Dielectric Relaxation of Rod-Like Poly(n-hexyl isocyanate) in Nonpolar Solvents[1]

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ABSTRACT: The complex dielectric permittivity of a low molecular weight sample of poly(n-hexyl isocyanate) has been measured over a range of audio frequencies in carbon tetrachloride, n-heptane, and cyclohexane in the range 15° to 55°. The change of the rate of dielectric relaxation with temperature is unusually rapid which indicates a failure of the rigid rod model applied to this system. Several alternatives are assessed and an explanation is presented which presumes a nonvanishing coefficient of linear expansion. Independent methods of evaluating this coefficient lead to the same result and it seems likely that local conformational changes with temperature cause a variation in the monomeric projection length.

During the past decade the poly(n-alkyl isocyanates) have been studied extensively. The motivation has been to characterize the change in molecular structure from rigid rod to random coil using primarily molecular weight and solvent as variables. The thesis research of Rubingh[2] (in which a survey including references to earlier work may be found) employed the techniques of light scattering, intrinsic viscosity, and dielectric relaxation. The viscoelastic behavior of poly(n-hexyl isocyanate) (PHIC) solutions was investigated subsequently.[3] The temperature dependence of the specific viscosity and light scattering of PHIC solutions was the subject of a recent study.[4] The present work reports the temperature dependence of the dielectric relaxation of rod-like PHIC in nonpolar solvents. The motivation for this work was to verify the rod conformation for PHIC using a technique, dielectric relaxation, which is unusually sensitive to molecular extension in solution. We then expected to be able to employ PHIC as a probe of the modification of the dielectric response due to long range dipole–dipole forces in polar solvents. The design of the total experiment has been described elsewhere.[5] The dielectric behavior of PHIC in nonpolar solvents proved anomalous, however, as reported below.

Experimental Section

A sample of PHIC, synthesized by anionic polymerization in toluene with sodium biphenyl as initiator, was given us by Professor Hyuk Yu of the University of Wisconsin–Madison. The weight average molecular weight was determined by light scattering by Rubingh[2] to be $10^5 \pm 5\%$ (g). Solutions in carbon tetrachloride, cyclohexane, and n-heptane were prepared with concentrations in the range 2.3×10^{-4} to 0.1×10^{-4} g/ml. The complex dielectric permittivity was determined at 15, 25, 35, 45, and 55° at 31 frequencies in the range 50 Hz to 100 KHz using a General Radio Company 1620-AP Capacitance Measuring Assembly with external frequency generation and continuous frequency determination. A Balsbaugh Laboratories three-terminal cell, surrounded by a specially constructed thermostat, was used. For each sample three concentrations were used which were $1x$, $2x$, $3x$ relative to each other. Errors in the dielectric loss measurement were usually ±1–2% with a precision ten times better. Errors in the dielectric permittivity measurement were usually ±0.0003 with a precision of ±0.00002. Since the error in the permittivity determination is dominated by its systematic component, increments of dielectric permittivity could be determined to an accuracy better than that estimated from the errors in the individual permittivities.

Solute Morphology

From the width at half-maximum of the dielectric loss–log frequency curve the ratio M_w/M_n may be estimated using the correlation found by Bur.[6] The width of our loss curves gives $M_w/M_n = 1.07$. The weight-average degree of polymerization, N_w, is sufficiently small so that the polymer may be expected to behave as a rigid rod. Evidence for this comes from much previous work on the poly(n-alkyl isocyanates) with the interpretation of experimental results on low molecular weight samples based on the Kirkwood–Auer–Riseman equations[7] (or modifications thereof). The KAR equations for intrinsic viscosity and dielectric relaxation time respectively are

$$[\eta] = \frac{4\pi N_0 N_w^{\,2} L_0^{\,3}}{M_0 9 \times 10^3 \ln (N_w L_0/b)} \tag{1}$$

$$\tau = \frac{\pi \eta_0 N_w^{\,3} L_0^{\,3}}{6KT \ln (N_w L_0/b)} \tag{2}$$

where M_0 is the molecular weight per monomer (127.188 g), L_0 is the mean monomer projection length, η_0 is the solvent viscosity, and b is an insensitive and poorly known parameter which may be taken equal to the molecular diameter (17 Å for PHIC). Although L_0 values determined from eq 1 and 2 or from light scattering studies and X-ray crystallography differ among themselves,[8] the predicted functional dependence on N_w and M_0 appears to hold. Actually the variables of the experiment are M_w and M_0 but a transformation may be effected using $N_w = M_w/M_0$. Bur and Fetters[8] made intrinsic viscosity determinations on solutions of well characterized low molecular weight samples of poly(n-butyl isocyanate) and poly(n-octyl isocyanate) and found the (derived) N_w, M_0 dependence of eq 1 consistent with the observations. The dependence of dielectric relaxation time on N_w predicted by eq 2 was verified by Bur and Roberts[9] for PBIC in carbon tetrachloride at 23° (our average relaxation time for PHIC in carbon tetrachloride at 25° lies on the Bur–Roberts line when compared at the same degree of polymerization with a hypothesis that L_0 is not different among the n-butyl and n-hexyl polymers) and by Rubingh and Yu[2] for PHIC in n-hexane at 25°.

Results and Discussion

Since low frequencies are employed in this work a conduction contribution to the dielectric loss may be observed. In fact a small increase in loss at the lowest frequencies was observed. The loss in excess of what might be expected by extrapolation of the loss–log frequency curve to low frequencies appeared to be inversely proportional to frequency and may be realistically attributed to conduction of the solvent and polymer. Measurements of the loss of the pure solvents showed similar dependence of the total loss. An estimate of the solution conductivity was made and the corresponding loss subtracted from the individual total losses observed. Only the losses at the lowest frequencies had significant changes from the total observed loss and the low frequency points are not strongly weighted in the

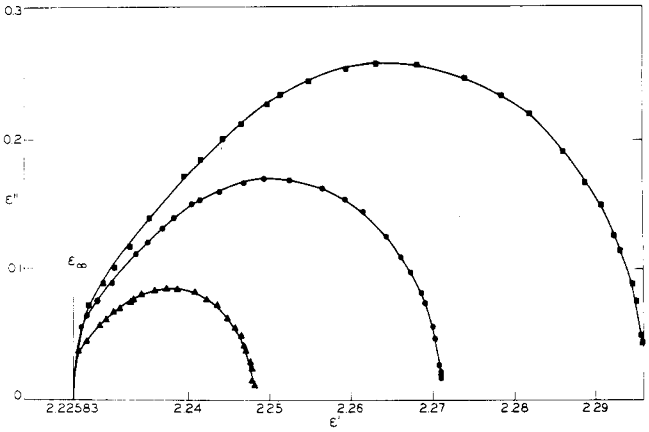

Figure 1. Cole–Cole plots for PHIC in carbon tetrachloride at 25°. Concentrations are $1x$, $2x$, $3x$; $3x = 2.51 \times 10^{-5}$ g/ml. The vertical bar shows the solvent dielectric constant.

subsequent analysis. The dielectric permittivity is unaffected by the presence of conduction.

The large dipole moments (about 1000 D) of the polymer molecules allow measurement on solutions of very low concentration. To verify the absence of close range solute–solute interactions and to suppress the effect of random errors (by expansion of the amount of raw data) three different concentrations for each solvent–temperature pair were employed. No systematic departures from linear dependence of the permittivity and loss on concentration could be detected and there was no apparent shift of the frequency of maximum loss with concentration (lines drawn from ϵ_∞ in Figure 1 should intercept points of the same frequency at relative distances $1x$, $2x$, $3x$). Shift factors, described below, also showed no systematic variation with concentration.

The entire range of dielectric absorption is covered by the available frequencies. This is evident from the Cole–Cole plots of Figure 1 in which the limiting value of the permittivity at high frequencies, ϵ_∞, coincides with the static dielectric constant of the solvent. This is in accord with previous work[10] and shows that no measurable dielectric dispersion, due to chain flexibility for example, occurs at higher frequencies.

In light of the finding (in previous work—described above) of the predicted functional dependence of eq 1 and 2 on N_w and M_0, one may inquire whether the KAR (and many similar models) prediction that $[\eta]$ and $T\tau/\eta_0$ are temperature independent holds. Recent data indicate that neither prediction is correct for PHIC.

Table I
Observed and Calculated Values of ϵ_r'' (Carbon Tetrachloride, 55°)

Frequency, Hz	ϵ_r'' Obsd	ϵ_r'' Calcd
99,965	0.117	0.154
75,088	0.143	0.175
59,325	0.179	0.197
49,825	0.206	0.215
39,953	0.237	0.241
30,026	0.275	0.277
20,078	0.321	0.323
17,036	0.338	0.339
13,977	0.352	0.352
12,022	0.361	0.359
9,960	0.365	0.363
9,001	0.367	0.363
7,485	0.365	0.359
5,917	0.352	0.346
4,999	0.336	0.332
4,001	0.285	0.308
2,994	0.273	0.269
2,407	0.239	0.237
2,000	0.207	0.209
1,499	0.170	0.167
1,196	0.142	0.138
1,000	0.116	0.118
793	0.099	0.095
698	0.087	0.084
500	0.059	0.061
400	0.046	0.049
200	0.016	0.025
120	0.008	0.015
100	0.000	0.012
60	0.000	0.007
50	0.000	0.006

In order to provide a basis for comparison of the different solvent–temperature–concentration runs, it is convenient to form the reduced quantities $\epsilon_r'' = \epsilon''/(\epsilon_0 - \epsilon_\infty)$ and $\epsilon_r' = (\epsilon' - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty)$ where ϵ'' is the dielectric loss, ϵ' is the dielectric permittivity, ϵ_0 is the limiting permittivity value at low frequencies (static dielectric constant of the solution), and ϵ_∞ is the limiting permittivity at high frequencies (static dielectric constant of the solvent). By virtue of the linear dependence of permittivity and loss on concentration these reduced quantities are concentration independent; it is also found that plots of ϵ_r'' (and ϵ_r') vs. log frequency have the same shape for each solvent–temperature pair. The various curves are shifted relative to each other along the log frequency axis. This finding means that although there is a distribution of molecular lengths in the polymer, when conditions are changed all relaxation times change by the same factor. Since this is a prediction of the KAR model, the result is perhaps not surprising. The translation of individual ϵ_r'' (or ϵ_r') versus log f curves so they superimpose was accomplished in the following manner. An interpolation formula for the loss measurements in carbon tetrachloride at 25° (these appear to be the most accurate as they employ the highest concentrations) was generated by fitting to the prediction generated from using an empirical distribution function for relaxation times. This function was

$$f(\tau) = H_1\delta(\tau_1) + H_2/\tau \qquad (\tau_2 \leq \tau \leq \tau_3)$$

with $H_1 = 0.08825$, $H_2 = 0.3365$, $\tau_1 = 1.566 \times 10^{-6}$, $\tau_2 = 8.714 \times 10^{-6}$, $\tau_3 = 1.309 \times 10^{-4}$. (The small (9%) delta function contribution is needed to account for a slight asymmetry of the loss–log frequency curve. This type of function was also used by Bur.[6]) Then the factor by which the frequencies of the other loss curves should be scaled to provide best (weighted least squares) superposition on the master curve was found. A master curve for the ϵ_r' data was generated from the distribution function and the ϵ_r' curves were shifted similarly. A second set of carbon tetrachloride determinations was made to test the reproducibility of the experiment. The set of superpositions was successful considering the experimental errors (a few percent for ϵ_r'' and ϵ_r' except for very low and very high frequencies). This does not necessarily mean that $T\tau \propto \eta_0$ but rather that the shift parameter (C) is merely length independent. A back calculation of ϵ_r'' for a (typical) concentration of 5.0×10^{-5} g/ml in carbon tetrachloride at 55° is shown in Table I. The residuals are used by the computer program to generate an estimate of the error in C. In this case we find $C = 2.04 \pm$

Table II
Temperature Dependence of Dielectric Relaxation[a]

	T, °C	ln $(T/C)_{\mathrm{obsd}}$	ln $(T/C)_{\mathrm{calcd}}$
Carbon tetrachloride	14.75	5.88	5.89
$\Delta H_\epsilon^{\mathrm{system}} = 3.878$	25.05	5.66	5.65
$\Delta H_{\mathrm{V}}^{\mathrm{solvent}} = 2.491$	34.75	5.45	5.45
$x = 1.557$	45.0	5.26	5.24
	55.2	5.04	5.05
n-Heptane	14.65	5.01	5.00
$\Delta H_\epsilon^{\mathrm{system}} = 3.168$	25.04	4.76	4.80
$\Delta H_{\mathrm{V}}^{\mathrm{solvent}} = 1.911$	34.75	4.66	4.64
$x = 1.658$	45.0	4.48	4.47
	55.2	4.31	4.31
Cyclohexane	14.45	5.93	5.94
$\Delta H_\epsilon^{\mathrm{system}} = 4.242$	25.04	5.68	5.68
$\Delta H_{\mathrm{V}}^{\mathrm{solvent}} = 2.905$	34.75	5.47	5.45
$x = 1.460$	45.0	5.23	5.23
	55.2	5.01	5.02

[a] The C values used are weighted averages of individual C's for each solvent-temperature combination. ΔH in cal.

0.04 which is typical of the derived errors in C found in this work. In the fitting process ϵ_∞ as well as C was treated as a variable. For the lower temperatures this made little difference, but at 45 and 55° the cell became more flexible and introduction of the sample caused a small change in geometrical capacitance which shifted the calculated values of all permittivities (but not ϵ_∞ which was derived initially from separate measurements on the solvent) by an amount which was a significant fraction of $\epsilon_0 - \epsilon_\infty$. With ϵ_∞ constrained to its expected value, the residuals would show very large systematic trends; with ϵ_∞ floating such trends were absent.

It became evident very early in this work that $C\eta_0 298.16/\eta_{\mathrm{CCl_4},25°}T$ did not equal unity as required by eq 1 but that this ratio depended both on solvent and on temperature.[5] The nature of the solvent effect is difficult to characterize by macroscopic methods but analysis of the temperature effect proves illuminating. Eyring's rate theory applied to dielectric relaxation yields[11]

$$\tau = \frac{h}{kT} \exp(-\Delta S_\epsilon/R) \exp(\Delta H_\epsilon/RT) \tag{3}$$

so a plot of ln (T/C) vs. $1/T$ may be expected to be linear with slope $\Delta H_\epsilon^{\mathrm{system}}/R$. The results of such plots are shown in Table II. Similarly one may write

$$\eta_0 = (hN_0\rho/M) \exp(-\Delta S_{\mathrm{V}}/R) \exp(\Delta H_{\mathrm{V}}/RT) \tag{4}$$

and if the temperature dependence of the density is absorbed into the activation enthalpy, one has $T\tau \propto \eta_0^x$ with $x = \Delta H_\epsilon^{\mathrm{system}}/\Delta H_{\mathrm{V}}^{\mathrm{solvent}}$ the so called "Kalman equation".[12] Although the Kalman equation generally holds (with x characteristic of the system), when the temperature dependent dielectric relaxation behavior of noncooperative processes is analyzed, the connection between relaxation time and shear viscosity is tenuous. Nevertheless, it has been common practice to doctor theories of dielectric relaxation by replacing η_0 by η_0^x thus producing an empirical expression. We have surveyed the available dielectric literature to investigate the dependence of x on molecular size and shape. In agreement with a similar study on a smaller sample by Higasi[12] we find that x is close to zero for small symmetrical molecules and tends to unity as the molecular size increases and the molecule becomes irregular in shape. A few instances are found where x exceeds unity but the difference between the value found and unity is less than the error of determination of x. Since the polymer is both large and irregular one expects to find $x = 1$ as predicted by the KAR equation. However the x values found for the systems of this work exceed unity by an amount about ten times the error in x. The difference among the x values (and the number of solvents employed in this study) is sufficiently small that it is not possible to make a strong statement as to whether the departure of x from unity is due to polymer properties alone or whether it depends on the solvent as well (in a specific manner).

Recently Pierre and Desreux[4] have published the results of a study of the temperature dependence of the specific viscosity of PHIC and their results may be interpreted as a failure of the KAR equation for intrinsic viscosity (applied to PHIC solutions).

Several explanations suggest themselves. One might empiricise the KAR equation for τ by replacing η_0 by η_0^x. This is essentially a statement that the local hydrodynamic interaction has been treated improperly. While there is obvious justification for this procedure with respect to the Debye equation[12] when applied to small molecules, in the present instance such substitution seems inappropriate since the polymer molecules are very large. In addition in retrospect the finding that x exceeds unity is without precedent. If the source of the anomaly is due to local solvent effects with the polymer conformation being unchanged with temperature, we may predict that the molecular dipole moment should not change with temperature. A discussion of the temperature dependence of the dipole moment appears below.

It would seem that the molecules do not behave as rigid rods. Among the possibilities are flexing of the polymer chain and cooperative local motions of the ends of the hexyl groups. Either process would be expected to make the relaxation of the orientation polarization less difficult (by providing additional relaxation pathways) and our survey of the x values indicates that the presence of intramolecular motion makes x smaller. This is not surprising since less drastic rearrangement of the neighboring solvent is required for reorientation of the molecular dipole.

Somewhat more attractive is the possibility that the configuration space available for local torsional motions is sufficient so that the pitch of the helix decreases with increasing temperature resulting in a decrease of the mean monomer projection length. In this case the molecular dipole moment would be expected to decrease with increasing temperature (see below).

Using the KAR dependence of τ and $[\eta]$ (or specific viscosity) on L_0 we found the required relative change of L_0 with temperature from ratios of $T/C\eta_0$ (our dielectric data) and from ratios of η_{sp}/c (work of Pierre and Desreux). The analysis requires values for L_0 and b. A range of values covering the physically reasonable L_0–b space was tried and the results were indistinguishable. The results using $L_0 = 1.94$ Å and $b = 17$ Å (at 35°) are shown in Figure 2. The solvent, molecular weight, and type and origin of the data points are indicated on the figure. A least-squares fit to the data gives $L_0/L_0(35°) = 1.0719 - 0.001242t - 0.000022t^2$. The dielectric points lie extremely close to the line (exception heptane 25°). The data show no consistent variation with molecular weight in the range 3×10^4 to 10^5 g but the lines derived from the Pierre and Desreux data for molecular weights 2×10^5 and 6×10^5 show significant deviations. It may be that these molecular weights have become so large that the samples lie outside the rod-like region. In that event the analysis presented here is inappropriate.

In principle one should be able to use the temperature dependence of the dipole moment to decide between the al-

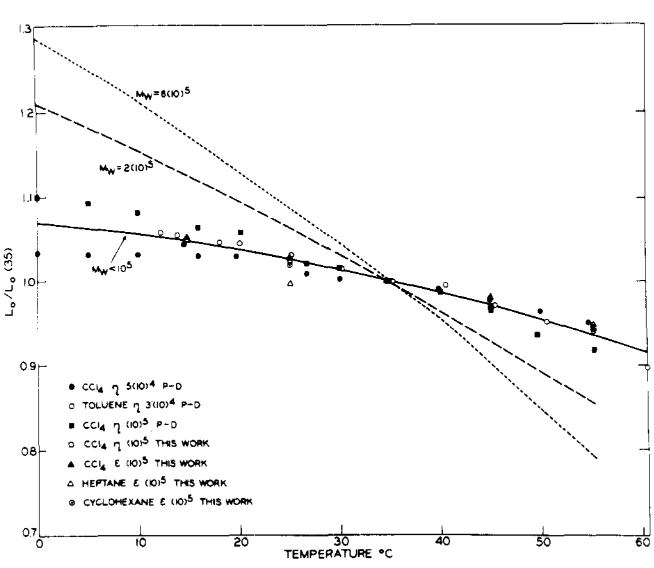

Figure 2. $L_0/L_0(35°)$ as a function of temperature.

ternatives of L_0 independent of temperature and L_0 variation with temperature as shown in Figure 2. From the values of ϵ_0 and ϵ_∞ we determined the average molecular dipole moment at each temperature (for carbon tetrachloride and for n-heptane separately) and attempted to determine the slope of a dipole moment vs. temperature plot. The expected change in dipole moment is small and the errors in the dipole moment determination are sufficiently large (due to the deliberate use of low concentrations) so that either hypothesis is consistent with the data. The dielectric relaxation time is a more sensitive probe of L_0 varying nearly as L_0^3 whereas the dipole moment is linear in L_0.

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References and Notes

(1) This work was supported by the National Science Foundation and by the University of Wisconsin Research Committee.
(2) D. N. Rubingh, Thesis, University of Wisconsin–Madison, 1973.
(3) N. Nemoto, J. L. Schrag, and J. D. Ferry, *Polym. J.*, in press.
(4) J. Pierre and V. Desreux, *Polymer*, **15**, 685 (1974).
(5) J. S. Anderson and W. E. Vaughan, *Annu. Rep., Conf. Electr. Insul. Dielectr. Phenom.*, in press.
(6) A. J. Bur, *J. Chem. Phys.*, **52**, 3813 (1969).
(7) J. Riseman and J. G. Kirkwood in "Rheology", Vol. 1, F. Eirich, Ed., Academic Press, New York, N.Y., 1956, p 508.
(8) A. J. Bur and L. J. Fetters, *Macromolecules*, **6**, 874 (1973).
(9) A. J. Bur and D. E. Roberts, *J. Chem. Phys.*, **51**, 406 (1969).
(10) H. Yu, A. J. Bur, and L. J. Fetters, *J. Chem. Phys.*, **44**, 2568 (1966).
(11) N. Hill et al., "Dielectric Properties and Molecular Behaviour", Van Nostrand-Reinhold, London, 1969.
(12) K. Higasi, "Dielectric Relaxation and Molecular Structure", Research Institute of Applied Electricity, Hokkaido University, Sapporo, 1961.

Light Scattering from Correlated Polymer Systems

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ABSTRACT: The use of irreducible representation coefficients for angular dependent correlations is proposed for light scattering from correlated polymer systems, which have long range orientational correlations. A set of rather general equations for this scattering is derived, using these irreducible representations. The general angular dependence of the scattering of plane polarized light is found, and analytic forms for the characteristic patterns of the V_v and H_v patterns are given. Furthermore, it is shown that the irreducible representations give rather remarkably simple equations for the molecular factor in the scattering cross section. Explicit expressions for thin, oriented rods are given.

The theory of light scattering of molecular systems in which the correlation length is short compared to the wavelength of the light is quite well understood. However, in systems in which the correlation length is long, such as polymeric materials, there is still some room for theoretical developments. There are effects, due to the persistence of long range correlations, which cannot be accounted for by simple theories.

In polymer materials, the studies of Stein and his school[1] reveal that the depolarized component has a peculiar angular dependence. The intensity pattern under crossed polarizers has a characteristic four-leaved clover shape, with axes at π/4 from the axes of the polarizers. The application of the standard theory leads to a maze of complicated integrals, and therefore, the approach has been to formulate a physically simple and reasonable model and then carry out the integrals of the standard theory.[2] This approach is quite successful when the scattering is intramolecular, and the correlation between the molecules is unimportant. A typical example is a spherulitic polymer material.

In fibrous materials, this simple approach cannot be carried to its end, due to the very difficult integrations, in the first place, and to the fact that the interfiber angular correlations cannot be ignored. The problem of the angular correlations is in itself a nontrivial one, and fitting the observations to a specific model may be a scientifically unattractive proposition.

The purpose of the present communication is twofold: first we use a general technique, Racah algebra, to find the angular dependence for the polarized light scattered from an arbitrary but isotropic system; second, we use irreducible correlation function expansions for the angular correlations. This produces some remarkable simplifications in the otherwise very complex equations.

In summary, the theoretical formulation is general and no specific model has to be formulated to interpret the angular dependence of the polarized light. The particular trick of using Racah algebra was first proposed by Ben-Reuven and Gershon,[3] in a study of dynamical effects in inelastic light scattering from molecular fluids. To treat the