Notes

The Rigidity of Polymer Molecules in Solution. Electric Dichroism of Poly(butyl isocyanates)

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Many large rodlike polymers are flexible in solution. This flexibility is often difficult to assess by dynamo-optical data such as that obtained by viscosity or flow birefringence techniques,[1] though its existence can complicate the interpretation of experimental results. We have been exploring the use of electric field induced dichroism and electric birefringence for obtaining structural parameters of polymeric molecules in solution. The dichroism is defined as the ratio of the difference between the extinctions measured parallel and perpendicular to the applied electric field to the isotropic extinction, $\Delta\epsilon/\epsilon = (\epsilon_{\parallel} - \epsilon_{\perp})/\epsilon$. The theory of electric dichroism of *rigid* molecules predicts that the dichroism at an absorption band maximum will be proportional to the square of the external field strength at low applied fields.[2] For poly(γ-benzyl L-glutamate) of molecular weights greater than 250,000 this proportionality is not observed;[3] on the contrary, the field-strength dependence of the reduced dichroism is largely linear. Since the hydrodynamic behavior of α-helical poly(γ-benzyl L-glutamate) molecules appears to deviate from that of rigid rods at molecular weights greater than 250,000,[4,5] flexibility was invoked as the explanation for this unexpected field strength behavior.[3] However, nonquadratic field strength dependence of electric dichroism and electric birefringence is expected at high field strengths and can have its origin in properties of the polymer and associated solvent other than rigidity. It has not previously been demonstrated that the electric dichroism of rigid polymer rods does in fact show the predicted quadratic dependence on field strength.

The results of several experiments have indicated that the poly(n-alkyl) isocyanates behave as very stiff rods in solution. Burchard[6] concluded from the value of the exponent a, 1.18, in the relation between the intrinsic viscosity $[\eta]$ and the molecular weight M

$$[\eta] = K_1 M^a$$

that poly(n-butyl) isocyanates (PBIC) appear to be very stiff electrically neutral polymers whose properties deviate from those expected for Gaussian behavior in solution. This conclusion was further strengthened by light-scattering measurements on poly(n-hexyl) isocyanates;[7] PBIC has been shown to be a rigid rod by dielectric measurements.[8] Thus these polymers provide a system for testing the validity of the application of electric dichroism theory to large polymers with respect to field strength dependence.

Fractionated PBIC samples of molecular weights in the range from 51,000 to 1,700,000 were used.[9] The solvent was Matheson Coleman and Bell "spectroquality" chloroform. The isotropic extinction coefficients, ϵ, were determined on a Cary Model 14 spectrometer at the same concentrations and spectral band widths used in the dichroism measurements. The electric dichroism apparatus and the methods of calculation are described elsewhere.[3,10] The higher molecular weight samples were heated with stirring in chloroform to ensure complete solution.

PBIC has a broad absorption band in the ultraviolet region with a $\lambda_{\max}$ of 254 nm. The dispersion of the electric dichroism parallels the absorption spectrum. All concentration and field strength studies were carried out at 254 nm.

The insert in the upper left of Figure 1 shows the dependence of the reduced dichroism on PBIC concentration for two different polymers. There is no significant change over a 20-fold increase in concentration, indicating an absence of aggregation effects. Further studies used a concentration of about $2.5 \times 10^{-4} M$.

In Table I are presented the coefficients determined for the equation

$$\Delta\epsilon/\epsilon = aE^2 + bE + c$$

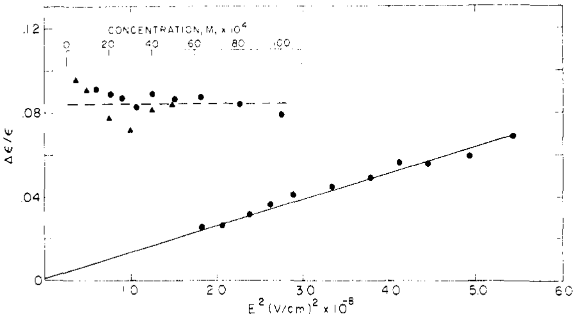

Figure 1. Field strength dependence of the reduced dichroism for polymer 2, M_w = 73,000. Upper left insert: concentration dependence of $\Delta\epsilon/\epsilon$ for PBIC in $CHCl_3$. Results for two different polymers are shown. The average value of $\Delta\epsilon/\epsilon$ = 0.084 ± 0.005.

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(1) See, for example, V. N. Tsvetkov in "Newer Methods of Polymer Characterization," Vol. 6, Bacon Ke, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter XIV.

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(9) These polymers were a gift of Dr. A. J. Bur, who also supplied the molecular weights and molecular weight distributions. We wish to thank Dr. Bur for these samples and for making his results available to us prior to publication.

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TABLE I
COEFFICIENTS OF THE EQUATION $\Delta\epsilon/\epsilon = aE^2 + bE + c$ DETERMINED BY COMPUTER LEAST-SQUARES FIT OF THE EXPERIMENTAL DATA

Polymer	M_w	$a \times 10^{10}$	$b \times 10^6$	$c \times 10^3$	$\sigma^a \times 10^3$
1	51,000	1.11		0.800	3.94
2	73,000	1.23		1.60	1.67
3	133,000	1.20	0.879	−0.648	3.45
4	380,000	1.36	1.31	−1.33	3.76
5	1,700,000	1.24	0.970	−0.719	2.84

[a] σ is the standard deviation of the experimental data from the calculated curve.

by a least-squares computer fit of the data. Figure 1 shows a plot of dichroism data obtained for polymer 2. Polymers 1 and 2, with lower molecular weights, showed a purely quadratic dependence of $\Delta\epsilon/\epsilon$ on field strength. However, the data for polymers 3–5 could be better fitted by the addition of a linear term in E.

The deviation of the field strength from quadratic dependence arising from induced polarization effects is expected to take a form very similar to the directly related deviations from the quadratic electric birefringence.[2] On this basis using the dipole moment data for the 133,000 molecular weight sample from ref 11, and reasonable values for the optical anisotropy, the maximum derivation at field strengths of about 20 kV/cm would lead to a change in slope from the initial slope of the curve of $\Delta\epsilon/\epsilon$ *vs.* E^2 of about 20%. The observed deviation for this sample is 60 ± 5%, clearly outside the range of the deviation from E^2 dependence expected from the polarization phenomena alone. The same is true for the higher molecular weight samples. For the highest, $M_w = 1.7 \times 10^6$, the dichroism in fact is *less* than that observed with the sample of M_w = 380,000, despite the fact that the former has a dipole moment of about 4500 D and the latter a dipole moment of about 2120 D units.[11] There is no mechanism which has been proposed to account for this except a difference in structure such as that produced by flexibility.

The onset of flexibility, as evidenced by the appearance of a significant term linear in E, occurs at a molecular weight between 73,000 and 133,000. This result is consistent with indications from dielectric relaxation studies that PBIC begins to deviate from a rigid rod above 80,000 molecular weight.[11]

The value of the reduced dichroism at a particular field strength should be roughly proportional to the dipole moment of the molecule since this is a major force in its orientation in an electric field. However, Table I shows that polymer 5, with a molecular weight of 1,700,000, has approximately the same field strength dichroism dependence as polymers 3 and 4, which are much smaller. Thus this polymer must be not only flexible but considerably folded.

These experiments demonstrate the validity of the theoretically derived quadratic field strength dependence of electric dichroism for rigid polymer molecules. Furthermore, deviations from quadratic field strength behavior are shown to occur with hydrodynamically flexible polymers and this property may be very useful in determining the flexibility of rodlike polymers.

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The Molecular Weight Fractionation of Polypropylene

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Several studies[1–10] of the fractionation of polypropylene have been reported in the past. This paper also deals with the fractionation of the same polymer, but it differs from the previous studies in the following areas: (1) use of 1,2,4-trichlorobenzene (TCB)–dimethyl phthalate (DMP) as the solvent–nonsolvent system; (2) comparison of the results obtained by fractional precipitation and chromatographic techniques; and (3) treatment of fractionation data according to Weibull's (or Tung's) distribution function.

Experimental Section[11]

A polypropylene homopolymer of Diamond Shamrock Corp. was used in this work. This product had the following physical properties: state, fluff; melt flow rate, 12 g/10 min; intrinsic viscosity in TCB ($[\eta]_{TCB}$), 1.230 dl/g; intrinsic viscosity in Decalin ($[\eta]_{DEC}$), 1.738 dl/g; and isotactic content, 95%.

Fractionation of the polymer was carried out by fractionational precipitation (FPF)[12] and chromatographic (CF)[13] methods. Thermal degradation was minimized by the addition of 0.3% Ionol–antioxidant to TCB and DMP, and also by maintaining a blanket of N_2 gas throughout the fractionation. Both $[\eta]_{TCB}$ and $[\eta]_{DEC}$ were measured at 135° in a Cannon–Fenske viscometer utilizing the classical expression

$$\lim_{c \to 0} (\eta_{sp/c}) = [\eta]$$

Results and Discussion

The following correlation was established between $[\eta]$ in the two solvents used

$$\log [\eta]_{DEC} = (0.15 \pm 0.05) + (0.95 \pm 0.11) \log [\eta]_{TCB} \quad (1)$$

This relation should be found useful as it is easier to run $[\eta]_{TCB}$ than $[\eta]_{DEC}$ because of poor thermal stability of DEC.

Integral molecular weight distribution curves were

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