Polymer Vol. 36 No. 24, pp. 4553–4559, 1995

0032-3861/95/$10.00+0.00

Kerr-effect measurements on poly(vinylidine fluoride), poly(methyl methacrylate) and their blends

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(Received 9 November 1994)

The dynamic electro-optical effect of poly(vinylidene fluoride) (PVDF), poly(methyl methacrylate) (PMMA) and their blends is reported. The response of PMMA exhibited one detectable relaxation in the vicinity of the glass transition, the time constant of which revealed that it is due to side-chain rotation. In contrast, two relaxations were detected in the PVDF melt. From the strength of the faster, the orientation correlation coefficients g_1 and g_2 can be calculated to be 0.5 and 15, respectively, indicating an antiparallel arrangement of the individual electric moments of the monomer units. The slow relaxation is suggested to be due to weakening of these correlations by the action of electric-field-injected charges. The kinetics of that distortion are enhanced by blending with PMMA, whereas the other relaxations of both components do not change with blending.

(Keywords: poly(vinylidene fluoride); poly(methyl nethacrylate); Kerr effect)

INTRODUCTION

The investigation of the interactions on a molecular level between blend components, and their thermodynamic and structural consequences, are important areas of study in current polymer research. There are a number of spectroscopic and relaxational techniques available which allow insight into certain aspects of the problem. A more complete picture is obtained by combination of the contributions of a large number of such investigation techniques. A rather unfamiliar type of such techniques are electro-optical investigations.

Isotropic materials can become birefringent under the action of a strong electric field due to the field-induced reorientation of induced or permanent electric moments. The field-induced reorientation of a certain molecule or group of atoms is controlled by the energetic interactions with the surroundings, of which chemical links are a limiting case. The electro-optical effect ('Kerr effect') consequently yields information on the strength and the relative orientation of electric moments and polarizabilities of a single molecule[1,2]. Moreover, conclusions can be drawn on the orientation correlations of molecules and atom groups in condensed systems[3]. Kerr-effect measurements allow an estimation of the conformation of macromolecules and the configuration of their subunits as a function of the temperature, the molecular weight, or, if dissolved, the concentration[4]. From this, in turn, conclusions can be drawn on the origin, the location, the strength and the consequences of interactions between the components of a solution or a blend. The electric-field-induced birefringence, finally, develops after a sudden switching-on of the field according to a characteristic temporal law until approaching its steady equilibrium value ('dynamic Kerr effect'). These dynamics yield additional information on the type and the time constant of orientational relaxations on a molecular level[5].

We report in this paper on the electro-optical investigations on poly(vinylidene fluoride) (PVDF), poly(methyl methacrylate) (PMMA) and their blends. These polymers are miscible over the whole composition and accessible temperature range, respectively[6]. The miscibility is due to strong interactions between the electric moments of the two polymers, and to hydrogen bonding between the oxygen of the carbonyl group of the PMMA side group and the acidic hydrogens of the PVDF monomer unit[7]. It has been concluded from dielectric measurements of semicrystalline materials that, on the one hand, the orientation correlations between the PVDF electric moments are disturbed and broken by the presence of PMMA, and that, on the other hand, the side-group rotation in PMMA is impeded by PVDF[8]. These specific interactions should also influence the electro-optical response. The latter is expected to be very strong because of the strong electric moments of the blend components. PVDF, however, is a semicrystalline material at ambient temperature and, consequently, is not transparent. Investigations on this polymer are therefore possible only in the melt or when crystallization has been suppressed. The latter holds for blends with PMMA content larger than 50%. Our investigations have been performed in the melt at temperatures between 180 and 210°C.

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BASIC FACTS AND EQUATIONS

Basically, the birefringence Δn of a material is proportional to the thermodynamic expectation value $< \Delta\alpha^o >$ of the anisotropy of the optical polarizability:

$$\Delta n = z < \Delta\alpha^o > \qquad (1)$$

If the anisotropy is caused by the orientation efficiency of an external electric field E_0, then using the Lorentz field approximation $c = E_i/E_0 = (\chi^o + 3)/3$ where E_i is the electric field inside the material and χ^o is the dielectric susceptibility at optical frequencies, and inserting the Maxwell formula $n^2 = \chi^o + 1$ where n is the average refractive index, it can be shown that[9]:

$$z = \frac{N(n^2+2)^2}{18n\epsilon_0} \qquad (2)$$

where N is the number density of the particles in the sample material and ϵ_0 is the permittivity of vacuum. The value $< \Delta\alpha^o >$ can be calculated by means of statistical mechanics, considering the disturbing contribution of the external electric field to the Hamiltonian of the system[9,10]. Expanding the corresponding expression into a power series, it is found that it exhibits only even powers in E_0 since the effect is related to a second-rank tensor. The first term of the series, taking into account only linear susceptibilities, is:

$$< \Delta\alpha^o > = \frac{\beta c E_0^2 < R >}{30} \qquad (3)$$

where $\beta = (kT)^{-1}$ and

$$< R > = 2\Delta\alpha^o\{f\mu^2[2(g_1 - 1) + g_2] + kT\Delta\alpha^s\} \qquad (4)$$

In this equation, f is:

$$f = \frac{1}{2}(3\cos^2\Theta - 1) \qquad (5)$$

where Θ is the angle between the electric moment vector μ and the long axis of the polarizability tensor of a single particle. In (4), $\Delta\alpha^s$ and $\Delta\alpha^o$ are the polarizability anisotropies in the static limit and at optical frequencies, respectively, of the particles. g_1 and g_2 are the orientation correlation factors, which are defined by:

$$g_1 = \sum_i < \cos\eta_{ij} >_i \qquad (6)$$

and

$$g_2 = \frac{1}{2}\sum_i < 3\cos^2\eta_{ij} - 1 >_i \qquad (7)$$

where η_{ij} is the angle between some reference directions in the particles i and j (cf. *Figure 7*). Obviously, g_1 is related to directed quantities like electric moments whereas g_2 is linked with the orientation of inversion symmetrical quantities, i.e. tensors of even rank like polarizabilities. It should be mentioned that g_1 and g_2 are defined under field-free conditions.

By combination of equations (1)–(3), it is found that:

$$\Delta n = \lambda B E_0^2 \qquad (8)$$

('Kerr law') where

$$B = z < R > \frac{(\beta c)^2}{30\lambda} \qquad (9)$$

is the 'Kerr constant', and the light wavelength λ is commonly introduced for historical reasons*. An inspection of equations (4) and (5) reveals that the 'moment term', the first one in equation (4), does not contribute to the Kerr constant if $\Theta = 54.7°$. Since, in most instances, the moment term exceeds the polarizability term (second term in equation (4)), remarkably, the sign of the birefringence is determined by the angle Θ: for $\Theta < 54.7°$, the sign of B is positive, whereas B is negative for $\Theta > 54.7°$.

An interpretation of the experimental results with respect to the orientation correlation parameters requires knowledge of the electric moment and the polarizability of a single particle. The equilibrium conformations of a monomer unit of the polymers as investigated here have therefore been simulated by use of a commercial simulation program based on a MNDO (modified neglect of differential overlap) algorithm[11]. From this, the electric moments and the polarizabilities have then been derived. The results are illustrated by *Figure 1*, and the numerical values are collected in *Table 1*. For PVDF, the electric moment vector is oriented perpendicularly to the longitudinal axis of the monomer unit such that $\Theta_{PVDF} = 90°$. In PMMA, the location and the strength of the electric moment is determined mainly by the carbonyl unit and to a lesser extent by the methoxy group. Therefore, μ_{PMMA} points roughly (but not exactly) into the direction of the carbonyl group of the repeat unit. The PMMA monomer unit polarizability main axis points into the direction of the side group, and the angle Θ_{PMMA} between μ_{PMMA} and $\Delta\alpha^s_{33}$(PMMA) amounts to $\Theta_{PMMA} = 59°$. This angle can be compared with that of $\Theta_{PMMA} = 60$–$70°$ from the literature[12]. Literature values for μ as derived from i.r. measurements are $\mu_{PVDF} = 7.56 \times 10^{-30}$ C m (ref. 13) and $\mu_{PMMA} = 5.56 \times 10^{-30}$ C m (ref. 14).

EXPERIMENTAL PROCEDURE AND SAMPLE MATERIALS

The samples were commercial-grade materials as described in *Table 2*. For sample preparation, pellets of the starting materials were first mixed in the desired ratio, then extruded three times and moulded at 200°C into plates with a thickness of 1 mm. Finally, samples with dimensions of 10 mm × 1 mm, where the long dimension is the optical path L, and the electric field is applied at the 10 mm × 5 mm face, were cut from these mouldings. Thermogravimetric measurements revealed that the materials are chemically stable for at least 4 h up to 380°C (PVDF) and 210°C (PMMA). Electro-optical measurements could therefore be performed in the temperature range between 180 and 210°C.

The experimental set-up is shown diagrammatically in *Figure 2*. The sample cell temperature was controlled to within ± 0.1°C. The electric field pulses were generated by a high-voltage supply, which was triggered by an external pulse generator. The high voltage pulse rise time was below 500 ns. A HeNe laser ($\lambda = 633.2$ nm) serves as a light beam. Its polarization direction was inclined by an angle $\pi/4$ with respect to the electric field. The light passes through the sample and then through a quarter-wave retarder in order to enhance the sensitivity of the arrangement. The analyser was inclined with respect to the extinction direction by a fixed angle $\alpha = -5°$. This allows detection of the sign of the birefringence. The transmitted light was registered by a photo-cell with a

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* Sometimes, and more correctly, the quantity $K = \lambda B$ is designated as the Kerr constant

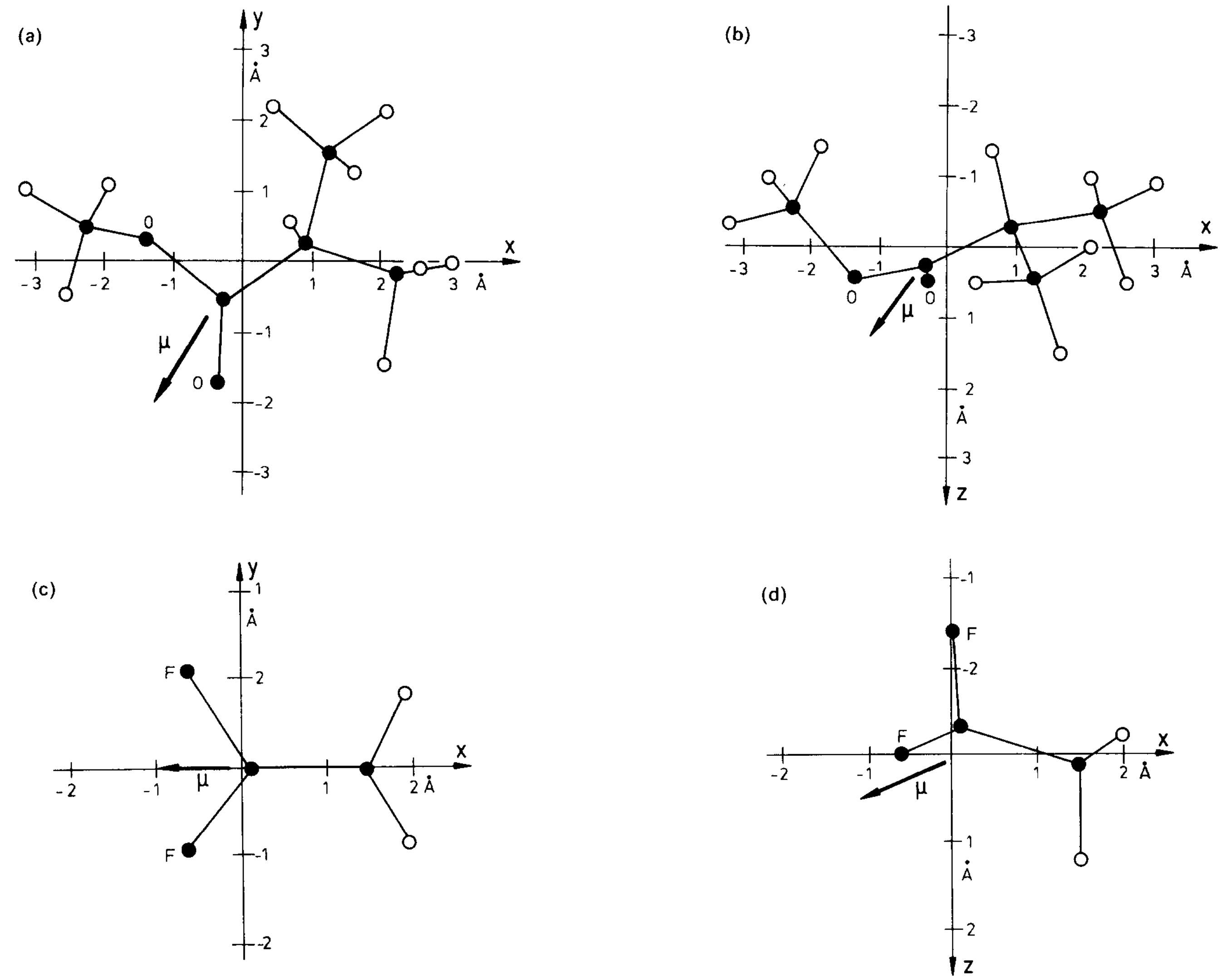

Figure 1 Monomer unit conformations. Left, *xy* plane; right *xz* plane; μ arrows indicate just directions, their lengths are not representative. Open circles, hydrogen atoms; unlabelled full circles, carbon atoms. (a, b) PMMA [-CHCH(-CH$_3$)(CO-O-CH$_3$)-]. The linking bonds to the adjacent monomer units have been neutralized by hydrogen (in order to simplify the calculation). (c, d) PVDF [-CH$_2$-CF$_2$-]

time constant of about 300 ns. The experimental arrangement allows a resolution of Δn of 10^{-10} and a temporal resolution of better than 10^{-6}s. The value of Δn was calculated from:

$$\Delta n = \frac{\lambda}{\pi L}\left\{\arcsin\left[\left(\frac{I_0}{I_E}\right)\frac{1}{2}\sin\alpha\right] - \alpha\right\} \qquad (10)$$

where I_E and I_0 are the light intensities with and without the electric field, respectively. The intrinsic birefringence Δn_0 of the material due to frozen stresses or slight orientations may amount to more than 10^{-4} despite suitable annealing. This value is larger by orders of magnitude than the electro-optical birefringence, which amounts to 10^{-8} or less. Therefore, Δn_0 must be carefully eliminated by an optical compensator prior to the measurements. Moreover, Maxwell forces on the samples, which can lead to pressure-induced birefringence of the same order as the desired effect, must be prevented by a fixed electrode arrangement.

RESULTS

Figure 3 shows a typical light intensity trace for PMMA after application and removal of a step-like electric field. Rise (τ_R) and decay (τ_D) times, respectively, differed remarkably: τ_R^{PMMA} amounts to about 20 ms whereas τ_D cannot be resolved ($\tau_D^{PMMA} > 500$ ns). The Kerr law is

Table 1 Calculated electric moments and polarizabilities of the monomer units of the investigated polymers (cf. *Figure 1*)

		PVDF	PMMA
Static polarizability (10^{-40} F m^2)	α^s_{11}	2.4	7.9
	α^s_{22}	2.7	5.6
	α^s_{33}	2.7	8.2
Electric moment (10^{-30} C m)	μ	6.7	5.6

Table 2 Sample materials

	PVDF	PMMA
Supplier	Solvay	Röhm, Germany
Grade	Y8N	X8N
Number-average molecular weight	38 000	65 000
Weight-average molecular weight	100 000	104 000
Equilibrium melting temperature, $T_m°$ (°C)	178	–
Glass transition temperature, T_g (°C)	–41	122

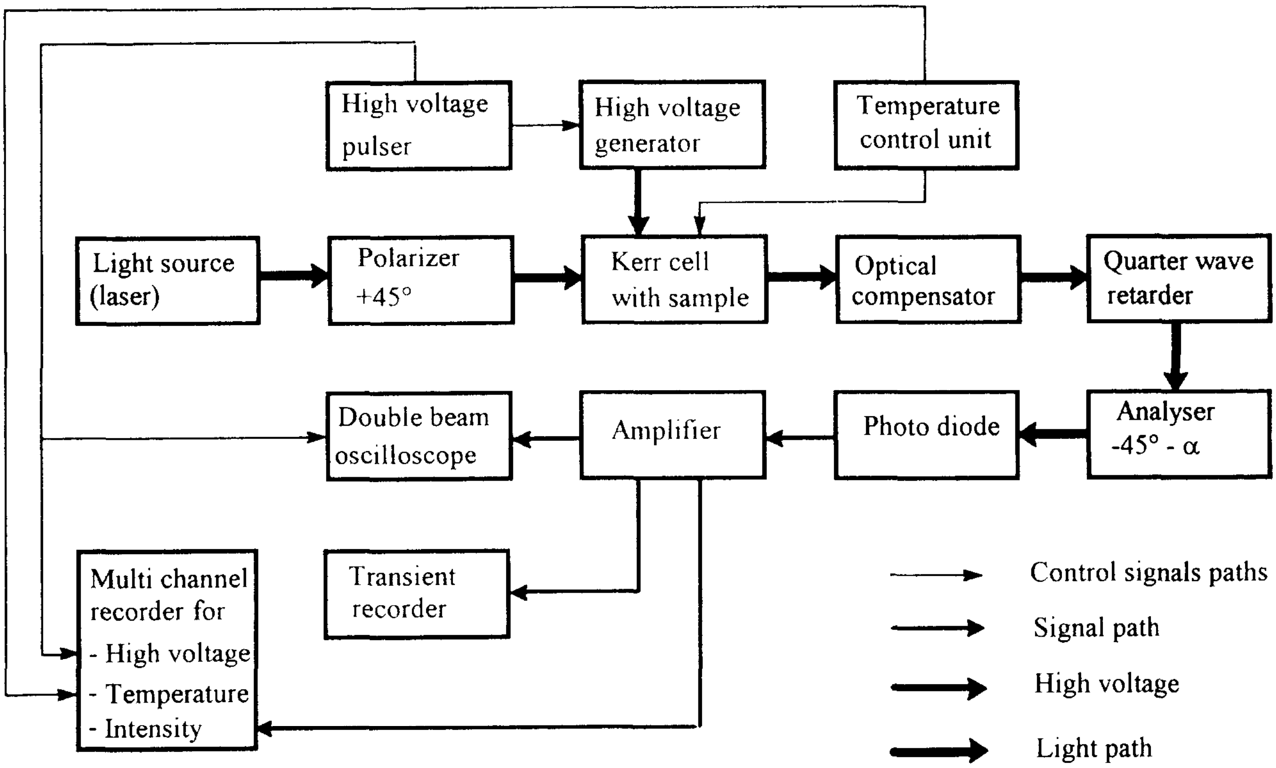

Figure 2 Experimental set-up

fulfilled. The Kerr constant is independent of temperature below and in the vicinity of the glass transition, and amounts to $B^{PMMA} = +1.5 \times 10^{-15}\,\mathrm{m\,V^{-2}}$. If the electric field is applied for longer than about 300 ms, the measured light intensity scatters irregularly. This can be attributed to the heating effects caused by electrical conductivity, which can cause flow birefringence, and to the action of electric-field-injected charges, which cause undefined electric field conditions in the bulk of the sample[15].

Figure 4 exhibits the birefringence transients of a PVDF sample at 201°C. Two distinct relaxations can be observed in the rise as well as in the decay transients, respectively. At first, a negative birefringence (I) develops quickly with a time constant of about $\tau_{\mathrm{I}}^{PVDF} \leq 1$ ms (*Figure 5*). The corresponding Kerr constant is $B_{\mathrm{I}}^{PVDF} = -4.3 \times 10^{-14}\,\mathrm{m\,V^{-2}}$. For longer times, a remarkably slower relaxation (II) with a positive birefringence becomes effective and approaches the overall final value after 2–4 ms. The associated Kerr constant amounts to $B_{\mathrm{II}}^{PVDF} = +2.7 \times 10^{-14}\,\mathrm{m\,V^{-2}}$. The relative strengths of the two relaxations are the same at rise and at decay. This is not self-evident[9]. Switching off the electric field consequently causes at first a rapid change of the sign of the birefringence, as can be seen clearly in *Figure 4*. Again, the birefringence equilibrium values of all partial relaxations and of the whole effect as well fulfil the Kerr law. As has been observed already for PMMA, the transmitted light intensity starts to change

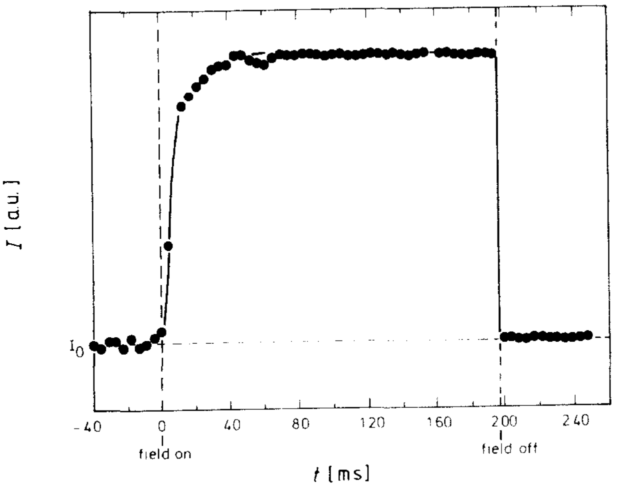

Figure 3 Electro-optical transient of a PMMA sample at 70°C. Shown is the transmitted light intensity I as a function of time. I_0 = light intensity with field off

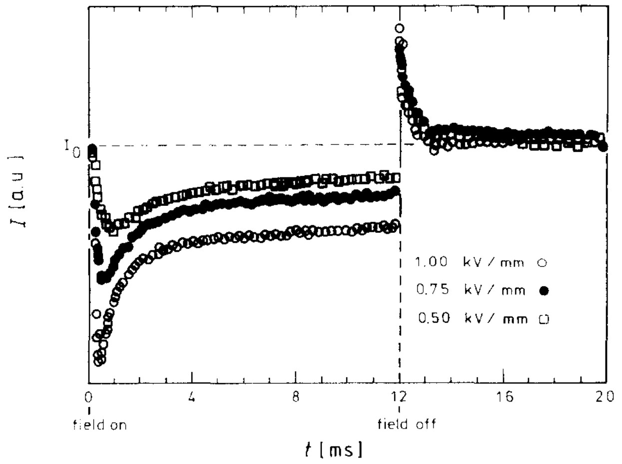

Figure 4 Electro-optical transients (transmitted light intensity I) of a PVDF sample at several electric field strengths as indicated. $T = 201$°C. I_0 = light intensity with field off

irregularly for longer electric field application times. This can again be attributed to a certain electrical conductivity and to the action of electric-field-injected charges, which cause undefined electric field conditions in the bulk of the sample. Moreover, PVDF degrades under the action of an electric field[15].

The electro-optical effect of PVDF is therefore stronger than that of PMMA by a factor of at least 10. The Kerr effect of blends is consequently dominated by the contribution of the PVDF component, and their transients have in principle the same course as those of pure PVDF. It turns out that the relative strengths of all relaxations are weighted by the composition in the limits of the accuracy of the Kerr-constants determination. The relaxation time of the slow PVDF relaxation (II), however, becomes remarkably smaller with increasing PMMA content (*Figure 6*). The two PVDF relaxations merge therefore at a PMMA content of about 50%. At still higher PMMA content, all the three relaxations—the two relaxations arising from PVDF and the PMMA relaxation—of the two components merge and are no longer distinguishable.

DISCUSSION

The electro-optical response of pure PMMA has been studied several times before[16–19]. Whereas the magnitudes of the effect as reported by those authors agree very well and coincide with that found here, the number of individual relaxations and their temperature dependence seem to vary irregularly with the specific sample material and experimental procedure, respectively. Most probably, the influence of injection of charges into the sample material and the material's conductivity have been underestimated so far. The relaxation time $T_R \approx 20\,\mathrm{ms}$ during rise corresponds to a Kerr relaxation frequency ν_K of $\nu_K = 1/(2\pi\tau_R) \approx 10\,\mathrm{Hz}$. This compares rather well with that (ν_ϵ) of about 4.5 Hz for the dielectric β relaxation at room temperature[14], considering that the relation $\nu_K \approx 1/(3\nu_\epsilon)$ holds for rotation diffusional reorientation[20], and proves that this relaxation is due to rotation of the methacrylate side group. The difference in rise and decay relaxation times has also been observed frequently[16,21], and has been attributed to ion implantation, electrostriction and free-volume effects[21].

The discussion of the magnitude of the Kerr constant of PMMA started in the cited literature from the assumption that the electric moment and the polarization major axis are oriented almost parallel, and, consequently, that the effect is determined by the moment term. This assumption has been based on the estimation of the group contributions to the electric moment and to the polarizability, neglecting the energetically determined equilibrium conformation of the monomer. Our computer simulations, however, yielded an angle of $\Theta = 59°$ and, consequently, a geometry factor $f = -0.1$. The relative orientation of electric moment and polarizability consequently weakens the moment contribution to the Kerr effect by a factor 10. From dielectric measurements, moreover, it is known that the orientation correlation parameter g_1 changes from 0.3 at room temperature to 0.9 at 160°C (ref. 22). Introducing all these values into equations (4) and (9), it is finally found that g_2 amounts to $g_2 = 1.5$ in the vicinity of the glass transition. This value is comparable to that of $g_2 = 1$ found by dynamic light scattering[23] and proves that the corresponding correlations are only weak.

The measured overall Kerr constant of PVDF is negative in accordance with the relative orientation of the electric moment and the polarizability, from which it follows that $f = -1$. Moment and polarizability contributions, respectively, to the whole Kerr effect would therefore relate as 700 : 1 if the values of *Table 1* are introduced into equation (4), and if no orientation correlations were present. Dielectric measurements at 185°C, i.e. in the melt, yielded the dielectric permittivity in the static limit $\epsilon^0 = 7$. Using the Onsager relation:

$$\epsilon^0 - \epsilon^\infty = \frac{3\epsilon^0}{2\epsilon^0 + \epsilon^\infty} \frac{N g_1 \mu^2}{3kT} \left(\frac{\epsilon^\infty + 2}{3} \right)^2 \qquad (11)$$

with $\epsilon^\infty = n^2 = 1.73^2 = 2.9$ and $N = 9.4 \times 10^{-27}\,\mathrm{m}^{-3}$, and introducing the computer-simulated μ value, it is found by dielectricity that $g_1 \approx 0.5$ in the melt at 185°C. Combining this value with the Kerr constant of the fast relaxation I and the computer-simulated polarizability values, it is finally found that $g_2 \approx 10$–15. There are obviously rather strong orientation correlations in the PVDF melt between the monomer units with electric

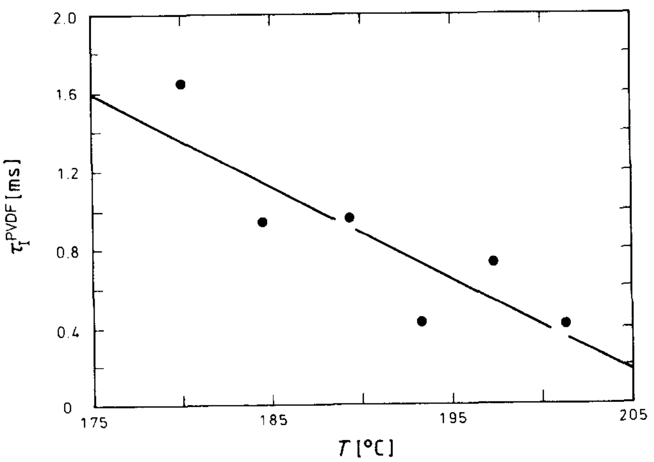

Figure 5 Relaxation time τ_I^{PVDF} of the fast PVDF relaxation as a function of temperature T in pure PVDF

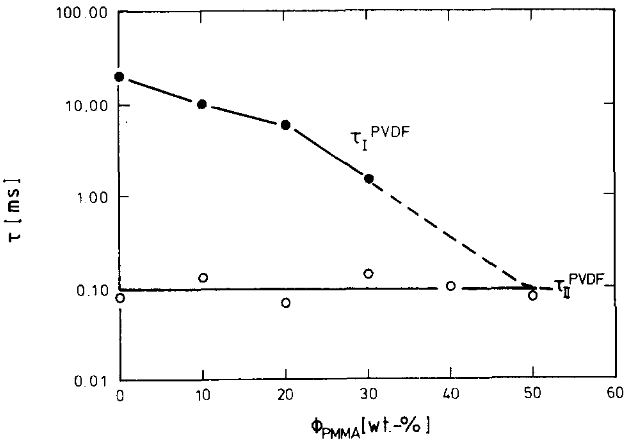

Figure 6 Relaxation times τ of the PVDF relaxations as a function of composition (PMMA content ϕ^{PMMA} in weight per cent) at 180°C. Note the logarithmic scale of the τ axis

moments aligned preferentially antiparallel such that g_1 is small and g_2 is rather large (*Figure 7*). Orientation correlations of that kind are clearly favoured for energetic reasons.

There is no obvious origin of the second relaxation (II) and no immediate correspondence to dielectric relaxation frequencies for the rise time of relaxation I (cf. *Figure 5*). The latter exceeds those of the known relaxations by orders of magnitude, and the reasons for the observed behaviour can only be speculated on. It is known from ferroelectric investigations on PVDF and from dielectric measurements with intermediate electric field strengths that the injection of charges plays an important role for the relaxational behaviour and the stability of dipole orientations[24]. We suggest therefore that the charges as injected in our experiments disturb the reorientation behaviour of the electric moments such that they break the orientation correlations present under the field-free conditions and expressed by g_1 and g_2. The corresponding field-induced diminution of the orientation correlation factor g_2 causes a likewise temporal diminution of the average orientation of the electric moments and finally a decrease of the electro-optical response. According to this interpretation, the fast relaxation I is the intrinsic electro-optical response of PVDF, which is deteriorated and disturbed by process II. The relaxation time of the latter reflects, therefore, the injection and the migration rates, respectively, of the injected charges.

Finally, the Kerr effect of the blends can be discussed. The Kerr constants of all relaxations are proportional to the content of the respective components. The relaxations as detected by electro-optics are therefore not influenced by blending, and the blend components do not interact with respect to these relaxations. Particularly, the orientation correlations in the melt are not changed by blending. It should be recalled that, in contrast, the orientation correlations of the electric moments in the interphase between PVDF crystals and their amorphous surroundings are remarkably disturbed by blending with PMMA[8]. Similarly, the reorientation rate of the electric moments is not influenced by the PMMA. However, the second relaxation, which we attribute to injected-charge-induced distortion of the orientation correlations between the PVDF electric moments, speeds up remarkably with increasing PMMA content.

In conclusion, Kerr-effect measurements reveal a distinct antiparallel alignment of adjacent electric moments of the PVDF chains in the melt. These orientation correlations are not influenced by blending with PMMA. They are, however, most probably disturbed and diminished by charges as injected by the action of the electric field, and this diminution is enhanced and accelerated by the PMMA. In contrast, the orientations of the electric moments of the PMMA are almost not correlated. This can be concluded by analysis of its electro-optical response, which is due to side-chain reorientation, i.e. by the so-called β relaxation. Since the Kerr effect of PVDF is stronger than that of PMMA by a factor of 10, the corresponding effect in the blends is ruled by the PVDF component, and the observation of mixing-induced changes in the behaviour of the PMMA is not possible.

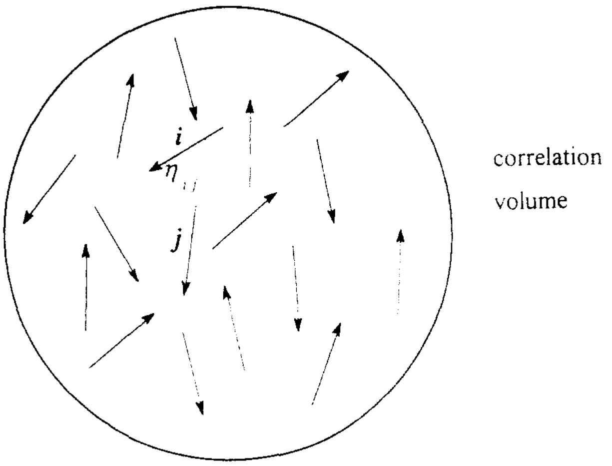

Figure 7 Schematic sketch of the orientation correlations between the electric moments in a PVDF melt at 185°C. On average, the moments as indicated by arrows are aligned antiparallel (here: from above to the bottom of the drawing plane). With respect to g_1, the cosines of the angles η_{ij} between a reference moment *j* and the surrounding moments are summed up (cf. equation (6)); only those within the correlation volume contribute to the sum whereas the contributions of those from the exterior average out. Since every second moment contributes by $\approx +1$ ($<\eta_{ij}>=0$) and by ≈ -1 ($<\eta_{ij}>=\pi$), the cosine sum and, consequently, g_1 remain small. However, g_2 becomes large since all moments contribute by $\frac{1}{2}(3\cos^2\eta_{ij}-1)\approx +1$ (equation (7))

ACKNOWLEDGEMENT

Financial support from the Deutsche Forschungsgemeinschaft (DFG grant number Ju 168/1-2) is gratefully acknowledged.

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