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Intrinsic Dynamic Viscoelasticity of Polystyrene in Good Solvent. A Test of the Nonuniform Expansion Theory

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Introduction

Experimental and theoretical studies on the structure and dynamics of long-chain polymers in solution are critical to understanding the relaxation processes of macromolecules that lead to their characteristic and extraordinary physical properties. Dynamic viscoelastic (VE) and oscillatory flow birefringence (OFB) experiments focus on the relaxations associated with the response of polymers in solution, which are subjected to a small shear.[1,2] Data from these experiments have been successfully treated[3] with the Rouse–Zimm bead–spring theory,[4,5] which models Gaussian chain configurations and includes hydrodynamic interactions by a preaveraged Oseen tensor. In comparison to this ideal chain model, infinite dilution dynamic storage and loss moduli, $[G'(\omega)]_R$ and $[G''(\omega)]_R$, of high molecular weight polymers in Θ solvents are in clear agreement with theory in the limit of nondraining polymer coils.[6,7]

The same is not true for polymers in good solvent. One method of modeling these results has been to allow the hydrodynamic interaction paramter h^* to vary from its nondraining limit of 0.25 toward the free-draining limit of 0. Allowing h^* to vary as a fitting parameter indicates that the introduction of excluded volume for the polymer chain shifts experimental data, including intrinsic viscosity, in the direction of the free-draining Rouse limit.[1,6] By this method dynamic VE, OFB, and intrinsic viscosity results have been treated with effective h^* values.

It has long been recognized[8] that this application of the Rouse–Zimm model is inconsistent because polymer chains in good solvent are expanded beyond the Gaussian configuration assumed by the calculation. Thus, despite the widespread success of the method in fitting data, it does not establish that an adjustable h^* corresponds to the correct physical interpretation of the data. Ptitsyn and Eizner[9] addressed the problem by introducing non-Gaussian chain statistics into the bead–spring theory and solving for the case of dominant hydrodynamic interaction. This model includes excluded volume with a uniform expansion as $\langle r_{ij}^2 \rangle = \sigma^2 |i-j|^{1+\epsilon}$ where $\langle r_{ij}^2 \rangle$ is the mean-square separation between the ith and jth bead. $\langle r_{ij}^2 \rangle$ is not a linear function of $|i-j|$, but expands according to the excluded-volume parameter ϵ, which ranges from 0 in Θ condition to 0.333 in good solvent cases. Tschoegl extended this approximate treatment to include arbitrary hydrodynamic interaction because it was found that the addition of ϵ alone could not account for the experimental results; an adjustable h^* was also required.[10] Equally good comparisons to data were obtained by setting $\epsilon = 0$ and varying h^* alone.[8]

In a recent paper[7] both the original Gaussian model and Tschoegl's extension have been applied to data from dilute solution VE experiments ($[\eta]$, $[G'(\omega)]_R$, and $[G''(\omega)]_R$ for polystyrenes of molecular weights from 1.79×10^5 to 2.06×10^7 in toluene). Generalized programs for calculation of eigenvalues and VE properties using the bead–spring model (Hookean springs) were provided by Sammler and Schrag.[11,12] For the original Zimm theory, h^* was determined from the Houwink–Mark–Sakurada (HMS) molecular weight exponent for $[\eta]$ and used to fit $[G'(\omega)]_R$ and $[G''(\omega)]_R$ vs $\omega\tau_1$. For the uniform expansion model ϵ was fixed from radius of gyration measurements by light scattering, the value of h^* consistent with this ϵ was determined from $[\eta]$, and the resulting calculations were compared to $[G'(\omega)]_R$ and $[G''(\omega)]_R$ vs $\omega\tau_1$. For PS in toluene both fits were excellent with the following parameters:[7] Gaussian ($\epsilon = 0$), $h^* = 0.04$; uniform expansion, $\epsilon = 0.192$, $h^* = 0.06$. These values of h^* are surprisingly small, tending toward the Rouse limit of $h^* = 0$.

Nonuniform Expansion Model

It has been shown by neutron scattering[13] and by direct perturbation calculations[14,15] that even the uniform expansion assumption is incorrect for real excluded-volume chains. These studies demonstrated that if $\langle r_{ij}^2 \rangle$ is cast in the Ptitsyn and Eizner form, ϵ depends on $|i-j|$. Descriptions of chain expansion in good solvents, which should provide a more accurate representation, are given by the renormalization group calculations of Miyake–Freed[16,17] and by the perturbation calculations of Barrett.[18] Recently Sammler and Schrag[12] have compared results obtained under the Gaussian, uniform expansion, and (Miyake and Freed) nonuniform expansion models. The eigenvalues in each model are dependent, in complicated ways, on the same hydrodynamic interaction parameter, $h^* = (\zeta/\eta_s)(1/12\pi^3 b^2)$, where ζ, η_s, and b are the monomeric friction factor, solvent viscosity, and equilibrium bead length, respectively. The calculations

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provide $\langle r_{ij}^2 \rangle$, the equilibrium mean-squared intersegment distances, which determine both the force constants for the Hookean springs and, through the preaveraged Oseen tensor, the hydrodynamic interaction. Sammler and Schrag observed that predicted dynamic VE and OFB properties are comparable from the three models. They concluded that long-chain structure parameters obtained by fitting measured dynamic properties with Gaussian model predictions can be expected to be at most only weakly dependent on solvent power.

We have taken a different approach that relies on data from independent experiments to determine some model parameters, which can then be used for tests of theoretical predictions against VE data. In the previous paper,[7] viscoelasticity for PS in toluene was compared directly to theoretical curves with the controlling parameters set by independent measurements. In general, this is desirable, and it is especially important for h^* because of objections[19] to the common method of using an adjustable h^* (with its implication of intermediate hydrodynamic interaction or partial draining) to account for the effects of chain expansion among different polymer–solvent pairs.

The Miyake–Freed theory is a chain conformation renormalization group method applied to calculation of distribution functions of regular stars. Linear chains are taken as the special case of two-arm stars. In addition to h^*, several variables must be assigned values or used as fitting parameters. These are (using Sammler and Schrag's notation) the following: d, the dimensionality of space [=3]; $\epsilon_0 \equiv 4 - d$ [=1]; f, functionality of star at the center bead [=2]; L/b, the ratio of the macroscopic coarse-grained length scale on which the cooperative excluded-volume effects appear (L) over the root-mean-square distance between connected beads in a quiescent solution (b); ν_0, the exponent for the microscopic bare excluded volume describing binary interactions between units $[=\{1 + (\epsilon_0/8)[\zeta_0/(1+\zeta_0)] + O(\epsilon_0^2)\}/2]$; ζ_0, the crossover parameter, which indicates the degree of excluded volume in the chain [0 (Gaussian $\leq \zeta_0 \leq \infty$ (full excluded volume)]. ζ_0 and L/b both depend on the degree of excluded volume, with ζ_0 describing global and L/b referring to local effects.

Results and Discussion

The PS–toluene system shows nearly full excluded volume on static conformations so the self-avoiding limit was chosen for ζ_0 and L/b. In this limit, L is set equal to b so that excluded volume acts over the smallest subdivision of the chain in this model, i.e., one bead. Sammler and Schrag's calculations also show that the effect of excluded volume is most enhanced as L approaches b.[12] To assess the sensitivity of the chain relaxation spectrum to these parameters, calculations similar to those described previously[7] were performed to determine the dependence of $[\eta]$ on the number of chain beads. For each set of h^* and N the relaxation spectrum $\{\tau_p\}$ was calculated. Since $[\eta] \sim \sum(\tau_p/N)$ and N is proportional to molecular weight, the slope of log $\sum(\tau_p/N)$ vs log N gives a, the HMS molecular weight exponent of viscosity. Values of a are plotted in Figure 1 as a function of h^*. At the expanded chain limit ($L/b = 1$) curves with ζ_0 = 10, 100, and 1000 are shown. Because there is only a slight change in the calculations for ζ_0 between 100 and 1000, ζ_0 = 1000 and L/b = 1 is taken as the good solvent limit. Using the experimental values[20] for intrinsic viscosity of polystyrene in toluene at 20 °C gives a = 0.724, and thus reading from Figure 1 yields the self-consistent h^* value of 0.25. This result is the limiting Zimm value for *nondraining* coils.

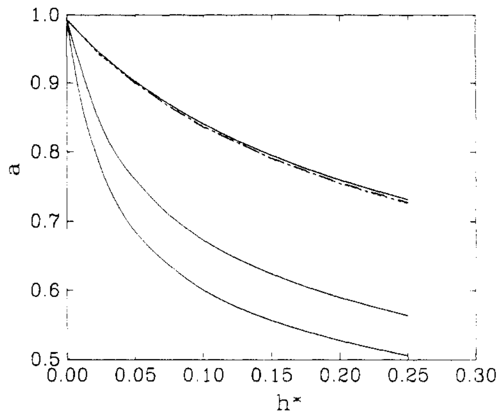

Figure 1. Relationship between HMS coefficient a and h^*, the hydrodynamic interaction parameter. Points are generated from calculations of $[\eta]$ using the bead–spring model: lower curve, Gaussian model; middle curve, uniform expansion model; upper set of curves, nonuniform expansion with ζ_0 = 10 (—), 100 (– –), and 1000 (- - -).

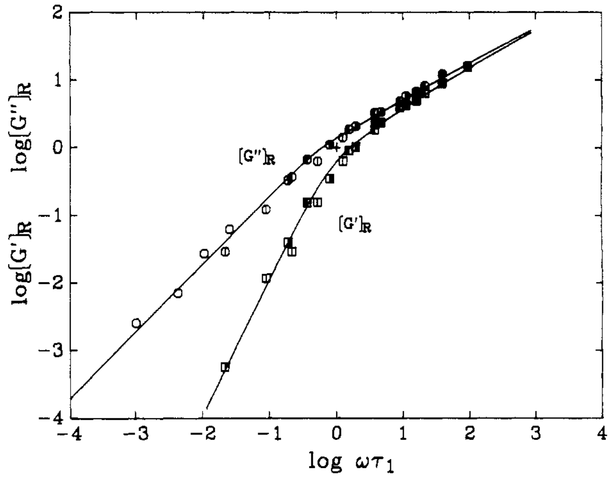

Figure 2. Log–log plot of $[G']_R$ and $[G'']_R$ versus log $(\omega\eta_s[\eta]M/S_1RT)$ (=log $\omega\tau_1$), measured in toluene at 20 °C. Molecular weights are indicated by: ○, □, 1.79 × 10^5; ⦶, ◫, 1.05 × 10^6; ◑, ◧, 3.75 × 10^6; ◐, ◨, 5.50 × 10^6; ●, ■, 20.6 × 10^6. Curves are Miyake–Freed nonuniform expansion theory with h^* = 0.25, ζ_0 = 1000, and L/b = 1.

Eigenvalues determined with these parameters were used to calculate $[G'(\omega)]_R$ and $[G''(\omega)]_R$. The results are shown in Figure 2 in comparison to intrinsic dynamic viscoelastic data taken with the multiple-lumped resonator. The agreement is excellent. The agreement of $[\eta]$, $[G'(\omega)]_R$, and $[G''(\omega)]_R$ with the Gaussian and the uniform expansion models was also good, and thus any preference for the fit to the Miyake–Freed theory is based on the belief that the theory provides a fundamentally more accurate representation of the chain configurations. Viscoelastic experiments cannot discriminate between the models.

The parameters used in this fit are reasonable for this polymer–solvent pair, and from hindsight the value of h^* = 0.25 is particularly interesting. The previous interpretation of partial draining behavior with h^* nearly reaching its Rouse limit is no longer required. Just as the Θ solvent results were fit with h^* = 0.25 in the Gaussian limit (the three models are the same in this limit), good solvent data can be fit with the same h^* if nonuniform expansion is considered. This result calls into question the common practice of varying h^* to fit VE and OFB data. At the same time it may lend support to the connection drawn[21] between the hydrodynamic renormalization group fixed point and the smallest eigenvalue from the Kirkwood–Riseman theory ($h^* \approx 0.25$). The veracity of the conformational distribution function may strongly affect the universality of the physics underlying polymer hydrodynamics.

The next challenge before eliminating variable h^* values will be to consider other polymer–solvent systems with intermediate chain expansion. Such experiments are presently under way in this laboratory. Success here will require choosing, and justifying from theory or experiment, appropriate values for the local and global excluded-volume parameters.

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Registry No. Polystyrene, 9003-53-6; toluene, 108-88-3.

Communications to the Editor

Polyphenylene Ether Based Thin-Film Nonlinear Optical Materials Having High Chromophore Densities and Alignment Stability

Challenges confronting the rational construction of poled polymeric nonlinear optical (NLO) materials[1] include maximizing chromophore number densities as well as achieving and preserving maximum electric field induced acentricity of the microstructure. Chromophore-functionalized glassy polymers represent an advance in this respect,[2] and we recently reported improved second-haromonic generation (SHG) efficiencies and temporal stabilities vis-à-vis guest–host "doped" systems.[3a] Nevertheless, current generation polystyrene-,[2,3] polyacrylate-,[4] and polyethylene-based[5] materials are intrinsically limited in a designed functionalization level to a maximum of one chromophore molecule per repeat unit (in most cases, considerably less has been achieved) and to architectures having undesired residual chain mobility, as suggested by T_g data.[2-6] This paper addresses several of these issues and describes the synthesis and characterization of a new class of highly functionalized SHG polymers derived from the robust, high-T_g (205–210 °C) thermoplastic poly(2,6-dimethyl-1,4-phenylene oxide) (PPO).[7] Although we illustrate with a well-characterized model chromophore, the synthetic approach should be general. To better define the transparency characteristics of the subject films, we also report the fabrication of a waveguide.

PPO was prepared by oxidative coupling of 2,6-dimethylphenol and was purified as described elsewhere[8] (Scheme I; $\bar{M}_n = 27\,000$).[9] Bromination[10] in refluxing tetrachloroethane afforded materials (PPO–Br$_x$) with functionalization levels on the order of 1.6–1.8 Br/repeat unit (predominantly methyl bromination) as ascertained by elemental analysis and ^{1}H NMR.[11] *N*-(4-Nitrophenyl)-*S*-prolinoxy- (NPPO-) was chosen as a model chromophore substituent since the optical properties of NPPOH have been extensively characterized[12] and since it is readily amenable to $\lambda = 1.064$ μm NLO experimentation. Reaction of PPO–Br$_x$ with NPPO$^-$ (from NPPOH + NaH) in dry *N*-methylpyrrolidone (NMP; 4 days at 60 °C) afforded the chromophore-functionalized polymer (PPO–(NPP)$_x$; Scheme I; 1.43–1.63 NPPO/repeat unit;[13] $T_g \approx 173$ °C) after precipitation with acetone, washing with H$_2$O, Soxhlet extraction with MeOH, and vacuum drying for 24 h at 60–70 °C. Polymer films were cast onto ITO-coated conductive glass from triply filtered NMP solutions in a class 100 laminar-flow clean hood. The solvent was slowly evaporated at 80 °C, and the resulting films were dried in vacuo at 150–170 °C for 24 h. These PPO–NPP films have excellent transparency characteristics (vide infra; $\lambda_{max} = 405 \pm 2$ nm; 405 ± 2 nm as a solution in NMP), adhere tenaciously to glass, and are impervious to most organic solvents. Film thickness were 1–4 μm by profilometry.

Contact poling of the PPO–NPP films was carried out at 160–170 °C (40 min) with 1.2 MV/cm fields using tech-

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