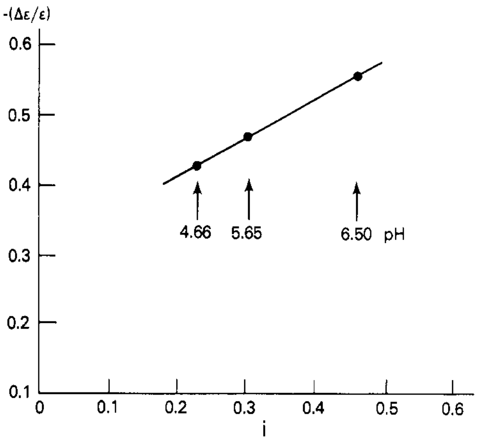

Figure 1. The electric dichroism of poly(A) as a function of the fractional charge density neutralized by condensed counterion in solutions of different pH. The calculation of *i* proceeds as described in the text. Values for this calculation were obtained from the data of D. N. Holcomb and S. N. Timasheff,[14] extrapolated to an ionic strength of 0.8×10^{-4} M K^+ from data at 0.15, 0.01, and 0.001 M KCl. The data are for poly(A) in appropriate 2×10^{-4} M buffers of 2-(*N*-morpholino)ethylsulfonic acid; λ 2520 Å, $E = 9280$ kV/cm.

polarization with respect to their equilibrium nuclear configuration in the absence of the field of either or both their valence electrons, and if they are polyelectrolytes, their associated counterion charges. In the experiment reported here, the counterion charge density of the polyelectrolyte, poly(A), is varied by varying the extent of its protonation in the pH range, 5 to 7, where it has a double helical configuration at the ionic strength used. The electric-field-induced dichroism at moderate fields has been shown to be linearly proportional to the orientation, which in turn has a linear dependence on the induced polariztion.[15,16]

The results are shown in Figure 1 where a linear relationship is observed to hold between the electric-field-induced dichroism of poly(A) and the fraction, *i*, of its phosphate charge which is neutralized by condensed alkali counterions. The predicted dependence of *i* on the pH was calculated from the theories of Manning[6] and of Record[7] who have predicted that *i* is related to the charge density parameter, $\xi = e^2/kTb$, and the degree of protonation of the polyelectrolyte, κ, by the relation $i = (1 - \xi^{-1})(1 - \kappa)$. In the charge density parameter, *e* is the charge on the electron (4.80×10^{-10} esu), ϵ is the bulk dielectric constant, *k* is Boltzman's constant (1.38×10^{-16} erg deg^{-1}/mol^{-1}), *T* is the absolute temperature, and *b* is the average spacing in angstroms of the projection of the charged groups on the axis of the fully extended polyion. Polyelectrolytes with univalent charges spaced less than 7.1 Å apart have such a high charge density that counterions condense from their uniform Debye–Hückel–Bjerrum atmosphere in the solvent to form a highly polarizable hydrated sheath around the polyelectrolyte. Poly(A) (and DNA) with $b \approx 1.7$ Å are just such polyelectrolytes and should be expected to demonstrate appropriate behavior, in this case the observed linear dependence of the dichroism on *i*. The dependence of *i* on α is given above. In turn, the variation of α with pH has been determined empirically from the data of Holcomb and Timasheff.[16] The dependence of the electric dichroism of the polyelectrolyte, poly(riboadenylic acid), on the degree of counterion condensation predicted by the theories of Manning[6] and Record,[7] is thus shown to be linear. Since the orientation is predicted to be linear in the polarization, this result encourages the development of a theory of the orientation of polyelectrolytes in electric fields which adequately accounts for the degree of charge neutralization of the polyelectrolytes by a polarizable distribution of counterions.

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Infinite-Dilution Viscoelastic Properties of Polystyrene of Very High Molecular Weight

Measurements of storage and loss shear moduli of various dilute polymer solutions, extrapolated to infinite dilution to yield the intrinsic moduli, have been compared with the predictions of the Zimm theory[1] as evaluated with exact eigenvalues for an arbitrary degree of hydrodynamic interaction;[2] good agreement has been obtained for flexible linear polymers[3] (provided the product of frequency and solvent viscosity is not so high that local constraints to flexibility influence the response), and conclusions have been drawn concerning the effects of branching and partial rigidity in other types of macromolecules.[4] In the present report, some data are given for flexible linear polymers of extremely high molecular weight.

Two polystyrene samples were generously furnished by Dr. T. Kotani of the Japan Synthetic Rubber Company (JSR). They had been prepared by emulsion polymerization and were believed free of branching.[5] Viscosity-average molecular weights $\bar{M}_\eta$ were determined from intrinsic viscosity measurements at low shear rates and weight to number average molecular weight ratios $\bar{M}_w/\bar{M}_n$ were determined from velocity centrifugation, both measurements in cyclohexane at the Θ temperature, at JSR; $\bar{M}_\eta$ was calculated from the equation $[\eta] = 76 \times 10^{-3} M^{1/2}$. These data are given in Table I. Before use, each sample was extracted with methanol in a Soxhlet extractor for over 12 h and dried under vacuum.

Two solvents were employed: toluene (a very good solvent) at 20 °C, viscosity 0.0059 P, density 0.867 g/mL; and decalin (Aldrich), 53% trans as determined by gas chromatography, 15 °C (the Θ temperature), viscosity 0.0287 P, density 0.887 g/mL.

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Table I
Characterization of Polymers

Code No.	BK2500	IK3000
$\overline{M}_\eta \times 10^{-6\,a}$	18	28
$M_w/M_n{}^a$	1.35	1.20
$[\eta]$, mL/g, decalin, 15 °C,^{b}	300	
$[\eta]$, mL/g, toluene, 20 °C,^{b}	~3100	

[a] At Japan Synthetic Rubber Company. [b] In this study.

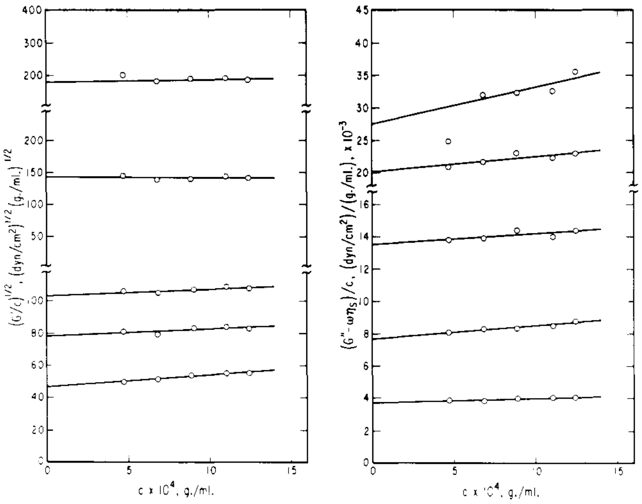

Figure 1. Plots of $(G'/c)^{1/2}$ and $(G''-\omega\eta_s)/c$ against concentration for sample BK2500 in toluene at 20 °C. The frequencies of measurement are, from bottom to top, 103, 418, 1027, 2509, and 6054 Hz.

Solutions were made up with weighed amounts of polymer in small volumetric flasks and stored for several months in the dark. Occasionally the flasks were gently inverted to promote mixing. The decalin solutions were heated to 50 °C for several days before use.

The intrinsic viscosity of BK2500 was measured in both solvents in a Cannon-Ubbelohde four-bulb shear dilution viscosimeter. In decalin, the shear rate was 6.3 to 74 s^{-1} and in toluene, the shear rate was 31 to 360 s^{-1}. No degradation could be detected when solutions were passed through the capillary more than once. In decalin, there was no detectable dependence of viscosity on shear rate; from the value $[\eta] = 300 \pm 10$ mL/g and the equation[6] $[\eta] = 77 \times 10^{-3} M^{1/2}$, M_η is calculated as 15×10^6, in reasonable agreement with the value from JSR. In toluene, the value of $[\eta]$ increased from 2080 to 2680 mL/g with decreasing shear rate, and a very rough extrapolation estimated the limiting value of 3100. This is much higher than would be predicted from the equation[6] $[\eta] = 4.16 \times 10^{-3} M^{0.788}$, which would be approximately 2170 mL/g. It may be consistent with the upward curvature of logarithmic plots of $[\eta]$ against M noted by McIntyre,[7] although data of Fujita[8] show linear plots over very wide ranges of M.

The storage and loss shear moduli, G' and G'', were measured in the Birnboim-Schrag multiple-lumped resonator apparatus[9] with computerized data acquisition and processing system. One aluminum alloy resonator, Mark IV-A, with five working frequencies, was used from 103 to 5800 Hz. The apparatus was filled very slowly by use of a syringe with a 15 gauge needle. The concentration ranges (c) were as follows: toluene, 0.47 to 1.24×10^{-3} g/mL for BK2500, 0.196 to 0.98×10^{-3} for IK3000, fresh solution for each experiment; decalin, 1.46 to 5.3×10^{-3} g/mL, two fresh solutions with two subsequent dilutions of each. At each frequency, $(G'/c)^{1/2}$ and $(G''-\omega\eta_s)/c$ were extrapolated to zero c in the usual manner as illustrated in Figure 1. (Here ω is radian frequency and η_s solvent viscosity.)

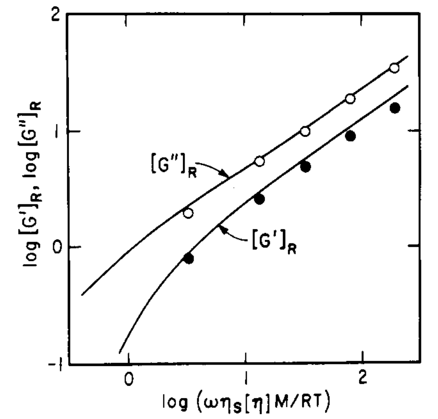

Figure 2. Reduced intrinsic moduli $[G']_R$ (filled circles) and $[G'']_R$ (open circles) plotted logarithmically against reduced frequency $\omega\eta_s[\eta]M/RT$ for BK2500 in decalin at 15 °C. Curves are for the Zimm theory.

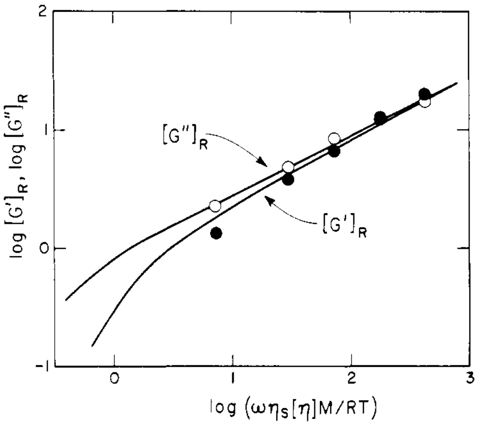

Figure 3. Reduced intrinsic moduli for sample BK2500 in toluene at 20 °C plotted logarithmically against reduced frequency as in Figure 1. Curves are for the Rouse theory.

From the limiting values of G'/c and $(G''-\omega\eta_s)/c$, viz., $[G']$ and $[G'']$, the reduced dimensionless intrinsic moduli, $[G']_R$ and $[G'']_{R'}$, were obtained by multiplying by M/RT.

In Figure 2, $[G']_R$ and $[G'']_R$ are plotted logarithmically against the usual reduced frequency $\omega[\eta]\eta_s M/RT$ for BK2500 in decalin and compared with the Zimm theory for dominant hydrodynamic interaction (hydrodynamic interaction parameter[3] $h^* = 0.25$, number of submolecules N very large). Despite the very high molecular weight, the agreement for $[G'']_R$ is quite good and $[G']_R$ falls near the theoretical curve but apparently with a somewhat lower slope. The data do not extend much into the terminal zone because of the large terminal relaxation time[3] ($\tau_1 = [\eta]\cdot\eta_s M/RTS_1 = 2.3 \times 10^{-3}$ s with $S_1 = 2.37$).

It has been suggested by de Gennes[10] that the behavior of flexible coil molecules in Θ solvents may be complicated by intramolecular entanglements, especially if the molecular weight is very high. That this is plausible can be seen from a rough calculation for the present samples in which the average concentration inside the polymer coil is taken as the reciprocal of the intrinsic viscosity. The product cM is then 50 000 to 60 000 which is sufficiently higher than the average entanglement spacing of the undiluted polymer,[11] $M_e = 18\,000$, to expect some effects of entanglement coupling which could prolong the longest relaxation times. Of course, the concentration of polymer segments is high only near the center of the coil and diminishes with radial distance with a Gaussian dependence. But no departure from the Zimm theory which might be attributed to intramolecular entanglements is evident in the frequency range covered here.

A similar plot for BK2500 in toluene is shown in Figure 3. In this case, the terminal zone is not seen at all. Quite good agreement for $[G'']_R$ is obtained with the Rouse theory, which neglects hydrodynamic interaction; the molecule, highly expanded as demonstrated by the high intrinsic viscosity, appears to be free draining. The points for $[G']_R$ lie close to the theoretical curve but with a slightly higher slope. The terminal relaxation time can be calculated from the same formula with $S_1 = 1.645$ (Rouse value) as $\tau_1 = 6.9 \times 10^{-3}$ s. Data for IK3000 in toluene were not reduced as in Figure 3 because $[\eta]$ in toluene was not available, but when plotted logarithmically as $[G']$ and $[G'']$ against log ω they were indistinguishable from similarly plotted data for BK2500. Also, plots at a finite concentration of about 0.8×10^{-3} g/mL for both samples were identical and similar in shape to Figure 3; at this concentration the product $c[\eta]$ is 2.5 for BK2500 and even greater for IK3000, so a partially free-draining type of frequency dependence might be expected from the behavior previously observed when coils overlap[12] and hydrodynamic interaction is shielded.[13,14] However, it is surprising that the behavior is so nearly Rouse-like after extrapolation to infinite dilution. (The lowest concentration corresponds to $c[\eta] \doteq 1.5$ which is half the value of the midpoint of the transition from Zimm-like to Rouse-like behavior with increasing concentration.) It may be noted that recent examination by Brueggeman, Minnick, and Schrag[15] of frequency dependences, mostly of semidilute solutions, shows Rouse-like behavior when $G'' - \omega\eta'_\infty$ rather than $G'' - \omega\eta_s$ is plotted logarithmically against frequency, where η'_∞ is the limiting value of η' ($= G''/\omega$) at high frequencies. For a very high molecular weight, $\omega(\eta'_\infty - \eta_s)$ is quite small compared with $G'' - \omega\eta_s$ at moderate frequencies, so the behavior observed here is consistent with the analysis of Brueggeman, Minnick, and Schrag.

The fact that the experimental $[G']_R$ has a slope lower than the Zimm theory in decalin and slightly higher than the Rouse theory in toluene has been mentioned. Actually, $[G']_R$ is nearly identical in the two solvents despite the large differences in $[G'']_R$. The significance of this observation is not clear at present.

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