Electro-optical properties of liquid crystal copolymers and their relationship to structural order

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A range of side chain liquid crystal copolymers have been prepared using mesogenic and non-mesogenic units. It is found that high levels of the non-mesogenic moieties may be introduced without completely disrupting the organization of the liquid crystal phase. Incorporation of this comonomer causes a marked reduction in the glass transition temperature (T_g), presumably as a result of enhanced backbone mobility and a corresponding lowering of the nematic transition temperature, thereby restricting the temperature range for stability of the liquid crystal phase. The effect of the interactions between the various components of these side-chain polymers on their electro-optic responses is described. Infrared (i.r.) dichroism measurements have been made to determine the order parameters of the liquid crystalline side-chain polymers. By identifying a certain band ($C{\equiv}N$ stretching) in the i.r. absorption spectrum, the order parameter of the mesogenic groups can be obtained. The temperature and composition dependence of the observed order parameter are related to the liquid crystal phase transitions and to the electro-optic response. It is found that the introduction of the non-mesogenic units into the polymer chain lowers the threshold voltage of the electro-optic response over and above that due to the reduction in the order parameter. The dynamic electro-optic responses are dominated by the temperature-dependent viscosity and evidence is presented for relaxation processes involving the polymer backbone which are on a time scale greater than that for the mesogenic side-chain units.

(Keywords: electro-optical properties; liquid crystal copolymers; structural order)

INTRODUCTION

Many liquid crystalline side-chain polymers have been reported to show electro-optical behaviour which is similar to that of traditional low molar mass mesomorphic compounds. This large scale motion is only possible for polymers at temperatures well above their glass transition and consequently such side chain liquid crystal polymers have been considered for use in optical data or storage devices[1–4]. Liquid crystal side chain polymers are molecular composites formed by the attachment of mesogenic moieties to a polymer backbone via some form of coupling unit. The interaction of these various normally incompatible components of such novel materials has a profound influence on the resultant molecular organization and the response of that organization to the application of electric fields. It has been proposed, for example, that by changing the number of side chains along the polymer backbone, the coupling between the mesogenic units and the polymer chain may be drastically altered[5]. As a result of the polymeric nature of the main chain, the viscosity of the liquid crystal phase is comparatively high, and as a consequence of this high viscosity the electric field response times of liquid crystalline polymers are appreciably longer than for low molar mass liquid crystals. Hence these polymeric materials are not suitable for use in dynamic display applications[6]. However, the very properties which make the materials unsuitable for the demands of dynamic electro-optical effects are attractive for the preparation of optical components such as non-linear optical waveguides for exploitation in optical processing and switching[7].

The electro-optical properties and the orientational order of these liquid crystalline side-chain polymer systems are of particular interest. A number of contributions concerned with these properties have appeared[1–3,6] although none has considered the systematic variation of properties and molecular organization with changing chemical configuration. In this paper we focus on a series of liquid crystal side-chain copolymers in which the density of mesogenic units attached to the polymer chain is systematically varied through the introduction of a non-mesogenic monomer. The state of order in these copolymers is evaluated through the use of infrared (i.r.) spectroscopy which selectively probes only the mesogenic side chains[8–10]. Carefully programmed electro-optic measurements are used to evaluate the relationships between chemical configuration, orientational order and electro-optical properties.

MATERIALS

The base liquid crystal homopolymer of I used has been the subject of a number of studies[1–3,6,11] and it shows similarities to low molar mass analogues, in that the liquid crystal director may be aligned by electric and magnetic fields, although this depends on rather flexible coupling between the mesogen and the polymer chain[12].

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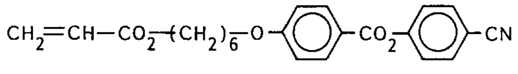
A range of copolymers was prepared by copolymerization of I with a monoacrylate group (II):



(I)

$CH_2{=}CH{-}CO_2{-}CH_2{-}CH_3$

(II)

Copolymers were prepared by free-radical polymerization under vacuum of I with varying proportions of ethyl acrylate (II) in chlorobenzene solution at 55°C, using 1% AIBN as an initiator. The resultant polymers were precipitated into diethyl ether at -10°C and purified by dissolving in dichloromethane, followed by reprecipitation into ether and subsequent drying in vacuum at 50°C. The synthesis and the characterization of the materials used in this work have been previously reported[13]. The homopolymer of I shows a nematic phase with a well defined nematic–isotropic transition at 135°C and a glass transition at 39°C. The copolymers prepared show similar behaviour with both decreasing nematic–isotropic transition temperature (T_{NI}) and glass transition temperature (T_g) with increasing fraction of II. For copolymers containing 55 mol% or more of II no liquid crystal phases are observed; the homopolymer of II does not exhibit any mesomorphic phases. The phase transition temperatures, the T_gs and the molecular weight data for the materials prepared are listed in *Tables 1* and *2*. The molecular weight data were determined using gel permeation chromatography (g.p.c.) (at the Polymer Supply and Characterisation Centre at RAPRA Technology Ltd) at room temperature in tetrahydrofuran solution.

EXPERIMENTAL

Phase behaviour

Differential scanning calorimetry was performed on 4–5 mg samples using a Perkin Elmer DSC-2C calorimeter. The phase transition temperatures thus obtained were compared with the temperatures of observed changes in the optical textures, noted from samples placed in a polarizing microscope (Swift MPB124) equipped with a variable temperature unit (Linkam TN601). In this case the phase transition temperature was obtained by monitoring the intensity of light passing through the microscope (with crossed polarizers) by means of a photoelectric cell connected to a microcomputer system.

Table 1 Thermal characteristics of copolymers used[a]

Concentration of ethyl acrylate[b] (mol%)	Glass transition (°C)	Nematic–isotropic transition (°C)
0	39	135
10	23	108
20	20	105
30	16	75
38	5	47
48	5	46
55	2	–[c]
67	–	–[c]

[a] All transition temperatures quoted refer to data obtained from differential scanning calorimetry measurements at a heating rate of 10 K min^{-1}

[b] Copolymer ratio determined by ^{1}H nuclear magnetic resonance (n.m.r.) spectroscopy

[c] No transition observed

Table 2 Molecular weight data obtained from a range of copolymer samples[a]

Ethyl acrylate content (%)[b]	Molecular weight (M_w)[c]	Molecular weight (M_n)[c]	Degree of polymerization[c]
0	9.13×10^4	5.2×10^4	155
10	7.06×10^4	4.75×10^4	100
20	7.94×10^4	4.88×10^4	140
30	8.12×10^4	3.49×10^4	130
38	8.00×10^4	4.00×10^4	155
48	7.06×10^4	3.01×10^4	120
55	6.24×10^4	2.78×10^4	145
67	7.06×10^4	3.21×10^4	172

[a] Determined by g.p.c. at room temperature in tetrahydrofuran

[b] Measured values from ^{1}H n.m.r. data

[c] Calculated from 'polystyrene equivalent' on the basis of the experimentally determined composition

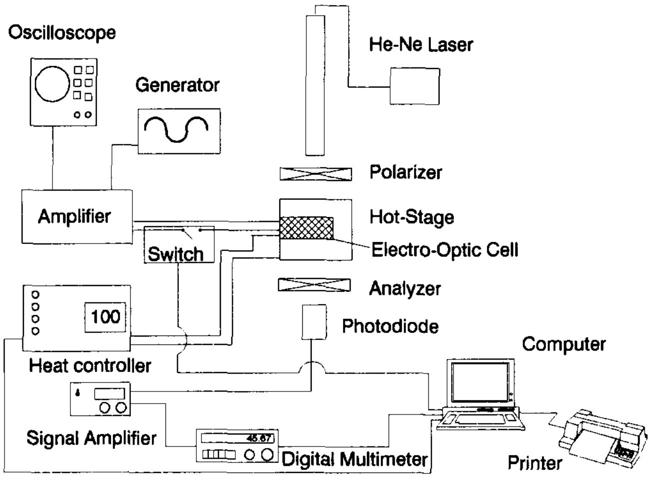


Figure 1 Schematic view of the arrangements used for the electro-optic measurements

Electro-optic measurements

The core of this work involves the measurement of changes in the optical properties of thin films of the liquid crystal copolymers induced through the application of electric fields. *Figure 1* shows the experimental arrangement used for these electro-optic measurements. The electro-optic cell (described later) was held inside a specially designed hot stage, the temperature of which was regulated by a three term PID controller (Eurotherm 820) providing a uniform temperature environment with fluctuations of ±0.25°C. The sample was mounted horizontally and hence the optical system consisting of a 5 mW helium–neon laser, polarizer and analyser (Ealing Electro-Optics) and photodiode was placed vertically on a specially modified optical track. Light intensities were obtained from the photodiode via a home built amplifier and a high resolution multimeter (Thurlby 1905a). Electric fields were provided by means of a power amplifier (Hewlett Packard 6827A) driven by a function generator (Thandar TG501). This arrangement provided waveforms in the frequency range of 0.05–30 kHz with peak-to-peak voltages in the range of 0–240 V. For some experiments a specially made high voltage amplifier producing waveforms with peak-to-peak voltages of 600 V was used. The applied peak-to-peak voltages were measured using a calibrated oscilloscope. The intensity of the transmitted light through this optical system was recorded as a function of time using a microcomputer system based around an IBM compatible PC. The resolution of the intensity data was ~0.15% of the 100% transmitted signal. Through the use of a specially written software system EOCS, sophisticated electro-optical experiments could be performed on a continuous or cyclic basis, involving temperature control, data recording, field switching and analysis[14]. For both the electro-optic and the order parameter measurements the nematic–isotropic transition of the particular cell arrangement was established *in situ* through small temperature increments coupled with long dwell times. No significant variations of these transition temperatures were observed with respect to those obtained through scanning calorimetry.

Electro-optic cell construction

We have followed similar procedures for the construction of electro-optic cells with predefined director orientation to those developed for low molecular weight liquid crystals[15,16]. The cells for electro-optic measurements were constructed from tin oxide coated glass slides (Z20 from Balzers Ltd) of 6 cm^2 area, and etched, using HCl with zinc metal powder as a catalyst, to give a 2 cm × 2 cm electrode. After cleaning in an ultrasonic bath and drying in an oven, the cell electrodes were coated with a thin layer of a polyimide precursor consisting of a 5% solution of Rodehftal 322 in dimethylformamide using a spin coater running at 4500 rev min^{-1}. These coated slides were heated in an oven for 30 min at 80°C, rubbed at room temperature in a single direction using controlled repeatable procedures with a cloth, heated again for 30 min at 130°C, and then finally for 1 h at 200°C in an oven.

Cell filling by means of capillary effects as widely used for low molar mass liquid crystal compounds was not possible due to the high viscosity of the polymers employed in this work. Consequently, cell construction involved the following procedure. A small portion of the selected polymer sample was carefully applied onto one of the treated glass electrodes, which was then heated for some time (typically 10 min) above its clearing point in order to allow the trapped air to escape. The second glass electrode was then mounted above the first electrode and the complete assembly inserted into a clamping frame. The assembly was retained in this frame while the electrodes were fixed permanently using 'Araldite Rapid' epoxy resin (Ciba Geigy). All the cells used in this work were prepared using 'Kapton' sheet (nominal thickness 0.025 mm) acting as a spacer between the electrodes. 'Kapton' is particularly useful for this purpose since it is a high temperature high stability polymer. The thickness of the cells was measured using both interferometric and micrometer techniques; both gave similar results with all cells prepared being in the range of 0.028–0.030 mm. The quality of the direction orientation induced by the electrode surface treatment was confirmed through examination with a polarizing microscope. The surface treatment described above results in an alignment in which the director pattern is parallel to the rubbing direction or the electrode surface. Complete and uniform director alignment was obtained by holding the completed electro-optic cell at a temperature 3°C below the measured clearing point for 24 h. This technique was successful in inducing a uniform director alignment in electro-optic cells containing the homopolymer of I, and 10, 20 and 30% of II, but not for cells with polymers containing 38% or more of II. Cells, particularly those prepared with copolymers containing 38 mol% of II or more, showed defects such as small disclination loops when examined using the polarizing microscope and clearly these defects will affect the behaviour of liquid crystals in external fields[17]. This series of materials all exhibit a positive dielectric anisotropy and thus application of a voltage across the cell voltages will result in a reorientation of the director pattern from parallel to perpendicular to the electrodes.

Order parameter measurement

The essential characteristic of the liquid crystal state is long range orientational order. For a nematic monodomain the mesogenic groups are preferentially aligned about the director and in such uniaxial systems this level of orientational order may be expressed in terms of the order parameter S:

$$S = (3\langle\cos^2\alpha\rangle - 1)/2 \qquad (1)$$

where α is the angle between the axis of an individual unit and the director n. Various techniques are available for the experimental evaluation of S[18]. Infrared spectroscopy provides a particularly useful approach for the evaluation of S in the case of copolymers. Macroscopic orientation of a sample leads to different absorption of i.r. radiation depending on the state of polarization[19]. A transition moment absorbs only the electric field component of the incident radiation which is parallel to its own direction. In the mid i.r. region, the transition moment is caused by a molecular vibration, which in many cases, is localized to particular chemical bonds. Thus by measuring the dichroism of the different absorption bands at particular wavelengths, information on the ordering of individual groups, e.g. mesogenic units, can be obtained. Here we describe how S is calculated from the measured dichroism. The dichroism is measured in terms of the dichroic ratio R, i.e. the ratio of the absorbance of radiation with the electrical field parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the director, which is determined by the direction of rubbing[19]:

$$R = A_\parallel / A_\perp \qquad (2)$$

This ratio and S are related by the well known formula:

$$S = \left(\frac{1}{3\cos^2(\psi - 1)/2}\right)\left(\frac{R-1}{R+2}\right) \qquad (3)$$

The first term on the right-hand side of equation (3) corrects for the situation where the angle ψ between the molecular axis and the transition moment is not zero. In this work we have employed the transition moment of the nitrile group to obtain R. This provides a direct measure of the anisotropy of the rigid component of the mesogenic side groups. We have estimated through the use of molecular modelling procedures that the angle between the nitrile bond and the molecular axis of the rigid group of the mesogenic unit I is $<6°$. Such a value results in an 'increase' in the measured S values to a maximum of 5%. In many cases, an optical S is defined which depends only on the measured absorption values:

$$S = \frac{R - 1}{R + 1} \tag{4}$$

Such an approach is used to calculate the S values in this work for any correction is constant. In order to perform the S measurements we must work with monodomain samples. This was achieved through the use of surface treatment in a similar manner to that employed for the preparation of the electro-optic cells. For the i.r. dichroism measurements we constructed cells using single crystals of KBr in the form of discs (20×4 mm) as the cell surfaces. In order to define the director orientation we followed the same procedure as utilized above for the construction of electro-optic cells from glass. After coating, mechanical and thermal treatment, the discs were assembled into a cell by pressing a polymer film between them at a temperature in the liquid crystal phase region. This resulted in films $\sim 10\ \mu$m thick. Annealing these cells at a temperature just below the liquid crystal clearing point leads to samples with a uniform macroscopic orientation. The level of alignment and cell thickness were assessed using similar procedures to those described earlier. Cells prepared using the homopolymer of I, and copolymers containing 10 and 20% of II showed good uniform director alignment. Unfortunately it was not possible to prepare completely successful cells based on copolymers containing 30% of II.

In order to measure the order parameter of the mesogenic groups, i.r. spectra of the materials were recorded at different temperatures in the nematic and the isotropic phase with a Perkin-Elmer 580B spectrometer. The i.r. beam was polarized by a wire grid on an AgCl substrate (Perkin-Elmer), and the resolution was better than $2\ \mathrm{cm}^{-1}$ in the examined wave number range. The cell was mounted in a specially constructed hot stage which was regulated using a three-term PID controller (Micror III) using a platinum resistance thermometer as the sensor. This provided a uniform temperature environment with a temperature regulation of $\pm 1°$C. With this method the temperature dependence of the C$\equiv$N stretching absorption and its dichroism was recorded. Particular attention was directed at ensuring that equilibrium conditions had been established at each temperature.

RESULTS

The reorientation of the liquid crystal director in the presence of an applied electric field is a well known property of the low molecular weight liquid crystal and it is used to particular effect in optical display devices[15]. In general optimum electro-optic investigations are performed on configurations in which a defined rest or 'off' state is imposed through, for example, the use of surface alignment. The polymers described here are expected to show a response to an electric field, although the nature of the response will depend upon the coupling of the mesogenic groups to the polymer backbone and the bulk viscosity of the complete polymer system. We may partition the electro-optic response into that which is equilibrium in nature and which results from the resistance to director reorientation arising from the curvature elasticity and that which is time dependent. The former allows the curvature elastic constants to be evaluated while the latter provides information on the viscosity of the material and the possible areas of application. In a low molar mass liquid crystal material the evaluation of these separate components is relatively straightforward. However, for polymeric liquid crystal systems the possibility of high bulk viscosities poses particular difficulties in the measurement of the true equilibrium or static properties. It is therefore essential to establish firmly the dynamic behaviour of this range of materials before examining the static properties.

Dynamic electro-optic properties

The basic premise of an electro-optic measurement is that the optical signal provides a direct or proportional measure of the state of the material in the cell. For a low molar mass system this is certainly a reasonable approach. However, for a side-chain liquid crystal polymer, there are two basic components; the highly polarizable side chains and the polymer backbone which is made up of units with relatively low polarizabilities. The consequence of this composite structure is that the optical signal is particularly sensitive to the former and not to the latter, unless variations in the chain orientation are coupled completely through to the mesogenic side chains. Neutron scattering measurements performed on the homopolymer of I show this coupling to be weak since the polymer chain trajectory is almost isotropic, although there is a slight tendency for positive coupling[20]. Conventionally the time taken for the liquid crystal director to undergo complete reorientation (in this case from parallel to perpendicular with respect to the cell electrode) under the influence of an electric field, τ^{on}, is expressed as the time taken for the intensity to change by 90% of the total range (as shown schematically in *Figure 2*). For such measurements it is vital that we can be certain that the material in the cell is in a predefined and steady-state condition. Now if we assume that all structural variations are coupled to the mesogenic side chains then, as discussed above, the transmitted light signal provides a convenient measure. However, we have adopted a different approach in order to avoid making the limiting assumption. Using the system described in the preceding section, we have implemented a cyclic experiment in which we use the values of τ^{on} to determine when a steady state is reached. The method involves applying an electric field, measuring τ^{on}, removing the

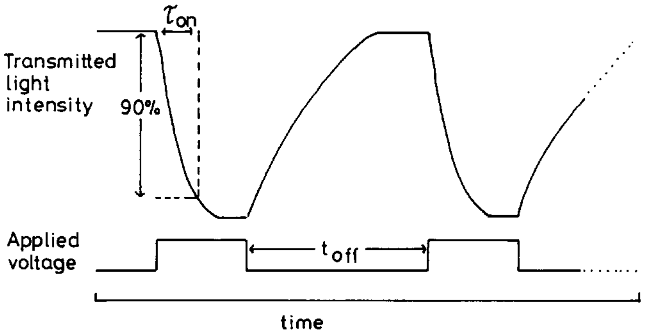


Figure 2 Timing arrangements used in the cyclic electro-optic experiment

field, waiting for a time t^{off} and then repeating the cycle. When t^{off} reaches and exceeds the true relaxation time for the polymer system, then τ^{on} will show reproducible values. The approach allows both τ^{on} and τ^{off} to be evaluated. The process is shown schematically in *Figure 2*.

In order to achieve complete switching we typically applied 155–160 V (peak to peak) at a frequency of 500 Hz. An example of the variation of the transmitted light intensity as a function of the applied voltage is shown in *Figure 3*. Reproducible switching effects were observed at temperatures close to the T_{NI} where the viscosity of the polymer is relatively low and measurements were made in the range of T_{NI} to $T_{NI} - 23°C$. Such switching effects were only measured for electro-optic cells prepared using polymers containing 0, 10 and 20% of II, although some qualitative measurements were possible for the polymer containing 30% of II.

Figure 4 shows τ^{on} as a function of the time for which the field is switched off before the τ^{on} measurement; each set of experiments was carried out at constant temperature. This figure is an example for 10% of II; all other samples show similar curves, although of course the time scales vary. These curves show several characteristic features. Initially τ^{on} is short, but this only arises from insufficient time allowed for complete relaxation to the predefined surface alignment state. As the time period for which the field is removed, t^{off}, increases, the following τ^{on} increases until a quasi-equilibrium is reached. From such curves we can obtain values for τ^{on} and τ^{off} which represent switching between equilibrium conditions. Repetition of the cyclic experiment at different but fixed temperatures allows the temperature variation of τ^{on} and τ^{off} to be mapped out. Near to the nematic–isotropic transition a response of the order of a few seconds can be observed, however as shown in *Figure 5*, there is a strong temperature dependence of the switching times.

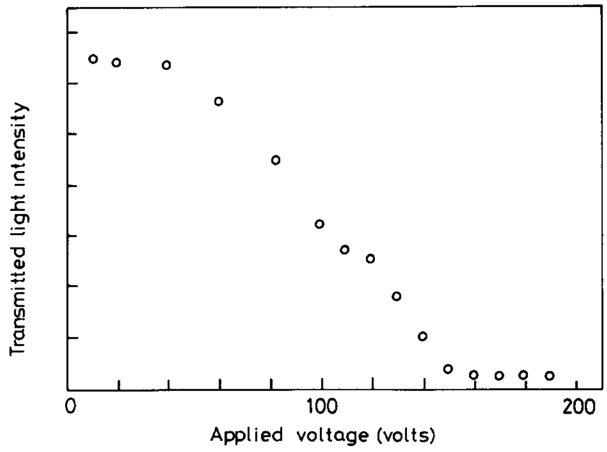


Figure 3 Plot of the transmitted light intensity through crossed polarizers as a function of the applied peak-to-peak voltage (500 Hz) for a prealigned electro-optic cell of thickness 28 μm prepared using the homopolymer of I, indicating the voltage required for complete switching

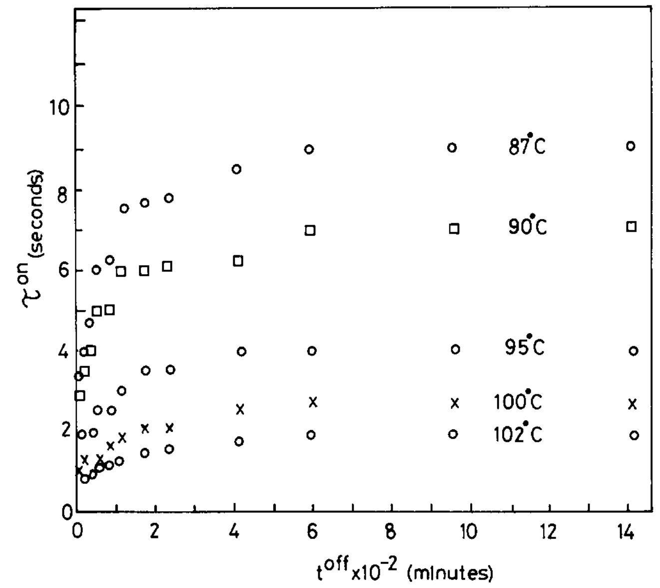


Figure 4 Plot of τ^{on} for the indicated temperatures showing the variation in τ^{on} for differing values of t^{off}, the time for which the field was left off prior to the measurement of τ^{on}. These data were obtained using the cyclic techniques described in the text for a prealigned electro-optic cell of thickness 28 μm, prepared using the copolymer with 10 mol% of II with an applied voltage of 155 V (peak to peak) at 500 Hz

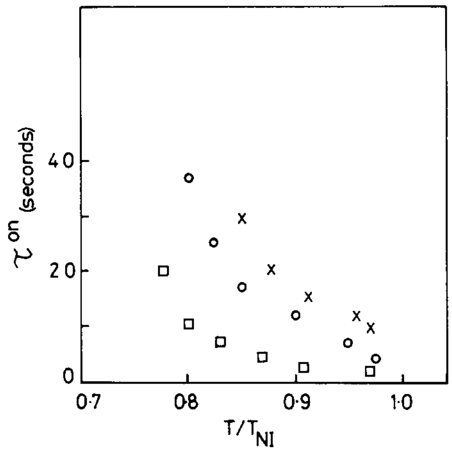


Figure 5 Plots of τ^{on} as a function of the reduced temperature T/T_{NI} for electro-optic cells prepared using the homopolymer of I (×) and copolymers containing 10 mol% of II (□) and 20 mol% of II (○). These values were obtained using the data from *Figure 4* and similar plots for the other materials

Conventionally the equations of motion for the liquid crystal director in a sandwich electro-optic cell in which the initial configuration is with the director parallel to the cell walls lead to an expression for τ^{on} as[20]:

$$\tau^{on} = \frac{d^2\eta}{\pi^2 K_{11}}\left[\left(\frac{U}{U_0}\right)^2 - 1\right]^{-1} \qquad (5)$$

where η, K_{11}, U and U_0 are the viscosity, the elastic constant, the applied voltage and the threshold voltage, respectively. It is expected, and it has been shown in a number of reports[1,2], that the strong temperature dependence of τ^{on} may be related to the significant temperature variation of η. We can introduce a modified relationship:

$$\tau^{on} = A\exp(-bT/T_{NI})\eta_0 \qquad (6)$$

where η_0 is an intrinsic viscosity and the other factors shown in equation (5) have been consumed into A. Thus

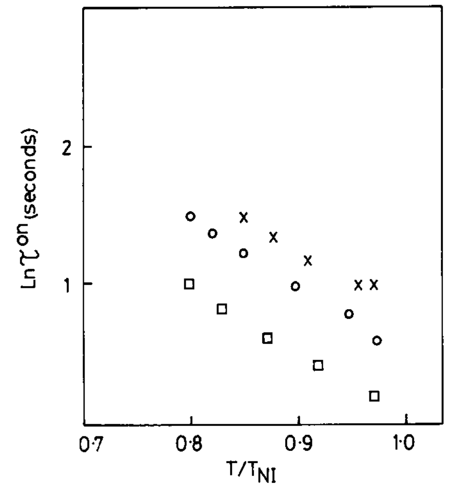


Figure 6 Plots of $\log \tau^{\mathrm{on}}$ against the reduced temperature T/T_{NI}. Symbols as in *Figure 5*

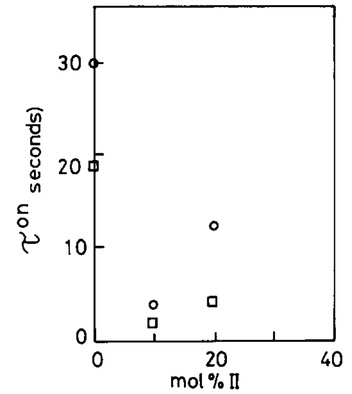


Figure 7 Illustrative example of the variation of τ^{on} for differing polymer compositions. The sets of data are obtained for fixed temperature offsets above T_g: (○) $T_g + 75°\mathrm{C}$; (□)$T_g + 82°\mathrm{C}$

if we plot $\ln(\tau^{\mathrm{on}})$ as a function of T/T_{NI} we should obtain a linear fit. Such a plot is shown in *Figure 6* and a reasonable linear fit is obtained for the data points taken close to the nematic–isotropic transition although such a plot does not take account of the temperature variation of U_0. There is a slight curvature indicative of the fact that these are glass-forming materials.

Figure 7 shows the variation in τ^{on} for changing polymer composition for measurements made at 75 and 82°C above T_g. Direct comparison of these data is complicated by the multitude of factors affecting the magnitude of τ^{on}. If we make corrections for the molecular weight dependence of η ($\eta \propto M_{\mathrm{W}}^{3.4}$) and the variations in the threshold voltages it is found that the τ^{on} values decrease with increasing concentration of II.

Of more significance in these studies is the relaxation time or τ^{off}. The cyclic experiment shown schematically in *Figure 4* obviously yields one measure of τ^{off} in which the equilibrium state of the material is probed by its response to the applied field. In essence this approach assesses whether the complete material system is in equilibrium. An alternative approach which is the more standard method reported in the literature is to measure the exponential decay of the transmitted light signal after the field is removed. As indicated above this is much more a measure of the state of alignment of the mesogenic units and may not indicate the state of the polymer chains. *Figure 8* shows the τ^{off} values obtained by the first method involving cyclic type experiments as a function of temperature for 10 and 20% of II and the homopolymer of I. These show similar temperature dependence of τ^{off} to that for τ^{on} (*Figure 6*), however the overall timescale is at least three orders of magnitude longer indicating the core of the problem in studying these materials. In general the switch off times, τ_{off}, as determined directly from the variation in the transmitted light intensity are somewhat shorter than those displayed in *Figure 8* evaluated using the cyclic approach. *Figure 9* shows the fractional difference in the τ^{off} values found using the two alternative procedures outlined above. The differences arise because in the cyclic experiments we are in fact determining the equilibrium relaxation time, whereas in the direct measurement we are considering the relaxation to the initial light intensity level, which does not necessarily indicate the equilibrium state of the whole system, but merely that of the mesogenic units. The fact that there is a difference indicates that the coupling between the mesogenic unit to the polymer backbone is not perfect and this has been confirmed at least for the homopolymer of I utilizing small-angle neutron scattering techniques. The fractional differences

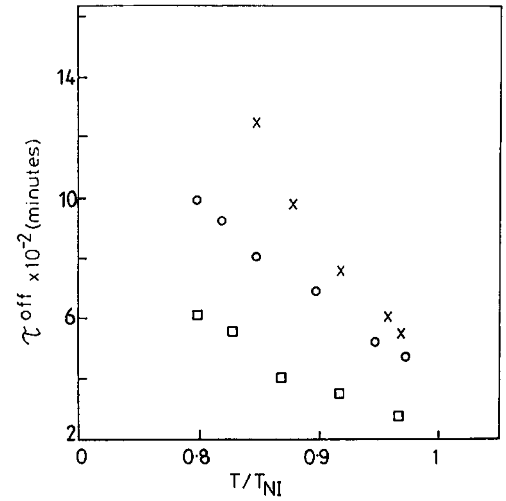


Figure 8 Plots of the relaxation time τ^{off}, obtained using the cyclic electro-optic procedures described in the text, as a function of the reduced temperature T/T_{NI}. Symbols as in *Figure 5*

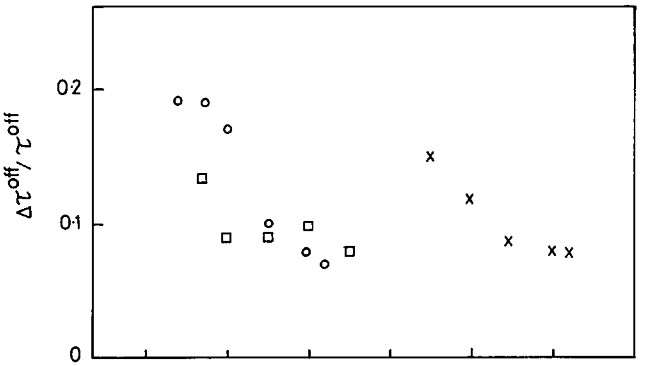


Figure 9 Plot of the fractional difference between τ^{off} measured using the cyclic electro-optic procedures and that measured using the direct optical signal. Symbols as in *Figure 5*

increase with decreasing temperature indicating a divergence of the relaxation rates of the polymer chain and the mesogenic units with temperature. In short, the optical signal does not necessarily indicate the relaxation of the backbone to its initial state. By considering the switch on time as a function of the allowed relaxation time, we reach a plateau when both the polymer backbone and the mesogenic elements have relaxed and hence the values of τ^{off} reported are those arising from the relaxation of a partially coupled system of the mesogenic and polymer backbone.

Static electro-optic properties

In this section we are concerned with evaluating the curvature elastic constants for the liquid crystal copolymers as a function of composition and temperature. This is achieved by measuring the threshold voltage required to induce director deformation in an electro-optic cell in which the director has a predefined surface alignment[20]. The general form of the relationship assuming strong anchorage is[21]:

$$U_c = \sqrt{K_{ii}/\varepsilon_0\Delta\varepsilon} \qquad (7)$$

where K_{ii} is a curvature elastic constant and $\Delta\varepsilon$ is the anisotropy of the permittivity. Equation (7) suggests that evaluation of K_{ii} will be a relatively straightforward procedure. However, the long time scale of both τ^{on} and τ^{off} presents particular experimental difficulties in measuring U_c reliably. In the first instance, ensuring that the sample is in total equilibrium involves leaving the sample for at least τ^{off}. *Figure 4* shows the variation of τ^{on} which may arise as a result of insufficient relaxation time. The 'simplest' method of measuring U_c is to determine the smallest voltage required to produce a significant optical change. Obviously the slow τ^{on} means that substantial time must be provided after each voltage step in order to ensure that a correct decision is made on whether any change has occurred.

The experimental arrangement used for the static properties is basically the same as that used for the dynamic electro-optic effects. Fields with a frequency of 500 Hz were employed for all measurements. The geometry of the cell and the type of predefined alignment results in the initial deformation, that is for voltages close to the threshold voltage, being dominated by splay deformation and hence these experiments provide an estimate for the splay elastic constant, K_{11}. From the dynamic electro-optics section we found how long each polymer takes to reach the equilibrium state after the application of a significant electric field, and so the threshold voltage measurements were made after the sample had been held at the fixed temperature for a period of more or at least equal to the relaxation time which we obtained as described in *Figure 4*. The threshold voltages were determined by an indirect method which avoids some of the difficulties outlined above. For particularly small voltages just above the apparent threshold voltage the steady-state transmitted light intensities were measured. A plot of these intensities as a function of the small applied voltages allowed, through extrapolation, the true threshold voltage to be estimated. Between each voltage step a period of typically 2–3 h was left for a steady state to be reached and this was checked by inspection of the transmitted light *versus* time function recorded. For all measurements the cell was held at those conditions for a period twice as long as required for a steady state to be reached. The direct measurement of the threshold voltage (not employed here) is somewhat less accurate as it is affected by the relatively large values of the response time[11] and may lead to considerable under estimation of K_{ii}.

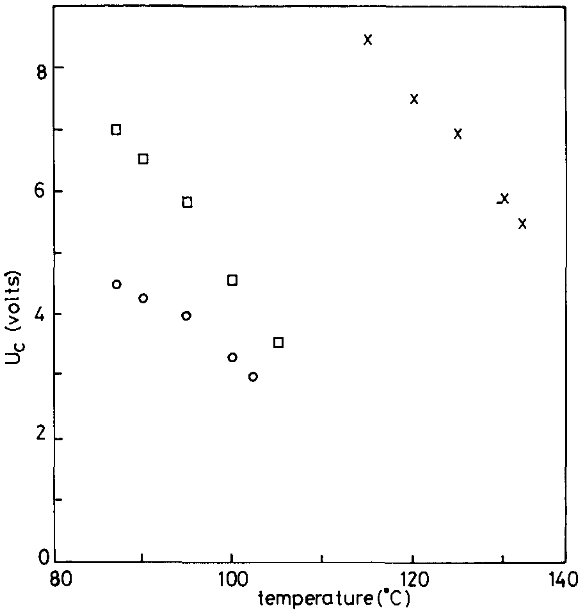


Figure 10 Plots of the measured electro-optic threshold voltages as a function of temperature. Symbols as in *Figure 5*

The results obtained for the homopolymer of I, 10 and 20% of II are presented in *Figure 10*. There is a steady reduction in the threshold voltage for both increasing temperature and content of II in the copolymers. In order to make comparisons between the threshold voltages for differing copolymer compositions we must have a knowledge of values of $\Delta\varepsilon$ for each copolymer composition, or make appropriate corrections. We have

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \qquad (8)$$

If we make the reasonable assumption, given the limited composition range, that the dielectric anisotropy of the mesogenic side chain may be approached through the additivity of the individual components we may write:

$$\Delta\varepsilon = \chi\varepsilon_{\parallel}^{I}(1-\chi)\varepsilon_{\parallel}^{II} - (\chi\varepsilon_{\perp}^{I} + (1-\chi)\varepsilon_{\perp}^{II}) \qquad (9)$$

where χ is the concentration of I and superscripts I and II relate to the two units of the polymer. We know that the dielectric anisotropy of the mesogenic units will be considerably greater than that for the II units. This is particularly so since neutron scattering experiments[20] show that the polymer backbone is only weakly coupled to the liquid crystalline order; essentially the polymer backbone is almost isotropic. This allows equation (8) to be simplified:

$$\Delta\varepsilon = \chi\Delta\varepsilon^{I} \qquad (10)$$

where $\Delta\varepsilon^{I}$ is the dielectric anisotropy of homopolymer I in the system. Equation (7) then becomes:

$$U_c(\chi)^{1/2} = (K_{ii}/\varepsilon_0\Delta\varepsilon^{I})^{1/2} \qquad (11)$$

Figure 11 shows the temperature dependence of the corrected threshold voltage. The threshold voltage of homopolymer I is typical of those reported in the

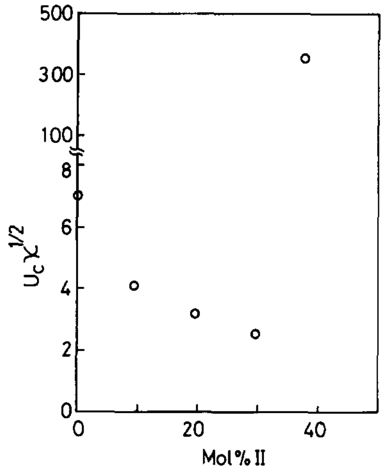


Figure 11 Data of *Figure 10* replotted to take account of the variation in Δε with copolymer composition as described in the text. Each point here was measured at a temperature 10°C below T_{NI} for that polymer composition. Similar behaviour was observed for other temperature offsets

literature and is similar to the threshold voltages found for low molecular weight liquid crystals[3]. Here we find that by increasing the concentration of II, the threshold voltage is decreased. There is a substantial reduction for the addition of 30 mol% of II which leads to a halving of the threshold voltage. We attempted to consider an extended composition range, but even for polymers containing 38 mol% of II the dominance of the viscosity and its effect on the temporal response of the material precluded reliable measurements in which the time dependence had been eliminated. The point plotted in *Figure 11* for 38 mol% of II represents a number of measurements made, although the high voltages required introduced the additional problems of dielectric breakdown and heating as observed in a previous study[12].

Order parameter measurement

The S measurements were made on prealigned cells using the procedures detailed earlier. The distinctive absorption band of the C≡N stretching vibration at 2235 cm^{-1} is well separated from other absorption peaks (*Figure 12*) and this allows reliable and reproducible values of $A_{\parallel}$ and $A_{\perp}$ to be obtained. The fact that this series of copolymers exhibits long relaxation times (*Figure 8*) again highlights the care that is needed in ensuring that equilibrium conditions are met and hence real S values are measured. Here we are interested in the variation of S with temperature. To ensure that for each temperature equilibrium conditions were established we held the sample at each temperature for periods up to 96 h during which repeated measurements were made to establish the steady state value for R. For example one particular sample (homopolymer of I) took 5 h to reach a steady state value for S after cooling from the isotropic phase, however the sample was left for 96 h to ensure that no fluctuation in S was observed (*Figure 13*). Values of $A_{\parallel}$ and $A_{\perp}$ were obtained with respect to the rubbing direction on the polyimide treated surfaces of the KBr crystals.

As expected, the i.r. spectra recorded from the samples in the nematic phase show a strong dichroism. The dichroism decreases with increasing temperature and finally drops to zero at T_{NI}. Spectra were recorded at a certain temperature within the nematic range. For all temperatures within the nematic range R for the C≡N absorption band was >1 indicating a parallel alignment of the mesogenic side chains with the rubbing direction. *Figure 12* shows the parallel and the perpendicular absorption for 20% of II at 80°C. In *Figure 14* the calculated S values according to equation (4) are plotted *versus* temperature. The variation of S with temperature shows the classical shape predicted by the Maier–Saupe theory[24]. The variation of the polymer composition leads to distinctive trends in the S *versus* temperature plots, however each individual curve has the same basic form.

Unfortunately it was not possible to prepare an aligned cell for the copolymer containing 30 mol% of II for i.r. studies. In general we found that the cells with predefined alignment based on KBr crystals were more difficult to

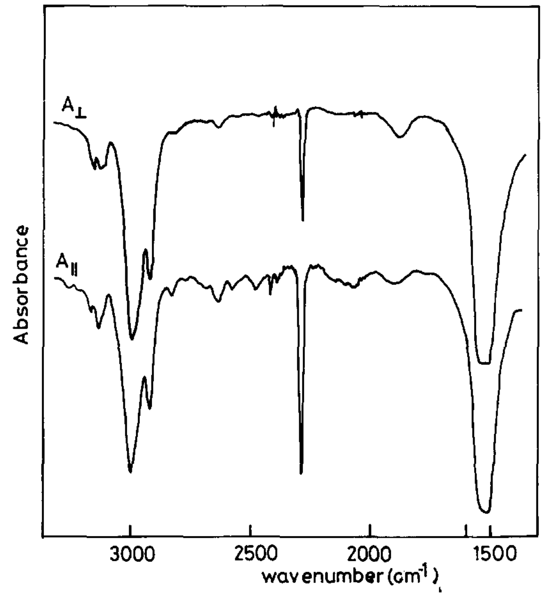


Figure 12 Measured i.r. spectra obtained using a prealigned cell containing copolymer with 20 mol% of II, with electric field vector parallel and perpendicular to the alignment direction. The sharp band for the C≡N stretching absorptions may be seen clearly at a wave number of 2235 cm^{-1}

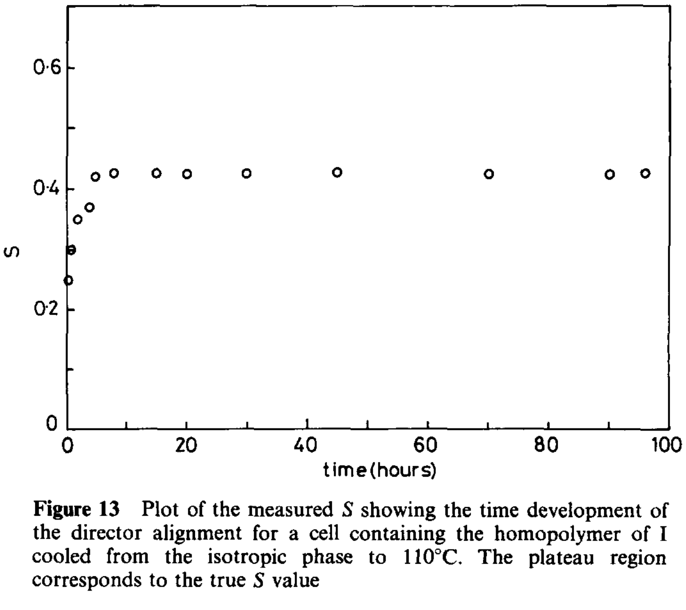


Figure 13 Plot of the measured S showing the time development of the director alignment for a cell containing the homopolymer of I cooled from the isotropic phase to 110°C. The plateau region corresponds to the true S value

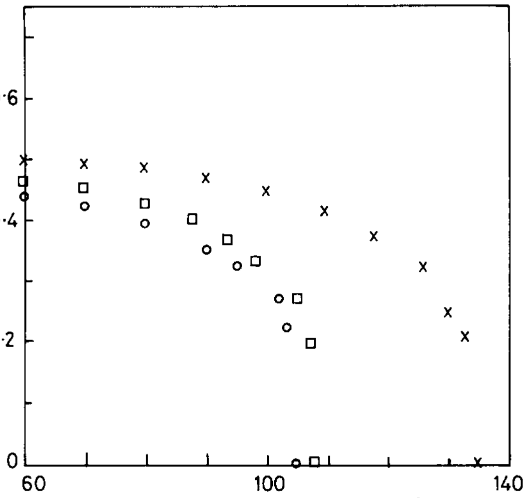


Figure 14 Variation of measured S obtained through measurement of the i.r. dichroism using prealigned cells as a function of temperature for the three polymers considered. Symbols as in *Figure 5*. Prior to each measurement at the specified temperature the sample was held at that temperature to ensure equilibrium conditions were established (*Figure 12*)

prepare than those based on the tin oxide coated glass, even though both contained barrier layers of polyimide.

Relationship of elastic constant K_{11} *with the order parameter* S

The establishment of the relationships between macroscopic properties such as the elastic constants and the molecular structural arrangements and chemical configurations of the constituent molecules remain a challenge in the area of liquid crystal physics. Some of the first calculations of the relative magnitude of the elastic constants were carried out by Saupe and Nehring[22]. Their approach was based on the Maier–Saupe mean field theory and they derived:

$$K_{\rm ii} = \frac{C_{\rm ii}S^2}{V^{7/3}} \tag{12}$$

where $C_{\rm ii}$ is a temperature-independent constant varying with molecular properties, and V is the molar volume, which is inversely proportional to the mass density ρ. Typical variations of ρ across the nematic phase range are small; for example, with low molar mass cyanobiphenyls $\rho^{7/3}$ varies by a maximum of 3.5%[23]. The temperature dependence of the elastic constant is therefore expected to be dominated by S. The prediction that $K_{\rm ii} \propto S^2$ may also be derived using the Landau–De Gennes approach in which the free energy of a system is expressed[24] in terms of a series expansion of S. In fact this latter approach highlights the extent of the approximation, for all terms higher than S^2 are neglected. This may be reasonable for consideration of systems in which $S \sim 0$ but as can be seen from the S values displayed in *Figure 14* this represents a severe approximation. This type of approach predicts that the rate K_{33}/K_{11} should be independent of the temperature and despite the apparent severe approximations, such an effect is indeed observed qualitatively for a number of low molar mass liquid crystalline materials[16].

Equation (11) may be written:

$$U_{\rm c}(\chi)^{1/2} = (K_{11}/\varepsilon_0 S\Delta\varepsilon_{\rm I}^*)^{1/2} \tag{13}$$

in which $\Delta\varepsilon$ is replaced by $S\Delta\varepsilon^*$, where $\Delta\varepsilon^*$ is the 'intrinsic' dielectric anisotropy, i.e. that for a perfectly aligned system. Since the dielectric permittivity is a second rank tensor we may write $\Delta\varepsilon = \Delta\varepsilon^* S$ if the variations in local fields and other local interactions do not vary with S. In the limited S *versus* temperature variation considered here this seems not unreasonable. The purpose of this restructuring is to allow the temperature and S variations on K_{11} to be considered independent of the effect of those variables of the dielectric properties. If we accept equation (12) then combination with equation (13) leads to:

$$U_{\rm c}^2\chi \propto S \tag{14}$$

Figure 15 shows the variation of $U_{\rm c}^2\chi$ with S for the three polymer systems for which complete data are available. From the experimental data there is a clear trend between the threshold voltage and S, but any reasonable fit to the data allowing the curve to pass through $U_{\rm c}^2\chi = S = 0$, would require a non-linear relationship at variance with the general prediction as described above. The fact that the experimental data suggest a more complicated relationship between deformation and the level of order involving other terms than S^2 is perhaps hardly surprising. *Figure 15* shows that even when the variation in S is taken into account there remain substantial differences between the threshold voltages for the three compositions. In other words if the lowering of the threshold voltage as a function of composition, as shown in *Figure 11*, was due to a reduction in S alone, then all three curves would superimpose. If we consider adding more terms such that, for example

$$U_{\rm c}^2\chi \propto aS + bS^2 + cS^3 \tag{15}$$

we could fit the data as shown by the broken lines in *Figure 15*. However this serves to highlight the main differences between the curves for the three materials; the coefficients a, b and c. In the formulation of equation (15), these would correspond to the temperature-independent elastic constants C_{11}. These data show that by changing the number of mesogenic units substituted along the backbone the intrinsic curvature elasticity may be reduced. The differences in the threshold voltages with respect to composition are sufficiently great that any small variations that might arise from the assumptions

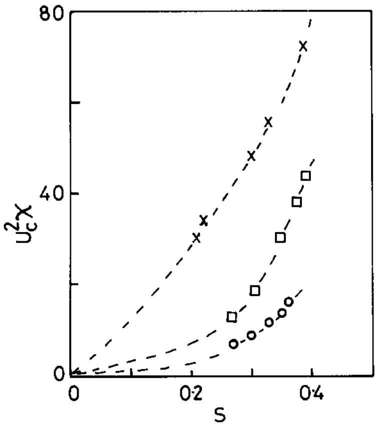


Figure 15 Plot showing the correlation between the function $U^2\chi$ obtained from the measured threshold voltages (*Figure 10*) and S for each polymer system. The broken lines are fits obtained to the polynomial described in the text

introduced in equation (13) do not detract from this principal observation.

DISCUSSION

It is found that the introduction of non-mesogenic unit moieties (II) into the polymer chain of a liquid crystal polymer (I) lowers the T_{NI}, and for a composition of >55% of II the organization of the liquid crystal phase is completely disrupted. Essentially we have reduced the density of the mesogenic units attached to the polymer chain. In contrast to simple molecular mixtures of the polymers of I and II[13] the inherent connectivity of a copolymer system allows substantial proportions of an incompatible component to be introduced without phase separation. Complementary to the reduction of T_{NI} with decreasing number density of mesogenic units there is a marked lowering of T_g, presumably as a result of enhanced backbone mobility. The latter effect has been confirmed in the dynamic electro-optic section although the response times are mostly dominated by the molecular weight. However the reduction in T_{NI} with composition occurs at a greater rate than the corresponding reduction in the glass transition, and the mobile liquid crystal phase region narrows until it is completely eliminated for composition of II of >55 mol%. It is unclear whether for higher concentrations of II the liquid crystal phase is not observed because of the kinetic restrictions rather than thermodynamic stability.

Although the reduction of the number of mesogenic units along the polymer is relatively limited from 0.5 to 0.35 (expressed as a fraction of the backbone carbon atoms) for the copolymers in which complete data were obtained, it has a marked impact upon the switching times, the threshold voltages and S. From equation (3), it is clear that an increasing proportion of ethyl acrylate (II) should reduce the magnitude of $\Delta\varepsilon$ and hence U_c should increase. The observation that U_c reduces with increasing non-mesogenic unit content indicates a reduction in the elastic constant K_{11}. It is clear that this reduction in the elastic constant is greater than can be attributed to the variation in order parameter of the mesogenic side chains with side-chain density. In the spirit of the approach of Nehring and Saupe[22] we may relate this to some reduction in the intrinsic curvature elasticity of the system. Although this appears at first sight to reflect the fact that obviously a reduction in the side-chain density will ease deformation, such effects are presumably already accounted for in the variation of the order parameter with composition. It seems more appropriate to attribute the reduction of the intrinsic elastic constant with composition to changing levels of interactions between the mesogenic units and the polymer backbone. Similar effects may appear when the nature of the attachment of the side chain is varied for example through differing coupling chain lengths and such work is in progress[25]. Although the introduction of the non-mesogenic units has an advantageous result in terms of the electro-optic response, the disadvantage of this approach is that when the ethyl acrylate content is large enough to provide considerable backbone flexibility, the nematic phase is lost.

In this study we have been particularly concerned to ensure that when considering the static electro-optic properties we have eliminated any effects arising from kinetic-based phenomena. This led to the development of the cyclic experiment in which the response time τ^{on} is utilized as the probe for equilibrium conditions. Comparison of those results for τ^{off} as a function of temperature with those measured using conventional optical relaxation techniques shows a significant difference which increases as the temperature is lowered (*Figure 9*). This graph underlines both the interactions which must exist between the mesogenic units and the polymer backbone and the fact that the interactions are weak. In other words reorientation in an electric field results in electrical energy coupling to the mesogenic units. Since the polymer chain is coupled to the mesogenic side chains[5] then this will also undergo motion. However, the response of the mesogenic units and that of the polymer need not be on the same time scale. The polymer chain may take much longer to reach equilibrium and because of the weak nature of the coupling this need not be evidenced by the orientation of the side chains. This is exactly what happens and it is the origin of the difference in *Figure 9*. The electric field results in reasonable rapid alignment of the mesogenic units through the coupling of the polymer chain. Removal of the field results in relaxation driven through the curvature elasticity back to the initial configuration, however, the side chains in part can relax independently of the polymer chain and this occurs slightly ahead of the polymer chain relaxation. The former contributes to the optical signal, the latter does not. This slower relaxation of the polymer chain is only detected since it influences the subsequent response to the electric field.

In other respects this range of copolymers behaved in a similar manner to many other reported liquid crystal polymers; for example, the (switch-on) time decreased as the temperature was increased above the glass transition; such effects are related to the reducing polymer viscosity. The response times for homopolymer of I which were reported in references 11, 26 and 27 are found to be slightly shorter than the response times for the homopolymer of I used in this work. This is in part due to the fact that the homopolymer studied here has a higher degree of polymerization than that used by the other authors. As was shown by Talroze *et al.*[28] the orientation response time is largely dependent on molecular weight rising with increasing degrees of polymerization; such an effect is sufficient to explain the longer response times reported here. In terms of the threshold voltages the values obtained here for the homopolymer are similar to those reported in the literature[26–28].

A similar series to that studied here has been reported by Hirai *et al.*[12] for the situation when the coupling chain length (n) is 2. In those materials the phase behaviour with composition of II is similar to that described here, in that with increasing concentration of II the liquid crystal phase region narrows and the nematic–isotropic transition is lowered. In the series with $n = 2$, Hirai *et al.*[12] found that reliable electro-optic switching could not be performed except with high concentration of II. This mirrors the results of this work with $n = 6$, in that threshold voltage falls with increasing concentration of II. For the series with $n = 2$ the proximity of the glass transition precludes detailed measurements of the static electro-optic properties.

Values of S for the homopolymer of I have been reported by Pranoto *et al.*[11,24] and Buerkle *et al.*[8]. The results are generally similar although the values given in references 8 and 28 are systematically some 6% higher than the values given in this work (*Figure 15*). The temperature dependence of S found in these various studies is the same and it is probable that the differences in absolute values arise from differences in the molecular weight of the polymers.

CONCLUSIONS

This study has focused on the properties of a series of copolymers with differing densities of mesogenic side chains attached to an acrylate backbone. It is found that reducing the density of the side chains through the introduction of non-mesogenic moieties disrupts the organization of the liquid crystal phase such that the nematic–isotropic transition is lowered together with a reduction in the glass transition. In the system considered here 55 mol% of the non-mesogenic unit II can be introduced before the nematic phase is completely destabilized within the accessible temperature range. The orientational order of the mesogenic units follows a similar temperature dependence for each of the differing copolymer compositions, although the magnitude of S is reduced. The effects of decreasing the steric crowding along the polymer chain is to lower the observed threshold voltages. This may be related to the reduction in the intrinsic elastic constants of the liquid crystal polymer. The variation in the copolymer composition leads to changes in the dynamics of the electro-optic response but these time scales are dominated by temperature and molecular weight effects. It is clear that the optical properties do not offer a direct probe of the overall state of the material, and that relaxation of the polymer chain may occur without affecting such optical properties. This has implications for the design of electro-optic measurements on liquid crystal polymers.

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