Communications to the Editor

Static and Dynamical Properties of Polystyrene in *trans*-Decalin

The scaling theories,[1-9] developed by de Gennes and others, have been successful in describing the static and dynamical properties of polymer solutions. Instead of the use of mean-field-type arguments of classical theories of the statistical thermodynamics of polymer solutions, such as the Flory–Huggins theory,[10] the ideas proposed by de Gennes are very different in spirit and are based upon an analogy with critical phenomena in magnetic systems. de Gennes took over the results of the renormalization group technique and evaluated the exponents in power-law relations by matching cross-over properties. Kosmas and Freed, who obtained the general scaling relations without recourse to renormalization group methods or to analogies with magnets or critical phenomena, have also derived static scaling relations for polymer solutions at finite concentrations.[11] Static properties of entangled polymer solutions have been checked by neutron experiments,[3] while Adam and Delsanti[12] have studied dynamical properties of polymer (polystyrene) solutions in a good solvent (benzene). The agreement between theory and experiments has been excellent. When the translational diffusion coefficient D in the dilute region was observed to behave as $D \sim N^{-0.55}$ instead of a predicted value $D \sim N^{-0.6}$ where N is the number of monomers per chain, Weill and des Cloizeaux[13] have shown that the dynamical properties of polymers converge more slowly to the asymptotic infinite molecular weight limit than static properties.

There is no doubt that the scaling theories of polymer solutions represent a fresh approach and a major advance to an interesting and important problem of concentrated polymer solution behavior. The relations, however, emerge from asymptotic dimensional analysis for infinitely long chains. Thus, at finite concentrations and at finite molecular weight, we expect deviations from simple scaling relations. In this communication, we wish to show some experimental evidence indicating the approximate nature of scaling theories under experimental conditions.

A brief experimental procedure is described as follows. Polystyrene (NBS 705 standard, $\bar{M}_w = 179\,300$, $\bar{M}_w/\bar{M}_n = 1.07$) was dissolved in benzene and freeze–dried in vacuum. *trans*-Decalin (Tokyo Kasei Kogyo Co. Ltd.) was dried in $CaCl_2$, passed through a silica gel column (1.5 cm diameter × 80 cm), and then fractionally distilled under dry helium at approximately 15 mmHg. The solutions were prepared under helium in a drybox. A 7 wt % polymer solution was filtered through a Millipore filter of nominal pore diameter of 0.22 μm. Solutions at lower concentrations were prepared by dilution, and those at higher concentrations were prepared by evaporation of the solvent. All samples with concentrations ranging from 0.2–35 wt % polymer were flame sealed. We used a 96-channel single-clipped photon correlation spectrometer for macromolecular diffusion studies and photon counting for scattered intensity measurements. Temperature of the sample at 30 °C was controlled to ±0.01 °C. We used an argon ion laser operating at $\lambda_0 = 488.0$ nm and an ITT FW 130 photomultiplier tube for photon detection.

In the osmotic compressibility $(\partial\pi/\partial C^v)_{T,P}$, we compute

$$\left[\frac{\partial \pi}{\partial C^v}\right]_{T,P} = \frac{H(\partial n/\partial C^v)_{T,P}{}^2 C^v RT}{R_c(0)} \qquad (1)$$

from the excess Rayleigh ratio $R_c(0)$ obtained from absolute excess scattered intensity extrapolated to zero scattering angle and $H = 4\pi^2 n^2/(N_A\lambda_0{}^4)$ with n, C^v, N_A, T, P, and R being the refractive index, the concentration in g/cm^3, the Avogadro number, the absolute temperature, the pressure, and the gas constant, respectively. At infinite dilution, $(\partial\pi/\partial C^v)_{T,P} = RT/\bar{M}_w$ and the initial slope at very low concentrations represents a finite value for A_2, as shown in Figure 1 where we have plotted $(\partial\pi/\partial C^v)_{T,P}$ vs. concentration measured at 30 °C, about 10 °C above the Θ temperature. However, at higher concentrations, the virial expansion

$$(\partial\pi/\partial C^v)_{T,P} = RT/\bar{M}_w + 2A_2RTC^v + \ldots \qquad (2)$$

no longer holds.

One of the consequences of the temperature–composition diagram of Daoud and Jennink is as follows. In the dilute region, $(\partial\pi/\partial C)_{T,P} \sim C^{\sim 0}$; in the semidilute region, $(\partial\pi/\partial C)_{T,P} \sim C^{5/4}$; in the concentrated solution region, $(\partial\pi/\partial C)_{T,P} \sim C^2$. Experimentally, as we have shown in Figure 1, we do not observe sharp breaks for a polymer solution of finite molecular weight in a Θ solvent. However, it should be noted that in the dilute solution region, we do have $(\partial\pi/\partial C)_{T,P} \sim C^{\sim 0}$, and in the semidilute region, we can find a concentration range where $(\partial\pi/\partial C)_{T,P} \sim C^{5/4}$ which eventually increases to C^2. The gradual transition for a polymer of finite molecular weight near the Θ temperature merely demonstrates a quantitative breakdown of the approximate nature of the scaling theory which is valid for a polymer of infinite molecular weight. If we take the overlap concentration

$$C^* = \bar{M}_w/(N_A\rho_s R_G{}^3) \qquad (3)$$

where ρ_s and R_G are the solvent density and the radius of gyration, respectively, we note that the $^5/_4$ exponent value indeed appears in the neighborhood of C^* over a very short range of C. Yet the overlap concentration C^*, though arbitrary in definition, represents an upper value for the cross-over to the semidilute region. It stretches our imagination to consider a 10 wt % polymer solution as the domain where the semidilute region emerges.

In photon correlation measurements, we have taken pains to reduce the presence of dust particles and to assure ourselves of the homogeneous nature of viscous concentrated solutions. Nonlinear least-squares methods of data analysis of correlation function data of concentrated solutions were used whereby we could estimate the presence of heterodyning during self-beating. Figure 2 shows a plot of $\mu_2/\bar{\Gamma}^2$ as a function of concentration at 30 °C. In the cumulants[14] fit, $\bar{\Gamma} = \int G(\Gamma)\Gamma\, d\Gamma$ and $\mu_2 = \int (\Gamma - \bar{\Gamma})^2 G(\Gamma)\, d\Gamma$ where $G(\Gamma)$ is the normalized distribution of line width. With K being the magnitude of the momentum transfer vector, the relation $\bar{D} = \bar{\Gamma}/K^2$ holds over the entire range of scattering angles measured. The drastic increase of the variance $(\mu_2/\bar{\Gamma}^2)$ is not predicted by the scaling theory. With a contracted coil behavior near the Θ temperature, the apparent polydispersity effect cannot be attributed to internal molecular motions for a polymer sample of only 179 300 molecular weight.

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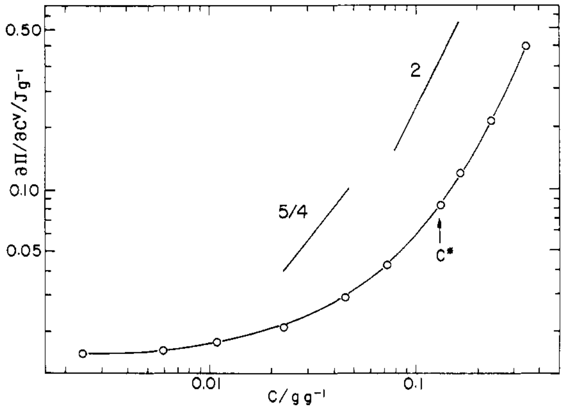

Figure 1. A plot of osmotic compressibility as a function of concentration for the polystyrene-*trans*-decalin system at 30 °C.

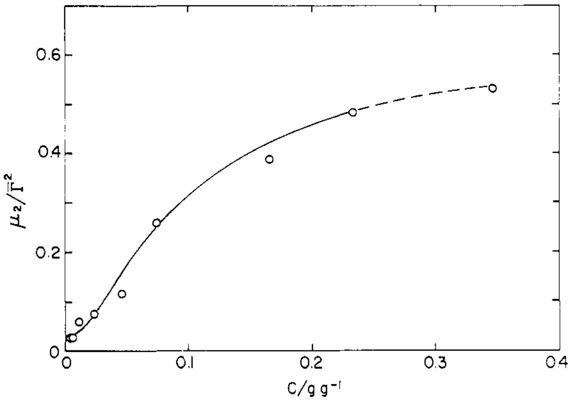

Figure 2. A plot of $\mu_2/\bar{\Gamma}^2$ vs. concentration for the polystyrene-*trans*-decalin system at 30 °C. All measurements were performed at θ = 90° except for the concentration at 34.5 wt % polystyrene where we used θ = 135°. Values of $\mu_2\bar{\Gamma}^2$ at high concentrations are approximate, as the cumulants expansion does not provide a good representation of the entire correlation function profile.

In a recent study,[15] we have established that the value of the asymptotic critical exponent β of a polymer solution (polystyrene with $\bar{M}_w = 1.56 \times 10^6$ in cyclohexane) be like that calculated for the Ising model provided that we use extended scaling.[16] Thus, it would be unreasonable to expect the limiting simple scaling relations to hold over the entire temperature-concentration diagram. The deviations suggest that we need correction terms (extended scaling) to simple scaling in order to predict generalized polymer solution behavior of finite molecular weights. A more detailed study and analysis of static and dynamical properties of polystyrene in *trans*-decalin is in progress.

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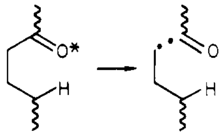
Photoenolization in Polymers. A Simple Way to Reduce Photodegradation

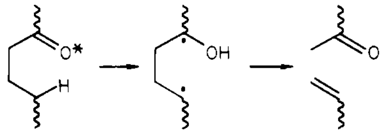
The elementary processes involved in polymer photodegradation frequently reflect the chemistry of excited carbonyl groups, particularly the Norrish type I and type II processes, reactions 1 and 2.[1]

type I



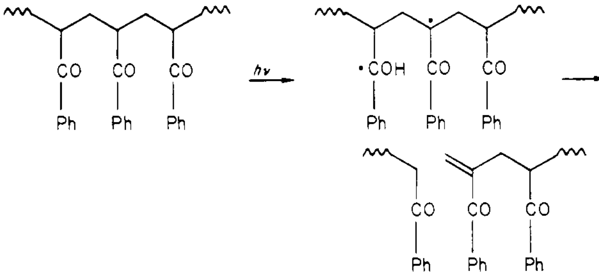
(1)

type II



(2)

In triplet state reactions the type II process tends to be more important whenever the C-H bond dissociation energy at the γ position is relatively low (e.g., tertiary hydrogens).[2] The photodegradation of poly(phenyl vinyl ketone), PPVK, is a typical example of this type of behavior, reaction 3.[3,4]



(3)

We have examined the possibility of using the high reactivity of carbonyl triplets in hydrogen abstraction processes in order to *prevent* the photodegradation. This can be achieved if a suitable reversible process can be found, which would effectively behave as an energy sink. The photoenolization of the *o*-methylbenzoyl group shows precisely this property,[5] and this communication reports the results of a comparative study of the photochemistry of PPVK, poly(*o*-tolyl vinyl ketone) (PTVK),[6] and a copolymer containing 11:89 tolyl vinyl ketone-phenyl vinyl ketone (Co-PT).[7]

The deaerated samples were irradiated in benzene at 30 °C with light of 366 nm using a high pressure mercury lamp and monochromator. Typical radiation dose rates were ca. 1-5 × 10^{-6} einstein L^{-1} s^{-1}.[8] Figure 1 shows a plot of the number of bonds cleaved (formally "moles" of

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