.4$ nm. The negative A_2 suggests that the MO solvent is a poor solvent for PTFE at 340 °C. Figure 3 shows a typical net intensity–intensity time correlation function. We first tried to examine the clarified oligomers at 340 °C and were satisifed with a lack of angular dissymmetry in intensity measurements and a lack of correlations over the entire correlator delay time range. From a simple cumulants analysis,[12] we note that the polydispersity index[13] is high, with $M_z/M_w \sim 2$. A detailed characterization is under way.

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Cyclobutene-Containing Monomers and Polymers. Polymerization and Cross-Linking via Thermally Generated Butadiene Units

New monomers and polymers have been synthesized that contain 1,2-disubstituted cyclobutene moieties capable of thermal ring-opening to 2,3-disubstituted butadiene groups. Model diamides and polyamides are described here.

The 1,2-cyclobutenedicarboxylic acid intermediate **1** was synthesized via the dicyano compound by published procedures.[1,2] The diacid chloride **2** was readily obtained with thionyl chloride.[3] Conversion of **2** to the N-substituted diamides **3–5** took place in good yield.[4] The diamides serve
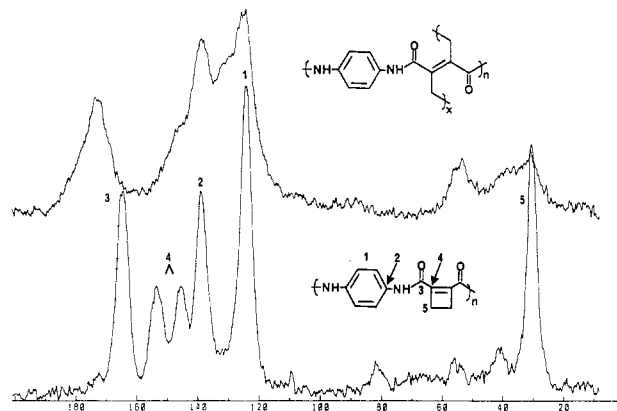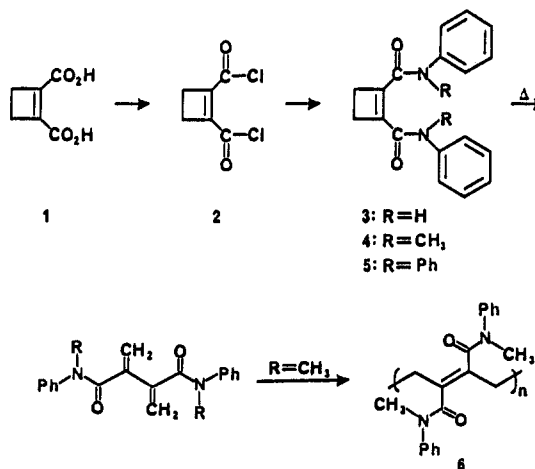

Figure 1. Cross-polarization/magic angle spinning ^{13}C NMR spectra of the cyclobutene-containing polyamide (lower trace) and its thermolysis product (upper trace).

both as models for aromatic polyamides and as precursors for a new family of disubstituted polybutadienes.

Previous work has focused mainly on the cycloaddition chemistry of several cyclobutenes and their butadiene derivatives.[5] Two reports have appeared, however, on the spontaneous polymerization of ring-opened compounds. Thermolysis of 1,2-dicyanocyclobutene gave a soluble polymer of undetermined structure,[3] while polyolefins containing cyclobutene units in their backbone became insoluble after thermolysis.[6] We have found that polymerization and cross-linking are also possible for other 1,2-disubstituted cyclobutenes and their polymers.

Thermolysis of the model diamides was monitored by DSC. All three compounds displayed melting endotherms followed by broad reaction exotherms over the range 200–250 °C with maxima of 210–220 °C. Thermolysis of **4** led directly to polybutadiene **6** (proposed structure; 1,2 incorporation is also possible), which was soluble in common organic solvents.[7] Further work is under way on the general polymerizability of the butadienes and on characterization of the monomers and polymers.

We have also synthesized polyamide **7** from **1** and p-phenylenediamine using a mild triphenylphosphine–hexachloroethane procedure.[8] Figure 1 shows the ^{13}C CP/MAS spectra of this polymer and its insoluble thermolysis product (proposed structure **8** leading to **9**). The changes in chemical shifts for the amide carbonyl and the alkene carbons are consistent with solution spectra for model diamides except that the solid polyamide shows *two* peaks for the alkene carbons. This may be due to restricted rotation caused by intramolecular hydrogen bonding that forces the two cyclobutene alkene carbons into different chemical environments.