repeat unit was substantially the same in both cases, within the standard deviation, i.e. 4.2 ± 0.5 kJ mol^{-1}, end group effects and surface free energy were different. These alone account for the thermodynamic stability of the lamellar crystals.

Conclusion

The conclusion must be drawn from these melting studies that little or no chain folding with regular adjacent re-entry of the chain, as observed in the crystal structure of polyethylene single crystals and cyclic hydrocarbons, can be present in the lamellae produced in slow melt crystallization of polyethylene. Differences in the thermodynamic stability of the lamellar crystals arise from the lateral surface free energy and the stem length.

References

1 Keller, A. *Rep. Prog. Phys.* 1968, **31**, 623
2 Flory, P. J. and Yoon, D. Y. *Nature* 1978, **272**, 227
3 Mandelkern, L. *J. Polym. Sci., C* 1975, **50**, 457; *Acc. Chem. Rev.* 1976, **9**, 8
4 Painter, P. C., Watzek, M. and Koenig, J. L. *Polymer* 1977, **18**, 1169
5 Dawson, I. M. and Vand, V. *Proc. Roy. Soc., (London)* 1951, **206A**, 555
6 Kay, H. F. and Newman, B. A. *Acta Cryst.* 1968, **B24**, 615
7 Flory, P. J. and Vrij, A. *J. Am. Chem. Soc.* 1963, **85**, 3548
8 Broadhurst, M. G. *J. Chem. Phys.* 1962, **36**, 2578
9 Hay, J. N. *J. Poly. Sci., Chem.* 1976, **14**, 2845
10 Hay, J. N. and Wiles, M. *Makromol. Chem.* 1977, **178**, 623; *J. Poly. Sci. Chem.* 1979, **17**, 2223
11 Blair, H. E., Salovey, R. and Huseby, T. W. *Polymer* 1967, **8**, 9
12 Blair, H. E., Huseby, T. W. and Salovey, R. *A.S.C. Polym. Rep.* 1968, **9**, 1106
13 Mandelkern, L. and Gopalan, M. *J. Chem. Phys.* 1967, **71**, 3833
14 Brown, R. G. and Eby, R. K. *J. Applied Phys.* 1964, **35**, 1156
15 Wunderlich, B. and Arakawa, T. *J. Polym. Sci. A* 1964, **2**, 3697

Kerr effect relaxation measurements on glassy amorphous poly(methyl methacrylate)*

B.-J. Jungnickel
Deutsches Kunststoff-Institut, Schlossgartenstrase 6 R, D-6100 Darmstadt, Germany

(*Received* 3 *November* 1980; *revised* 6 *March* 1981)

Introduction

Optically and structurally isotropic materials can become birefringent under the influence of an electric field (Kerr effect). Between the steady state value of the birefringence Δn_0 and the intensity of the electric field E_0 the relation

$$\Delta n_0 = B \cdot \lambda \cdot E_0^2 \tag{1}$$

almost always holds, where λ is the wavelength of the used light and B is the so-called Kerr constant. Theoretically it can be shown relatively easily, that B contains information on molecular electrical parameters such as dipole moments and anisotropies of electric, optical and hyperpolarizabilities[1]. Furthermore, in a system of coupled molecules the Kerr constant gives hints to orientation correlations. Therefore, for polymers information on chain conformation and interactions between the chains can be obtained[2].

The term 'static Kerr effect measurements' is used, only if the steady state value of the birefringence is considered. This value, however, will be obtained only after a certain time following a sudden application of the electric field (*Figure 1*). For 'dynamic Kerr effect measurements', the corresponding time function $\Delta n_R(t)$ as well as the function $\Delta n_D(t)$ which describes the decay of the birefringence after switching off the field are additional sources of information. The relaxation depends on the character of the reorientation process (e.g. rotational diffusion or large angle jumps) and the magnitude of the mobility of the molecules[3]. In the case of polymers, conclusions are possible on the conformational and reorientational dynamics of the chain as a whole and its subunits. The curves $\Delta n_D(t)$ and $\Delta n_R(t)$ can be calculated for different models of molecular rearrangement.

Based on these considerations and theoretical calculations many successful investigations on reorientational dynamics and molecular electrical parameters were car-

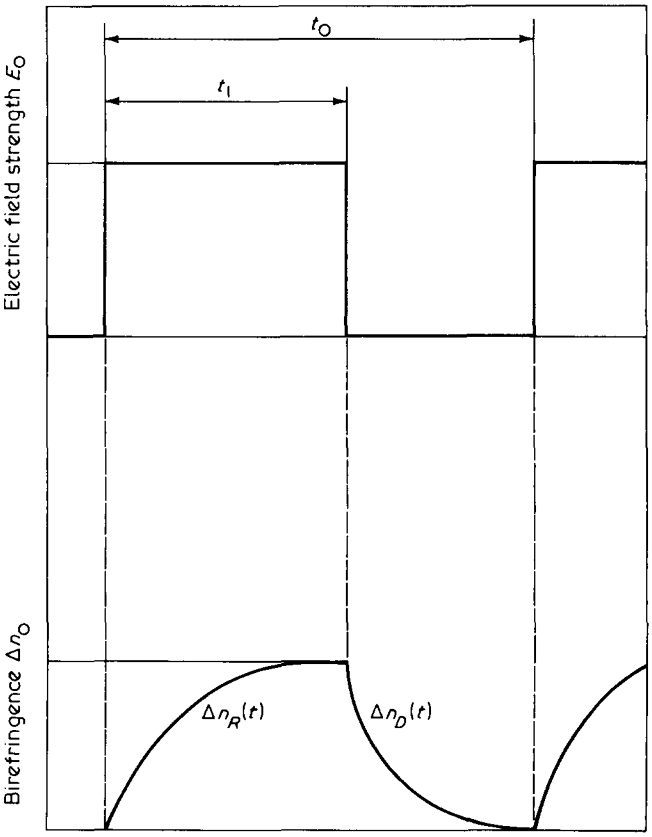

Figure 1 Schematic diagram of electric field and birefringence transients

---

* Partly presented as paper at EPS-Conference on 'Structure and Motion in Polymeric Glasses', Noordwijkerhout, The Netherlands, 22.4.80–25.4.80

0032–3861/81/060720–06$02.00

ried out for low molecular weight substances, oligomers and polymers in solution. The present work is concerned with studies of the dynamic Kerr effect of glassy amorphous poly(methyl methacrylate), PMMA.

The relaxational behaviour of glassy amorphous PMMA after mechanical disturbances[4,5], in alternating electric fields[6-8] (dielectric relaxation) or in quasielastic light scattering experiments[9,10] has already been investigated in detail (see *Table 4*). Until now, however, the knowledge of the dynamics of the corresponding molecular rearrangement processes is relatively limited. The different dispersion regions and relaxation times observed can be attributed rather uniquely to certain motions of certain molecular subunits. Details of these processes, such as the cooperativity and the specific course of these motions are essentially unclear. It is to be expected, that electro-optical investigations yield useful additional and valuable information.

Experimental

The measuring principle and technique are known from the literature[1]. Differing from the usual arrangement we used an optical compensator in addition to the crossed polarizers and analysers having an angle of ± 45 to the electric field to measure the value and sign of the birefringence (*Figure 2*). It gives an additive birefringence with known sign and is characterized by its optical retardation angle δ_0. The birefringence due to the Kerr effect can then be calculated by

$$\Delta n = \frac{\delta \cdot \lambda}{2\pi \cdot L} \tag{2}$$

(L = length of the sample) with

$$\delta = \delta_0 - \arccos\left[1-(1-\cos\delta_0)I(E)\cdot I^{-1}(O)\right] \tag{3}$$

($I(E)$ and $I(O)$ = light intensity at the multiplier with and without electric field respectively). Since almost always, δ is small this gives approximately

$$\delta = \delta_0\left(1-\sqrt{I(E)\cdot I^{-1}(O)}\right) \tag{4}$$

with an error of $<1.5\%$, if $\delta < 10^\circ$. Therefore from the signal the square root is extracted.

An intermittent high voltage is applied to the Kerr cell for measurements of the dynamic Kerr effect. At low frequencies the birefringence signal is recorded on a multichannel-X-time-recorder together with the high voltage and the temperature. At higher frequencies the signals are displayed on a double beam oscilloscope, from which photos are then taken.

As sample material, we used Plexiglas GS 218 (n_{20}^{D} $= 1.491$; absorption coefficient $\mu < 1.7 \, . \, 10^{-4}$ mm^{-1}; dielectric loss angle tan δ'(50 Hz) = 0.06) from Röhm GmbH, Darmstadt/Germany. This PMMA is especially developed for optical purposes. The samples must be absolutely optically homogeneous to avoid stress or orientation birefringence. To achieve this, the samples were annealed at $T_G + 5^\circ C = 120^\circ C$ for 24 h and then slowly cooled for a few days. The sample (see *Table 1*) has rectangular shape, an optical path length of 70 mm and end faces of 2 x 9 mm^2. For geometrically optical reasons these faces must be exactly smooth and parallel. This is achieved by preparing them with a special micro milling cutter (Jung GmbH, Germany). The samples were immersed into silicon oil to prevent electric breakdown and to improve the optical coupling between sample and cell windows. By monitoring the sample temperature it could be excluded, that heating effects due to the electric field and additional birefringence due to temperature gradients occur. The electrodes are made from stainless steel, pressed against the sample unprotected against carrier injection.

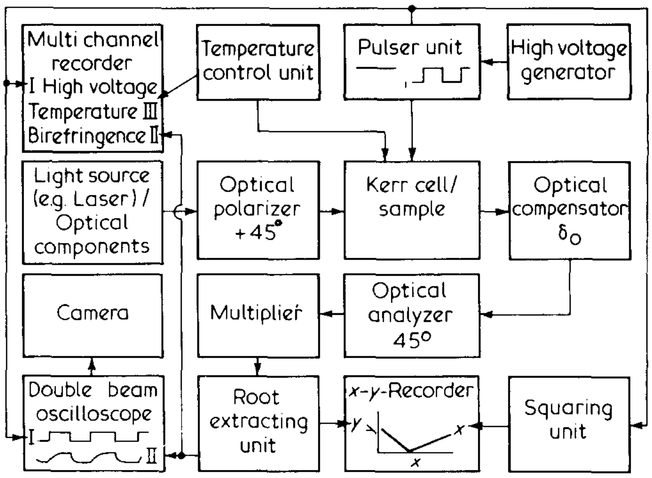

Figure 2 Schematic diagram of electro-optical measuring arrangement

Table 1 Essential properties of experimental arrangement

Length/width/height of sample	70 mm/2 mm/9 mm
Maximal electric field strength (for liquids or immersed solids)	15 MV m^{-1}
Temperature range	Room temperature–250°C
Wavelength of light source (tunable laser)	in general 514.5 nm
Smallest reproducible birefringence	$\approx 10^{-9}$
Range of relaxation times detectable	
– oscilloscopic	2 ms–5 s
(resolution limit	2 ms)
– by recorder	>5 s
error of relaxation times	⩽10%

Results

The following results all relate to measurements at room temperature. The relaxation curves $\Delta n(t)$ of glassy amorphous PMMA at two different field strengths are given in *Figure 3*. It is clear that both rise and decay transients can be considered as being additively composed of a fast component, taking a few seconds, and a slow component which approaches its steady state value on a time scale of hours. In the following, the last component will be indicated by number three. The shape of the fast component can be further resolved by the oscilloscopic technique (*Figure 4*). It is found that this component can again be split into two parts.

Both transients (rise and decay) of the faster component

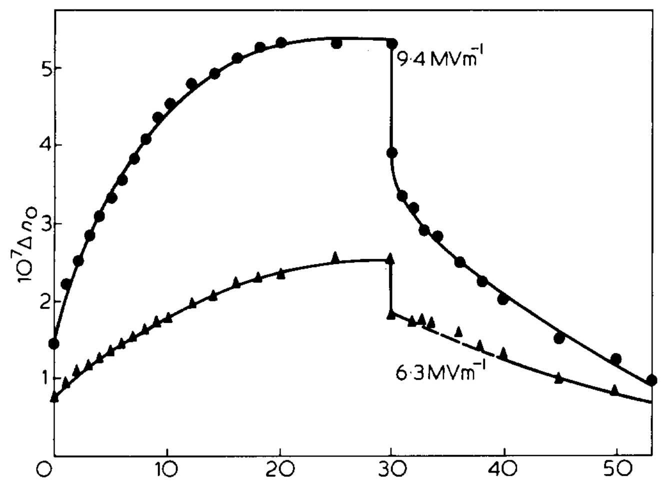

Figure 3 Rise and decay transients of birefringence at room temperature for PMMA at different electric field strengths

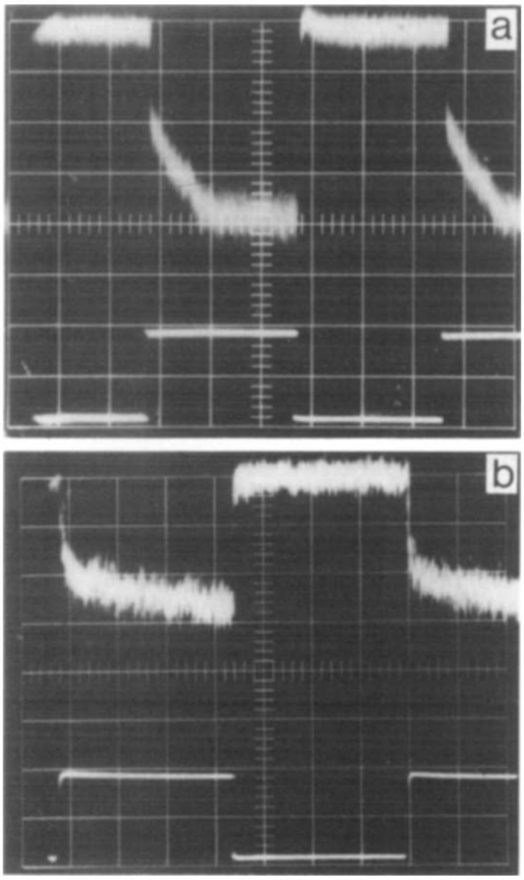

Figure 4 Electric field (below) and birefringence (above, display of $I(E)$ for $\delta_0 = 0$, see equation 3) transients at room temperature for PMMA. $E_0 = 9.4$ MV m^{-1}. (a) Grid scale = 1.07 s (b) grid scale 0.027 s

(number one) cannot be resolved with our experimental arrangement (see *Table 1*). This restriction also holds for the decay curve of the medium component (number two). However, the corresponding steady values of the birefrigence $\Delta n_0^{(i)}$ can be estimated as a function of the field strength for all three components (*Figure 5*). The observed linear dependence on the square of the field strength indicates that the Kerr law is fulfilled up to field strength of 10 MVm^{-1}. The corresponding Kerr constants as well as the time constants of all three relaxation components both for rise (τ_R) and decay (τ_D) transients are summarized in *Table 2*.

Discussion

The reorientational dynamics of polymer chains or their subunits has been discussed extensively in the literature. Various possible mechanisms were proposed and calculated. The best known models are the multi-side-model[11,12], the fluctuation diffusion model[3] and the rotational diffusion model[13,14]. In the latter it is assumed that the orientation distribution function of the molecules behaves according to the Fick law. The reorientation proceeds via small angle steps. In the fluctuation diffusion model it is assumed, that fluctuations in the environment of a molecule make reorientations possible. If this occurs the molecule reorients by large angle jumps. In the multi-side-model the transition probabilities between different

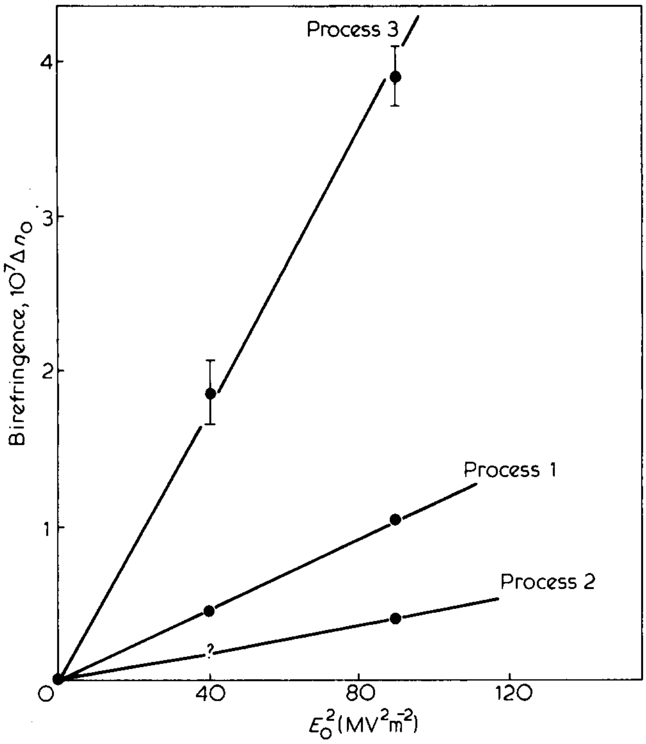

Figure 5 Kerr plot of steady birefringence for all detectable relaxation processes. Glassy–amorphous PMMA at room temperature. The error bars indicated for process three points apply for all others too. The question mark (process two) indicates, that this point was measured with this value, but (compare with the length of the error bars) it is difficult to separate it from the noise

Table 2 Kerr constants B and time constants τ (half maximum values) for the detectable relaxation processes in glassy amorphous PMMA at room temperature

Process No.	τ_R	τ_D	B (10^{-15} V^{-2} m)
One	<2 ms	<2 ms	2.2
Two	0.8 s	<2 ms	0.9
Three	6.0 h	13.2 h	8.6

Table 3 Properties of the different reorientation models

	Fluctuation diffusion	Rotational diffusion	Multi-side-model
Relation between Δn_R and Δn_D	$\Delta n_D(t) = \Delta n_0 - \Delta n_R(t)$	No analytical relation between $\Delta n_D(t)$ and $\Delta n_R(t)$	Depending on the symmetry and the multiplicity of the specific model
Relation between τ_R and τ_D	$\tau_R = \tau_D$	$\tau_R \gg \tau_D$	
Analytical expressions for Δn_D	Different analytical expressions possible for $\Delta n_D(t)$	$\Delta n_D(t) = \Delta n_0 \exp(-6\,\theta t)$ θ = rotational diffusion coefficient	
Relation between electro-optical and dielectric (τ_ϵ) relaxation times	$\tau_\epsilon = \tau_D$	$\tau_\epsilon = 3\tau_D$	

Table 4 Choiced relaxation times of the most important processes in some usual experimental techniques. Glassy amorphous PMMA at room temperature. Interpretations given by the corresponding authors. Partially calculated by $\tau = (2\pi f_M)^{-1}$ from maximal damping in the frequency region (no relation between process here and in *Table 2*)

Method	References	Process 1	Process 2		Process 3
Mechanical	5		71 ms	Side group rotation (β-relaxation)	Practically measureless (α-relaxation)
	4		20 ms		
	15	10^{-7} s; CH_3–side group rotation	36 ms		
Dielectric	7		15 ms	Side group rotation (β-relaxation)	Practically measureless α-relaxation
	15		6 ms		
Polarizing current (cf. text: discussion process three)	22				30 min Dipole orientation
Quasi-elastic	9	4.5 ms; torsional vibration of main chains	53 ms	Free volume relaxation	
Light scattering	10	3 ms	59 ms		
Kerr effect	This work	(rise) $\leqslant$ 2 ms (decay) $\leqslant$ 2 ms	(rise) 800 ms (decay) $\leqslant$2 ms		(rise) 6.3 h (decay) 13.2 h Dipole orientation by mean chain motion

equilibrium positions, which are separated by energy barriers, are considered. The mathematical treatment of these models leads to specific conditions according to which the analytical expressions for $\Delta n_R(t)$ and $\Delta n_D(t)$ as well as the corresponding relaxation times, must behave (*Table 3*). Furthermore, relations can be derived which relate electro-optical relaxation times to those found by other experimental techniques, in particular dielectric relaxation times.

Frequently, the transition curves can be approximated by an expression $\Delta n = \Delta n_0 \exp(-t\cdot\tau^{-1})^{\beta}$[16], where β is the so-called 'Williams–Watts-parameter'. In the case of rotational diffusion the deviation of β from unity indicates a distribution of relaxation times.

It is attempted in the following to discuss the experimental results in terms of these models.

Process three. From theoretical considerations it is known that for the fluctuation diffusion model, the rise and decay curves are symmetric[3] and that in the rotational diffusion model the decay proceeds exponentially[17] (*Table 3*). Considering this, our experimental results for process three coincide best with the predictions of the rotational diffusion model. This leads to a rotational diffusion constant $\theta_3 = (6.3 \pm 0.3)\ .\ 10^{-3}\ h^{-1}$. The analysis can proceed according to an algorithm given by Nishinari *et al.*[14] provided it is known whether the relaxation is governed by polarizability or dipole reorientation. A polarizability anisotropy of $\Delta\alpha \approx 10^{-33}$ Fm^2 is obtained, if polarizability reorientation is assumed. This value differs from those given in the literature by a factor 10^8,[18]. This is structurally impossible. The assumption of a dipole reorientation mechanism, however, leads to dipole moments of 10^{-26} Cm. This is physically reasonable, although it is larger than that of the monomer unit ($5.3.\ 10^{-30}$ Cm,[19]) by a factor of about 1500. This experimental result indicates a large cooperativity of chain parts reorienting via small angle steps at room temperature. In the glassy state, it can be interpreted in terms of a 'correlation volume' containing this amount of monomer units and therefore having a diameter of about 7 nm. The magnitude of this value coincides with that of the 'cooperative rearrangement region' as expected by Donth[20] and Adam *et al.*[21] in their fluctuation theory of glass transition and glassy state. According to these authors, the cooperative rearrangement regions are the smallest regions in which changes in configuration are possible without distortion of the surroundings. Configurational changes can take place if the enthalpy fluctuations have sufficient magnitude. Glass transitions can be explained by relating cooling rate $\dot{T}$ (in general: measuring time) and the fluctuation frequency $\nu(T)$ (in general: relaxation time). The fluctuation frequency is determined by the size of the cooperative rearrangement regions through thermodynamic considerations.

Conclusions on a possible dipolar origin of relaxation process three can also be drawn from the relatively large absolute value of the Kerr constant B_3. In general, such values can only be achieved by dipole reorientation. Furthermore, it can be remarked, that under comparable conditions the direct current through a PMMA sample, after an application of an electric field, decays with half life times comparable to ours for process three. This polarizing current should be governed mainly by dipole orientation[22] (*Table 4*). All these observations, in particular the magnitude of order of the relaxation times and the cooperativity of process three suggest a relationship with the α-relaxation which can be observed by other experimental techniques.

In general, injection of carriers into the sample material via the electrodes cannot be excluded. However, there has been no exact knowledge on the extension and velocity of this process until now and therefore on the inner field in dependence on time[31]. It is possible that the Kerr effect relaxation behaviour is affected by such carrier injection. In the present case, however, this seems to be improbable because of the relatively small d.c. conductivity of PMMA ($<10^{-16}\ \Omega^{-1}\ \mathrm{cm}^{-1}$), the identity in the shape of the rise and decay transients and especially the fulfilment of the Kerr law.

If one considers the rearrangement region as a particle which moves in a matrix consisting of the same material, then from the rotational diffusion constant and the dimension of the rearrangement region, the viscosity of PMMA can be calculated[1,23]. The resulting value of about 10^{10} Poise coincides relatively well with that of 10^{11} Poise found by extrapolation of rheometrically measured melt viscosities to the glass transition temperature[12,8].

Processes one and two. It is rather difficult for various reasons to comment on the relaxation processes one and two. In the case of process two it is remarkable that the rise and decay transient times differ by two magnitudes of order. Williams[25] observed a similar behaviour for oligomeric PMMA just above T_G (he found $\tau_R \approx 10\tau_D$). This means that, due to the application of the electric field, the relaxational conditions are greatly changed. Indeed, in the torsional pendulum experiment, the application of an electric field of 6 MVm^{-1} to a sheet-like PMMA sample causes a shift of the frequency-temperature-curve in the α-region by about 10°C to higher temperatures compared to the field-free experiment[26]. For our PMMA, this indicates a shift of glass temperature from 115°C to 125°C. This could explain a frequency shift by two magnitudes of order. A possible explanation is a hindrance of the course of the relaxation by electrostriction and an interference of electrostriction and free volume[27,28]. Then, however, one would also expect an influence on relaxation process three. It is apparent that measurements on dependence of temperature, or, for instance, measurements of dielectric behaviour under the influence of a strong electric field in a wide range of frequencies are required in order to solve this discrepancy. Such measurements are presently under progress. Other possible explanations for the difference between τ_R and τ_D are heating effects and ion implantation and migration[25,28]. These causes, however, seem improbable since the corresponding relaxation behaviour is too slow compared with the electro-optical relaxation. This objection applies to electrostriction also[29].

For most of the possible explanations of the difference between τ_R and τ_D it seems, that at the very least the decay transition time τ_D is uniquely related to the Kerr effect. Unfortunately, only an upper limit of two milli-seconds can be given for τ_D because of the limited resolution power of our experimental arrangement. Also an analysis of the slope of the transients one and two is not possible. Because of the limited information the nature of these processes can only be open to conjecture. One of them must surely correspond to the β-relaxation, that is rotation of the side groups. The dipoles of the PMMA monomer units lie in these side groups and make an angle of about 70° with the axis of rotation[30]. Therefore, such a rotation can be induced by an electric field and must consequently yield a component in the Kerr effect with dipolar origin.

Finally, for the sake of comparison, in *Table 4*, the relaxation times of different relaxation processes from the literature are shown. They correspond to room temperature and are estimated by different experimental methods available. It is true, they cannot fully agree, e.g. because some experiments are concerned with rotational movements of chain parts, others with oscillating or rectilinear movements. In spite of consideration of these restrictions, it can be seen that the values, including Kerr effect data, differ quite considerably. Assuming that $\tau_D^{(2)} = 2$ ms and remembering that $3\tau_D = \tau_R$ (see *Table 3*) it seems, that relaxation process two corresponds to the β-relaxation. But only further experimental and theoretical efforts can confirm this as certain.

Acknowledgement

The financial support of the Deutsche Forschungsgemeinschaft (special research branch 'chemistry and physics of macromolelules') is gratefully acknowledged. I also express my thanks to the Röhm GmbH for supplying the PMMA.

References

1 Fredericq, E. and Houssier, C. 'Electric Dichroism and Electric Birefringence', Clarendon Press, Oxford, 1973

2 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience Publishers, New York–London–Sydney–Toronto, 1969

3 Beevers, M. S., Crossley, J., Garrington, D. C. and Williams, G. *J. Chem. Soc. Faraday Trans.* 1976, **72**, 1482

4 Koppelmann, J., Leder, H. and Royer, F. *Colloid Polym. Sci.* 1979, **257**, 673

5 Heijboer, J. 'IUPAC Int. Symp. on Macromol.', Madrid, 1974

6 Williams, G. *Trans. Faraday Soc.* 1966, **62**, 2091

7 Koppelmann, J. *Progr. Colloid Polym. Sci.* 1979, **66**, 235

8 Kunststoff-Handbuch (Ed. by Vieweg, R. and Esser, F.) Vol IX 'Poly(methacrylates)', Hanser-Verlag, München, 1975

9 Cohen, C., Sankur, V. and Pings, C. J. *J. Chem. Phys.* 1977, **67**, 1436

10 Jackson, D. A., Pike, E. R., Powles, J. G. and Vaughan, J. M. *J. Phys. C: Sol. State Phys.* 1973, **6**, L55

11 Williams, G. *Europhys. Conf. Abstr.* 1980, **4A**, 5

12 Fröhlich, H. 'Theory of Dielectrics', Oxford University Press, Oxford, 1949

13 Benoit, H. *Ann. Phys.* 1951, **6**, 561

14 Nishinari, K. and Yoshioka, K. *Kolloid-Z./Z. Polym.* 1969, **235**, 1189

15 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley & Sons, London, 1967
16 Williams, G. and Watts, D. C. *Trans. Faraday Soc.* 1970, **66**, 80
17 Benoit, H. *J. Chim. Phys.* 1950, **47**, 719
18 Fischer, E. W., Wendorff, J. H., Dettenmaier, M., Lieser, G. and Voigt-Martin, J. *J. Macromol. Sci. Phys.* 1976, **B12**, 41
19 Salovey, R. *J. Polym. Sci.* 1961, **50**, S7
20 Donth, E. *Plas. Kautsch.* 1978, **25**, 617
21 Adam, G. and Gibbs, J. H. *J. Chem. Phys.* 1965, **43**, 139
22 Mazur, K. *Jpn J. Appl. Phys.* 1978, **17**, 265
23 Broersma, S. *J. Chem. Phys.* 1960, **32**, 1626
24 Knappe, W. and Schönewald, H. *Kunststoffe* 1970, **60**, 657
25 Williams, G. personal communication, 1980
26 Jungnickel, B.-J. unpublished results, 1980
27 Wendorff, J. H. personal communication, 1980
28 Beevers, M. S., Elliot, D. A. and Williams, G. *Polymer 1980*, **21**, 13
29 Fuhrmann, J. *Kolloid-Z./Z. Polym.* 1972, **250**, 1075
30 Smyth, Ch. P. 'Dielectric Behavior and Structure', McGraw Hill, New York, 1955
31 Sessler, G. M. (Ed.) 'Topics in Applied Physics', Vol 33, Electrets, Springer-Verlag, Berlin u.a., 1980