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Aggregation of Poly(*n*-hexyl isocyanate) in Toluene. A Dielectric and Electric Birefringence Study

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ABSTRACT: Measurements have been made by dielectric relaxation and electric field birefringence on poly(*n*-hexyl isocyanate)–toluene solutions. Four molecular weights in the range 62 000 to 290 000 have been studied over a wide concentration range. The results by the two methods are in good accord and suggest the existence of both linear head-to-tail and antiparallel side-by-side aggregation for the low molecular weight samples and only antiparallel side-by-side aggregation for the high molecular weight samples. The relative amounts of aggregation have been shown to be concentration and temperature dependant.

The solution properties of poly(alkyl isocyanates) have attracted much interest recently because of their apparent helical conformation and high chain stiffness. Of these isocyanates both the highly polar *n*-butyl isocyanate (PBIC) and *n*-hexyl isocyanate (PHIC) have been studied in various solvents by light scattering,[1,2] viscosity,[3-5] infrared spectroscopy,[6] electric birefringence,[7,8] and dielectric relaxation methods.[9-11] It has been shown by several authors that both these polymers can be described by a wormlike chain model.

It is generally concluded that aggregation does not occur with these systems. However, this conclusion appears to have been made for measurements with nonpolar solvents over a restricted concentration range or for polar solvents. While it is well known that highly polar polypeptide (helical and rodlike) molecules do not generally form aggregates in polar solvents they do so in nonpolar solvents.[12-15] It is therefore perhaps surprising that the isocyanates with similar characteristics do not show the same behavior in nonpolar solvents.

We have chosen to examine this behavior in well fractionated PHIC samples in toluene solutions. Measurements were made by dielectric relaxation and electric field birefringence, both methods being sensitive to structural changes, over a large concentration range. For these solutions temperature dependence studies were also made. The results clearly indicate the existence of aggregation in these solutions and further, we believe, explain the discontinuities recently recorded in temperature dependence studies.[16,17] Finally we compare salient characteristics of the current results with those obtained with polypeptides in nonpolar solvents.[18]

Experimental Section

The PHIC samples were kindly donated by J. Pierre of Professor Desreux's group at Liège University. They were prepared according to the method described by Shashoua[19] and fractionated by precipitation using the carbon tetrachloride–methanol system. Their weight average molecular weights determined by light scattering in chloroform were 62 000, 90 000, 140 000 and 290 000, and these samples will be denoted PHIC (62 000), PHIC (90 000), PHIC (140 000) and PHIC (290 000), respectively. The ratio of the weight to the number average molecular weight as determined by gel permeation chromatography in tetrahydrofuran (THF) at 25 °C was less than 1.2, indicating a low polydispersity.

Solutions were made up with freshly distilled toluene on a gravimetric basis, and measurements were made at room temperature of 23.0 ± 0.5 °C, unless otherwise stated.

The dielectric absorption measurements, in the range 20 Hz to 2 MHz, were made on the two impedance bridges described previously[20] and a General Radio 1616 bridge. Two stainless steel cylindrical cells of air capacitance 13 and 196 pF were used. They were enclosed in a thermostatically controlled chamber which maintained their temperature to within ±0.1 °C.

The birefringence measurements were made by the pulsed dc field method. The sample cell (length 7.5 cm) was placed between crossed Glan-Thomson polarizers with the applied field at 45° to the polarizer azimuth. The system was such that the beam of the low powered He-Ne laser (λ 633 nm) probed the field induced birefringence which was recorded as an intensity change via a red sensitive photomultiplier–storage oscilloscope system. The pulsed dc field was from 0 to 2.5 kV cm^{-1} and of duration variable from 10 μs to 10 ms. This apparatus which included novel features in the cell design will be described in greater detail elsewhere.[21]

Theory

Macromolecules in solution are free to orientate, being on average randomly oriented in the absence of an applied field. If these molecules are polar they tend to align under the application of an electric field. In this situation the polarizability produced is measured through the dielectric constant, and the induced or inherent optical anisotropy is manifest through the induced birefringence. Both the dielectric and the birefringence techniques give information on dipole moments and rotational relaxation times and both have been used in the present work. Each method has its advantages. At low frequencies of applied field we measure the dielectric constant ϵ_0, at high frequencies, where the dipoles have insufficient time to obtain an equilibrium distribution at each stage of the alternating cycle, we measure ϵ_∞. The dielectric increment $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$ is related to the mean-square dipole moment $\overline{\mu^2}$ by the following:

$$\frac{\overline{\mu^2}}{M} = \frac{9kT}{4\pi N_A} \frac{(2\epsilon^2 + n^4)}{\epsilon^2(n^2+2)^2 d} \frac{\Delta\epsilon}{w} \tag{1}$$

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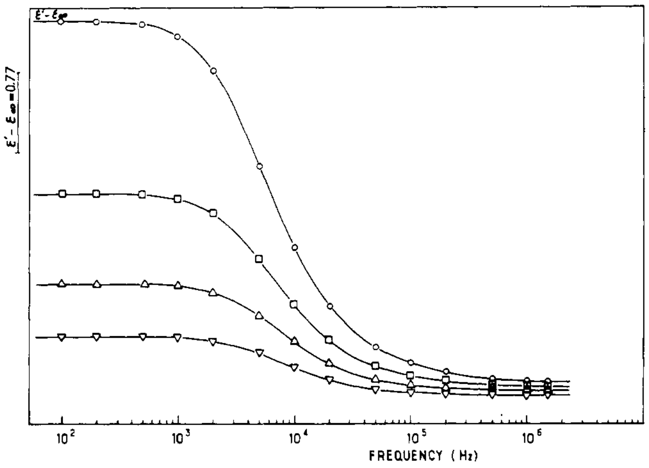

Figure 1. Dielectric absorption curves for PHIC (90 000) in toluene at various concentrations: (○) $w = 5.1 \times 10^{-3}$ g/g; (□) $w = 2.6 \times 10^{-3}$ g/g; (△) $w = 1.4 \times 10^{-3}$ g/g; and (▽) $w = 7.6\ 10^{-4}$ g/g.

where M, w, d, n, ϵ, N_A, k, and T are the mass of solute particles, weight fraction of solute in solution, density of solution, refractive index of solvent, dielectric constant of solvent, Avogadro number, Boltzmann constant, and temperature of the solution in K, respectively. This is obtained from the Barriol Weissbecker formulation[22] based on the Onsager internal field concept[23] for the relation between the applied and effective field orienting the particle. Although this relation is still under discussion, its applicability to similar macromolecular systems has been discussed previously.[15]

The induced birefringence (Δn) may be expressed as a function of the applied field strength E, for low field strengths, the refractive index (n) of the medium, and the volume fraction c_v through the specific Kerr constant K_{sp}, where

$$K_{sp} = \Delta n / c_v n E^2$$

Further[24]

$$K_{sp} = \frac{2\pi}{15n^2}(g_1 - g_2)^0 \left\{ \frac{\mu^2}{k^2T^2} + \frac{(\alpha_1{}^E - \alpha_2{}^E)}{kT} \right\} \qquad (2)$$

where $(g_1 - g_2)^0$ is the optical anisotropy factor, μ is the permanent dipole moment, and $(\alpha_1{}^E - \alpha_2{}^E)$ is the electrical polarizability factor. Here it is assumed that the molecules are rodlike, the dipole moment lies along the major particle axis 1, and the axes of electrical and optical polarizabilities coincide. The minor axis 2 is taken as being cylindrically symmetric ($\mu_2 = \mu_3 = 0$).

The dielectric relaxation gives a critical frequency f_c related to a macromolecular rotation time τ_D ($f_c = \frac{1}{2}\pi\tau_D$). Assuming a Debye type relaxation τ_D is related to the rotational diffusion constant D_r by

$$D_r = \pi f_c = \frac{1}{2\tau_D}$$

It should be noted that f_c, the critical frequency, was taken to be that where the real part of the dielectric constant $\epsilon' = (\epsilon_0 + \epsilon_\infty)/2$.

For the case of pulsed field birefringence the decay of the birefringence after cessation of the applied field may be defined by[25]

$$\Delta n = \Delta n_0 \exp(-t/\tau_B)$$

This corresponds to the situation where the molecular array is reverting to a random situation under the influence of Brownian forces. Δn_0 is the birefringence at a time $t = 0$ given by the termination of the applied field, and $\tau_B = 1/(6D_r)$ (note $\tau_D = 3\tau_B$).

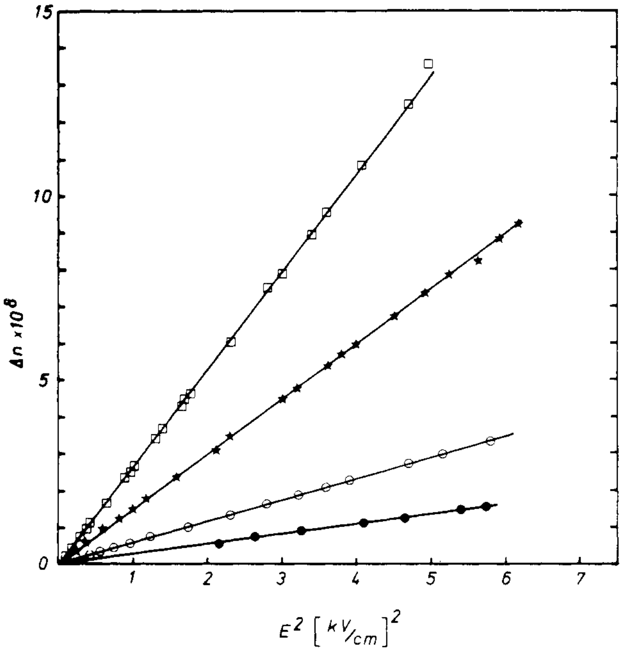

Figure 2. Birefringence vs. applied field squared for PHIC (90 000) in toluene: (□) $w = 5.07 \times 10^{-3}$ g/g: (★) $w = 2.81 \times 10^{-3}$ g/g; (○) $w = 1.04 \times 10^{-3}$ g/g; (●) $w = 5.73 \times 10^{-4}$ g/g.

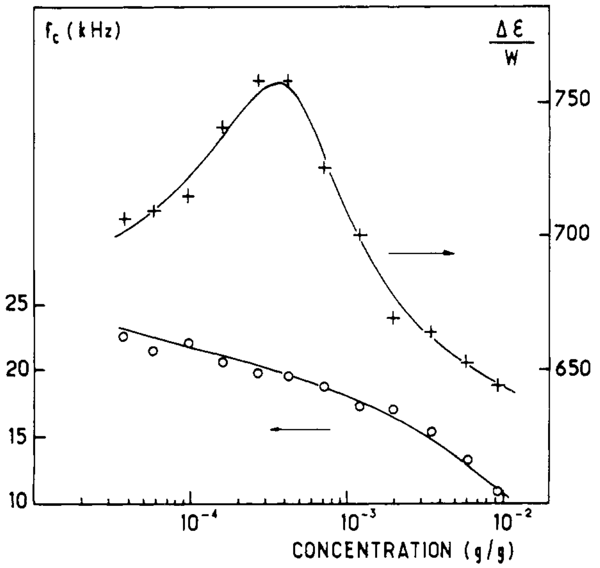

Figure 3. Variation of critical frequency f_c and specific dielectric increment $\Delta\epsilon/w$ with concentration for PHIC (62 000) in toluene.

Results and Discussion

(I) Concentration Studies. Although the possibility of aggregation has been mentioned in connection with viscosity measurements,[4] it has not been discussed. We believe that the results reported herein represent the first detailed study of these effects.

Typical variations of the real part of the dielectric constant with frequency are shown in Figure 1 and of the birefringence with applied field squared in Figure 2 for PHIC (90 000) in toluene. The variations of $\Delta\epsilon/w$ and f_c with concentration for PHIC (62 000) and PHIC (90 000) are shown in Figures 3 and 4. The corresponding Kerr constant behavior with concentration for PHIC (90 000) is given in Figure 5. It can be seen that $\Delta\epsilon/w$ goes through a maximum at a concentration of around 5×10^{-4} g/g for the two low molecular weight samples, whereas f_c shows a continuous increase with dilution. No

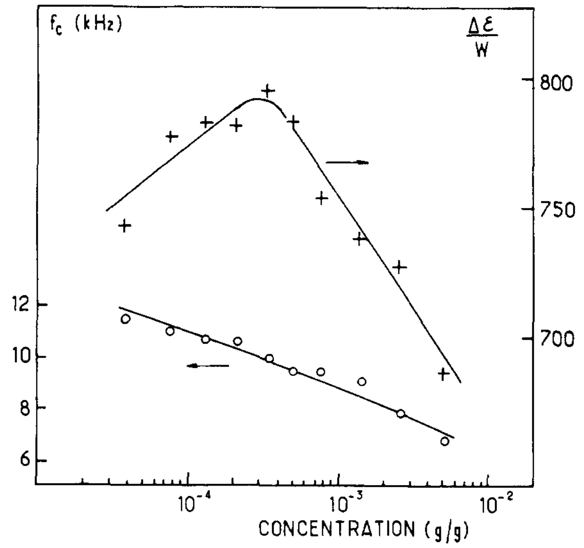

Figure 4. Variation of critical frequency f_c and specific dielectric increment $\Delta\epsilon/w$ with concentration for PHIC (90 000) in toluene.

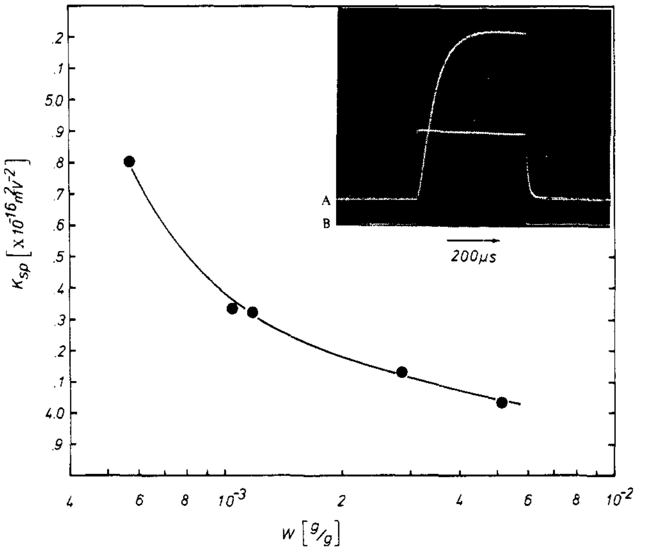

Figure 5. Concentration dependence of the specific Kerr constant for PHIC (90 000). Values of K_{sp} carry a ±5% uncertainty. The inset shows a typical birefringence transient (A) with the applied dc field (B); by quadratic detection $\Delta n = 9 \times 10^{-8}$, $E = 1.86$ kV cm^{-1}, and $w = 5.07 \times 10^{-3}$ g/g.

maximum in $\Delta\epsilon/w$ was observed for the high molecular weight samples (Figure 6) whereas f_c tended toward constancy at low concentrations. This behavior will be discussed below.

Furthermore, the absorption curves (Figure 1) are slightly broader than the ideal Debye relaxation curve at low concentration and always show an increased broadening with increasing concentration (Figure 7) indicating greater polydispersity at higher concentrations. As the recorded changes in $\Delta\epsilon/w$ and f_c with concentration are relatively small it is necessary to comment on the possible effects of experimental error in these measurements. The experimental uncertainty is within the area represented by the symbols in these figures. In Figures 3 and 4 we believe that the scatter of the experimental points around the mean estimated curves is due not to experimental imprecision but to small fluctuations in the aggregation state when the solutions are "handled" for dilution. In Figure 6 error bars have been included where the possible error becomes significant. Here the uncertainty arises at the highest concentrations for PHIC (290 000) when f_c becomes low, because the low frequency limiting of ϵ_0 is not fully saturated at the low frequency limit of the apparatus.

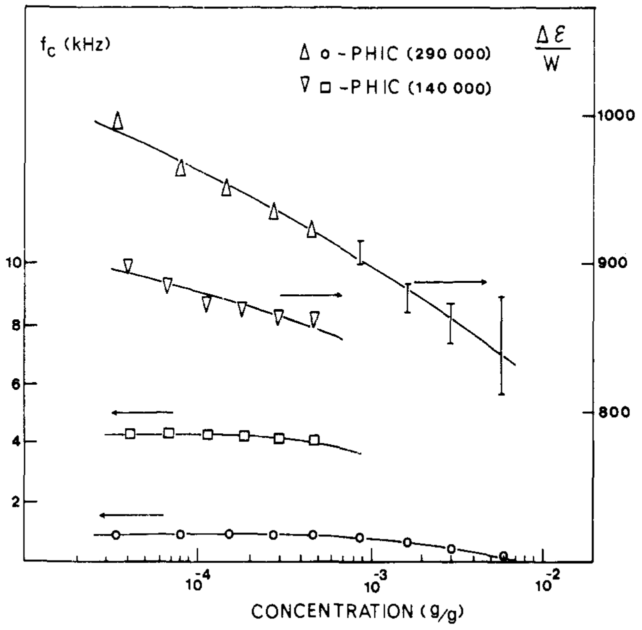

Figure 6. Variation of critical frequency f_c and specific dielectric increment $\Delta\epsilon/w$ with concentration for PHIC (140 000) and PHIC (290 000) in toluene.

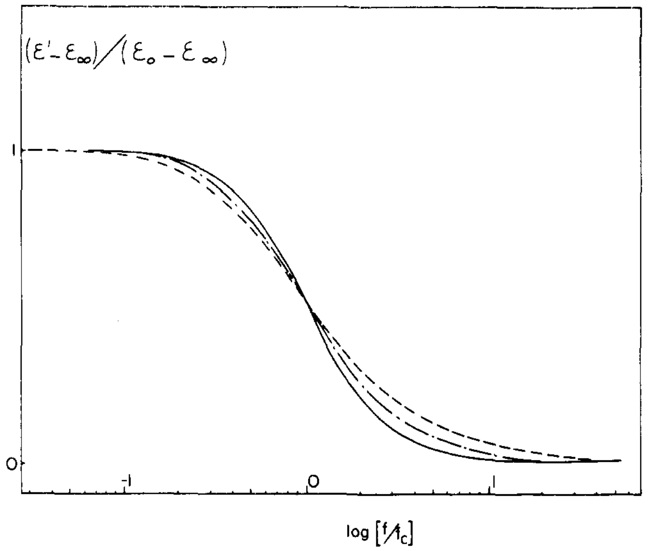

Figure 7. Comparison of the dielectric absorption curves at two extreme concentrations with the Debye curve for single relaxation time, $M = 62\,000$: (—) Debye curve, (- · -) $w = 3.85 \times 10^{-5}$ g/g, (- - -) $w = 5.07 \times 10^{-3}$ g/g. All the curves are normalized and superimposed such that their midpoints coincide.

Analysis of the birefringence decay by the peeling method[26] for this sample shows the existence of at least two relaxation times (Figure 8). The values of the two times recorded were invariant (see Table I), within the quoted experimental error, with concentration. However, there was a slight increase in the relative contribution of the long relaxation time (τ_{high}) with increasing concentration for a given field strength.

Before attempting to explain the results in terms of molecular models it is useful to convert the observed experimental parameters into microscopic quantities. It can be seen from the inset of Figure 5 that the area above the risetime of this transient birefringence response is very much greater than that below the decay curve. This means that the permanent dipole moment is much greater than any induced dipole mo-

Table I
Values for PHIC (90 000) in Toluene

w, g/g	$(\overline{\mu_D{}^2})^{1/2}$, D Eq 1	$(\overline{\mu_D{}^2})^{1/2}$, D Eq 3	$(\overline{\mu_B{}^2})^{1/2}$,D	$\tau_D/3$, μs a	$\tau_D/3$, μs b	τ_B, μs Low	τ_B, μs High
1×10^{-3}	770	1090	1060	6.0	4.4	5 (±1)	25 (±2)

[a] At concentration 1×10^{-3} g/g. [b] Limiting value at lowest concentration. A value of $(g_1 - g_2)^0 = 4.1 \times 10^{-3}$ was used in the calculation of $(\overline{\mu_B{}^2})^{1/2}$. This was obtained using the relationships given in ref 8.

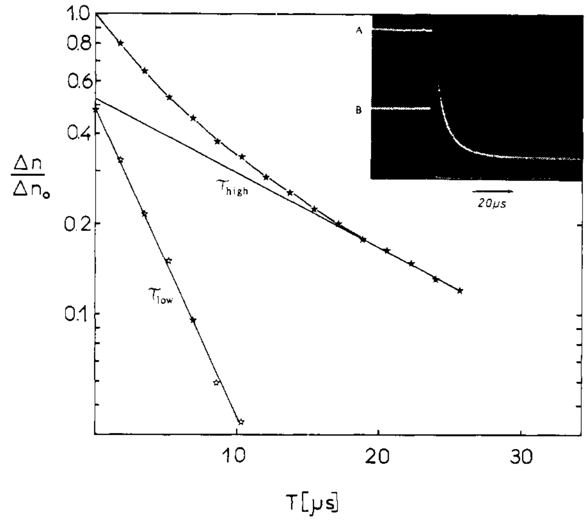

Figure 8. Normalized birefringence decay with time (★) for PHIC (90 000) in toluene. The lines τ_{low} (☆) and τ_{high} are obtained using the peeling method. The inset shows the actual birefringence decay (A), by quadratic detection, with time for a field E = 1.86 kV cm^{-1} (B), $w = 5.07 \times 10^{-3}$ g/g.

ment and dominates in the orienting mechanism.[27] Therefore in the following calculations induced dipole contributions are neglected. Thus in Table I are presented the values for $(\overline{\mu^2})^{1/2}$, the effective dipole moment, and τ, the rotational relaxation time calculated for both the dielectric and electric birefringence measurements for the sample PHIC (90 000).

For the sake of comparison, the same relation between the applied field and the directing field must be used when calculating the value of $\overline{\mu^2}$ by birefringence $\overline{\mu_B{}^2}$ and by dielectric $\overline{\mu_D{}^2}$ measurements. Supposing the two fields are equal (a hypothesis sometimes used for a long thin molecule of axial ratio larger than 10),

$$\overline{\mu_D{}^2} = \frac{\Delta\epsilon}{w}\frac{3kTM}{4\pi N_A d} \tag{3}$$

whereas $\overline{\mu_B{}^2}$ is given by eq. 2. In Table I we also give $\overline{\mu_D{}^2}$ calculated from eq 1. Both values of $\overline{\mu_D{}^2}$ were calculated by taking M = 90 000. The results show that the two techniques lead to identical dipole moment values. However, because aggregation is present, they are apparent values which cannot be used in a straighforward manner to determine the true dipole moment per monomer.

It is interesting to note that if we use a projection length onto the helix axis of L_0 = 1.3 Å per monomer unit and the Broersma equation[28] we obtain a relaxation time of τ_B = 4.6 μs. This can be seen to be in good agreement with the values of $\tau_D/3$ for dilute solutions and τ_B from the smaller relaxation time. The concord of the τ and μ values for the two techniques justifies their parallel use.

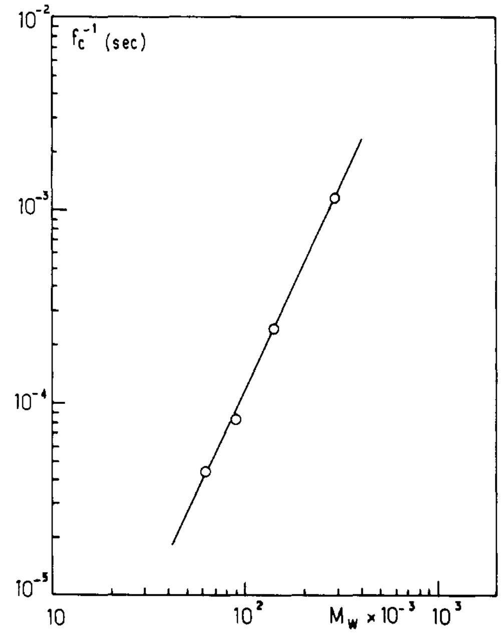

Figure 9. Variation of $1/f_c$ with molecular weight for PHIC in toluene. Low concentration limiting values are taken for f_c in all the cases.

The value of L_0 = 1.3 Å was obtained for poly(butyl isocyanate) (closely related to PHIC) in THF solutions where no aggregation occurs.[8] At higher concentrations it can be seen that $\tau_D/3$ becomes intermediate to τ_B low and high, thus indicating the average nature of this parameter. Since at low concentrations $\tau_D/3$ is effectively the single molecule relaxation time, a plot of log (τ_D ($c \rightarrow 0$)) vs. log M_w may be used to indicate the chain rigidity. As can be seen from Figure 9, this graph is linear with a slope of 2.15 indicating the reasonable rigidity of the chain and thus justifying the calculation of τ above. On this assumption it is noteworthy that the high τ_B value corresponds (Figure 8) to a M_w = 180 000, or twice the original particle length. Further it is estimated from the birefringence relaxation curves that such aggregates comprise about 15% of the solution volume at $c = 1 \times 10^{-3}$ g/g.

In order to explain the behavior of $\Delta\epsilon/w$, K_{sp} (or $\overline{\mu^2}$), and f_c (or $\tau_D{}^{-1}$, $\tau_B{}^{-1}$) with concentration for PHIC in toluene we invoke a model of aggregation. First we consider the PHIC samples of lower molecular weight (62 000 and 90 000). Between the lowest and the critical concentrations $\overline{\mu^2}$ is increasing while f_c is decreasing (or τ_D increasing) which could occur if there were predominant head-to-tail aggregation of the dipolar molecules. Above the critical concentration $\overline{\mu^2}$ decreases which suggests that a maximum may have been reached in the length of the head-to-tail linearly aggregated molecules and that now there are increasing amounts of antiparallel aggregation. This fits well with the behavior of f_c which continues to decrease (or $\overline{\tau_D}$ which increases). This

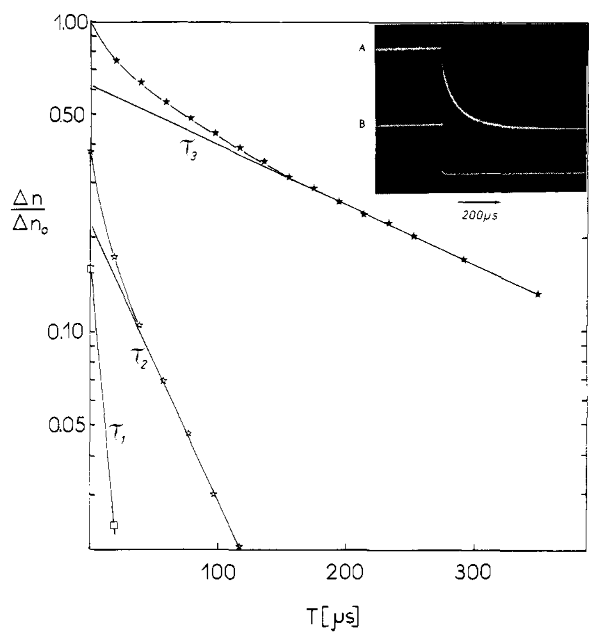

Figure 10. Normalized birefringence decay with time (★) for PHIC (290 000) in toluene. The lines τ_1 (□), τ_2 (☆), and τ_3 are obtained using the peeling method. The inset shows the actual birefringence decay (A), by quadratic detection, with time for a field E = 2.48 kV cm^{-1} (B), w = 1.12 × 10^{-3} g/g.

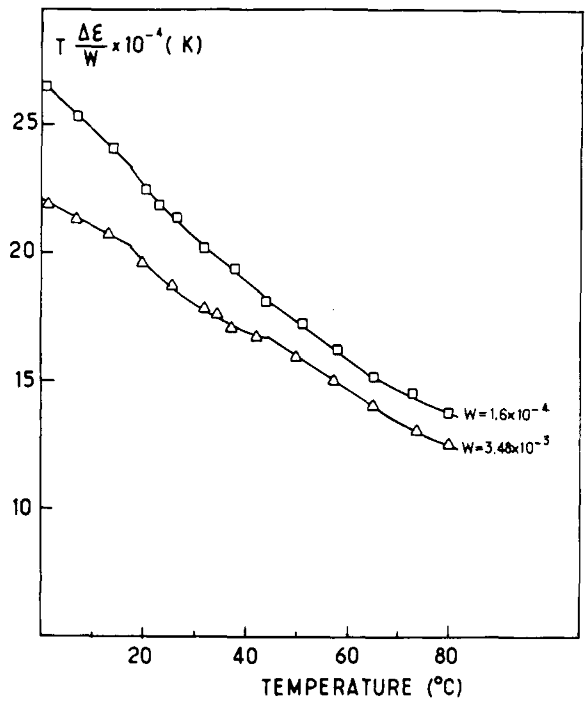

Figure 11. Variation of $(\Delta\epsilon/w)T$ with temperature for PHIC (62 000) in toluene at two extreme concentrations.

model for aggregation is further supported by the existence of at least two relaxation times from the birefringence measurements, Figure 8. The notion of a maximum length above which the aggregation becomes antiparallel is supported by the measurements on the higher molecular weight samples (140 000 and 290 000). Here no maximum in $\Delta\epsilon/w$ is recorded with concentration, and in fact this quantity decreases continuously with increasing concentration. The behavior of f_c with concentration is however more complex. Rather than decrease continuously it shows a plateau region at lower concentrations and then a decrease with increasing concentrations. It is difficult to specify exactly what this behavior means, apart from perhaps gradual increase in the anti-parallel type aggregates of larger sizes or changing particle flexibility which undoubtedly has a convoluting effect on the measurements. Certainly the analysis of the birefringence decay under these conditions is complex. The birefringence decay plot shows at least two and probably three relaxation times, Figure 10. It is difficult to specify the meaning of the very short relaxation time τ_1, apart from mentioning that it may not be a dipolar relaxation mechanism but rather a relaxation process characterizing the kinetics of aggregate formation and dissociation.

It is useful to compare the current results with those obtained for poly(γ-benzyl L-glutamate) (PBLG) in dioxane where aggregation effects are well documented.[12-15,18] Both solute systems are highly polar, rigid (at lower molecular weights) in nonpolar solvents. Apart from the fact that the overall magnitude of the changes in $\Delta\epsilon/w$, K_{sp}, f_c, and τ_B with concentration is much smaller for PHIC than PBLG solutions, the trends in the results are the same. Even for high molecular weight samples the observed behavior of $\Delta\epsilon/w$, K_{sp}, f_c, and τ_B with concentration is similar. It should also be noted that PBLG–dioxane measurements showed a critical concentration[18] which reduced in value with increasing molecular weight.[29] This may be expected for the PHIC–toluene solutions, but sample availability has limited our studies to only four molecular weights. Finally we note that the maximum length and maximum dipole moment supported by a linear head-to-tail aggregate joint are of the same order for the two systems.

(II) Temperature Studies. It is well known, for example, with PBLG–dioxane solutions, that increasing temperature acts as a disaggregating mechanism.[15] We have therefore studied the temperature dependence of $\Delta\epsilon/w$ and f_c at two concentrations, one above and one below the critical concentration, in the hope of recording differences corresponding to the different amounts of aggregation. As can be seen from Figures 11 and 12 an anomalous behavior is recorded between 20 and 40 °C in both cases for PHIC (62 000) at all concentrations, the effect being bigger in the ($\Delta\epsilon/w$) vs. T dependence the greater the concentration. In these measurements the solution requires no "handling" since it is maintained in the same, once positioned air-tight cell, thus reducing relative errors. These discontinuities are no artifacts: they have previously been reported in light scattering,[16] viscosity,[16] and dielectric measurements[17] on various poly(alkyl isocyanates). Besides the discontinuity the $\Delta\epsilon/w$ vs. T plot shows several other interesting features. The slopes of the $\Delta\epsilon/w$ vs. T curves (Figure 11) are different below 20 °C as a function of concentration but approximately parallel above 40 °C, and further with increasing concentration $\Delta\epsilon/w$ becomes smaller at a given temperature.

We believe that these characteristics of the $\Delta\epsilon/w$ and $\eta_0 f_c/T$ vs. T plots (Figures 11 and 12) can be visualized as the superposition of two effects: (i) an overall gradual change in the molecular flexibility of the PHIC Molecule with temperature and (ii) the aggregate structure in these solutions. The first effect would give a slowly decreasing value of $\Delta\epsilon/w$ and increasing value of $\eta_0 f_c/T$ with increasing temperature at a fixed concentration. The second effect is more complex because a changing aggregate structure changes the effective concentration and molecular weight of the component molecules contributing to $\Delta\epsilon/w$ and $\eta_0 f_c/T$. If there were no aggregation present in the solutions it would be expected that the curves of $\Delta\epsilon/w$ and $\eta_0 f_c/T$ vs. T would coincide and be independent of temperature. It has been suggested[30] that the anomalies recorded with temperature are due to helix–helix conforma-

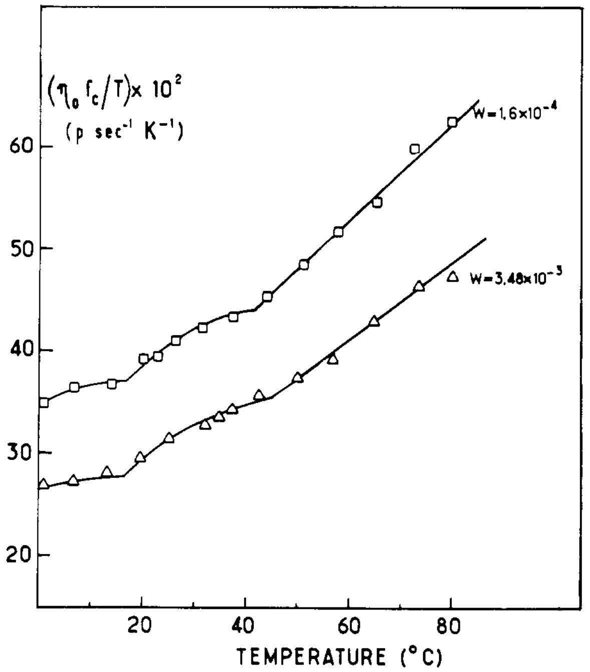

Figure 12. Variation of $\eta_0 f_c/T$ with temperature for PHIC (62 000) in toluene at two extreme concentrations.

tional changes alone. While such an effect cannot be totally excluded by the present results it cannot account for the displacement with concentration of the $\Delta\epsilon/w$ and $\eta_0 f_c/T$ vs. T curves nor the concentration dependence of the magnitude of the discontinuity in $\Delta\epsilon/w$ vs. T for the PHIC–toluene system concerned. Thus we invoke the following explanation.

Below ~20 °C both linear head-to-tail and antiparallel side-by-side aggregates exist in solution. The higher the concentration the greater is the amount of aggregation. As described previously above a critical concentration the amount of antiparallel structure has a predominant effect over that of the linear head-to-tail type and it would thus be expected that the effective concentration of PHIC molecules contributing to $\Delta\epsilon/w$ at fixed T will be less. This has the effect of reducing $\Delta\epsilon/w$ with increasing concentration because the measured w is the actual amount of PHIC weighed into solution. Further the differing slopes at high and low concentration (Figure 11) reflect the differing amounts and relative contribution of the aggregates with concentration. The marked decrease in $\Delta\epsilon/w$ and increase in $\eta_0 f_c/T$ at ~20 °C corresponds to the onset of the breaking of head-to-tail aggregates with the antiparallel aggregates relatively unaffected. This temperature would then correspond to the thermal energy required to initiate the breaking of linear head-to-tail aggregates. Thus the magnitude of the sudden decrease in $\Delta\epsilon/w$ becomes greater the more head-to-tail aggregates there are available to be broken (i.e., at higher concentrations). This process appears to be finished by around 40 °C and the $\Delta\epsilon/w$ and $\eta_0 f_c/T$ curves become approximately parallel but displaced relatively. It is proposed that this displacement is a reflection of the antiparallel aggregates still remaining in solution, and further that the magnitude of the differences reflects the relative amounts of these aggregates in each of the solutions due again to the different effective concentrations. Earlier studies on high molecular weight ($M_w > 150\,000$) samples[17] do not show the anomalous behavior but do show the displacement of the concentration curves. This is consistent with our picture of a maximum critical length supported by the aggregates, above which only antiparallel aggregation appears to take place.

Conclusion

The preliminary measurements reported herein show clearly that aggregation occurs in PHIC–toluene solutions and further that this behavior is similar to but of smaller magnitude than that recorded in PBLG–dioxane solutions. It is tempting therefore to suggest that when aggregation occurs in such polar rodlike solute molecules–nonpolar solvent systems a typical behavior is recorded. This suggestion is in agreement with the predictions of Tobolsky[31] who proposed that the isolated helical macromolecule is abnormal. In the light of these measurements, made over a wide concentration range, and the molecular weight dependence of the critical concentration it may be necessary to revise the results of previously reported studies on polyisocyanates where conclusions were based on measurements made over a small concentration range. This is particularly important when results are extrapolated to zero concentration.

We envisage these studies being extended to polar solvents where aggregation is less likely, to the mixing of polar–nonpolar solvents to study aggregate breaking, and to the other poly(alkyl isocyanates).

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