ABB bond angle by the introduction of additional AB–BB bond interactions.[9]

We have determined analytical expressions for the relaxation frequencies for the model in the nondraining limit.[9] The model displays two (±) branches like those discussed by Fixman and Evans;[10] however, the gap between the branches is not associated with $[\eta]_\infty$. This gap is, perhaps, related to a second plateau[11] at higher frequencies (up by 10^2 Hz) with a calculated $[\eta]_\infty'$ down from $[\eta]$ by 10^{-2}–10^{-5} depending on the model parameters. Neglecting terms of order N^{-1} ($N + 1$ is the number of B segments), the dimensionless relaxation frequencies, $\lambda_{k\pm}$, are given by[9]

$$\lambda_{k\pm} = \tfrac{1}{2}\{\lambda_k^*[1 - \tfrac{1}{2}\epsilon_3(1 + \gamma)] + (1 + \gamma)(\epsilon_2 + \epsilon_3)\} \pm \tfrac{1}{2}\{(\lambda_k^*[1 - \tfrac{1}{2}\epsilon_3(1 + \gamma)] + (1 + \gamma)(\epsilon_2 + \epsilon_3))^2 - 4\gamma\lambda_k^*(-\tfrac{1}{2}\epsilon_3\lambda_k^* + \epsilon_2 + \epsilon_3)\}^{1/2} \quad (1)$$

where $\lambda_k^* = 4 \sin^2 [\pi k/2(N + 1)]$, $\gamma = \zeta_B/\zeta_A$ is the ratio of B to A friction coefficients, $\epsilon_2 = (\sigma_B/\sigma_A)^2$, and $3k_BT\epsilon_3/2\sigma_B^2$ is the strength of the AB–AB interaction. The complex frequency dependent viscosity, $[\eta(\omega)]$, is then obtained from the familiar equation,

$$[\eta(\omega)] = \frac{N_Ak_BT}{M\eta_0} \sum_{k,\alpha=\pm} \left[i\omega + \frac{6k_BT\lambda_{k\alpha}}{\sigma_B^2\zeta_B} \right]^{-1} \quad (2)$$

We have evaluated (1) and (2) for some values of the model parameters. A slight plateau is found in the appropriate first plateau frequency regime for large side groups ($\zeta_A > \zeta_B$ and $\sigma_A > \sigma_B$), giving $[\eta]_\infty/[\eta]$ values of a reasonable order of magnitude. An example is displayed in Figure 2 (solid lines) for various values of N with the effective Rouse predictions (dashed lines) wherein the A_i–B_i units are combined into effective, C_i, Rouse ones. Note that the difference between the model and effective Rouse curves for $\omega \rightarrow 0$ and $N = 99$ arises from the $O(N^{-1})$ corrections to (1) which have been included in the calculations.[9] Approximate values of $[\eta]_\infty$ are taken from the curves of Figure 2 from the inflection region on the curves. A plot of $[\eta]_{\text{inflection}}^{\text{approx}}$ vs. N in the insert in Figure 2 demonstrates the approximate molecular weight independence of $[\eta]_{\text{inflection}}^{\text{approx}}$ for large molecular weights in conformity with experimental $[\eta]_\infty$. (At lower molecular weights an N dependence emerges in both cases.) The plateau region in Figure 2 is not as flat and wide as observed experimentally, but perhaps this can be remedied by adjusting the parameters and by introducing additional bond angle constraints as noted above. An additional generalization involves the inclusion of non-nearest-neighbor (i–i ± 2, etc.) interactions as in the model of Simon[12] which does not contain the important side-group motions.

The model is, thus, seen to display the correct qualitative form of $[\eta]_\infty$ as arising from hindered rotation potentials in agreement with the Monte-Carlo calculations of Fixman.[7] Our model, however, explicitly includes the side groups, so studies of perpendicular dielectric relaxation[13] and side-group contributions to flow birefringence can be made within our model.

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Ronald S. Adler* and Karl F. Freed
The James Franck Institute and
The Department of Chemistry
The University of Chicago
Chicago, Illinois 60637

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Dependence of the Electric Field-Induced Orientation of Poly(riboadenylic acid) on Its Polyelectrolyte Properties

The interpretation of the results of electrooptic measurements on the natural nucleic acids and polynucleotides has been hampered by the lack of a suitable theoretical treatment of the mechanism for the orientation of polyelectrolytes in moderate and strong electric fields. Although at least three such treatments have been attempted[1-3] and the subject has been discussed at some length,[4] recent advances in polyelectrolyte theory have not yet been applied successfully to this problem. In an extensive paper on the dichroism of poly(A)[5] we demonstrated the applicability of one of the predictions of polyelectrolyte theory to electrooptic measurements, the independence or stability of the "condensed" counterion density of polyelectrolytes of sufficiently high linear charge density. In a further attempt to understand the orientation of these macromolecules in electric field, we have perturbed their ionic environment to produce predictable changes (from the recent polyelectrolyte theories of Manning,[6] Record,[7] Mandel,[8,9] and McTague and Gibbs[10] and their respective colleagues) in the "condensed" counterion density and observed the resulting effect on the electric-field-induced dichroism. We report here briefly one such experiment, which together with our earlier result[5] and with other measurements[11] support the contention[1,2,12] that the polarization of condensed counterions on these highly charged polyelectrolytes, as described by the polyelectrolyte theories, plays as important a role in their field-induced orientation as they do in their dielectric properties.[13] Hogan et al.[14] have recently adopted a mechanism for the electric-field-induced orientation which differs from the one advanced here and depends on the anisotropic local fields established in the vicinty of the polyelectrolyte as a result of counterion flow. The constancy of the orientation of poly(A) in buffered solutions of different ionic strength[5] does not, however, seem to be in accord with the requirements of their mechanism.

Orientation in an electric field is due to the torque exerted by the field on the induced and/or permanent dipole moments of the molecules in the field. Very large moments can be induced in macromolecules through

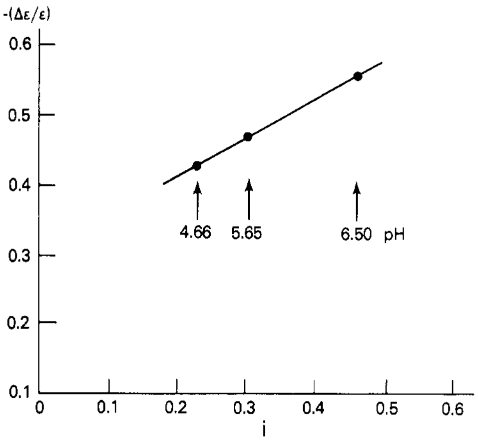

Figure 1. The electric dichroism of poly(A) as a function of the fractional charge density neutralized by condensed counterion in solutions of different pH. The calculation of i proceeds as described in the text. Values for this calculation were obtained from the data of D. N. Holcomb and S. N. Timasheff,[14] 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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Elliot Charney

Laboratory of Chemical Physics,
National Institute of Arthritis, Metabolism
and Digestive Diseases,
National Institutes of Health,
Bethesda, Maryland 20014

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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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