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Liquid-crystal side-chain copolymers composed of a non-chiral mesogenic monomer and a chiral non-mesogenic monomer

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A series of copolymers was prepared from a mesogenic monomer, 4-cyanobiphenyl-4-(6-acryloyloxy-hexyloxy) benzoate (**1**) and a chiral non-mesogenic monomer (S)-methyl(2-methyl-3-methacryloyloxy) propionate (**2**). The reactivity ratios for the copolymerization of the two monomers were found to be $r_1 = 0.15$ and $r_2 = 3.00$, indicating the greater tendency for the less bulky chiral monomer to be incorporated into the copolymer chains preferentially. Examination of the mesogenic behaviour showed that samples with compositions of mole fraction $F_2 \leq 0.6$ exhibited a nematic phase which was stable over a temperature range of about 85°C. There was no evidence that the interaction of monomer **2** with mesogen **1** was strong enough to induce a chiral nematic phase in the copolymers. A crosslinked sample was also studied and it was observed that the alignment of the mesogenic phase was very sensitive to the application a uniaxial tensile force.

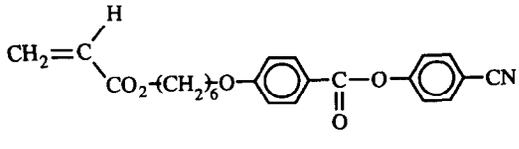
(Keywords: copolymerization; reactivity ratios; liquid crystal polymers)

Introduction

Investigations into the properties of chiral side-chain liquid-crystal polymers have increased since it was found that the chiral nematic and chiral smectic phases exhibit interesting optical and electrical behaviour. The usual approach to synthesizing these materials is to locate the chiral unit, either in the terminal group of the pendent mesogen[1] or in the spacer linking the mesogen to the polymer backbone[2]. Dissolution of a small liquid-crystal molecule in the liquid-crystal phase of a polymer may also influence the nature of the phase, and it was decided to examine whether this principle could be applied to wholly polymeric systems. This can be achieved by copolymerizing two monomers, one of which is a known mesogen but not chiral, while the other is chiral but not mesogenic.

Previous work, using a mesogenic monomer based on itaconic acid[3], showed that smectic phases were observed but that copolymerization with a chiral monomer did not induce any form of chiral mesophase. As this could have been due to the high levels of ordering in the system, a comonomer pair was selected that was more likely to produce a nematic phase where the lower degree of ordering might make the system more susceptible to external influences.

The monomers selected were 4-cyanophenyl-4-(6-acryloyloxyhexyloxy) benzoate (**1**):



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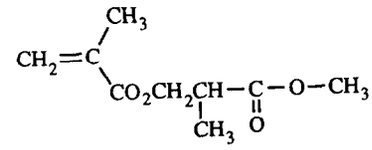
and (S)-methyl(2-methyl-3-methacryloyloxy) propionate (**2**):



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Monomer **1** forms a nematic mesophase when polymerized and monomer **2** can be prepared in an optically pure form with specific rotation in CH_2Cl_2 of $[\alpha]_D^{26} = 22°$.

Experimental

Monomers. Monomer **1** was synthesized according to the method reported by Portugall *et al.*[4] with minor modifications.

The chiral monomer **2** was prepared using the following procedure. Methacryloyl chloride (4.6 g, 4.3 ml, 4.4 mmol) in anhydrous benzene (10 ml) was slowly added dropwise to a stirred solution of the readily available (S)-(+)-methyl-3-hydroxy-2-methylpropionate (5 g, 42 mmol), triethylamine (4.45 g, 44 mmol) and 2,6-di-t-butyl-4-methyl phenol (*c.* 0.2 g) in benzene (30 ml) at 0°C. The reaction was allowed to warm up to room temperature after the addition, and stirring was continued overnight. Diethylether (100 ml) and water (50 ml) were then added and the mixture was shaken. The organic layer was separated and washed several times with water (3 × 50 ml), then dried ($MgSO_4$). Thin layer chromatography analysis indicated that three products were present (other than the starting materials) and that these had R_f values of 0.17, 0.23 and 0.30 (10% ethyl acetate in 40–60 petroleum ether). After careful

separation by flash chromatography using 5% ethyl acetate in 40–60 petroleum ether as the eluent, the products were analysed by n.m.r. and i.r. spectroscopy. The product having $R_f = 0.23$ was found to be the desired methacrylate ester.

Yield: 4.75 g, 58%; isolated as an oil. $[\alpha]_D^{26} = +21.97°$ (CH_2Cl_2). ^1H n.m.r: δ ppm ($CDCl_3$, 90 MHz) 1.22 (d, 3H) H–C–CH_3; 1.93 (s, 3H) vinyl–CH_3; 2.85 (m, 1H) tertiary C–H; 3.67 (s, 3H) RCO_2CH_3; 4.27 (d, 2H) HC–CH_2–OCO; 5.51 (s, 1H) vinylic H, *trans* to carbonyl; 6.06 (s, 1H) vinylic H, *cis* to carbonyl. I.r.: $\bar{\nu}$ (thin film on KCl) 1730, 1720, 1640, 1200, 1160 (s) cm^{-1}.

$C_9H_{14}O_4$ (186 g mol^{-1}): calculated C 58.06%, H 7.53%; found C 58.29%, H 7.59%.

Copolymerizations. Reactions were initiated, under nitrogen, in benzene solutions of the two monomers using 2,2′-azobisisobutyronitrile (0.5 mol%) as the radical source. The temperature was 60°C and reactions were terminated at $\leq$ 15% conversion, by precipitation in ethanol. Samples were purified by repeated dissolution - precipitation and finally dried in vacuum at 60°C for several days.

Characterization. Copolymer compositions were determined using ^1H n.m.r. by comparing the integration values of two separate distinguishable sets of resonances, each of which corresponds to a distinct environment in the comonomers. This was also confirmed using elemental analysis. Number-average molar masses were measured using a membrane osmometer (Knauer) with chloroform as solvent, at an operating temperature of 33°C. The M_n values lay in the range 65 000–126 000. Transition temperatures were established using a Perkin–Elmer DSC 2 with a scanning rate of 20°C min^{-1}. Both heating and cooling cycles were measured repeatedly for all samples. Optical textures were observed using a hot-stage polarizing microscope.

Crosslinking reaction. The monomer **2** had a tendency to crosslink when homopolymerized and this was used to prepare a crosslinked copolymer. A sample with composition $F_2 = 0.35$ was allowed to run to *c.* 30% conversion. Unreacted monomer and sol material were removed from the gel by washing with chloroform. The gel was then carefully deswollen with methanol and dried *in vacuo* for 48 h at 40°C.

Results and discussion

Copolymerization. The copolymerization reaction was characterized by plotting the mole fraction of monomer **2** in the copolymer, F_2, against its mole fraction in the feed, f_2, as shown in *Figure 1*.

The data deviate quite markedly from an ideal copolymerization and the solid line represents a non-linear least squares best fit, from which the monomer reactivity ratios can be estimated. These were $r_1 = 0.15$ and $r_2 = 3.00$. Clearly, monomer **2** is incorporated preferentially and this may result in extended sequences of **2** in the copolymer chains. The increased reactivity of **2** over **1** is due partly to the radical reactivity of the methacrylate being enhanced by the destabilizing inductive effect of the vinyl methyl group and partly to steric

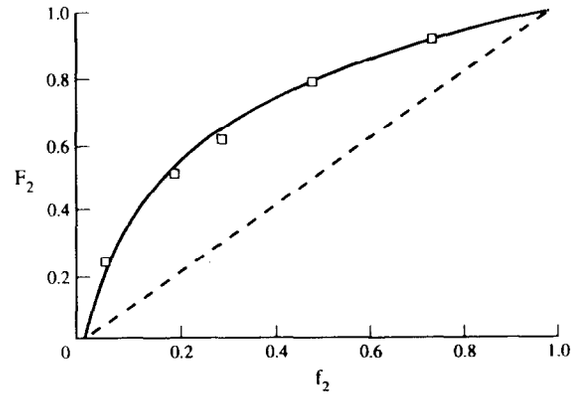

Figure 1 Copolymer composition F_2 against feed composition f_2. Solid line represents the best fit to the experimental points

effects. There was also a tendency for some crosslinking to occur at high concentrations of **2**, which was most obvious in the homopolymerization of **2**. This may be caused by hydrogen abstraction at the tertiary chiral carbon in **2**, and the possibility that an element of branching is present in the copolymers cannot be discounted.

Mesomorphic properties. The transition temperatures and optical textures for the various samples were measured and the results are summarized in *Table 1*.

The liquid-crystalline behaviour of the hompolymer of **1** has been reported previously[4] and the data obtained here are similar. On cooling from the isotropic melt, nematic droplets are formed that coalesce to produce a marbled nematic texture. A similar texture was observed for copolymer **3a**, which was retained on quenching the sample below the glass transition temperature (T_g), thereby locking it into the glassy state. Further increases in the content of **2** in the copolymers tended to weaken the mesomorphic order. Sample **3b** formed only a planar type of texture after annealing for about 24 h near the clearing temperature (T_{N-I}). A Schlieren texture, characteristic of the nematic phase, was observed after this annealing period. Homeotropic and planar birefringent areas were produced and only after prolonged annealing did the former eventually develop birefringence. This behaviour was exaggerated in sample **3c**, where the birefringence was very weak and was only strengthened when the sample was sheared. No mesomorphic behaviour was detectable in samples with $F_2 > 0.61$.

The dependence of the transition temperatures on the copolymer compositions and the stability ranges for the mesomorphic phases are shown in *Figure 2*. There is a sharp fall in the clearing temperature as the content of

Table 1 Copolymer compositions and transition temperatures for the homopolymer of **1** and the copolyers of **1** and **2**

Sample number	F_2	T_g(°C)	T_{N-I}(°C)	Optical texture
1	0.00	37	126	Marbled nematic
3a	0.24	23	102	Marbled nematic
3b	0.51	8	81	Planar/Schlieren
3c	0.61	11	(80)	Weak birefringence
3d	0.79	22		
3e	0.92	22	–	

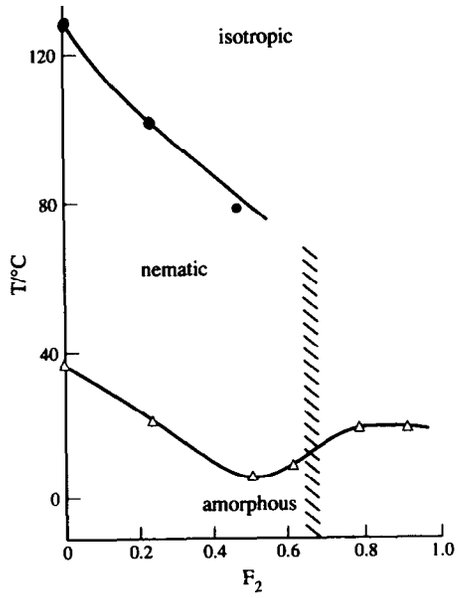

Figure 2 Phase transition temperatures as a function of copolymer composition F_2: △, T_g; ●, T_{N-I}

the chiral monomer in the copolymer increases, which is mirrored by a decrease in T_g. This is due to the disruptive influence of monomer **2**, which may be magnified by the tendency for long sequences of **2** to be incorporated in the chains, as indicated by the monomer reactivity ratios. This would result in the mesogenic groups being widely spaced, making organization into a stable liquid-crystal phase more difficult.

The only mesogenic phase detected was nematic. No optical texture was observed that would indicate the formation of a chiral nematic structure, although weak perturbation by **2** could produce a helical structure with a very long pitch length, and the weak planar texture for sample **3b** might suggest this possibility. This was rather unconvincing, however, and the observations are in keeping with theoretical approaches[5–7] that argue the need for a chiral dopant to be highly asymmetric and planar, if significant interaction between it and the mesogenic units is to be generated. Monomer **2** does not appear to have these necessary attributes and so its influence is weak or non-existent.

Crosslinked copolymers. Liquid-crystal elastomers have received some attention recently because of their thermoelastic and photoelastic properties. A copolymer, with $F_2 \approx 0.35$, was crosslinked and found to have retained the nematic phase with a clearing temperature of 110°C. This transition was much broader than in the uncrosslinked sample and occurred over a 25°C range as measured by differential scanning calorimetry; an uncrosslinked sample covered the transition in only 3°C. Optical observation showed a brightly coloured marbled texture similar to sample **3a**. The T_g was 18°C and so the sample behaved like an elastomer at ambient temperatures. The behaviour of a film was investigated at 25°C, at which temperature the unstretched elastomer was turbid. Application of a uniaxial deformation led to the sample becoming transparent, and illustrated the fact that a small applied force was very effective at orienting the mesogenic groups in the sample. This sensitivity of a mesogenic polymer to orientation by application of a mechanical force has been noted by others and has been reviewed recently by Finkelmann and Brand[8]. These elastomeric structures will be examined in greater detail and reported in the near future.

Acknowledgements

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