Table II
Values of the Perturbation Terms of Φ_0

m	$\Phi_0^{(m)} \times 10^{-23}$
0	2.8182
1	0.0298
2	0.0056
3	0.0020

It is seen that the convergence of Φ_0 is rather good and that the difference between the Φ_0 in the Zimm version and the Auer–Gardner value of 2.862×10^{23} in the Kirkwood–Riseman version is much smaller than expected. This is a justification for the approximation that the center of mass is fixed conveniently instead of the center of resistance.[10]

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Rheological Studies on Concentrated Solutions of Poly(α-methylstyrene)

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ABSTRACT: A cone and plate rheometer has been used to study the creep and recovery of solutions of poly(α-methylstyrenes) over a range of shear stresses encompassing both linear and nonlinear viscoelastic response. The steady state viscosity η_κ and the recoverable compliance R_κ determined after steady state flow at shear rate κ are discussed in terms of the reduced rate of shear $\eta_0 R_0 \kappa$ (subscripts zero refer to the limit of small κ). A total strain criterion for the onset of nonlinear behavior in creep is found. It is observed that the recoverable compliance as a function of the time θ of recovery is independent of the shear stress over the range studied for reduced times of recovery $\theta/\eta_0 R_0$ less than 5. For longer times the recoverable compliance decreases with increasing shear stress.

In recent investigations in our laboratory[1,2] the steady state compliance of concentrated solutions of macromolecules has been studied over a range of κ for which the viscosity decreases markedly.[1,2] In those studies, the steady state recovery function R_κ was determined from the recovery $\gamma_{R,\sigma}(S,\theta)$ after creep under a shear stress σ for a time S as the limit

$$R_\kappa = \lim_{S,\theta \to \infty} R_\sigma(S,\theta) = \lim_{S,\theta \to \infty} \frac{\gamma_{R,\sigma}(S,\theta)}{\sigma} \tag{1}$$

where θ is the time of recovery after cessation of steady state flow at a shear rate $\kappa = \sigma/\eta$ with η_κ the steady state viscosity. We denote the limiting value of R_κ for small σ by R_0; this quantity is often denoted simply as the steady state compliance $J_e{}^0$.[3] In this study we report similar rheological measurements on solutions of three poly(α-methylstyrene) polymers kindly provided by Professor Nagasawa (Nagoya University). The preparation and characterization of these polymers has been reported elsewhere, along with data on the shear stress and the first normal stress difference N_1 as functions of κ for concentrated solutions of the polymer in α-chloronaphthalene.[4] Of particular interest was a comparison of data on R_κ determined by recoil experiments with a quantity we will designate S_κ determined from the first normal stress difference measured in steady state flow:

$$S_\kappa = \left(\frac{N_1}{2\sigma^2}\right)_\kappa \tag{2}$$

Of course, for a simple fluid,[5]

$$S_0 \equiv \lim_{\kappa = 0} S_\kappa = R_0 \tag{3}$$

but little is known about the more general relation between S_κ and R_κ for κ large enough, for example, so that η_κ decreases with increasing κ. Thus, it is convenient to maintain separate symbols for the parameters R_κ and S_κ.

Experimental Section

Polymers received from Professor Nagasawa designated as poly(α-methystyrene) samples PαS-9, -12, and -13 were each vacuum dried at room temperature for several days before use. They were then dissolved in methylene chloride at room temperature (about 1 g/dl) and sufficient reagent grade α-chloronaphthalene was added to each solution so that the desired concentration of polymer in α-chloronaphthalene would be obtained on evaporation of the methylene chloride. The methylene chloride solution was filtered and the methylene chloride was evaporated by passing filtered, dry nitrogen over the solution until it reached a constant weight. The concentration of the final solution was checked by a dry weight analysis in which an aliquot was redissolved in methylene chloride. The polymer was then quantitatively precipitated in methanol, washed with methanol, dried, and weighed.

A Waters Gel-Permeation Chromatograph was used to determine the elution profiles of each of the polymers studied here. The chromatograph has previously been calibrated to give $[\eta]M$ as a function of the elution volume V_e using a series of anionically prepared polystyrenes in tetrahydrofuran (THF). The poly(α-methylstyrene) samples were injected onto the column as 0.5 g/dl solutions in THF (0.5 ml injection volume).

Rheological data were obtained with a rotational rheometer described elsewhere.[1] The rheometer, which employs a drag-cup torque transducer and cone and plate platens, can be used to determine the creep, recovery, and steady state flow properties by methods discussed in detail in ref 1. In experiments described here, a cone with an angle of 2° and a radius of 1.89 cm was used throughout.

Table I
Rheological Parameters Determined for Poly(α-methylstyrene) Solutions

Polymer	$10^{-6}M_w{}^b$	c, g/ml^b	$\eta_0(50\ °C)^b$	$S_0(50\ °C)^b$	$R_0(0\ °C)^{a,b}$	c, g/ml^c	$\eta_0(50\ °C)^c$	$\eta_0(0\ °C)^c$	$R_0(0\ °C)^c$
PαS-9	1.19	0.268	2.45×10^4	2.24×10^{-5}	4.35×10^{-5}	0.276	2.10×10^4	9.5×10^5	4.95×10^{-5}
PαS-12	1.82	0.192	0.582	4.99	13.4	0.194	0.625	1.04	14.3
PαS-13	3.30	0.188	4.26	4.50	13.4	0.192	2.05	4.20	23.8

[a] Based on an analysis with the flow curve η vs. κ as discussed in the text. [b] Reference 4. [c] This study.

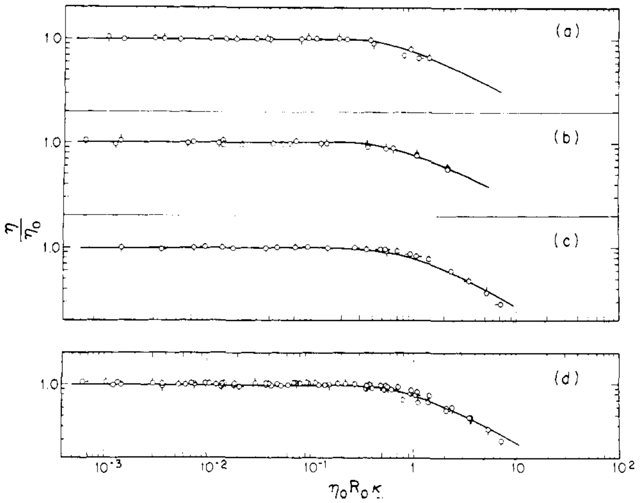

Figure 1. Reduced flow curves for solutions of poly(α-methylstyrene) in α-chloronaphthalene. (a) PαS-9 (0.268 g/ml), temperatures 0.8 °C (ȯ) 32.3, (○—) 49.8 °C (ϙ). (b) PαS-12 (0.192 g/ml), temperatures 0.0 (ȯ), 51.56 °C (ϙ). (c) PαS-13B (0.188 g/ml), temperatures −4.4 (ȯ), 0.0 (—○), 29.3 (ϙ), 43.7 °C (○—). (d) Composite curve for PαS-9 (ȯ), PαS-12 (○—), and PαS-13B (ϙ).

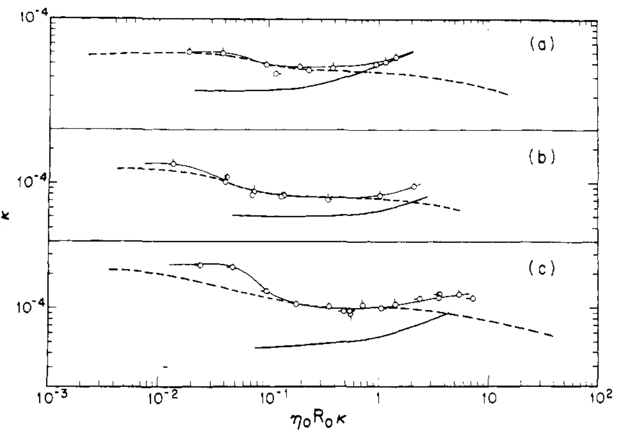

Figure 2. Steady-state recoverable compliance $R_\kappa(\infty,\infty)$ vs. the reduced shear rate for (a) PαS-9, (b) PαS-12, and (c) PαS-13B. The symbols are identified in the caption for Figure 1. The dashed lines show $R_0(\infty,\theta)$ vs. $\eta_0 R_0 \kappa$ with $\kappa^{-1} = \theta$ for these polymers. The heavy curves show S_κ of Sakai et al.[4] for (a) PαS-9, (b) PαS-12, and (c) PαS-13N.

Results and Discussion

(a) Steady State Flow Properties. Reduced flow curves log η_κ/η_0 vs. log $\eta_0 R_0 \kappa$ and plots of the reduced recoverable compliance log $R_\kappa(T/T_0)$ vs. log $\eta_0 R_0 \kappa$ are given in Figures 1 and 2. Values of η_0 and R_0 are entered in Table I. It can be seen that the data obtained for a given sample at temperatures in the range 0 to 50 °C are superposed by the reduction parameter $\eta_0 R_0$, as is expected for a thermorheologically simple material.[6] Moreover, as can be seen in Figure 1d, the flow curves for the three samples are superposed as well on the reduced plot. The flow curves shown in Figures 1a and 1b agree satisfactorily with the data reported by Sakai, Fujimoto, and Nagasawa [4]at 50 °C for samples PαS-9 and -12, allowing for the probable uncertainty in c, see Table I. On the other hand, the limiting viscosity η_0 found here for the PαS-13 solution is less than half the value reported by Sakai et al. We attribute this to some degradation of the polymer, either in the polymer as received or as processed in our laboratory. Analysis of the elution volumes $(V_e)_{max}$ corresponding to the extremum in the refractive index vs. V_e can be made to assess this conclusion if it is assumed that the calibration curve for ln $[\eta]M_w$ vs. V_e applies to these polymers (as would be expected). With the Mark–Houwink coefficients K and a chosen to obtain a reasonable correlation between M_w reported by Sakai et al. (see Table I) and $[\eta]M_w$ determined from $(V_e)_{max}$ for PαS-9 and -12, we obtain a molecular weight of 2.2×10^6 for sample PαS-13, a decrease of about 30% in M_w from the value reported by Sakai et al. This is within probable experimental error of the more accurate estimate that M_w is decreased by 20% to 2.60×10^6 calculated from the difference between values for η_0 reported here and by Sakai et al. (see Table I) under the assumption that $\eta_0 \propto M_w{}^{3.4}c^4$. Since the samples of P$\alpha$S-13 studied here and by Sakai et al. appear to differ, in the following we will designate these as PαS-13B and PαS-13N, respectively, where necessary.

The dependence of R_κ on $\eta_0 R_0 \kappa$ given in Figure 2 differs markedly from the dependence of S_κ on $\eta_0 R_0 \kappa$ reported by Sakai et al. in two respects: (1) the limiting value S_0 at small κ reported by Sakai et al. is consistently smaller than R_0 found here, and (2) the data reported for S_κ vs. κ exhibit an increase of R_κ as κ increases, as compared with the initial decrease in R_κ with increasing κ found here and with other polymers.[1,2] An increase of R_κ with increasing κ is observed for all three samples for $\eta_0 R_0 \kappa$ greater than about 1.

The reduced flow curve given in Figure 1d can be used to estimate R_0 from the flow curves (log η_κ vs. log κ) given by Sakai et al. These R_0 should be consistent with those reported here since this procedure minimizes the effects of possible errors in concentrations, polymer molecular weight or heterogenity, etc., in comparisons of R_0 with S_0 for the samples of Sakai et al. Estimates of R_0 so determined (reduced to 0 °C by the factor $T/273$) are entered in Table I. Inspection of Table I shows that estimates of R_0 so calculated for PαS-9 and -12 are close to the values found here and are larger than S_0 reported by Sakai et al. Their data for S_κ are plotted vs. $\eta_0 R_0 \kappa$ in Figure 2 (using R_0 determined from their flow curves) for comparison with R_κ. It is seen that the two functions differ markedly and show no indication of convergence at small κ. Thus, it appears that either the limiting behavior S_0 at small κ has not yet been reached in the normal stress experiment, or that there is an experimental inconsistency between the determinations of N_1 by Sakai et al and γ_R in this study.

In previous work by Plazek and collaborators[7,8] and in our laboratory[9] it has been found that the data on R_0 for polymers with a narrow molecular weight distribution can be fitted reasonably well by the relation

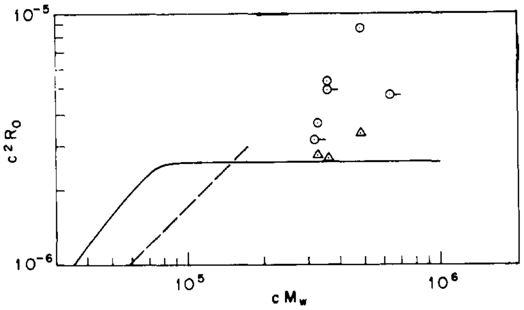

Figure 3. The limiting value R_0 of the steady state compliance at low stress multiplied by c^2 vs. cM_w determined in this study by recoil measuremnts (○) and from the flow curves of Sakai et al.[4] as described in the text (○–). The value of $R_\sigma(\infty,\infty)$ determined in the "nonlinear plateau" region with $0.1 < \eta_0 R_0 \kappa < 5$ is also shown as $c^2R_\sigma(\infty,\infty)$ *vs.* cM_w (△). For each series of points, the data from left to right are for samples 9, 12, and 13, respectively. The dashed line shows the Rouse equation and the solid curve shows the correlation between c^2R_0 and cM_w observed with polystyrenes.[7–9]

$$c^2R_0 = (2M_c'/5RT)(cM/M_c')^\alpha \tag{4}$$

with

$$\alpha = \begin{cases} 1 \text{ for } cM \le M_c' \\ 0 \text{ for } cM > M_c' \end{cases}$$

Graessley[10] suggests that M_c' is equal to $k\rho M_e$, where M_e is the molecular weight between entanglement loci, ρ is the polymer density, and k is a constant of the order 8–10. Equation 4 reduces to the steady state compliance $(R_0)_{\mathrm{ROUSE}}$ equal to $(2/5)(M/cRT)$ calculated by Rouse[11] for $cM < M_c'$. In fact, a slightly better fit with experimental data (for cM near M_c') is obtained with $\alpha = 1.43$ for $cM \le M_c'$. The values of R_0 determined in this study and those deduced from the flow curves reported by Sakai et al. are compared with the data on polystyrenes and eq 4 in Figure 3.

It appears that R_0 for PαS-9 is in reasonable accord with the correlation observed with polystyrene, which would be expected if M_c' is similar for these two polymers. Values of R_0 for PαS-12 and PαS-13N are about 1.5 times higher than might have been expected and R_0 for PαS-13B is 2.5 times larger than expected. These discrepancies may probably be attributed to molecular weight polydispersity, this effect being the more severe with sample PαS-13B which has apparently suffered some degradation. If it is assumed (cf. ref 10) that $(R_0)_{\mathrm{ROUSE}} \propto (M_{z+1}M_z/M_w)$, and that this relation holds in eq 4 even for $cM > M_c'$, then these discrepancies can be accounted for if the samples have a Schulz–Zimm molecular weight distribution with M_w/M_n equal to 1.2 for PαS-12 and 13*N* and 1.67 for PαS-13B. If we presume that the change in PαS-13 has been caused by random chain scission beginning with a monodisperse polymer (assuming a "short zip length"[12]), then one break per molecule will result in 1.36-fold reduction in M_w and cause M_w/M_n to increase to 1.47. These figures are in reasonable accord with the observed effects.

Also included in Figure 3 are values of R_κ determined here in the plateau region beyond the initial drop of the steady state compliance from the value R_0 as κ increases (see Figure 2). Interestingly, this R_κ appears to be at the level expected for R_0 for a monodisperse polymer, suggesting that the effects of polydispersity on R_κ that cause the increase in R_0 at small κ are eliminated at larger κ, a point of view expressed previously by Masuda.[13] We will return to this observation below.

(b) Creep and Recovery as a Function of Shear Stress. The transient creep compliance $J_\sigma(t) = \gamma(t)/\sigma$ has been determined as a function of σ, where $\gamma(t)$ is the strain at time t following application of a shear stress σ. In addition, the transient recovery $R_\sigma(\infty,\theta)$ following cessation of steady state flow at a shear stress σ (e.g., at a shear rate $\mathrm{K} = \sigma/\eta$) has been determined. In previous studies[2] we have reported that $J_\sigma(t)$ is equal to the limiting value $J_0(t)$ at small σ for all σ provided the total strain $\gamma(t)$ is below some critical value γ^*. In order to illustrate this effect it is useful to plot the quantity

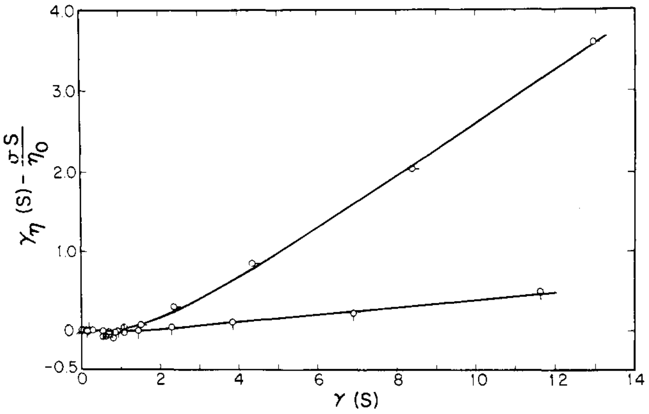

Figure 4. The difference $\gamma_\eta - \sigma S/\eta_0$ vs. $\gamma(S)$ for PαS-9 (0.6 °C) showing the onset of nonlinearity at $\gamma^* = 1.2_5$ for data at stresses of 4850 (ϙ), 15 670, (ȯ), and 15 720, (○–).

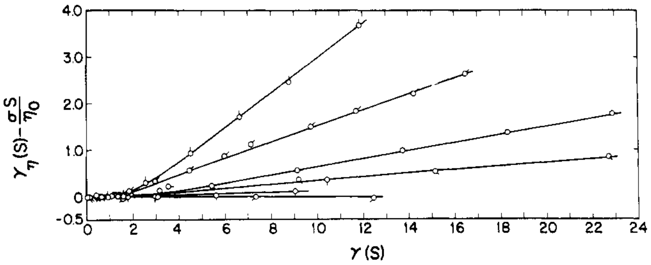

Figure 5. The difference $\gamma_\eta - \sigma S/\eta_0$ vs. $\gamma(S)$ for PαS-12 (0.25 °C) showing the onset of nonlinearity at $\gamma^* = 1.7_5$ for data at stresses of 980 (ϙ), 2340 (○⸜), 3370 (○–), 6050 (○′), and 8.910 dyn/cm² (○⸜).

$$\Delta\gamma(t) = \gamma_\eta(t) - \sigma t/\eta_0 \tag{5}$$

$$\gamma_\eta(t) = \sigma\{J_\sigma(t) - R_\sigma(\infty,t)\} \tag{6}$$

vs. $\gamma(t)$, as is done in Figures 4–6. If linear viscoelastic behavior is obtained, $\Delta\gamma(t)$ is zero. Of course, in the limit of steady state flow attained for large t, $\Delta\gamma(t)$ is equal to $\sigma t(\eta_0 - \eta_{\mathrm{K}})/\eta_0\eta_{\mathrm{K}}$. The data in Figures 4–6 show that $\Delta\gamma(t)$ is zero within experimental error provided $\gamma(t)$ is less than a critical strain γ^* of about 1.2_5, 1.7_5, and 1.0 for samples PαS-9, -12, and -13B, respectively, irrespective of σ over the range studied. This is similar to behavior found with other polymers,[2] but at the present time there are not sufficient systematic data to distinguish with certainty among the effects of concentration, molecular weight, and molecular weight polydispersity on γ^*. Comparison of all the available data suggests, however, that γ^* may be decreased by increased polydispersity, an effect illustrated by γ^* for samples PαS-12 and -13B, and by increased concentration, as illustrated by data samples PαS-9 and -12.

The recoverable compliance $R_\sigma(\infty,\theta)$ as a function of the time θ of recovery following steady state flow under a shear stress σ is shown as a function of θ in Figure 7 for samples PαS-9, -12, and -13B. It can be seen that for the behavior at short time, e.g., θ/η_0R_0 less than about 5, $R_\sigma(\infty,\theta)$ is independent of σ, even for σ large enough so that the steady state viscosity η_κ is less than η_0. The data in this region show $R_\sigma(\infty,\theta)$ to be nearly independent of θ as well. The data on sample PαS-9 and PαS-13B contrast sharply in that a substantial further increase to a (terminal?) plateau is observed with the

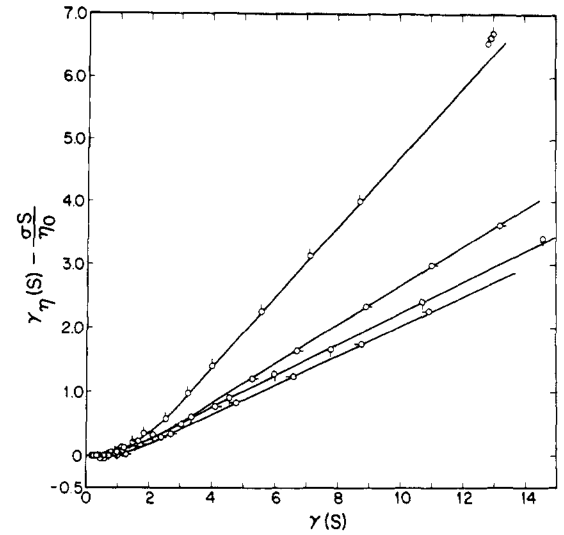

Figure 6. The difference $\gamma_\eta - \sigma S/\eta_0$ vs. $\gamma(S)$ for PαS-13B (1 °C) showing the onset of nonlinearity at $\gamma^* = 1.0$ for data at stresses of 3540 (–○), 4540 (○̣), 6340 (○̇), and 8.270 dyn/cm^2 (○).

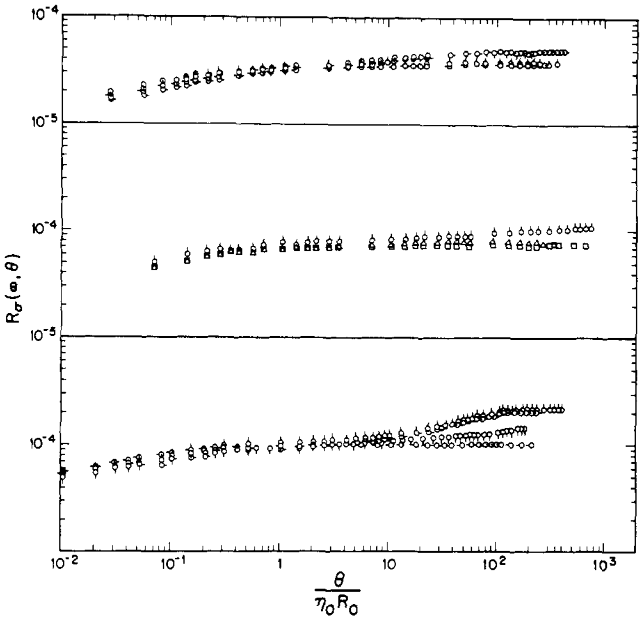

Figure 7. The recoverable compliance following steady state flow vs. the reduced time of recovery. Top: PαS-9 (0.8 °C) for stresses of 383 (○–), 761 (○̣) 1940 (○̇) and 3830 dyn/cm^2 (–○). Middle: PαS-12 (0.25 °C) for stresses of 103 (○–, ○̣), 143 (–○), 289 (○̇), 511 (△), and 952 dyn/cm^2 (□). Bottom: PαS-13B (0 °C) for stresses of 100 (○–), 199 (○̇), 402 (○̣), and 433 dyn/cm^2 (–○).

latter for $\theta/\eta_0 R_0$ greater than 5, whereas only a modest rise is observed with PαS-9 in the similar time interval. An intermediate increase of $R_\sigma(\infty,\theta)$ at large $\theta/\eta_0 R_0$ is observed with sample PαS-12. In all three cases, the increase in $R_\sigma(\infty,\theta)$ becomes smaller with increasing σ until finally $R_\sigma(\infty,\theta)$ is nearly a continuation of the plateau level observed with $\theta/\eta_0 R_0 < 5$. It is this R_κ, plotted as the triangles in Figure 3, that appears to be in accord with the compliance predicted by eq 4 for monodisperse polymers.

Conclusions

The decrease of R_κ with increasing κ found here is consistent with our previous results on concentrated solutions of polystyrene, polyisobutylene, poly(vinyl acetate),[2] and a heterocyclic polymer BBB,[1,14] including some blends of monodisperse polystyrenes.[9] Since with the polymers we have studied previously R_κ was found to decrease (or remain constant) with increasing κ, one of the initial motivations for this study was the comparison of R_κ with S_κ for samples for which S_κ was reported to increase with increasing κ.[4] Because the anticipated equivalence of R_0 and S_0 has a firm theoretical basis[5] and should be expected to apply here, the substantial discrepancy between R_0 found here and S_0 reported by Sakai et al. is unexpected. One possible explanation is that the limiting value of S_κ was not, in fact, reached. In that case the comparison of our results with those of Sakai et al. would indicate that for the samples studied here in the limiting value S_0 is reached only at smaller values of $\eta_0 R_0 \kappa$ than are required for R_κ to reach its limiting value R_0. Indeed, a comparable disparity between R_κ and S_κ has been reported by Stratton and Butcher[15] for data in the range $\eta_0 R_0 \kappa > 1$, but in their case the data on R_κ and S_κ converged for $\eta_0 R_0 \kappa$ less then about 0.1. Similarly, comparisons to be published elsewhere between R_κ determined in our laboratory and S_κ determined by Masuda in Graessley's laboratory have shown that S_κ tends to lie a little below R_κ in the nonlinear region for anionically polymerized polystyrene. The phenomenon may be of general importance, indicating that the determination of S_0 (or, equivalently, R_0) by normal stress measurements may be made even more difficult than is generally appreciated by a tendency of S_κ to be relatively constant over an extended range of κ in the span $0.01 < \eta_0 R_0 \kappa < 1$, allowing false (low) estimates of S_0 from data confined to this range of κ.

Although the composite reduced flow curve η_κ/η_0 vs. $\eta_0 R_0 \kappa$ given in Figure 1d does not extend very far into the nonlinear range, the curve does coincide very well with reduced flow curves for anionically polymerized polystyrenes,[1,9] lending confidence to the estimates of R_0 reported here. For this flow curve, determined with polymers with a narrow molecular weight distribution, $\eta_\kappa/\eta_0 = 0.75$ when $\eta_0 R_0 \kappa = 1$, i.e., when κ^{-1} equals the "time constant" τ_0 defined by $\eta_0 R_0$.

Inspection of Figures 1 and 2 shows that R_κ begins to deviate from R_0 at even smaller κ, where the effects on η_κ are yet negligible. Just as one sometimes loosely compares the "experimental time" κ^{-1} with the average molecular relaxation time constant, here represented by $\eta_0 R_0$, it is natural to make a comparison between R_κ at a reduced shear rate $\eta_0 R_0 \kappa$ and $R_0(\infty,\theta)$ at a reduced reciprocal time $\eta_0 R_0 \theta^{-1}$. Thus, in Figure 2 $R_0(\infty,\theta)$ is plotted as a function of $\eta_0 R_0 \theta^{-1}$ for comparison with the nonlinear function R_κ vs. $\eta_0 R_0 \kappa$. It may be seen that a good correspondence is found between R_κ and $R_0(\infty,\theta)$ with samples PαS-9 and -12 for $\eta_0 R_0 \kappa < 1$ and that the data on PαS-13B are at least in qualitative accord. It will be of interest, therefore, to examine the correspondence between R_κ and $R_0(\infty,\theta = \kappa^{-1})$ in future studies. (Alternatively, the comparison might be made between R_κ and the dynamic storage compliance $J'(\omega)$, with $\omega = \kappa$, inasmuch as $J'(\omega)$ and $R_0(\infty,\theta = \omega^{-1})$ are similar in the region of θ of interest here.) At this point, it appears that a general agreement between R_κ and $R_0(\infty,\theta = \kappa^{-1})$ would be fortuitous, even if such should be limited to the region $\theta > \eta_0 R_0$ of the terminal response. Nonetheless, at the present time, such a correspondence may be the best available way to predict R_κ if the nonlinear data are lacking.

It is also worth noting that $R_0(\infty,\theta)$ reaches its terminal level R_0 only for $\theta/\eta_0 R_0$ greater than 100 to 1000 for the samples studied here. Presumably, a comparable time is required for the normal stress to reach its steady state value N_1.

The total strain criterion for the appearance of nonlinear creep behavior found here will be discussed in more detail elsewhere. Of course, if σ is small enough, the creep behavior should be linear whatever the imposed strain, so that the strain criterion is by itself not sufficient to specify the conditions for nonlinear behavior. In addition, the inverse rate of deformation $(d\gamma(t)/dt)^{-1}$ must also be large compared with some material response time, such as η_0R_0. For these samples studied here, for example, it is necessary for $\eta_0R_0\kappa$ to be less than 0.01 to ensure linear viscoelastic behavior. For stresses which lead to larger steady state rate of shear κ, the creep behavior will become nonlinear when $\gamma(t) > \gamma^*$. The molecular origin of this behavior is presently a matter for speculation. Following Graessley's[16] analysis of η_κ, we assume that linear viscoelastic behavior will obtain so long as the κ is much less than the reciprocal of a time constant associated with the diffusion processes tending to maintain the molecular distribution characteristic of the quiescent state and that for larger κ the entanglement density is affected with increasing κ. Thus, for large K, approximately equal to $\kappa > (100\eta_0R_0)^{-1}$ for solutions studied here, nonlinear creep behavior develops when the molecular distribution is perturbed so far from the quiescent state that it cannot return to that state in the time available as limited by the deformation rate. This condition, which is given by the critical strain γ^*, may be related to the deformation required to achieve a given separation of the molecular centers of gravity.

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Diffusion of Polystyrene in Binary Solvents Near the Theta State

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ABSTRACT: The diffusion coefficient D of polystyrene near the unperturbed state has been measured by photon-correlation spectroscopy in mixtures of carbon tetrachloride and methanol as a function of polymer molecular weight M (33 000 to 10^6) and concentration c (up to 10 mg/mL) for three solvent compositions with CCl_4 volume fractions $\phi = 0.815$, 0.8025, and 0.790. The hydrodynamic radius a varies as M^b where b decreases from 0.524 through 0.503 to 0.469 (±0.005) as ϕ changes from 0.815 through 0.8025 to 0.790. Thus the intermediate composition represents the "diffusion theta state" with a varying as $M^{1/2}$. The slope of the D–c plots also indicates that A_2 is closest to zero for $\phi = 0.8025$. All three plots of log a against log M are linear and intersect at $M = 80\,000$, so that for $M < 80\,000$, a is greater for the subtheta molecule ($\phi = 0.790$) than the supertheta ($\phi = 0.815$). These results are at variance with the work of Dondos and Benoit who found that A_2 was zero at $\phi = 0.815$ and $[\eta]$ varied as $M^{1/2}$ for $\phi = 0.790$. They also observed nonlinear Stockmayer–Fixman plots which they attributed to a molecular-weight dependence of the preferential adsorption.

In recent years a number of investigations of the equilibrium and dynamic properties of polystyrene molecules in mixed solvents have been carried out using light-scattering and viscometry techniques.[2,3] From such measurements information has been obtained on the second virial coefficient A_2 of the solution, the radius of gyration of the polymer molecule, and the preferential adsorption λ' shown by the polymer for one component of the mixed solvent; λ' is the volume occupied by the excess molecules of the good solvent surrounding a polymer molecule divided by the mass of the polymer molecule. In particular, for systems exhibiting relatively large values of λ', the results of a light-scattering investigation by Dondos and Benoit[2] led them to propose that λ' is a function of polymer molecular weight M through a term depending on polymer segment density: $\lambda' = \lambda'_\infty + A/M^{1/2}$, where A is a constant and λ'_∞ is the limiting value of λ' at large M.

One system of interest which they investigated was polystyrene in mixtures of carbon tetrachloride (solvent) and methanol (precipitant) at 25 °C for volume fractions of carbon tetrachloride ϕ around 0.8. They found that λ' was large for this system, with $\lambda'_\infty = 0.49$ cm^3 g^{-1} and $A = 35$ cm^3 g$^{-1/2}$ for $\phi = 0.79$, and $\lambda'_\infty = 0.43$ cm^3 g^{-1} and $A = 30$ cm^3 g$^{-1/2}$ for $\phi = 0.815$. Furthermore, A_2 was zero when $\phi = 0.815$ whereas the intrinsic viscosity $[\eta]$ varied as $M^{1/2}$ for $\phi = 0.79$. For a single solvent these two conditions are associated with the Flory theta state and coincide at the theta temperature. The failure of these conditions to coincide at a particular mixture composition for the given temperature was explained by Dondos and Benoit in terms of the preferential adsorption which causes the composition of the solvent within the molecule to be different from that outside. As a result the intramolecular and intermolecular segment interactions will be different. The variation of $[\eta]$ as $M^{1/2}$, which implies an unperturbed molecular state, will occur at a different solvent composition to the condition $A_2 = 0$, which corresponds to a zero excluded volume term between molecules. Thus they concluded it was not possible to define a true theta state for a mixed solvent