polymer papers

The alignment of polar mesogens in electroactive polymers

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We have studied the polar alignment produced in a range of comb polymers with a methacrylate backbone and oxynitrostilbene mesogenic groups attached to the backbone at variable densities by a 3 or 6 carbon spacer. These polymers, when poled, display second order non-linear optical activity, piezoelectricity and pyroelectricity. The magnitude of these effects depends upon the degree of polar ordering of the side groups and we have therefore investigated the efficiency of the poling process using the pyroelectric coefficient and thermally stimulated currents as primary diagnostic techniques. For constant poling conditions it is found that the polarization and pyroelectric response are not linearly related to the volume fraction of mesogen, i.e. samples of high mesogen concentration display lower polarization and pyroelectric activity than might be expected from extrapolation of low concentration data. Indeed, for the 6 carbon spacer material there would appear to be an optimum mesogen concentration around 30 mol%. Also, though the 3 and 6 carbon spacer materials are similar at low mesogen concentration, the latter material gives a lower response when it forms a liquid crystalline phase at high concentrations. We therefore suggest that the polar mesogens tend to pack anti-parallel at higher concentrations and that this interaction is not readily overcome by the applied field. Though these polymers are brittle at high mesogen concentration, ductile thin films can be cast if the density of side chains is reduced to 10 mol%. Despite the reduction in mesogen concentration, the pyroelectric activity is not proportionally reduced, implying more effective poling due to reduced interaction between the mesogens.

(Keywords: poling; liquid crystalline behaviour; non-linear optical activity; pyroelectricity)

INTRODUCTION

In order for materials to exhibit piezoelectricity, pyroelectricity or optical second harmonic generation, they must be macroscopically non-centrosymmetric. In the case of polymeric materials, the macroscopic centre of symmetry arising from the random arrangement of molecules is destroyed by the application of a static electric field which produces a preferential alignment. The field is usually applied at high temperatures and removed at low temperatures when the polarization is frozen in.

The effectiveness of this operation, known as poling, will determine the subsequent activity of the sample. We have therefore been investigating the polar order produced in a number of side-chain electroactive polymers, some of which are liquid crystalline. The thermally stimulated current (TSC) technique was first used to characterize the degree of polarization produced but since this technique must destroy the polarization in order to measure it, the pyroelectric coefficient was also used as an alternative measure of the degree of poling. This latter measurement is non-destructive, simple and rapidly performed.

A review of materials and target properties of polymers exhibiting non-linear optical (NLO) activity is given by Ulrich[1]. As would be expected, at moderate fields, before dipolar orientation nears saturation, linear relationships between pyroelectric activity and NLO coefficients have been reported[2,3] with Pockels coefficients up to 10 pm V^{-1} being obtained for the side chain polymers of the present study.

EXPERIMENTAL

Materials

The polymers studied were homopolymers of (4-(3-oxypropane)-oxy-4′-nitrostilbene methacrylate) (MO3ONS), the same material with a 6 carbon spacer (MO6ONS), and copolymers of these polymers with methyl methacrylate (*Figure 1*). These materials were supplied by Hoechst-Celanese (Robert Mitchell Research Centre, Summit, NJ, USA)[4] and the research was undertaken as part of a major collaborative research programme.

In the first instance, homopolymer samples were provided. These were found to be very brittle and could not be handled as free films. Initially it was thought that this might be due to too low a molecular weight but high molecular weight samples ($M_n > 10^6$) were also found to be brittle. This was somewhat surprising since the mesogens were on a methacrylate backbone and methyl methacrylate films can be readily cast and handled. A number of copolymers with a range of concentrations of the stilbene mesogen were therefore prepared to ascertain whether good mechanical properties could be combined with good NLO properties.

The compositions of the materials studied are summarized in *Table 1*, together with their glass

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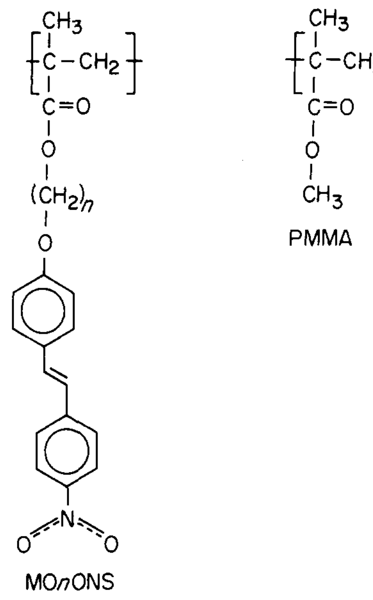

Figure 1 MO*n*ONS and PMMA repeat units

Table 1 Compositions of the materials studied

Mesogen	Mole fraction (%)	Volume fraction (%)	T_g (°C)	T_{cl} (°C)
MO3ONS	100	100	114	-
	50	78	116	-
	10	29	117	-
MO6ONS	100	100	71	153
	70	91	82	122
	50	80	83	-
	30	63	94	-
	10	31	112	-
	5	17	114	-
PMMA	0	0	119	-

transition temperatures and clearing temperatures, if any. (The MO6ONS polymer showed liquid crystalline behaviour which disappeared in the lower copolymers.)

Sample preparation

Samples were generally prepared by solvent casting from 10% solutions on to aluminized thin glass slides. Solvents used were dimethyl sulphoxide, cyclopentanone or benzonitrile and all solutions were filtered using 0.2 μm filters. Cast films were first allowed to dry in clean conditions at room temperature followed by a further drying step under vacuum at about 20°C above the T_g of the polymer to remove all traces of the solvent. A second aluminium or gold electrode was then evaporated onto the upper surface of the film for poling and pyroelectric or TSC measurements.

Poling

The films were poled by applying a d.c. field between the evaporated electrodes. The pyroelectric response of the samples increased with poling temperature up to the T_g of the polymer, but no further increase was obtained above this temperature using a constant poling time of 2 min. Samples were therefore compared by poling for 2 min at their respective T_gs and maintaining the field while the sample was cooled to room temperature at 10°C min^{-1}.

For those samples which exhibited liquid crystalline behaviour, d.c. poling at higher temperatures in the liquid crystalline phase was not generally successful due to high conductivity and electrical breakdown. At low fields, below breakdown, there was no suggestion that poling in the liquid crystalline region led to increased alignment. Unfortunately therefore, the self-aligning properties of the liquid crystalline phase were not exploited.

Pyroelectric and TSC measurements

Pyroelectric measurements were obtained by varying the temperature of the poled sample using a triangular waveform of amplitude 3°C, period 100 s and mean temperature 20°C, using a dry nitrogen gas flow and fast response heater. The charge or current generated was measured using a Keithley electrometer and the pyroelectric coefficient was obtained from the ratio of the first Fourier coefficient of the current or charge signals and the signal from a fine-wire thermocouple mounted in the gas flow immediately above the sample.

To obtain the polarization, the depolarization current was logged as samples were heated at 10°C min^{-1} to a temperature above their T_g[5,6]. Typically two peaks in the current–temperature plot were obtained, the first being due to dipolar reorientation and the second due to the release of trapped charge. The area under the dipolar curve was used to measure the total polarization.

Dielectric measurements

Dielectric measurements were carried out in the temperature range −40°C to 180°C and a frequency range from 0.1 Hz to 100 kHz using a Schlumberger 1260 gain-phase analyser for the higher frequencies but with the addition of a Kistler charge amplifier for the lower frequencies, as described previously[7]. The low frequency, high temperature data were complicated by the presence of ionic conductivity and only the 10 Hz data are reported in this publication.

RESULTS

Pyroelectric measurements

The pyroelectric coefficient, γ, was found to vary linearly with poling field, E, as shown in *Figure 2*. It is immediately apparent that the variation with mesogen concentration is surprisingly small.

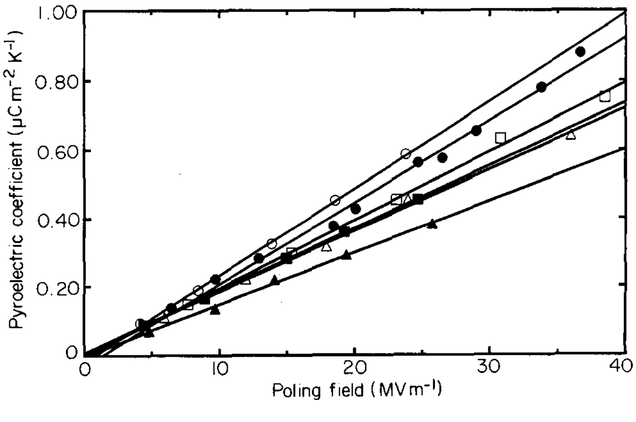

Figure 2 Pyroelectric coefficient γ of MO3ONS and MO6ONS copolymers *versus* poling field. ●, 100% MO6ONS; ■, 50% MO6ONS; ▲, 10% MO6ONS; ○, 100% MO3ONS; □, 50% MO3ONS; △, 10% MO3ONS

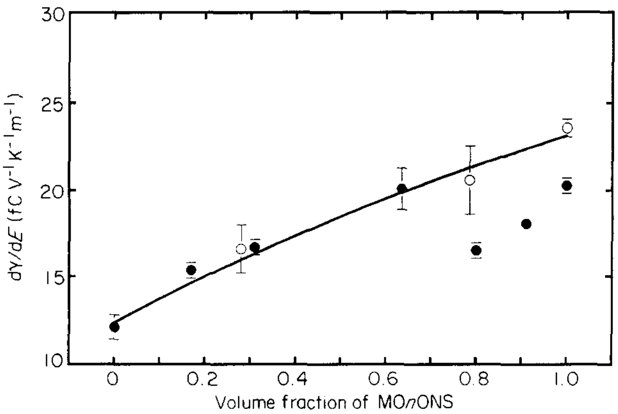

Figure 3 dγ/dE *versus* copolymer fraction. ●, MO6ONS; ○, MO3ONS

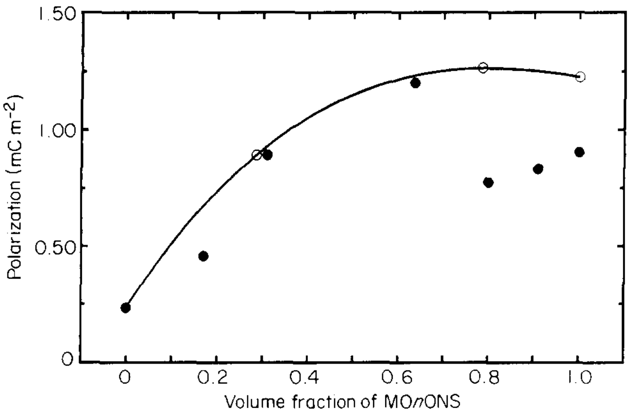

Figure 4 Polarization *versus* copolymer fraction. ●, MO6ONS; ○, MO3ONS

A clearer summary of the results is given in *Figure 3*, where the slopes, dγ/dE, of the lines in *Figure 2* are shown plotted as a function of the volume fraction of mesogen. We see that, for the 6 spacer copolymers, this normalized measure of the pyroelectric response approaches a plateau value at a volume fraction around 65% (mole fraction 30%) and the response then clearly falls. It is interesting to note that this fall occurs just prior to the onset of obvious liquid crystalline behaviour. The MO3ONS copolymers do not show the clear drop in response nor do they show evidence of liquid crystalline behaviour.

The shape of the curves would therefore appear to be related to the interactions between the mesogens which results in liquid crystalline behaviour but which makes orientation by the electric field more difficult. The X-ray evidence of Findlay[8] shows that the side chains are interdigitated in the liquid crystalline phase of the MO6ONS homopolymer, presumably in an anti-parallel alignment which minimizes their dipole moment and impedes poling.

It is not certain from the above data whether the drop in response at the onset of liquid crystalline behaviour is due to a change in the mechanism of pyroelectricity or a change in the effectiveness of poling. This was clarified by the TSC measurements.

TSC and dielectric measurements

The polarization of films poled at the same poling field are shown in *Figure 4* as a function of mesogen concentration. Now we see a drop in the polarization of MO6ONS just prior to the onset of liquid crystalline behaviour, thus the lower pyroelectric response arises from a less effective poling of the liquid crystalline material rather than a difference in the pyroelectric mechanism.

The TSC curves themselves are shown in *Figure 5* for poly(methyl methacrylate) (PMMA) and the MO6ONS copolymers and homopolymer. There is a suggestion from these data that, in addition to the clear shift in T_g, the relaxation behaviour around room temperature is varying markedly with composition. Dielectric measurements were therefore undertaken to further investigate the relaxation behaviour of these materials.

The 10 Hz dielectric data shown in *Figures 6* and *7* show a progressive reduction of the β relaxation and an increase in the dielectric increment above T_g as the concentration of mesogenic side chains is increased. It is particularly important to note that the β relaxation is absent in the homopolymer.

Ageing experiments

For a practical application of these materials it is extremely important that their response and hence their polarization does not decay significantly with time. Comparison of the decay in relative polarization for the 100% MO6ONS homopolymer, the 10% MO6ONS copolymer and PMMA are shown in *Figure 8*. In each case the sample was repeatedly poled then kept at room temperature for progressively increasing time before the polarization was measured by TSC. It can be seen that the polarization of the homopolymer is much more stable

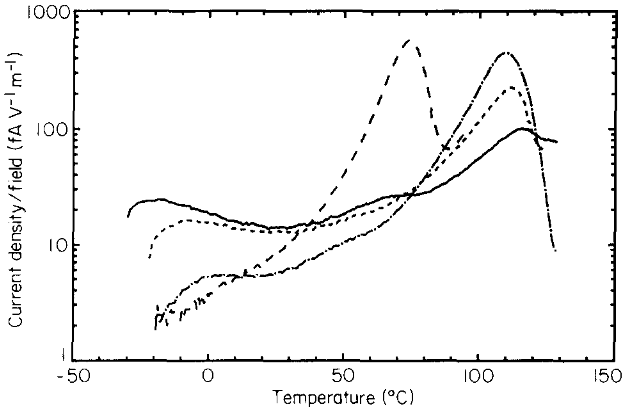

Figure 5 Thermally stimulated current data. ·······, PMMA, – – – –, 10% MO6ONS; – · – ·, 30% MO6ONS; — — —, 100% MO6ONS

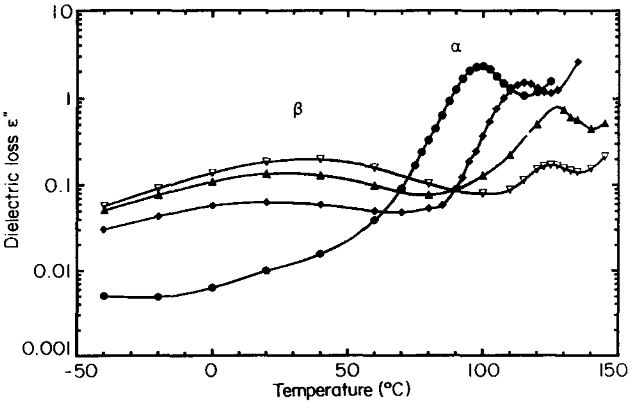

Figure 6 Dielectric loss at 10 Hz *versus* temperature. ▽, PMMA; ▲, 10% MO6ONS; ◆, 30% MO6ONS; ●, 100% MO6ONS

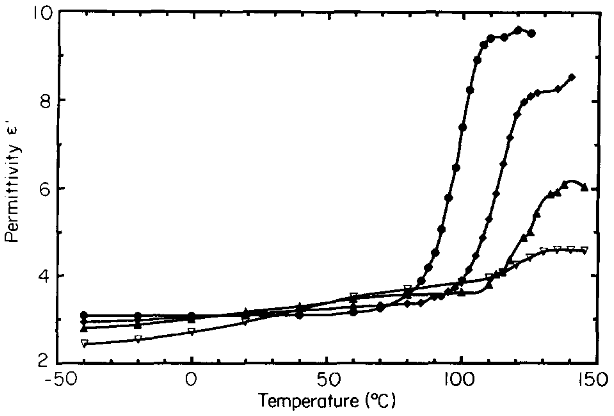

Figure 7 Permittivity at 10 Hz *versus* temperature. ▽, PMMA; ▲, 10% MO6ONS; ◆, 30% MO6ONS; ●, 100% MO6ONS

than that of either PMMA or the 10% copolymer in spite of the fact that the T_g for the latter two polymers is about 115°C compared with 71°C for the homopolymer. It therefore appears that the stability of the homopolymer arises from the absence of the β relaxation. This conclusion is consistent with the rapid fall in second harmonic intensity which has been observed in a poled guest/host system consisting of an azo dye in PMMA which has also been attributed to the β relaxation in the host polymer[9].

DISCUSSION

The above data show that the poling process is not achieving as high a degree of polar alignment as might be expected by extrapolating the initial slope of *Figure 4* despite the fact that the plots of pyroelectric coefficient against poling field show no incipient saturation. The coefficients are also small by comparison with 10% MNA in PMMA for example[3]. We believe that this is due to a strong anti-polar pairing of the side groups which is more pronounced in liquid crystalline MO6ONS but which also causes a reduction of polarization in the higher concentrations of MO3ONS.

The net result of these dipole interactions is that the activity of poled samples of these materials is a maximum at a mole fraction of mesogens of about 30%, as measured by pyroelectric response and by total polarization. A similar conclusion has been reached by Amano *et al.*[10] who reported that second harmonic generation saturated at 25 mol%, a similar concentration to that reported here.

It is concluded that the dipolar pairing immobilizes the dipoles so that in the homopolymer no β relaxation is observed and the materials are difficult to pole even at the glass transition. The dipolar pairing can be regarded as cross-linking the chains. A high degree of cross-linking is known to lead to brittle behaviour, which is consistent with the brittle nature of the homopolymer even at high molecular weight. At a molecular level, however, this lack of ductility probably relates to the absence of the β relaxation.

CONCLUSIONS

Measurement of the pyroelectric coefficient has been shown to provide a good qualitative measure of the degree of polar ordering which can be achieved in a series of comb polymers with polar side groups. The pyroelectric results have been confirmed by TSC measurements of polarization.

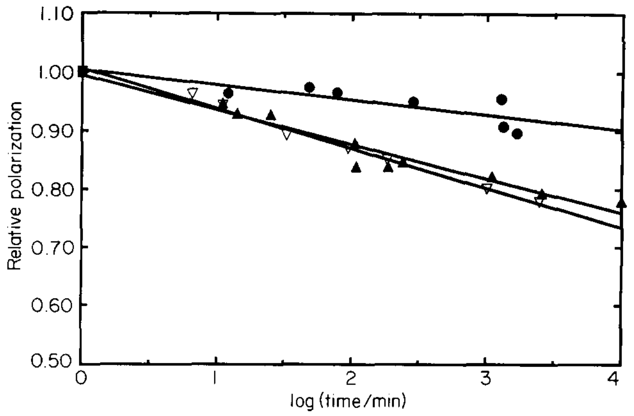

Figure 8 Decay of polarization with time. ▽, PMMA; ▲, 10% MO6ONS; ●, 100% MO6ONS

The side chain homopolymers are not sufficiently ductile to produce self-supporting films. This is attributed to the dipolar interactions which effectively cross-link the chains and suppress the β relaxation, making the material brittle and also impeding poling.

Copolymerization offers a route to obtaining adequate ductility. To a large extent the reduced concentration of active side chain groups is compensated by more effective poling.

For higher response materials new side groups are required with a reduced tendency to anti-polar alignment or, ideally, a tendency to polar alignment. It is not obvious that liquid crystalline polymers are required though it may be expected that if polar liquid crystalline domains are formed they would show strong orientation in relatively weak electric fields.

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