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Fractal Dimension of a Cross-Linking Polymer at the Gel Point

Many models have been proposed to describe cross-linking polymers at their gel point. The most accepted ones are based on the classical theory of Flory,^{4,5} Stockmayer,⁶ and Zimm⁷ and on the percolation model.⁸⁻¹⁰

The fractal dimension d_f of a molecular cluster is defined by

$$R \sim M^{1/d_f} \quad (1)$$

where R is the radius of gyration and M is the molecular weight. The fractal dimension at the gel point was found to be¹⁰

$$d_f = 4, \quad \text{Zimm-Stockmayer (Cayley tree)} \quad (2a)$$

$$d_f = 2.5, \quad \text{percolation cluster at threshold} \quad (2b)$$

However, recent computer modeling¹¹ of the kinetic gelation suggests that a different value for d_f should be expected.

Recently, a theory³ has been derived for predicting the frequency dependence of the complex viscosity in terms of the arbitrary fractal dimension of the molecular cluster. In the regime of large molecular weights where both the hydrodynamic and excluded volume effects are fully screened, the frequency dependence of the viscosity is shown to be

$$\eta^*(\omega) \sim \omega^{-2/(d_f+2)}, \quad 0 < \omega \quad (3a)$$

$$\eta^*(\omega) \sim M^{2/d_f}, \quad \omega \rightarrow 0 \quad (3b)$$

This theory has been compared to experimental observations and is known to reproduce the high-concentration behavior of unentangled linear polymers. It makes it possible to draw conclusions regarding the global structures of polymeric systems from measurements of the complex viscosity as a function of frequency.

Chambon and Winter¹ measured the evolution of the rheological behavior during the cross-linking of polymers, using stoichiometrically balanced poly(dimethylsiloxane) (PDMS) as a model polymer in which two-functional and four-functional molecules end-linked by hydrosilation reaction. A discrete set of stable samples represented the continuous evolution of the cross-linking reaction. The samples were prepared by poisoning the catalyst at several different extents of reaction. For the rheological experiments it was important that the samples were cross-linked at rest and, therefore, had no memorized flow history. The molecular weights of the prepolymers were below the entanglement limit to reduce the effect of physical entanglements.

The storage modulus G' and the loss modulus G'' have been measured as a function of frequency, applying time-temperature superposition to stretch the frequency range to about 5 decades. At low extent of reaction, the storage modulus was smaller than the loss modulus, $G' < G''$. With increasing extent of reaction, the two moduli increased in value and became more similar until, at a

critical extent of reaction, they were found to completely grow together. At this state of the material, the storage and the loss moduli were congruent functions and they could be described by a "power law"

$$G'(\omega) = G''(\omega) = A\omega^\alpha, \quad \alpha = 1/2 \quad (4)$$

where A is a material constant. Winter and Chambon² hypothesized that the power law relation is valid not only in the experimental region but in the entire frequency range $0 < \omega < \infty$. On the basis of this hypothesis, the Kramers-Kronig relation gives $\alpha = 1/2$ as the only possible value for the exponent. Beyond the critical extent of reaction, the storage modulus was always larger than the loss modulus, $G' > G''$, over the entire frequency range.

Winter and Chambon² could also show that the one sample which exhibited congruent behavior was at the phase transition from viscoelastic liquid to viscoelastic solid. We therefore know that the complex viscosity

$$\eta^*(\omega) = [(G'/\omega)^2 + (G''/\omega)^2]^{1/2} \quad (5)$$

of the PDMS at the gel point is

$$\eta^*(\omega) = A\omega^{-1/2} \quad (6)$$

Comparison of eq 3 and 6 gives the result that the fractal dimension of the PDMS cluster at the gel point is

$$d_f = 2 \quad (7)$$

Although the dimension of the percolation cluster at the percolation threshold is closer to this value than the dimension of the Cayley tree of the classical theory, it seems that the cluster at the gel point is not a percolation cluster at the threshold. The fractal dimension at the gel point is the same as that of an isolated linear chain of infinite length under θ -conditions. This is surprising because the polymer at the gel point is a highly branched macromolecule. Furthermore, it is to be pointed out that the experimental observation^{1,2} of the congruency $G' \sim \omega^{1/2} \sim G''$ at the gel point is a direct manifestation of the fractal dimension of the system although this behavior is reminiscent of the Rouse spectrum valid for an isolated linear flexible chain of infinite length.

Although the Rouse model of networks also predicts $G' \sim \omega^{1/2} \sim G''$ for intermediate frequencies, the standard arguments¹² show that this intermediate frequency range is restricted to less than a decade for molecular weights between cross-links employed in ref 1 and 2. This is to be contrasted with the observed congruency (eq 6) over more than 5 decades in frequency.

Since the molecular weight of the growing cluster diverges at the gel point, the experimental complex viscosity at $\omega = 0$ also diverges, in accordance with eq 3.

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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 polyethylene² 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 complex³ 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 polymers²⁻⁵ 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

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

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

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

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 Decomposition⁹ (MSVD). The technique is a modification of the eigen-