Dielectric and dynamic Kerr effect studies of poly(n-butyl isocyanate) and poly(n-octyl isocyanate) in solution

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Static and dynamic Kerr effect studies on poly(n-butyl isocyanate) (PBIC) and poly(n-octyl isocynate) (POIC) in CCl_4 solution are reported and are compared with dielectric studies. The variation of dipole moment μ and Kerr constant factors θ_1 and θ_2 with temperature suggest the chains for $M_W \sim 10^5$ depart from a rod-like conformation, and this is also indicated by a detailed analysis of the dynamic Kerr effect and dielectric data. It is shown that the ratio of areas for the rise and decay transients for the Kerr effect are inconsistent with the simple model for rotational diffusion. In addition the averaging process involved in the apparent dielectric relaxation time $\langle\tau_D\rangle$ and the Kerr effect decay average relaxation time $\langle\tau_{K,d}\rangle$ is examined and it is shown that for rigid-rod, coil and Kratky–Porod behaviour that $\langle\tau_D\rangle/\langle\tau_{K,d}\rangle \simeq \langle A_D/A_K\rangle$ a factor which would be 3 for rotational diffusion, and is found to be ~1 for PBIC and POIC again indicating the departure from simple rotational diffusion for the present samples.

INTRODUCTION

The motions of high molecular weight polymers in solution may be studied using a variety of techniques. Dielectric[1] and Kerr effect relaxation techniques[2–4] are of special interest since they give information on the reorientational motions of dipolar molecules. The dielectric relaxation experiment may yield information* on the vector time-correlation function $\langle\cos\theta(t)\rangle = \langle P_1(\cos\theta(t))\rangle$, while the decay transients from Kerr effect relaxation experiments may yield $\langle 3(\cos^2\theta(t) - 1)/2\rangle = \langle P_2(\cos\theta(t))\rangle$. A comparison of the results from the two experiments may assist in defining the mechanism for reorientation in a given system with a greater confidence than one may have from either experiment on its own, and this has been found useful for low frequency motions in glass forming systems[4–6].

The poly(n-alkyl isocyanates), along with the synthetic polypeptides, are rod-like molecules up to moderately high molecular weight and, since the dipole moment vectors lie along the long axis of the chain, are particularly well suited to study by dielectric and dynamic Kerr effect techniques. Dielectric studies of poly(n-butyl isocyanate) have been reported by Yu and coworkers[7], Bur and Roberts[8], Dev and coworkers[9], Pierre and Marchal[10] and by Bur and Fetters[11] and for poly(n-hexyl isocyanate) by Bur and Fetters[11]. Kerr effect studies of poly(n-butyl isocyanate) have been reported by Jennings and Brown[12]. These studies indicate that the molecules are rod-like for $M_W < 10^5$ but coil-up at higher molecular weight. The present work describes dynamic Kerr effect studies made on a narrow fraction sample of poly(n-butyl isocyanate) (PBIC) and an unfractionated sample of poly(n-octyl isocyanate) (POIC), and emphasizes the comparison of rise and decay transients, the comparison with dielectric relaxation data and the extent to which the observed reorientational motions are consistent with rigid-rods moving by small-angle steps (rotational diffusion).

EXPERIMENTAL

PBIC having $M_n = 1.2 \times 10^5$ and $M_w = 1.33 \times 10^5$, and POIC (unfractionated) having $M_w = 3.0 \times 10^5$ were kindly provided by Dr A. J. Bur of the National Bureau of Standards, Washington D.C. The solvent was CCl_4 and solutions were made with intermittent shaking for 24 h before study.

Kerr effect measurements were made using an apparatus constructed in this laboratory, the details of which are available[13]. For the static Kerr constant measurements of phase retardations from only a few minutes of arc – with no upper limit to the maximum observable phase retardation – voltages up to 15 kV (from a Brandenberg Model 707R supply) were applied to a Kerr cell of optical path length 7.45 cm with an interelectrode spacing near 1 mm. The Kerr cell was very similar to that described by Champion and coworkers[14]. The light source used for static measurements was a He/Ne laser (Spectra-Physics Model 133) operated at 632.8 nm. Static Kerr constants were measured (visually) using a quarter-wave retarder (F. Wiggins and Sons Ltd) cut for use at 632.8 nm, in conjunction with a polarizer and analyser (Glan-type prisms from Ealing Beck Ltd). For dynamic Kerr constant measurements a voltage transient having a step-rise, a plateau and a step-decay was generated and was applied to the Kerr cell, the optical transient being observed in the quadratic mode of detection (i.e. with quarter-wave retarder removed). For the range 1.5×10^{-6} to 4×10^{-3} sec a transient, 0.8 to 3.2 kV in magnitude, was obtained using a pulse-former[15] and a pulse amplifier[16]. The rise and decay times were better than 6 and 17 μsec, respectively and the plateau lengths were in the range 100 μsec to 4 msec. For the range 10^{-2} to 12 sec a transient, up to 4 kV in magnitude, was obtained using the

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* We consider here, for simplicity, the random Brownian motions of a rigid dipole vector μ, so $\langle\cos\theta(t)\rangle = \langle\mu(0)\cdot\mu(t)\rangle/\mu^2$.

Brandenberg supply unit in conjunction with a relay and a reed switch. The rise and decay times were better than 0.5 and 0.6 msec, respectively. For times exceeding 12 sec the Brandenberg unit was connected by a simple switch to the Kerr cell. Optical transients were detected using a Mullard 56 AVP photomultiplier and displayed either on a Storage oscilloscope (Tektronix Model 7313 dual-trace oscilloscope) and photographed, or on a chart recorder. For weak optical transients a signal-average (Princeton Applied Research Waveform Eductor, Model TDH9) was used and the averaged transient displayed on a chart recorder. In order that any desired portion of the optical transient, as displayed on the oscilloscope, might be examined in detail, the triggering of the oscilloscope was synchronized with the high voltage pulse using a delay circuit[13]. This involved passing a monostable rectangular pulse through a differentiating circuit to yield two 'spikes' of opposite polarity and whose separation was adjustable up to 200 msec. It was then possible to trigger the oscilloscope at a chosen time relative to the step-on or step-off voltage pulse.

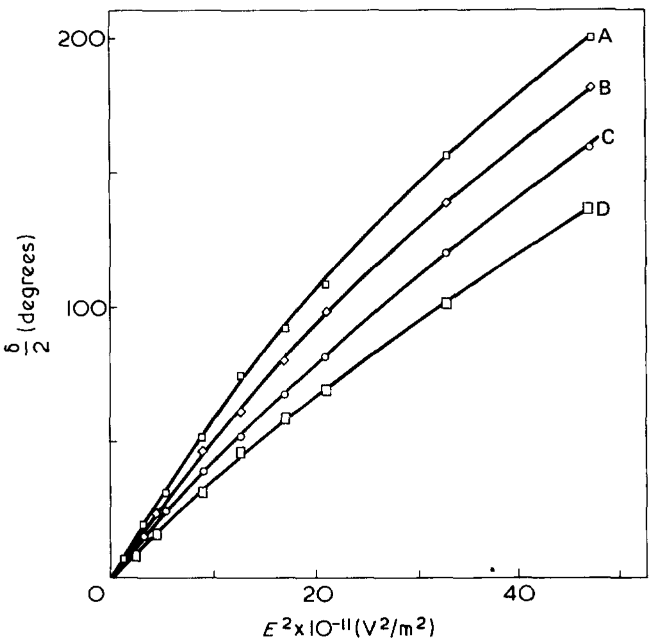

Figure 1 ($\delta/2$) against E^2 for a 3.02 mg/ml solution of POIC in CCl$_4$. Here $\delta = 2\pi l \Delta n/\lambda$, where l, Δn and λ are cell-length, optical birefringence and the wavelength of the light respectively: A, 288K; B, 298K; C, 308K; D, 318K

Having obtained optical transient data, a correction procedure quoted by Jones[17] was used when the observed relaxation was affected by the time-constant of applied pulse and the detector–recorder circuitry.

Temperature was controlled using a thermostatically controlled liquid circulated around a jacket which surrounded most of the Kerr cell. Dielectric measurements were made using a General Radio 1620.A Bridge (10^2 to 10^5 Hz) and a Scheiber Bridge (10^{-2} to 10^2 Hz) in conjunction with a two-terminal coaxial cell.

RESULTS

Static Kerr effect

As one example, *Figure 1* shows plots of the phase retardation (δ) (in degrees) against E^2, at four temperatures for a solution of POIC in CCl$_4$. Similar plots were obtained for PBIC in CCl$_4$. The optical retardations are very large for only modest values of E and arise from the combination of a large molecular dipole moment and anisotropy of molecular polarizability. The plots are linear for small E but a curvature is observed at large E, being due to saturation effects well-known for other macromolecules in solution e.g. poly(γ-benzyl glutamate)[18,19]. The solution Kerr constants $B_{12} = \delta/(2\pi E^2 l)$ obtained from the low field data are shown in *Table 1*. The effective solute contribution to B_{12} is calculated assuming the alligation formula $B_{12} = B_1 f_1 + B_2 f_2$, where f_1 is the mole fraction. The solvent Kerr constant $B_1 = 0.91 \times 10^{-15}$ V^{-2} m so B_{12} is essentially due to the solute contribution. The B_2 values thus derived may be converted[20] into effective molecular Kerr constants K_m. It is usual[2] to regard K_m as being due to the term θ_2 involving the permanent dipole moment μ and the term θ_1 due only to induced dipole moments, and $K_m = (\theta_1 + \theta_2)2\pi/9$. For the case of a rod-like molecule whose dipole moment lies along the long axis, Z say, and has a polarizability ellipsoid of axial symmetry about Z, then:

$$\theta_1 = \frac{2}{45kT}(b_1 - b_2)^2 \qquad \text{(1a)}$$

$$\theta_2 = \frac{2\mu^2}{45(kT)^2}(b_1 - b_2) \qquad \text{(1b)}$$

Table 1 Kerr constant B_{12} and dipole moments μ for PBIC and POIC in CCl$_4$

(a) PBIC	B_{12} (10^{-13} V^{-2} m)				μ (10^{-27} C m)			
C (kg/m^3)	293.2K	303.2K	313.2K	323.2K	293.2	303.2	313.2	323.2
1.02	27	23	19	16	4.3	4.23	4.13	3.90
0.66	20	17	13	11	4.20	4.13	4.07	3.90
0.51	14.	13	10	8	4.0	4.17	3.84	3.67
0.26	8	6	5	4	4.17	4.13	4.03	3.97
0.12	3.5	3.0	2.5	2.0	4.43	4.40	4.13	3.57
(b) POIC	B_{12} (10^{-13} V^{-2} m)				μ (10^{-27} C m)			
C (kg/m^3)	288.2K	298.2K	308.2K	318.2K	288.2K	298.2K	308.2K	318.2K
3.02	45	40	34	28	3.40	3.77	3.74	3.23
0.300	5.0	4.0	3.5	3.0	3.67	3.70	3.43	3.57
0.034	0.55	0.50	0.35	0.30	–	–	4.03	4.20
2.72					3.73*	3.73	3.67	3.60

* Dielectric measurements

Table 2 Molecular Kerr constant factors for PBIC and POIC in CCl_4

PBIC					POIC				
T (K)	K_m^*	θ_2^*	$(b_1 - b_2)$	θ_1^*	T (K)	K_m	θ_2	$(b_1 - b_2)$	θ_2
293.2	7.5 ± 0.2	2.0	4.0	1.7	288.2	8.7	2.3	5.9	3.8
303.2	6.1 ± 0.2	1.6	3.6	1.3	298.2	7.2	1.9	5.2	2.9
313.2	4.8 ± 0.1	1.3	3.1	1.0	308.2	6.2	1.6	5.0	2.6
323.2	3.8 ± 0.1	1.0	2.9	0.8	318.2	5.2	1.4	4.6	2.2

* See text for units of θ_1, θ_2 and $(b_1 - b_2)$ and K_m

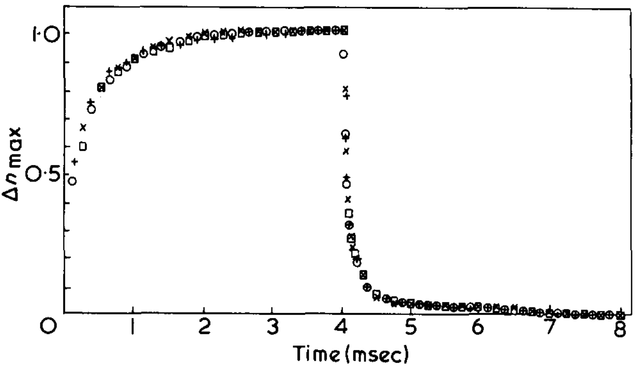

Figure 2 $(\Delta n(t)/\Delta n_{max})$ against time for POIC in CCl_4 at 293K: X, 630 kV/m; O, 980 kV/m, □, 1300 kV/m, +, 1680 kV/m, corresponding to $\frac{1}{2}\delta_{max}$ being 10.2°, 24.5°, 41.5° and 65.5° respectively

where $(b_1 - b_2) \equiv \Delta b$ is the anisotropy of polarizability of the molecule. For the case where $\theta_2 \gg \theta_1$, K_m is determined by μ and $(b_1 - b_2)$ and since μ may be determined by a separate experiment (e.g. dielectric permittivity) $(b_1 - b_2)$ and hence θ_1 may be estimated. *Table 2* summarizes the K_m and θ_2 values thus deduced. K_m is in units of 10^{-18} $V^{-2}m^5mol^{-1}$ and θ_2 in $10^{-51}FV^{-2}m^4$. We have deduced values of μ from the Kerr constant data at high fields. For $\theta_2 \gg \theta_2$, which is the case here (see also Jennings and Brown[12]), then the ratio of the slope (m) to the intercept (C) for the plot of $(\delta/2E^2)$ against E^2 is given by[18]:

$$\frac{|m|}{C} = \frac{2}{21} \cdot \left(\frac{\mu}{kT}\right)^2 \tag{2}$$

Table 1 includes the values for μ deduced by this method. Bur and Roberts[8] give $\mu = 3.83 \times 10^{-27}$ C m for the present sample of PBIC in CCl_4, (their sample 21) and we see that the values of μ in *Table 2*, deduced from equation (2), are in reasonable agreement. We deduced μ for the present sample of POIC from our permittivity measurements and the agreement between μ (diel.) and μ (Kerr, equation 2) is good. The values for μ (Kerr, equation 2) have been used in equation (1b) to obtain $(b_1 - b_2)$ and hence θ_1. *Table 2* includes $(b_1 - b_2)$ and θ_1, where $(b_1 - b_2)$ is quoted as $(10^{-38}\ F\ m^2)$ and θ_1 as $(10^{-56}\ FV^{-2}m^4)$. The following features are noted: (i) μ, K_m, θ_2, θ_1 and $(b_1 - b_2)$ all decrease with increasing T; (ii) $\theta_2 \gg \theta_1$, as expected[12].

Dynamic Kerr effect and dielectric relaxation

The normalized transient birefringence $(\Delta n(t)/\Delta n_{max})$ for the 'quadratic' mode of detection is given by the relation[18]:

$$\frac{\Delta n(t)}{\Delta n_{max}} = \frac{\delta}{\delta_{max}} = \frac{2 \sin^{-1} (V(t)/V_0)^{1/2}}{\delta_{max}} \tag{3}$$

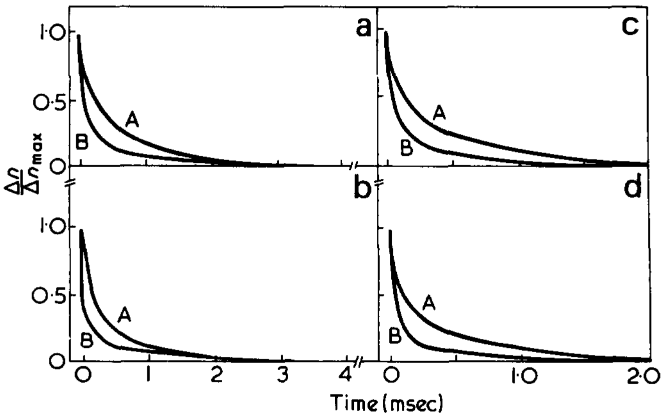

Figure 3 $(\Delta n(t)/\Delta n_{max})$ against t for (a) PBIC in CCl_4, C = 1.02 kg/m, T = 293K; (b) PBIC in CCl_4, C = 1.02 kg/m, T = 323K; (c) POIC in CCl_4, C = 3.0 kg/m, T = 288K; (d) POIC in CCl_4, C = 3.0 kg/m, T = 318K. A, $1 - R$; B, D. Here $R = \Phi_r(t)$ and $D = \Phi_d(t)$

where $V(t)$ is the photomultiplier signal at time t, V_0 corresponds to the signal for $\delta = \pi$. Since $V = V_0 \sin^2(\delta/2)$, δ_{max} is the maximum phase retardation. For $\delta < (\pi/4)$, equation (3) is approximated by $(\Delta n(t)/\Delta n_{max}) = (V/V_{max})^{1/2}$ so the square root of the observed normalized transient is proportional to the normalized birefringence. The phase retardations for the PBIC and POIC solutions may be very large (see e.g. *Figure 1*) so we have checked the transients at different levels of δ. As one example *Figure 2* shows $(\Delta n(t)/\Delta n_{max})$ for different values of $\alpha = (\delta/2)$ produced by changing E. The transients superpose for all values of E, showing that the transients obey relation (3) with relaxation functions being independent of field for the range studied here. For the results given below $\delta_{max} < \pi/4$ in all cases, so the simple quadratic approximation was applied.

Figures 3a–3d show representative normalized transients for the PBIC and POIC solutions. The rise transients are far slower than the decay transients, similar to that observed for poly(γ-benzyl glutamate) in solution[18], being indicative of a small angle rotational diffusion mechanism. We may define a relaxation time $\tau_{K,d}$ as being the time required for the decay transient to reach $(1/e)$ of its initial value, and also $\tau_{K,r}$ for the rise transient to reach $(1 - e^{-1})$ of its final value. These values are summarized in *Table 3*. The plots of $\log_{10}(\Delta n(t)/\Delta n_{max})$ against t^{-1} are strongly curved, indicative of a broad distribution of relaxation times both for rise and decay transients for both polymers. This will be discussed further below in connection with dielectric results, but it is convenient to define a relaxation time $\langle \tau_{K,d} \rangle$ obtained from the area below the Kerr effect decay transient.

Table 3 Relaxation data for PBIC and POIC in CCl_4

(a) PBIC $C = 1.0$ kg/m^3; pulse magnitude 1.3×10^6 V/m

T (K)	$\tau_{K,d}$ (μsec)	$\tau_{K,r}$ (μsec)	$\langle\tau_{K,d}\rangle$ (μsec)	$\langle\tau_D\rangle$ (μsec)
293.2	124	360	293	195*
303.2	103	320	280	
313.2	84	280	254	
323.2	68	220	190	

* Taken from ref 8 and adjusting to $C = 1$ kg/m using Figure 3 of this ref

(b) POIC $C = 3.0$ kg/m^3; pulse magnitude 5.8×10^5 V/m

T (K)	$\tau_{K,d}$ (μsec)	$\tau_{K,r}$ (μsec)	$\langle\tau_{K,d}\rangle$ (μsec)	$\langle\tau_D\rangle$ (μsec)
288.2	68.5	255	150	215
298.2	51.5	213	131	180
308.2	44.5	172	130	141
318.2	37.5	155	115	106

$$\langle\tau_{K,d}\rangle = \int_0^\infty \left(\frac{\Delta n(t)}{\Delta n_{\max}}\right) \mathrm{d}t \tag{4}$$

Table 3 includes these values and we see that $\langle\tau_{K,d}\rangle$ is about $2\tau_{K,d}$ for PBIC and near $3\tau_{K,d}$ for POIC, and the difference means that the tail of the transient, due mostly to the higher molecular weight species, makes a very important contribution to $\langle\tau_{K,d}\rangle$.

DISCUSSION

The observation of large K_m values for both PBIC and POIC is to be interpreted in terms of a model of the chain as an extended helical structure whose dipole moment lies along the chain contour[7–9]. The values of θ_2 are about 10^5 greater than θ_1 for both polymers, which might have been anticipated since μ and $(b_1 - b_2)$ are proportional to chain length L for a rod, thus θ_2 is proportional to L^3 and θ_1 is proportional to L^2 (see equation 1). The observed values of μ and $(b_1 - b_2)$ decrease with increasing temperature (*Tables 1* and *2*) which suggest an increasing tendency for the chains to coil-up. The deviations from rod-like behaviour have been observed by Bur and Roberts[8], both in average dielectric relaxation times and dipole moments, for increasing molecular weight, so the present results provide additional evidence for the internal flexibility of the chain. Thus on the basis of the results for the static Kerr constant and dipole moment, we suggest that the chains deviate from rod-like molecules and that this becomes increasingly important as the temperature is raised. This has implications for the interpretation of the dynamic Kerr effect and dielectric relaxation results.

The interpretation of the dynamic Kerr effect results is made complicated by the fact that the rise and decay transients are not characterized by single exponential decay functions. The dielectric data are also not characterized by a single relaxation time[7–11], and this has been closely examined by Bur[22]. He found the half-width $(W/2)$ of the ϵ''-vs. $\log f$ plot was near 2.8 for $(M_W/M_N) = 1.5$ for PBIC. The present PBIC sample (sample 21) gave $(W/2) = 2.05$, which is much broader than a single relaxation time curve $(W/2 = 1.14)$. A further complication arises due to the fact that the magnitude of the dynamic Kerr effect is related, through θ_2, to $\mu^2\Delta b$ while the magnitude of the dielectric relaxation is related to μ^2. For a distribution of molecular weights the Kerr effect relaxation and dielectric relaxation reflect different averages of the relaxation of the species in solution.

Table 4 The dielectric relaxation function $\psi_D(t/\langle\tau_D\rangle)$ for POIC

$\mathrm{Log}_{10}(t/\langle\tau_D\rangle)$	$\psi_D(t/\langle\tau_D\rangle)$	$\mathrm{Log}_{10}(t/\langle\tau_D\rangle)$	$\psi_D(t/\langle\tau_D\rangle)$
−3.00	0.999	−0.50	0.574
−2.50	0.994	0.00	3.936
−2.00	0.961	0.50	0.192
−1.50	0.890	1.00	0.053
−1.00	0.759		

The dielectric behaviour in the frequency domain is related to the behaviour in the time domain according to the relation[23]:

$$\psi_D(t/\langle\tau\rangle) = \frac{\displaystyle\int_0^\infty [\epsilon''(x)/\epsilon''_m] \cos x \, \mathrm{d}x/x}{\displaystyle\int_0^\infty [\epsilon''(x)/\epsilon''_m] \, \mathrm{d}x/x} \tag{5}$$

$x = \omega t \equiv (\omega/\omega_m)(t/\langle\tau\rangle)$ where $\omega_m\langle\tau\rangle = 1$ and subscript m implies the maximum loss condition. We have* evaluated $\psi_D(t/\langle\tau\rangle)$ for a 2.7 kg/m^3 solution of POIC in CCl_4 and the values are given in *Table 4*. It is possible to compare the form of the dielectric decay function with that for the Kerr effect decay function $\psi_{K,d}(t)$ for POIC. This is conveniently achieved using the Williams–Watts empirical relation[23]: $\phi(t) = \exp - (t/\tau_0)^{\bar\beta}$ which gives an adequate fit to both $\psi_{K,d}(t)$ and $\psi_D(t)$ for POIC. We find that $\bar\beta$ was 0.52 ± 0.02 and 0.49 ± 0.02 for $\psi_{K,d}(t)$ and $\psi_D(t)$, respectively, thus although both the Kerr effect and dielectric relaxation curves are broad, phenomenologically they have similar functional forms.

The question of the applicability of the model of rotational diffusion (*RD*) to the Kerr effect and dielectric relaxation of PBIC and POIC is difficult to answer in relation to actual relaxation times due to the effects of a molecular weight distribution. For the present systems, however, one test of the applicability of the *RD* model may be made irrespective of the form of the distribution of molecular weights. *Table 2* indicates $\theta_1 \ll \theta_2$ for both polymers, the same results for PBIC was obtained by Jennings and Brown[12] from a.c. Kerr effect measurements. For this case the *RD* model gives the following relations*:

$$\Phi_r(t) = \frac{\Delta n_m - \Delta n_r(t)}{\Delta n_m}$$

$$= \frac{\int p(M)\mu^2(M)\Delta b(M)\,[\tfrac{3}{2}\phi_{1M}(t) - \tfrac{1}{2}\phi_{2M}(t)]\,\mathrm{d}M}{\int p(M)\mu^2(M)\Delta b(M)\mathrm{d}M} \tag{6a}$$

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* These calculations were kindly carried out by Mrs E Houston and the late Mr M. E. Baird of UWIST, Cardiff. Note that $(W/2) = 2.3$ for these results, indicating $\bar\beta \simeq 0.48$.

* In equation (24) of ref 4 $[1 - \Phi_r(t)]$ should be replaced by $\Phi_r(t)$; no conclusions are affected.

Table 5 Relaxation times obtained from moments of the distribution of molecular weight

(a) μ^2 $(M) = n\mu_0^2$							(b) μ^2 $(M) = 2\mu_0^2 n n_q$					(c) μ^2 (M) given by equation (11) with $\langle M\rangle = 1.33 \times 10^5$ and $M_q = 8 \times 10^4$				
$\alpha = 3.0$			$\alpha = 2.7$		$\alpha = 2.0$		$\alpha = 3.0$			$\alpha = 2.0$		$\alpha = 3.0$			$\alpha = 2.0$	
2λ	R_D	R_K	R_D	R_K	R_D	R_K	2λ	R_D	R_K	R_D	R_K	2λ	R_D	R_K	R_D	R_K
0.10	2.40	2.20	2.13	2.04	1.64	1.65	0.10	2.06	1.96	1.47	1.48	0.10	2.24	2.25	1.60	1.59
0.13	2.84	2.69	2.48	2.30	1.82	1.83	0.13	2.39	2.26	1.59	1.62	0.20	3.57	3.32	2.07	2.07
0.20	3.93	3.70	3.30	3.12	2.22	2.25	0.20	3.20	3.00	1.89	1.93					
0.50	9.20	8.65	7.11	6.80	3.80	3.90	0.50	7.14	6.50	3.12	3.17					
1.00	19.5	19.0	13.4	14.2	6.16	6.50	1.00	15.2	13.0	5.10	5.00					
2.00	44.5	47.1	–	–	10.5	11.57	2.00	36.1	27.0	9.00	8.33					

$$\Phi_d(t) = \frac{\Delta n_d(t)}{\Delta n_m} = \frac{\int p(M)\mu^2(M)\Delta b(M)\phi_{2m}(t)\mathrm{d}M}{\int p(M)\mu^2(M)\Delta b(M)\mathrm{d}M} \tag{6b}$$

where $\phi_{1M}(t) = \exp\,[-2D(M)t]$; $\phi_{2M}(t) = \exp\,[-6D(M)t]$, $p(M)$ is the molecular weight distribution function, and $D(M)$ is the rotational diffusion coefficient of species of molecular weight M. From equation (6):

$$\frac{\int \Phi_r(t)\mathrm{d}t}{\int \Phi_d(t)\mathrm{d}t} = 4 \tag{7}$$

The experimental values for this ratio are found to be 1.8 and 2.4 for PBIC and POIC, respectively, which are considerably less than the factor 4 required by the *RD* mechanism. This suggests that the PBIC and POIC chains are not rigid-rods moving by the *RD* mechanism, but are flexible giving rise to internal modes of motion in addition to overall (stiff-chain) motions. We had already noted the temperature dependence of μ, θ_2 and $(b_1 - b_2)$ and had suggested that the chains tend to coil-up at these molecular weights. Bur and Roberts[8] have shown that PBIC for $M_W > 4 \times 10^5$ exhibits dielectric relaxation behaviour consistent with a coiled configuration in which the chain dynamics are described not by an *RD* mechanism but by a Rouse–Zimm set of internal relaxation modes. The present Kerr effect data shows that for the PBIC ($M_W = 1.33 \times 10^5$) and POIC ($M_W = 3.0 \times 10^5$) studied here, the chains are beginning to depart from (a) the rigid-rod configuration – as evidenced by μ, θ_2 and $(b_1 - b_2)$ and (b) an overall *RD* mechanism as the process of reorientation – as evidenced by the area analysis (equation 7).

The interpretation of the relaxation times is made complicated by the presence of a distribution of molecular weights. $\tau_{K,d}$ is $\frac{1}{3}$ to $\frac{1}{4}$ of $\tau_{K,r}$ for POIC and about $\frac{1}{3}$ of $\tau_{K,r}$ for POIC. The values of $\langle\tau_{K,d}\rangle$ (see equation 4) are about $2\tau_{K,d}$, we see that $\langle\tau_{K,d}\rangle$ and $\langle\tau_D\rangle$ are quite similar for both POIC and PBIC. The question that now arises is, how may the average relaxation times $\langle\tau_{K,d}\rangle$ and $\langle\tau_D\rangle$ be related to the relaxation times of the constituent chains? Writing:

$$\epsilon''(\omega) = \int C(M) \frac{\omega\tau(M)}{1 + \omega^2\tau^2(M)} \mathrm{d}M \tag{8}$$

$C(M)\mathrm{d}M$ is the contribution to the magnitude of the dielectric process from species between M and $M + \mathrm{d}M$, and is proportional to $p(M)\mu^2(M)\mathrm{d}M$. Differentiation of equation (8) yields for the maximum loss condition:

$$\omega_m^{-1} = \langle\tau_D\rangle = \left[\frac{\int p(M)\mu^2(M)\tau^2(M)\mathrm{d}M}{\int p(M)\mu^2(M)\mathrm{d}M}\right]^{1/2} \tag{9}$$

The Kerr effect average relaxation time from equation (4) is:

$$\langle\tau_{K,d}\rangle = \frac{\int p(M)\mu^2(M)\Delta b(M)\tau(M)\mathrm{d}M}{\int p(M)\mu^2(M)\Delta b(M)\mathrm{d}M} \tag{10}$$

Note that in equations (8) and (9) we assume that a given molecular weight species would give a single relaxation time process which is reasonable in the light of Bur's dielectric results[22] for well-fractionated PBIC. Thus $\langle\tau_D\rangle$ and $\langle\tau_{K,d}\rangle$ correspond, via equations (9) and (10) to different average relaxation times with respect to the distribution function $p(M)$.

Bur and Fetters[11] have found that fractions of PBIC have symmetrical molecular weight distribution functions so it is reasonable* to represent $p(M)$ as a normal distribution function about an average molecular weight $\langle M\rangle = M_N$. We may now relate $\langle\tau_D\rangle$ and $\langle\tau_{K,d}\rangle$ to moments of the distribution if we specify how $\mu^2(M)$, $\Delta b(M)$ and $\tau(M)$ depend upon M. Following the dielectric studies of Bur and Roberts[8] we write $\tau_K(M) = A_K M^\alpha$, $\tau_D = A_D M^\alpha$, where $\alpha = 2.7$ for rigid-rods (valid up to $M_W = 4 \times 10^5$ for PBIC) and $1.5 < \alpha < 2$ for coiled chains. $\mu^2(M)$ is expressed by the Kratky–Porod relation[11]:

$$\mu^2(M) = 2\mu_0^2 n_q^2[(M/M_q) - [1 - \exp - (M/M_q)] \tag{11}$$

$n_q = (\mu_q/\mu_0)$, μ_q is the 'persistent' dipole moment, $(M/N_q) = (n/n_q)$ where n is the number of repeat units in the chain and μ_0 is the dipole moment per repeat unit. For $(M/M_q) \ll 1$ we have the rigid rod result $\mu^2 = n^2\mu_0^2$, while for $(M/M_q) \gg 1$ we have the result for a coil, $\mu^2 = 2\mu_0^2\, n n_q$. In order to deduce $\langle\tau_D\rangle$ and $\langle\tau_{K,d}\rangle$ from equations (9) and (10) we assume $\Delta b = A'M^s$, where $s = 1.0$. Writing the relaxation times for the average molecular weight $\langle M\rangle$ as $\tau_D(\langle M\rangle) = A_D\langle M\rangle^\alpha$ and $\tau_{K,d}(\langle M\rangle) = A_K\langle M\rangle^\alpha$, we have deduced $R_D = \langle\tau_D\rangle/\tau_D(\langle M\rangle)$ and $R_K = \langle\tau_{K,d}\rangle/\tau_{K,d}(\langle M\rangle)$ for different values of α, for different ranges of equation (11) and for different values of the parameter 2λ which characterizes the normal distribution. The details of the calculation procedure are summarized in the Appendix, and the results are given in *Table 5*. For a given distribution of molecular weight,

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* Note: Bur[22] used a rectangular distribution of molecular weights to analyse dielectric data for PBIC.

Table 6 Apparent activation energies (Q/kJ/mol) for the relaxation of PBIC and POIC in CCl_4

	PBIC	POIC
Kerr rise transient	12.4	12.5
Kerr decay transient	14.8	13.9
Dielectric	–	16.2
(Solvent viscosity	10.2	10.2)

(2λ = constant), both $\langle\tau_{K,d}\rangle$ and $\langle\tau_D\rangle$ exceed $\tau_{K,d}(\langle M\rangle)$ and $\tau_D(\langle M\rangle)$, respectively, by a factor which increases as 2λ is increased. This applies to all ranges of $\mu^2(M)$ (in *Table 5*). The significant feature is that for a given molecular weight distribution (2λ = constant) the ratio $(R_D/R_K) \simeq 1.0$ for this range of α at all ranges of $\mu^2(M)$. Thus:

$$\frac{\langle\tau_D\rangle}{\langle\tau_{K,d}\rangle} = \frac{A_D}{A_K} \cdot \frac{R_D}{R_K} \simeq \frac{A_D}{A_K} \qquad (12)$$

This result, equation (12), indicates that although $\langle\tau_{K,d}\rangle$ and $\langle\tau_D\rangle$ are obtained as a result of different averages over the constituent species, for the present systems $\langle\tau_D\rangle/\langle\tau_{K,d}\rangle$ is numerically close to $\tau_D(\langle M\rangle)/\tau_{K,d}(\langle M\rangle)$, and gives an estimate of the ratio (A_D/A_K). For rotational diffusion of a rigid-rod the dielectric and Kerr effect decay relaxation times are in the ratio $(A_D/A_K) = 3.0$. Inspection of *Table 3* shows that $\langle\tau_{K,d}\rangle$ and $\langle\tau_D\rangle$ are quite similar, indicating $(A_D/A_K)_{\text{expt}} \sim 1$, and thus not consistent with simple rotational diffusion, as was suggested above from the ratio of areas of rise and decay-transients. These observations, taken together with the observed variation in μ and Δb with temperature, suggest that internal mechanisms for motion play an important role in the relaxation of high molecular weight PBIC and POIC, and provide additional confirmation of the conclusions, from dielectric studies, of Bur and Roberts[8]. Finally, we note that the variation of the apparent relaxation times with temperature yield 'activation energies' which are comparable with that from the solvent viscosity η, and these are shown in *Table 6*.

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APPENDIX

We write $p(M)$ as a normal distribution function $p(M) = (4\pi^2\sigma^2)^{-1/2} \exp - \{[M - \langle M\rangle]^2/2\sigma^2\}$. Now $(M_W/M_N) = \langle M^2\rangle/\langle M\rangle^2 = 1 + [\sigma/\langle M\rangle]^2 \equiv 1 + 2\lambda$. *Table A1* gives $\langle M^n\rangle/\langle M\rangle^n$ for n = 1 to 12.

Table A1

n	$\langle M^n\rangle/\langle M\rangle^n$
1	1
2	$1 + 2\lambda$
3	$1 + 6\lambda$
4	$1 + 12\lambda + 12\lambda^2$
5	$1 + 20\lambda + 60\lambda^2$
6	$1 + 30\lambda + 180\lambda^2 + 120\lambda^3$
7	$1 + 42\lambda + 420\lambda^2 + 840\lambda^3$
8	$1 + 56\lambda + 840\lambda^2 + 3360\lambda^3 + 1680\lambda^4$
9	$1 + 72\lambda + 1512\lambda^2 + 10080\lambda^3 + 15120\lambda^4$
10	$1 + 90\lambda + 2520\lambda^2 + 25200\lambda^3 + 75600\lambda^4 + 30240\lambda^5$
11	$1 + 110\lambda + 3960\lambda^2 + 5540\lambda^3 + 277200\lambda^4 + 332640\lambda^5$
12	$1 + 132\lambda + 5940\lambda^2 + 110880\lambda^3 + 831600\lambda^4 + 1995840\lambda^5 + 665280\lambda^6$

R_D and R_K of the text for $\mu^2(M) \propto M^1$ or M^2 may be deduced from those moments. For example for $\mu^2(M) = n^2\mu_0^2$, $\Delta b = A'M$ and $\alpha = 2.7$, $R_D = [\langle M^{7.4}\rangle/\langle M^2\rangle]^{1/2}$ and $R_K = [\langle M^{5.7}\rangle/\langle M\rangle^3]$. Hence R_D and R_K may be evaluated for given values of λ. For the Kratky–Porod relation for $\mu^2(M)$, equation (11), R_D and R_K are obtained as follows. Expanding the exponential term in equation (11) leads to:

$$\mu^2(M) = 2\mu_0^2 n_q^2 \left[\sum_{m=2}^{\infty} \frac{(-1)^m}{m!} \left(\frac{M}{M_q}\right)^m \right] \qquad (A1)$$

from Equation (A1) and equations (9) and (10) of the text we obtain:

$$\langle\tau_{K,d}\rangle = A \sum_{m=2}^{\infty} (-1)^m \frac{\langle M^{m+\alpha+1}\rangle}{m!M_q^m} \Bigg/ \sum_{m=2}^{\infty} (-1)^m \frac{\langle M^{m+1}\rangle}{m!M_q^m}$$

$$= \tau_{K,d}(\langle M\rangle) \sum_{m=2}^{\infty} \frac{(-1)^m}{m!} \left(\frac{\langle M\rangle}{M_q}\right)^m \cdot f_{m+\alpha+1} \Bigg/ \sum_{m=2}^{\infty} \frac{(-1)^m}{m!} \left(\frac{\langle M\rangle}{M_q}\right)^m f_{m+1} \qquad \text{(A2)}$$

$$\langle\tau_D\rangle = A \left[\sum_{m=2}^{\infty} (-1)^m \frac{\langle M^{m+2\alpha}\rangle}{m!M_q^m} \Bigg/ \sum_{m=2}^{\infty} (-1)^m \frac{\langle M^m\rangle}{m!M_q^m} \right]^{1/2}$$

$$= \tau_D(\langle M\rangle) \left[\sum_{m=2}^{\infty} \frac{(-1)^m}{m!} \left(\frac{\langle M\rangle}{M_q}\right)^m f_{m+2\alpha} \Bigg/ \sum_{m=2}^{\infty} \frac{(-1)^m}{m!} \left(\frac{\langle M\rangle}{M_q}\right)^m \cdot f_m \right]^{1/2} \qquad \text{(A3)}$$

where $f_i = \langle M^i\rangle/\langle M\rangle^i$. R_D and R_K are obtained by summing the series for given values of α at a given value of $\langle M\rangle/M_q$. In *Table 5* the values of $\langle M\rangle = 1.33 \times 10^5$ and $M_q = 8 \times 10^4$ were chosen in order to be approximately applicable to the PBIC studied here. Note $M_q = 8 \times 10^4$ was determined for $\mu^2(M)$ by Bur and Roberts[8] from dielectric studies.