The effect of the molecular weight on the electro-optic properties of methacrylate-based side-chain liquid crystal polymers

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A series of methacrylate-based side-chain liquid crystal polymers has been prepared with a range of molecular weights. For the high molecular weight polymers a smectic phase is observed with a very narrow nematic range; however, for low molecular weight polymers only the nematic phase is observed. A marked reduction in the glass transition temperature, T_{SN} and T_{NI} is observed with a reduction in the molecular weight. The orientational order parameters for these polymers in the liquid crystal phase have been determined using infra-red dichroism. It is found that the higher the molecular weight of the polymer, the greater is the threshold voltage of the electro-optic response and the lower the order parameter. The increase in the threshold voltage with increasing molecular weight may be related to the intrinsic curvature elasticity and hence to the coupling between the mesogenic units and the polymer backbone.

(Keywords: molecular weight; properties; methacrylate)

INTRODUCTION

The design principles of side-chain liquid crystal polymers are well established[1]. These molecular composites consist of a flexible polymer backbone and a rigid mesogenic unit, joined as a side-chain to the polymer backbone by means of a flexible coupling chain. Although there were initial suggestions that the spacer chain would decouple the motion of the mesogenic unit from the polymer backbone, it is now clear that the relatively short length of the coupling chains leads to some interaction between the mesogenic units and the polymer backbone chains. The theoretical predictions of Warner and others[2–4] have been substantiated by a number of neutron scattering studies[5–10]. In the nematic phase, the coupling in methacrylate-based systems appears to be negative, in the sense that the polymer chains lie preferentially perpendicular to the mesogenic units[5,10]. This is in contrast to the positive or parallel arrangement found in acrylate-based materials[7]. For the smectic phase of the methacrylate-based polymers, the density wave of the layered structure of the mesogenic units acts to confine the polymer chain to a layer perpendicular to the mesogenic units[5,6,8–10], although there is some possibility of interlayer hopping by the polymer chain[11]. By suitable chemical design[12,13], polymers can be synthesized that will exhibit the well known electric and magnetic field effects displayed by their low molar mass counterparts[14]. In such electro-optic effects, what is the role of the polymer backbone? It is clear that the polymeric nature of the liquid crystal phase strongly affects the response times through a highly temperature-dependent viscosity. Furthermore, the electro-optic response of a side-chain liquid crystal polymer is particularly sensitive to the thermal history of each sample, and this may be related to the coupling of the side-chain organization to the very long relaxation time of the polymer backbone[15].

In this paper, we focus on the role of the polymer backbone in determining the static properties of the liquid crystal phase. In particular, we centre our attention on the influence of the molecular weight upon the curvature elasticity, which determines the ease with which the director pattern may be modified using external electric fields. We shall consider a series of methacrylate-based side-chain liquid crystal homopolymers in which the molecular weight is systematically varied. The state of orientational order in these homopolymers is evaluated through the use of infra-red spectroscopy which selectively probes only the mesogenic side-chains. Carefully programmed electro-optic measurements are used to evaluate the relationships between the variations in molecular weight, orientational order and electro-optic properties.

EXPERIMENTAL

Materials

A series of methacrylate-based side-chain liquid crystal homopolymers with the repeat unit I have been prepared by free-radical polymerization[16].

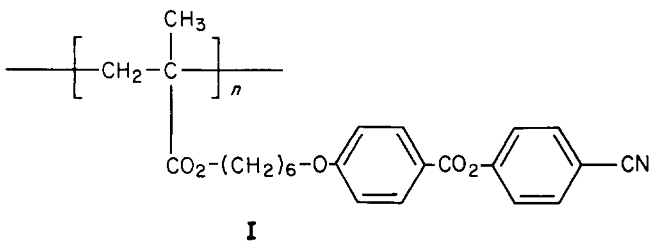

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Table 1 Molecular weight and phase transition data

Polymer	M_w[a]	DP_n[a]	T_g[b] (°C)	T_{SN}[b] (°C)	T_{NI}[b] (°C)
1	1.84×10^5	338	46	117	120
2	6.87×10^4	112	41	113	117
3	9.36×10^3	19	31	90	97
4	4.28×10^3	9	21	–	78
5	2.76×10^3	3.8	6	–	61

[a] Determined by g.p.c.

[b] Determined using a Perkin-Elmer DSC2-C and a heating rate of 10°C min^{-1}

The standard conditions used (initiation by azobis-(isobutyronitrile) in chlorobenzene at 55°C) have been modified to give a range of molecular weights by increasing the initiator concentration and by the addition of various amounts of dodecanethiol[17] as a chain transfer agent[18]. Both of these modifications reduce the molecular weight of the polymer produced. The liquid crystal phase behaviour of these homopolymers varies with the molecular weight as shown in *Table 1*. On reducing the molecular weight, all of the phase transitions — glass transition temperature, T_g, smectic to nematic transitions, T_{SN} and nematic to isotropic transitions, T_{NI} — are depressed (*Table 1*), as has been seen for polyacrylate- and polysiloxane-based side-chain liquid crystal polymer systems[19,20]. The high molecular weight polymers exhibit two endotherms close together in the d.s.c. curve. The lower of these corresponds to a smectic–nematic phase transition. The smectic phase, identified as smectic A by Davidson *et al.*[21], occurs over the greater part of the liquid crystal range. A nematic phase is seen over a narrow temperature range close to the clearing point. This phase shows a characteristic nematic optical texture when examined in a polarizing microscope. On cooling, a dense scattering texture forms. When polymers 2 and 3 are annealed in the smectic phase, clear focal conic textures, a fingerprint of the smectic phase, are observed. The high viscosity of polymer 1 prevents the formation of such large-scale textures. The low molecular weight polymers, 4 and 5, show a single endotherm in the d.s.c. curve and at all temperatures in the liquid crystal phase range; the optical textures observed in the polarizing microscope are characteristic of a nematic phase. In contrast to the higher molecular weight polymers, annealing these textures simply enhances the nematic textures; there is no evidence whatever for focal conic or other smectic textures.

When interpreting the phase behaviour of these materials we have to be cautious in attributing effects solely to differences in molecular weight: in the lowest molecular weight member of this series a significant fraction of end groups will be fragments of the chain transfer agent, consisting of a long alkyl chain bound through a sulfur atom. The molar fraction of attached chain transfer agent has been found, by micro-analysis for the sulfur content of the polymers[16], to be 0.20 for polymer 5 and 0.14 for polymer 4. In order to ascertain whether the plasticizing effect of the dodecyl chains was responsible for the anomalous phase behaviour, we prepared a series of copolymers of monomer I and dodecyl methacrylate, under polymerization conditions similar to those employed for the preparation of polymer 2. These copolymers exhibited nematic and smectic phases even when 15 mol% of the non-mesogenic monomer had been incorporated. Essentially their phase behaviour was that of the high molecular weight homopolymers rather than the low molecular weight homopolymers.

The molecular weight data for the homopolymer series were determined by g.p.c. (Rapra Ltd) at room temperature in tetrahydrofuran, using a combination of concentration and viscosity detectors and Unical universal calibration software[16].

Methods

An electro-optic experiment involves the measurement of changes in the optical properties of thin films of liquid crystal polymers induced through the application of electric fields. The experimental arrangement used for these electro-optic measurements has been described in detail elsewhere[15,22]. The electro-optic cell (described below) was held inside a temperature-controlled stage providing a uniform temperature environment of ±0.25°C. The optical system consisted of a 5 mW helium–neon laser with crossed polarizer and analyser system and a photo-diode with an amplifier for intensity measurements. Electric fields were provided by means of a power amplifier (Hewlett Packard 6872A) driven by a function generator (Thandar TG501). This arrangement provided waveforms in the frequency range of 0.05–30 kHz with peak-to-peak amplitudes in the range 0–240 V. 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. Through the use of a specially written software system, EOCS, sophisticated electro-optic experiments could be performed on a continuous or cyclic basis, involving temperature control, data recording, field switching and analysis[15]. The electro-optic cells with predefined direction orientation were constructed from patterned tin oxide coated glass slides. After cleaning in an ultrasonic bath and drying, the cell electrodes were coated with a thin layer of polyimide precursor consisting of a 5% solution of Rodehftal 322 in diemthylformamide using a spin-coater. These coated slides were rubbed in a single direction with a cloth and then heat-treated in order to retain the surface treatment. A small portion of the selected polymer sample was carefully applied onto one of the treated glass electrodes, and then heated above its clearing point in order to allow the trapped air to escape. The second glass electrode was then mounted above the first electrode using Kapton sheet (0.025 mm thick) as spacers. The quality of the director orientation was confirmed through examination with a polarizing microscope. Complete and uniform director alignment was obtained by holding the completed electro-optic cell at a temperature 1°C below the measured clearing point for 15 h. This technique was successful in inducing a uniform director alignment in electro-optic cells for all materials used in this work. In all cases the predefined director alignment was parallel to the electrode surface and to the direction of rubbing. Some cells showed small numbers of defects, such as small loops, when examined using the polarizing microscope; however, these largely disappeared after holding the cells at elevated temperatures.

The orientational order parameter, S, for each polymer sample at a variety of temperatures, was measured using infra-red dichroism employing a Perkin-Elmer 580B spectrometer fitted with a wire-grid polarizer and heating stage[22]. The order parameter measurements were made

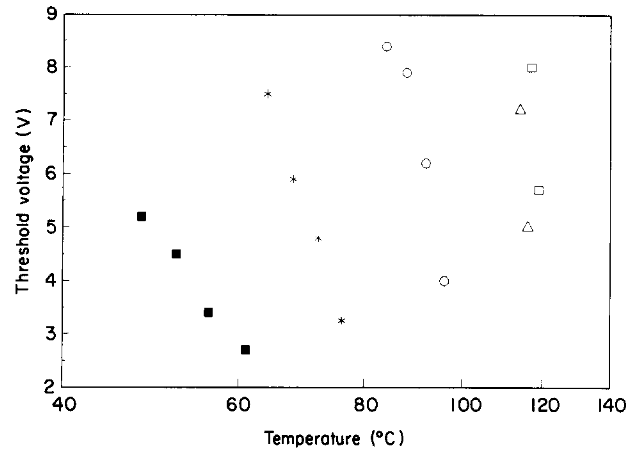

Figure 1 Experimental threshold voltages for a molecular weight series of methacrylate-based side-chain liquid crystal polymers plotted as a function of temperature. The symbols refer to the polymers listed in *Table 1*: □, polymer 1; △, polymer 2; ○, polymer 3; *, polymer 4; ■, polymer 5

using monodomain samples prepared as pre-aligned cells similar to those used for the electro-optic measurements but using crystals of potassium bromide as the cell windows[22].

RESULTS

Static electro-optic properties

We have used the experimental arrangement described above to evaluate the static electro-optic properties for each member of the molecular weight series of the side-chain liquid crystal polymers shown in *Table 1*. In these experiments we determine the minimum or threshold electric field required to distort the surface predefined director orientation. In this geometry the electric field perturbs an initial planar surface alignment and this mode of deformation is dominated by the splay component of the curvature elasticity, k_{11}, for small deformations. The threshold voltage, U_{th}, is related to the curvature elasticity, assuming strong anchorage, by[14]:

$$U_{th}=\sqrt{\frac{k_{11}}{\varepsilon_0\Delta\varepsilon}} \tag{1}$$

where $\Delta\varepsilon$ is the anisotropy of dielectric permittivity. From this equation, it can be seen that the evaluation of k_{11} should be a straightforward procedure through the measurement of U_{th}. However, for a polymer system a number of particular problems arise in evaluating U_{th}, each of which relates to the high viscosity of the polymer. The most challenging is to ensure that, before starting any measurements, the sample is in a state of complete equilibrium. For each of the samples considered, and for each temperature of measurement, we have established the real relaxation time of the polymer system through the use of cyclic electro-optic measurements[15,22]. All threshold voltage measurements were made after the sample had been held at the required temperature for a period at least three times longer than the relaxation time. As the response time is long, particularly at low applied voltages, we determined the threshold voltage from a plot of the change in the transmitted optical intensity as a function of the applied small voltages. By extrapolation, this method allowed both the true threshold voltage to be estimated and any dynamic effects to be excluded. After each voltage step, samples were left for 3–5 h in order to reach a steady state and the approach to steady state was monitored through measurement of the transmitted light. Typically, at each stage the sample was held for a period 10 times longer than the response time to the applied electric field.

The results obtained for the materials in this study are presented in *Figure 1*. There is a marked reduction in the threshold voltage for both increasing temperature and reducing molecular weight. In this series of polymers, the chemical composition, other than the proportion of end-groups, is unchanged and hence $\Delta\varepsilon$ should also be unchanged. *Figure 2* makes a direct comparison of the threshold voltages obtained for temperatures in the nematic phase range at a constant step below T_{NI} for the series of polymers prepared. It is clear that there is an increase in the threshold voltage with increasing molecular weight. Indeed, if the slight reduction with reducing molecular weight in $\Delta\varepsilon$, due to the end-groups of the polymer chains, is taken into account then the trend in the reduction of U_{th} will be even more marked. It is emphasized that any dynamic effects arising from viscosity have been eliminated through the procedures outlined above. Some previous studies[23–25] have dealt with measurements of the threshold voltage for methacrylate polymers. The values of U_{th} reported are broadly similar to those found in this study, although direct comparison is not possible since in those reports no molecular weight data were given. The marked increase of the threshold voltage with temperature follows similar trends to those observed for polyacrylate-based materials[15,22,25]. It is noticeable that there is no sudden step in the threshold voltage at the transition from nematic to smectic phases for polymer 3. In the electro-optic cells employed in this study the initial director pattern is parallel to the electrode surface. As a consequence, the first stages of deformation involve only splay-type deformation. For a smectic phase, although the other curvature elastic constants are considered almost infinite, the value of k_{11} is usually similar to that observed for the nematic phase[14]. This arises from the fact that bending of the smectic layers (or splay of the director pattern) is the only relatively facile deformation process for the smectic phase.

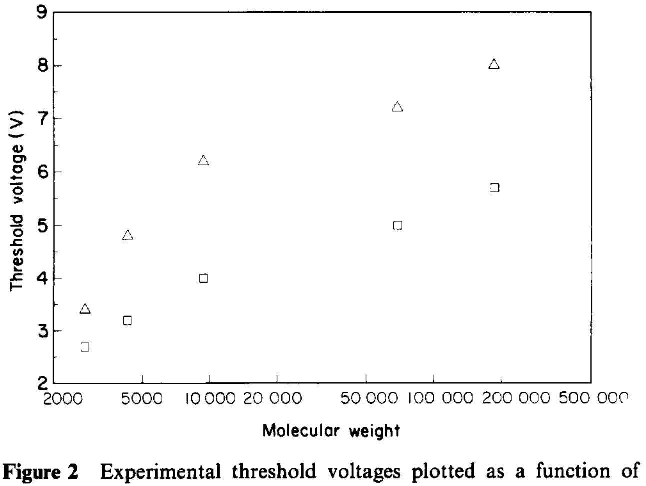

Figure 2 Experimental threshold voltages plotted as a function of molecular weight for measurements performed in the nematic phase range at $T_{NI}-T=1$°C (□) and $T_{NI}-T=3$°C (△) for each of the polymers listed in *Table 1*

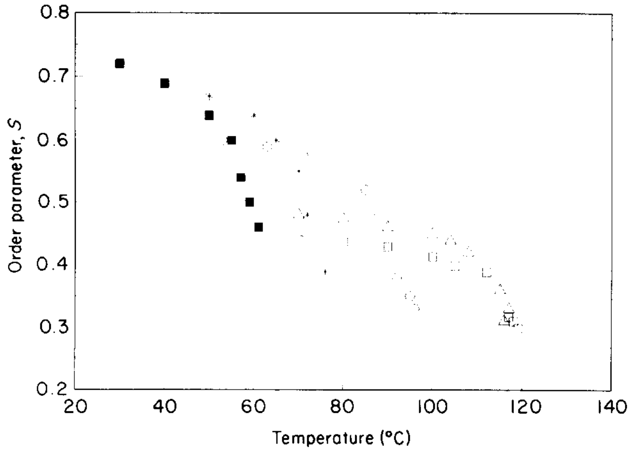

Figure 3 Order parameter S plotted as a function of temperature for the polymers listed in *Table 1*. Key as in *Figure 1*

Order parameter

We have measured the order parameter of the mesogenic side-chains through the dichroic ratio of the absorption peak at $2235\,\mathrm{cm}^{-1}$ which arises from the C≡N bond stretching vibration, in relation to a predetermined director alignment or rubbing direction. This dichroism may be used to define an optical order parameter, S, which in effect assumes that the absorption moment of the C≡N bond is parallel to the long axis of the mesogenic unit[22,26]. This order parameter measures directly the orientational order of the side-chains. Since these liquid crystal polymers exhibit long relaxation times, considerable care was taken to ensure that equilibrium conditions were achieved. Each sample was held for up to 130 h before the final measurements were performed, although the changes in dichroic ratio that occurred as a result of temperature steps were usually established within 10 h. Measurements were made for each sample over a range of temperatures to include both nematic and smectic phases where appropriate. The resultant order parameters are plotted as a function of temperature in *Figure 3*. The variation of the order parameter with temperature for each sample shows the classical shape predicted by the Maier–Saupe theory[27]. The variation of the polymer molecular weight leads to distinctive trends in the order parameter *versus* temperature plots, although each individual curve has the same basic form. It is clear from *Figure 3* that the materials with the highest molecular weight exhibit the lowest order parameters; this effect has also been observed by Boeffel *et al.*[28] for some acrylate-based side-chain polymers. Although it might appear that the lower order parameters for the higher molecular weight polymers reflect an incomplete monodomain formation due to the high viscosity, there was no experimental evidence to suggest that the measurements shown were anything other than the true steady-state values. The values and temperature dependence of the order parameter observed for polymer 2 closely follow those obtained for a nematic acrylate-based material with the same mesogenic side-chain and the same degree of polymerization[22].

Elastic constants

Current microscopic models of curvature elasticity in liquid crystal polymers are restricted to the main-chain variety and we must rely on the traditional approach used for non-polymeric liquid crystal systems. Nehring and Saupe used the Maier–Saupe mean field theory to establish the relationship[27,29]:

$$k_{ii}=\frac{c_{ii}S^2}{V^{3/7}} \qquad (2)$$

where c_{ii} is a constant dependent upon molecular properties and V is the molar volume. This type of relationship predicts that the value of the elastic constant is dominated by the order parameter S. It should be noted that this approach is very much first order, neglecting any higher order dependence of S, or indeed higher order orientational parameters. It predicts that the splay, twist and bend curvature elastic constants are equal. However equation (2) does provide a route to illuminating the molecular weight dependence of the threshold voltage. If we take account of the dependence of $\Delta\varepsilon$ upon S we may combine equations (1) and (2) to give[22]:

$$U_{\mathrm{th}}^2 \propto S \qquad (3)$$

The purpose of this restructuring is to allow the effect of temperature/order parameter variations on k_{11} to be considered independently of the effect of those variables on the dielectric properties. *Figure 4* shows the variation of U_{th}^2 with the order parameter S for each of the polymers considered in this study. From the experimental data there is a clear trend between the threshold voltage and the order parameter, but any reasonable fit to the data allowing the curve to pass through $U_{\mathrm{th}}=S=0$ would require a non-linear relationship at variance with the general prediction described above. *Figure 4* shows that even when the variation in order parameters is taken into account, there remain substantial differences between the different members of this molecular weight series. In other words, if the variation in the threshold voltages shown *Figure 2* were due to the reduction in order parameter alone, then all five curves in *Figure 4* would superimpose. This is not the case, and within the framework of equation (2) we can relate the differences in the slope of these curves to the temperature-independent coefficients c_{11}, which are clearly affected by the molecular weight. The variation in slope with molecular weight indicates that there is strong coupling between the mesogenic side-groups and the polymer chain, and that this plays a significant part even in the static electro-optic properties. The curvature of the plots in *Figure 4* is similar to that

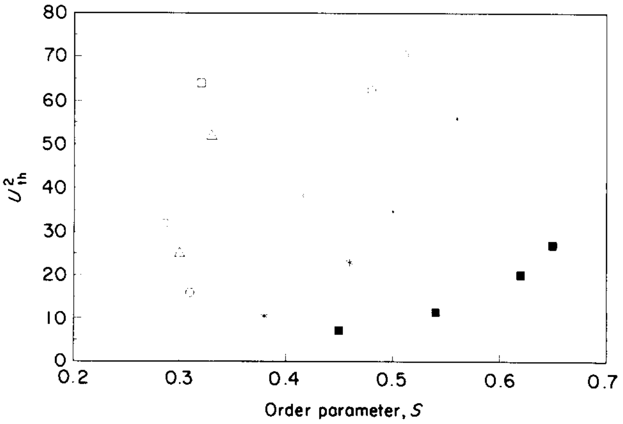

Figure 4 Plot of the square of the measured threshold voltage against the order parameter at the temperature of measurement for each of the polymers listed in *Table 1*. Key as in *Figure 1*

observed in studies of polyacrylate-based polymers[22]; this indicates that the non-linear dependence of U_{th} on S is a more general feature of side-chain liquid crystal polymers.

DISCUSSION

Variation of the degree of polymerization in this series of methacrylate-based side-chain liquid crystal polymers has impact upon the phase behaviour, the order parameter and the electro-optic properties. It is found that decreasing the molecular weight lowers the phase transition temperatures. For high molecular weight materials (polymers 1, 2 and 3) a smectic phase is observed with a very narrow nematic range. However, at lower molecular weight (polymers 4 and 5), only the nematic phase is observed. Complementary to the reduction of the clearing temperatures with decreasing molecular weight, there is a marked lowering of the glass transition temperatures. It is clear that increasing the molecular weight will not significantly change the magnitude of $\Delta\varepsilon$, and hence if the curvature elastic constant is unaffected by the degree of polymerization, the threshold voltage should be constant. The observation that U_{th} increases with increasing molecular weight indicates an increase in the elastic constant k_{11}. We attribute the increase of the elastic constant with molecular weight to changing levels of interaction between the mesogenic units and the polymer backbone. There is evidence for this from small-angle neutron scattering experiments carried out by Hardouin and co-workers[9,30] on different molecular weight siloxane-based polymers. They found that the anisotropy of the radius of gyration increased by 30–40% with the approximate doubling of the molecular weight. It is possible to divide the contribution of the polymer chain to the apparent curvature elasticity into two components. The first arises from the elasticity of interactions between chains as might arise from entanglements. Such effects have been observed in the electro-optic properties of crosslinked side-chain liquid crystal polymers[31,32]. The increase in the threshold voltage with crosslinking was very substantial. It would perhaps be expected for uncrosslinked polymers that the threshold voltage would be much lower when the molecular weight falls below that critical weight required for entanglements and that this additional elasticity would increase with increasing temperature. The second contribution arises more directly from the coupling of the mesogenic units to the polymer backbone and is perhaps typified by the increase in the threshold voltage which arises as the coupling chain is shortened[14,33]. It is not clear in this study which of these possible contributions is the dominant process in the molecular weight dependence of the threshold voltage.

SUMMARY

This study has focused on the properties of a series of polymers with differing molecular weights based on the methacrylate backbone. It is found that reducing the molecular weight lowers the phase transition temperatures and eventually leads to destabilization of the smectic phase. The effect of reducing the molecular weight of the polymer is to lower the observed threshold voltage. This may be related to an increase in the intrinsic elastic constants of the liquid crystal polymers. It is found that there is strong coupling between the mesogenic side-chain groups and the polymer chain and that the elasticity of the polymer chain plays a part in the static electro-optic properties. The orientational order of the mesogenic units follows a similar temperature dependence for each of the polymer molecular weights, although the magnitude of the order parameter is much reduced as the molecular weight increases.

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