

Infinite-Dilution Viscoelastic Properties of Poly(*n*-hexyl isocyanate)

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ABSTRACT: The storage and loss shear moduli, G' and G'' , have been measured for dilute solutions of three samples of poly(*n*-hexyl isocyanate) with molecular weights (M) from 0.99 to 10.0×10^5 , by use of the Birnboim—Schrag multiple-lumped resonator. The frequency range was 100 to 6000 Hz, the concentration range 0.2 to 5×10^{-3} g/ml, and the temperatures 0° , 10° , 25° , and 37.8°C . Two solvents were used: Tetralin, and a Tetralin—Aroclor 1254 mixture in proportions close to 1:1 by weight. The molecular-weight distributions were found to be narrow from dielectric dispersion measurements. The extrapolated intrinsic moduli, $[G']$ and $[G'']$, were compared with predictions of various theories. For $M=0.99 \times 10^5$ in both solvents, the low-frequency behavior agreed with the Kirkwood—Auer theory for rigid rods, with the relaxation time predicted from molecular dimensions. Over the entire reduced frequency range, the data could be described closely by a hybrid relaxation spectrum of one terminal relaxation time separated by a gap from a sequence of times spaced as in the Zimm theory (as previously found for poly(γ -benzyl-L-glutamate)). For $M=3.3 \times 10^5$, in Tetralin, the data could be described by the Zimm theory with free draining (*i.e.*, Rouse) and finite number of submolecules $N=10$ or by the Harris—Hearst theory with free draining and a persistence length of 400 Å. For $M=3.3 \times 10^5$ in Tetralin—Aroclor, the molecule appeared more flexible, as shown by a fit to the Zimm theory with $N=200$ and the hydrodynamic interaction parameter $h^*=0.10$. For $M=10.0 \times 10^5$ in Tetralin, the data were described by the Harris—Hearst theory with slight hydrodynamic interaction and a persistence length of 63 Å. The appearance of increased flexibility in the presence of chlorinated hydrocarbon solvent and the decrease in persistence length with increasing molecular weight are consistent with other physical measurements, especially recent experiments of Yu and Rubingh, though the dynamic measurements appear to sample molecular motions which are weighted by shorter lengths than are equilibrium measurements.

KEY WORDS Viscoelasticity / Dilute Solutions / Multiple-Lumped Resonator / Intrinsic Modulus / Poly(*n*-hexyl isocyanate) / Harris—Hearst Theory / Kirkwood—Auer Theory /

Viscoelastic properties of dilute solutions of flexible linear polymers, extrapolated to infinite dilution, have been successfully interpreted¹ by the theory of Zimm² and modifications thereof, based on the bead-spring model of a linear macromolecule. Certain polymers with helical structures, which have much more extended dimensions as deduced from a variety of physical measurements, behave somewhat differently. A recent study of dynamic viscoelastic properties of poly(γ -benzyl-L-glutamate)³ indicated that at low frequencies the response to oscillating shear is primarily a rigid body rotation but at higher frequencies additional loss mechanisms appear, tentatively ascribed to bending motions.

In the present study, dynamic viscoelastic properties of poly(*n*-hexyl isocyanate) have been investigated for three different molecular weights and two different solvents. This molecule is highly extended, as shown by measurements of intrinsic viscosity,⁴⁻⁶ light scattering,⁵⁻⁷ dielectric properties,^{6,8,9} and measurements of forward depolarized Rayleigh spectra.¹⁰ Such data are generally consistent with rigid rod-like behavior at lower molecular weights and random-coil-like behavior at very high molecular weights, with a gradual transition in the molecular weight range from 150,000 to 350,000.⁶ The light scattering and dielectric dispersion data can be interpreted by the Kratky—Porod wormlike coil

model,¹¹ but with a persistence length which decreases progressively with increasing molecular weight. Our viscoelastic measurements similarly show a marked molecular-weight dependence for the molecular motions sampled in this type of experiment.

EXPERIMENTAL

Materials

The polymer, synthesized by anionic polymerization in toluene with sodium biphenyl in tetrahydrofuran as initiator, was generously given us by Professor Hyuk Yu. The sample with lowest molecular weight (Code IV) had a sufficiently sharp molecular-weight distribution, so it was used without fractionation. Other samples were subsequently fractionated by precipitation with methyl alcohol from carbon tetrachloride solution, and two fractions were used. Intrinsic viscosities $[\eta]$ were measured in carbon tetrachloride or *n*-hexane with a Cannon—Fenske variable shear viscometer; in the solvents used for viscoelastic measurements, intrinsic viscosities were obtained, either with the variable shear viscometer or by conventional capillary viscosimetry, and also from the multiple-lumped resonator measurements at low frequencies. The weight-average molecular weight M_w of one sample was determined by light scattering by Dr. D. N. Rubingh,⁶ viscosity-average molecular weights M_v were calculated from intrinsic viscosities in carbon tetrachloride at 25.0° by an equation of Berger and Tidswell,

$$[\eta] = 1.52 \times 10^{-5} M_v^{1.10} \quad (1)$$

or, in *n*-hexane, by interpolation from the data of Rubingh.⁶ Measurements of dielectric dispersion were also made on solutions in carbon tetrachloride at a concentration of about 4×10^{-4} g/ml in the frequency range from 50 to 10⁷ Hz, with equipment generously made available by Professor W. E. Vaughan. The width at half-height, $W/2$, of the dielectric loss ϵ'' (measured in logarithmic decades) was used to estimate the distribution ratio M_w/M_n , as described by Bur and Roberts;⁸ this ratio was less than 1.1 for all samples. Characterization data are given in Table I.

The solvents were pure Tetralin (Aldrich Chem-

Table I. Data for characterization of polymers

Sample code	IV	I ^a	IIIf4 ^a
$\bar{M}_v \times 10^{-5}$	0.99	—	10.0
$\bar{M}_w \times 10^{-5}$	—	3.3	—
$W/2$, decades	1.5	1.5	1.3
\bar{M}_w/\bar{M}_n	<1.1	<1.1	<1.1
$[\eta]$, CCl ₄ , 25°C, ml/g	478 ^b	—	—
$[\eta]$, <i>n</i> -hexane, 25.0°C, ml/g	—	—	3,520 ^b
$[\eta]$, Tetralin, ml/g	326 ^d	990 ^c	2,560 ^b
	350 ^e	950 ^d	—
$[\eta]$, Tetralin—Aroclor	289 ^c	840 ^c	—
	288 ^d	860 ^d	—
L , contour length, Å	1,270	4,200	12,700

^a Fractionated.

^b By Cannon—Fenske variable shear viscometer at 25.0°C.

^c By conventional capillary viscosimetry at 25.0°C.

^d From MLR measurements at 25.0°C.

^e From MLR measurements at 0.0°C.

Table II. Viscosities and densities of solvents

Solvent	Temp, °C	η_s , poise	ρ , g/ml
Tetralin	0.0	0.0358	0.986
	25.0	0.0200	0.966
	37.8	0.0157	0.956
Tetralin—Aroclor	10.0	0.1200	1.199
	25.0	0.0675	1.186

icals) and a mixture of Tetralin and Aroclor 1254 (Monsanto Lot KB-162) containing 49.9-% Aroclor by weight. Their viscosities (η_s) and densities (ρ) are listed in Table II; the former are obtained by the multiple-lumped resonator in the course of the viscoelastic measurements. From comparison of the intrinsic viscosities, it is evident that the molecules are somewhat less extended in Tetralin relative to carbon tetrachloride or *n*-hexane and still less in Tetralin—Aroclor.

Solutions were made up by weight with very gentle stirring at room temperature, and the polymer concentration (c) in g/ml was calculated assuming additivity of volumes, taking the density of the polymer as 1.00 g/ml. The most concentrated solution was measured first and then sequentially diluted to several lower concentrations, usually a total of five or six. The concentration ranges were from 0.7 to $5 \times$

10^{-3} g/ml for the sample of lowest molecular weight, from 0.5 to 2.8×10^{-3} g/ml for the next higher, and from 0.2 to 1.0×10^{-3} g/ml for the highest molecular weight.

Method

The storage and loss shear moduli, G' and G'' , of the solutions were measured with the Birnboim—Schrage multiple-lumped resonator (MLR) with computerized data acquisition and processing system.^{12,13} All solutions were measured with a resonator with 5 working resonances from 100 to 6000 Hz, and for the two higher molecular weight samples in Tetralin an additional resonator with 4 working resonances from 160 to 3400 Hz was used. By making measurements at different temperatures, a wider effective frequency range was achieved.

RESULTS

The quantities $(G'/c)^{1/2}$ and $(G'' - \omega\eta_s)/c$, where ω is the frequency in radians, were plotted against

c and extrapolated to zero c at each frequency, as described in previous studies,^{14,15} to give the corresponding intrinsic quantities $[G']$ and $[G'']$. An example is shown in Figure 1. The initial concentration dependences may be described by the ratios γ' and γ'' which are, respectively, the limiting value at low concentrations of the ratio $(G'/c)^{-1} d(G'/c)/dc$ and the corresponding expression with $G'' - \omega\eta_s$ substituted for G' . These ratios decreased monotonically with increasing frequency, as is usually observed.^{14,15} The ratio $\gamma = \gamma'/\gamma''$ at low frequencies, sometimes used to test the applicability of certain molecular theories, showed considerable scatter; it was about 3 ± 0.3 .

The extrapolated values $[G']$ and $[G'']$ were reduced to $[G']_R = [G']M/RT$ and $[G'']_R = [G'']M/RT$ and are plotted logarithmically against the reduced frequency $\omega\eta_s[\eta]M/RT$ in Figures 2—5.

Lowest Molecular Weight

For $M = 0.99 \times 10^5$, the data in two solvents,

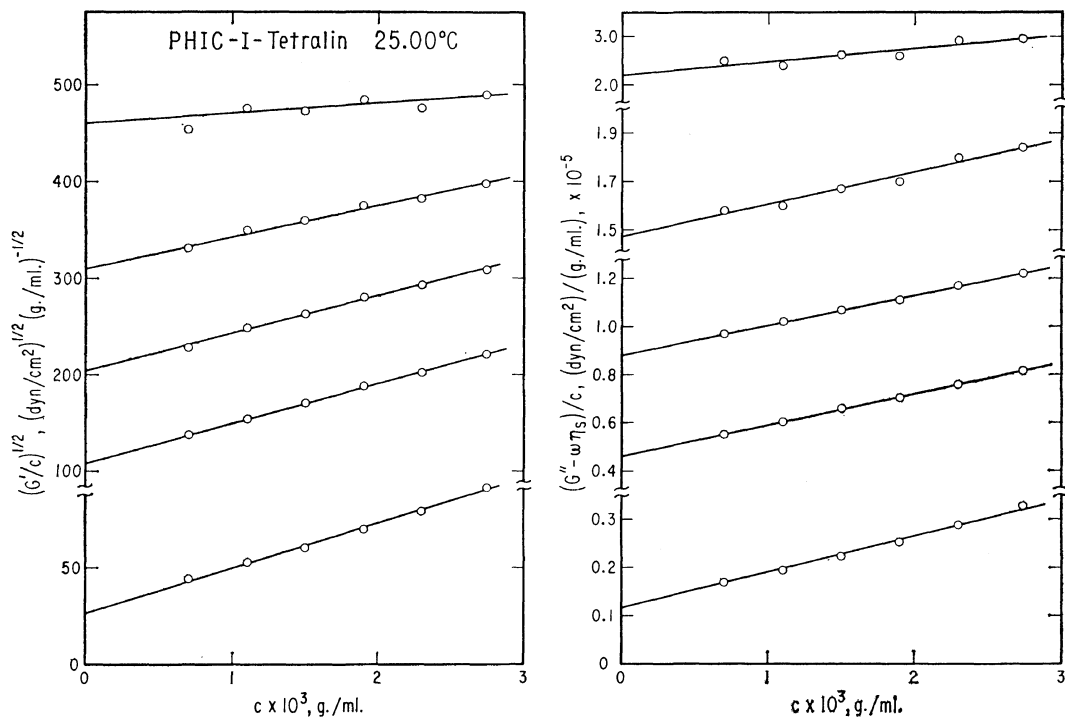


Figure 1. Plots of $(G'/c)^{1/2}$ and $(G'' - \omega\eta_s)/c$ against c for $M = 3.3 \times 10^5$ in Tetralin at 25.0°C , at 5 frequencies (Hz) as follows, bottom to top: 107, 427, 1040, 2520, and 6060. Note that several different ordinate scales are used.

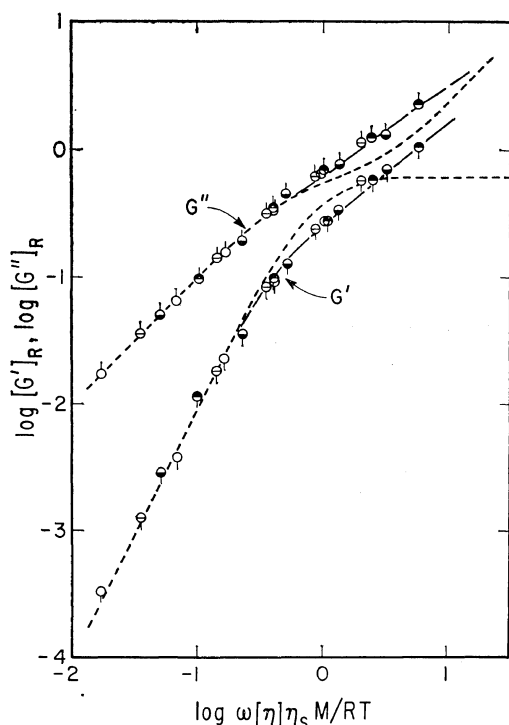


Figure 2. Logarithmic plots of reduced intrinsic shear moduli $[G']_R$ and $[G'']_R$ against $\omega[\eta]_s M/RT$ for $M=0.99 \times 10^5$. Open circles: in Tetralin at 25.0°C; slotted circles, in Tetralin at 0.0°C; bottom half black, in Tetralin—Aroclor at 25.0°C; top half black, in Tetralin—Aroclor at 10.0°C. Short dashes, Kirkwood—Auer theory; long dashes, hybrid model theory with $\tau_1/\tau_0=0.116$, $m_1=0.25$, $m=1.90$.

each at two temperatures, fall closely together on the same pair of curves when reduced in this manner (Figure 2). This indicates that the molecular flexibility is essentially the same in the two solvents despite the difference in average dimensions inferred from the intrinsic viscosities. At low frequencies, the data agree closely with the Kirkwood—Auer theory¹⁶ for rigid rods; on the reduced plot, the critical parameter¹⁵ is $j_{eR}^0 = \lim_{\omega \rightarrow 0} [G']_R/[G'']_R^2$, which is 1.00 for rigid rods and 0.206 for nondraining flexible coils. The experimental value is about 0.94 (Table III). Moreover, the experimental relaxation time τ_0 ($=m[\eta]_s M/RT$, where m is $5/4$)³ agrees very well with that calculated¹⁶ for end-over-end rotation as

Table III. Viscoelastic parameters

$M \times 10^{-5}$	0.99	3.3	10.0
j_{eR}	0.94	0.32	—
$\log \tau_0$, Kirkwood—Auer fit	-4.49 ^a		
$\log \tau_0$, Hybrid fit	-4.31 ^a		
$\log \tau_1$, Hybrid fit	-5.24 ^a		
$\log \tau_0$, eq 2	-4.49	-3.23	
$\log \tau_1$, Zimm		-3.79 ^a	
		-3.94 ^b	
q , Å		400	63

^a For Tetralin solvent at 25°C.

^b In Tetralin—Aroclor, reduced to the viscosity of Tetralin at 25°C.

$$\tau_0 = \pi \eta_s L^3 / 18kT \ln(L/b). \quad (2)$$

This is also shown in Table III. Here the length L is calculated from the degree of polymerization and a projection length per monomer unit taken as 1.8 Å; the unit length b is taken as 6.2 Å. It seems clear that the molecular response would correspond to rigid body rotation if low-frequency oscillating flow alone were considered.

At higher frequencies, however, the data deviate from the rigid rod prediction, as found also for poly(γ -benzyl-L-glutamate).³ Following the treatment used for the latter polymer, it was found that the data conform closely to the prediction for a hybrid spectrum consisting of one rigid body relaxation time and a series of Zimm relaxation times, with a gap between:

$$[G']_R = m_1 \omega^2 \tau_0^2 (1 + \omega^2 \tau_0^2)^{-1} + Z'(\omega \tau_1) \quad (3)$$

$$[G'']_R = m_1 \omega \tau_0 (1 + \omega^2 \tau_0^2)^{-1} + Z''(\omega \tau_1) \quad (4)$$

where Z' and Z'' are the reduced moduli specified by the Zimm theory with the number of submolecules N indefinitely large and the hydrodynamic interaction parameter $h^*=0.25$; τ_1 is the longest relaxation time in the Zimm spectrum. A good fit is obtained with $m_1=0.25$ and $\tau_1/\tau_0=0.116$. For this case, $j_{eR}^0=0.96$, in close agreement. Although τ_0 does not agree quite so well with that calculated from equation 2, the latter value is very sensitive to the somewhat uncertain choice of the monomer projection length. As for poly(benzyl glutamate), the Zimm relaxation times are not attributed to configurational changes of a bead-spring model, but rather to

some kind of flexural motions of a rather stiff structure.

Intermediate Molecular Weight

For $M=3.3 \times 10^5$, the frequency dependences are different in the two solvents, though the compliance parameter j_{eR}^0 is 0.32 in both, intermediate between the predictions for rigid rods and nondraining coils. In Tetralin, the data are plotted both as reduced complex modulus and as the complex intrinsic viscosity ($[\eta]' = [G']_R / \omega \eta_s$, $[\eta]'' = [G]''_R / \omega \eta_s$) normalized by the zero-frequency intrinsic viscosity $[\eta]$ for comparison with theories (Figure 3). The results can be fitted by the free-draining Zimm theory (*i.e.*, Rouse, with

$h^*=0$) with an unusually small number of sub-molecules, $N=10$. This describes the behavior within the frequency range studied, although it will not be satisfactory at high frequencies.¹⁷ Alternatively, the results agree reasonably well with the Harris—Hearst theory¹⁸⁻²⁰ with random fluctuations of curvature of the worm-like coil introduced by thermal motion. The form of the frequency dependence is determined by the parameters λL and λb , where L is the contour length (calculated from a monomer projection of 1.8 Å) and $\lambda = 1/2q$, q being the Kratky—Porod persistence length. The choice of $\lambda L=5$ corresponds to $q=400$ Å. The parameter λb , a measure of hydrodynamic interaction, is taken as 0. The position on the logarithmic frequency scale is predicted in terms of a reduced frequency ω_R (inset in Figure 3) which is $(\omega[\eta]\eta_s M/RT)8qL[1-(q/L)(1-e^{-q/L})]\langle R_G^2 \rangle$, where $\langle R_G^2 \rangle$ is the square of the radius of gyration determined from light scattering;⁸ it agrees with that calculated.

In Tetralin—Aroclor, the frequency depend-

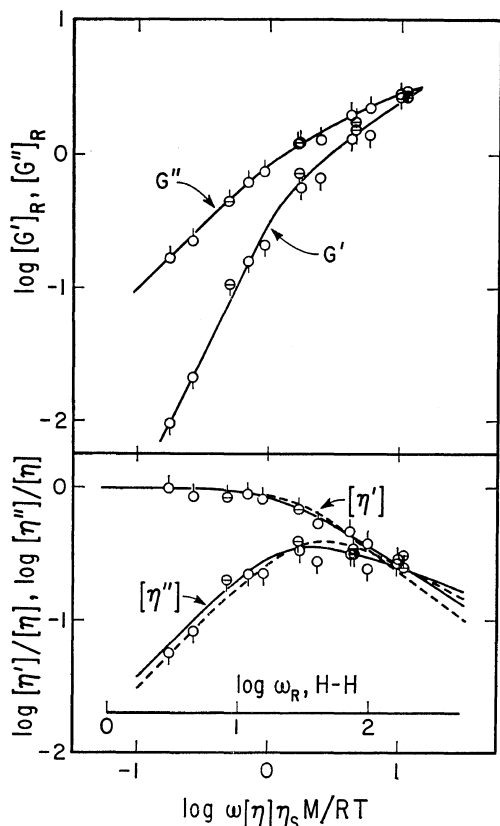


Figure 3. Logarithmic plots of reduced intrinsic shear moduli (top) and components of relative complex intrinsic viscosity (bottom) for $M=3.3 \times 10^5$ in Tetralin. Open circles, 25.0°C; slotted circles, 0.0°C. Solid curves at bottom drawn for Zimm theory with $N=10$, $h^*=0$; dashed curves drawn for Harris—Hearst theory with $\lambda L=5$, $\lambda b=0$ (inset abscissa scale).

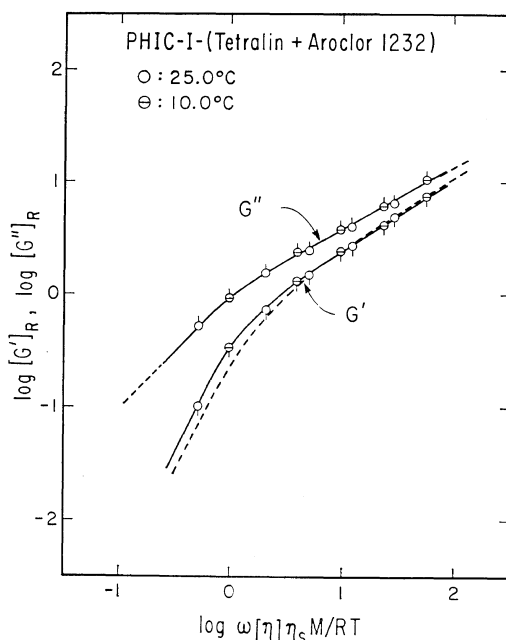


Figure 4. Logarithmic plots of reduced intrinsic shear moduli for $M=3.3 \times 10^5$ in Tetralin—Aroclor. Open circles, 25.0°C; slotted circles, 10.0°C. Dashed curves drawn for Zimm theory with $N=200$, $h^*=0.10$.

ence is qualitatively more like that predicted by the bead-spring model, and can be fitted fairly well by the Zimm theory with $N=200$ and $h^*=0.10$, corresponding to the standard behavior of a flexible coil in a good solvent (Figure 4). This indicates a significant increase in flexibility induced by the chlorinated hydrocarbon, despite the fact that the average dimensions, as gauged by the intrinsic viscosity, are only moderately decreased (Table I).

Highest Molecular Weight

For $M=10.0 \times 10^5$ (in Tetralin only), the terminal zone is not encompassed and j_{eR}^0 is not available. The data are plotted as both intrinsic modulus and intrinsic viscosity in Figure 5, and are fitted to the Harris—Hearst theory with $\lambda L=100$ and $\lambda b=10^{-3}$ (slight hydrodynamic interaction).²¹ This corresponds to $q=63 \text{ \AA}$, so the apparent persistence length decreases sharply

with increasing molecular weight. (Because of the sharp convergence of $[G']_R$ and $[G'']_R$ in the frequency range covered here, the Zimm theory cannot describe this behavior.)

DISCUSSION

Qualitatively, it may be concluded that (a) molecular flexibility increases markedly with molecular weight and (b) the presence of Aroclor appears to increase flexibility for $M=3.3 \times 10^5$ but not for $M=0.99 \times 10^5$.

Studies⁶ of light scattering and intrinsic viscosity in *n*-hexane, when fitted to the Kratky—Porod model, have also shown a persistence length which decreases with increasing molecular weight. (This effect was not observed by Berger and Tidswell,⁵ but their molecular weights did not exceed 400,000.) However, the persistence lengths from these methods are larger than those derived from fitting viscoelasticity measurements to the Harris—Hearst theory. For $M=3.3 \times 10^5$, $q=1000 \text{ \AA}$ from light scattering, 400 \AA from viscoelasticity; for $M=10.0 \times 10^5$, the values are 450 \AA and 63 \AA respectively. In any case, the dependence of q on molecular weight indicates the inadequacy in these treatments of the wormlike coil model.

The effect of Aroclor in increasing flexibility is similar to that of chloroform; intrinsic viscosities and persistence lengths are smaller in this than in other organic solvents.⁵ Also, poly(*n*-butyl isocyanate) has unusually small intrinsic viscosities in chloroform. The effect may be due to a specific interaction of the partially chlorinated hydrocarbons with the carbonyl group of the isocyanate.²² Its absence for low molecular weight (Figure 2) presumably means that the persistence length is greater than the contour length so that the behavior is rod-like even in the presence of the Aroclor.

It is of interest that the hybrid model equations 3 and 4 provide a good description of viscoelastic behavior for two stiff polymers as different as poly(γ -benzyl-L-glutamate) and poly(*n*-hexyl isocyanate), when L/q is small (*e.g.*, less than 4); further studies may show whether this model has general validity. However, the motions associated with the additional relaxation times of the hybrid model remain to be

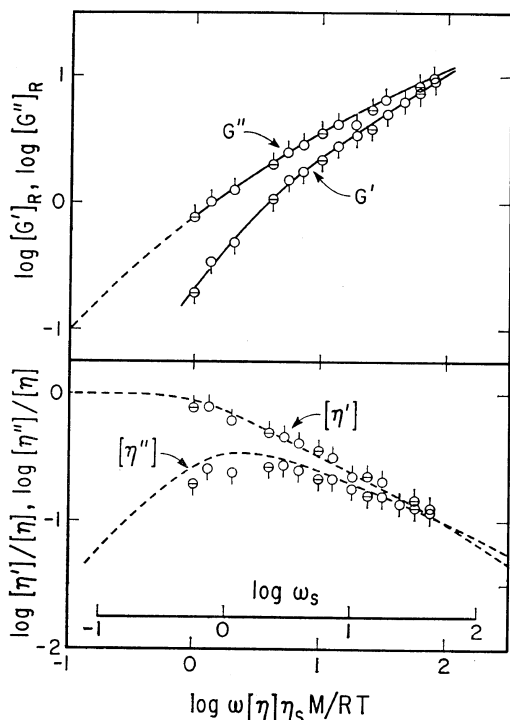


Figure 5. Logarithmic plots of reduced intrinsic shear moduli (top) and components of relative complex intrinsic viscosity (bottom) for $M=10.0 \times 10^5$ in Tetralin at 25.0°C . Dashed curves drawn for Harris—Hearst theory with $\lambda L=100$, $\lambda b=10^{-3}$ (inset abscissa scale).

identified. The steric restrictions which are responsible for the extended configurations of poly(*n*-hexyl isocyanate) undoubtedly leave room for small local adjustments which could permit bending and rotational modes of motion. It is puzzling, however, that these are unaffected by the presence of Aroclor, while the motions associated with longer, less rectilinear molecules are facilitated.

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REFERENCES

1. K. Osaki, *Advan. Polym. Sci.*, **12**, 1 (1973).
2. B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).
3. T. C. Warren, J. L. Schrag, and J. D. Ferry, *Biopolymers*, **12**, 1905 (1973).
4. A. J. Bur and L. J. Fetters, unpublished work.
5. M. N. Berger and B. M. Tidswell, IUPAC International Symposium on Macromolecules, *J. Polym. Sci., Polym. Symp. Ed.*, **42**, 1063 (1973).
6. H. Yu and D. N. Rubingh, in preparation; D. N. Rubingh, Ph. D. Thesis, University of Wisconsin, 1973.
7. L. J. Fetters and H. Yu, *Macromolecules*, **4**, 385 (1971).
8. A. J. Bur and D. E. Roberts, *J. Chem. Phys.*, **51**, 406 (1969).
9. A. J. Bur, *ibid.*, **52**, 3813 (1970).
10. C. D. Han and H. Yu, *ibid.*, **61**, 2650 (1974).
11. O. Kratky and G. Porod, *Rec. Trav. Chem.*, **68**, 1106 (1949).
12. J. L. Schrag and R. M. Johnson, *Rev. Sci. Instrum.*, **42**, 224 (1971).
13. D. J. Massa and J. L. Schrag, *J. Polym. Sci., Part A-2*, **10**, 71 (1972).
14. R. M. Johnson, J. L. Schrag, and J. D. Ferry, *Polymer J.*, **1**, 742 (1970).
15. Y. Mitsuda, J. L. Schrag, and J. D. Ferry, *J. Appl. Polym. Sci.*, **18**, 193 (1974).
16. J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19**, 281 (1951).
17. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York, 1970, p 233.
18. R. A. Harris and J. E. Hearst, *J. Chem. Phys.*, **44**, 2595 (1966).
19. J. E. Hearst, R. A. Harris, and E. Beals, *ibid.*, **45**, 3106 (1966).
20. J. E. Hearst, E. Beals, and R. A. Harris, *ibid.*, **48**, 5371 (1968).
21. We are much indebted to Professor J. E. Hearst for loan of the computer program with which the necessary numerical calculations were performed.
22. M. Goodman and S. Chen, *Macromolecules*, **3**, 398 (1970).