A new class of main-chain liquid crystalline polymers based on an unsymmetrically disubstituted cyanostilbene

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A new series of liquid crystalline (LC) monomers based on an unsymmetrically disubstituted cyanostilbene containing hydroxy- and carboxylic acid groups has been synthesized and characterized. The monomers could be polymerized in the presence of *N,N*-dicyclohexylcarbodiimide and 4-pyrrolidinopyridine to give a new class of main-chain LC polymers which may have potential applications in the field of non-linear optics.

(Keywords: thermotropic main-chain polymeric liquid crystals; synthesis; characterization)

INTRODUCTION

The first liquid crystalline (LC) polymers were reported by Flory[1] who demonstrated that solutions of rigid-rod chain polymers exhibit liquid crystallinity at a certain critical concentration. In 1975 de Gennes[2] suggested that thermotropic LC polymers could be fabricated by a combination of rigid and flexible units. In the same year, the first LC polymers were reported by Roviello and Sirigu[3]. Although polyesters are the most commonly studied LC polymers[4] a number of polyethers have also been synthesized and are reported to possess lower melting temperatures and a broader mesophase stability range than analogous polyesters[5].

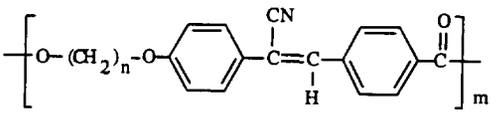
The rigid unit does not have to exhibit liquid crystallinity in itself in order to act as a mesogen in LC polymers[6]. The critical requirements for the mesogen are those of rigidity and asymmetry in shape[7]. The most commonly used rigid unit consists of a number of aromatic rings connected in the *para* position by short, stiff links in order to maintain the linear arrangement. Examples of links that satisfy the conditions for the development of liquid crystallinity in polymers include carbonyls[4], direct bonds[8,9], azo groups[10] and substituted stilbenes[11,12].

Main-chain LC polymers containing non-centrosymmetric arrangements of electric dipole moments can exhibit second-order non-linear optical effects[13]. Warner[14] has proposed that certain stereoregular, main-chain polymeric liquid crystals would have a very large, long-time dielectric susceptibility, χ, of unusual temperature dependence:

$$\chi \sim \text{constant} \times \exp(+h/k_B T)$$

with a large ultimate low temperature value $\chi \sim \chi_0 N$, where χ_0 is a susceptibility characteristic of a simple dielectric fluid, N is the degree of polymerization and h is the defect energy. The response would be caused by polarizing molecular defects (de Gennes hair pins) in the nematic ordering.

As part of our work on the synthesis of novel materials with second-order non-linear optical properties[15–20], we now report on a novel class of main-chain polyesters of structure I which exhibit liquid crystallinity.



I

The conjugated mesogen which is substituted with electron donating and electron withdrawing groups at opposite ends should satisfy the requirements for second-order non-linear optical behaviour by lending itself to non-centrosymmetric molecular alignment[13].

EXPERIMENTAL

Instrumental

I.r. spectra were recorded as KBr discs using a Perkin Elmer 1600 FTIR spectrophotometer. Solution ^{1}H n.m.r. and ^{13}C n.m.r. spectra were recorded using a Varian VXR 400 S spectrometer operating at 399.952 and 100.577 MHz, respectively, using $CDCl_3$ or acetone-d_6 as solvent. Studies of thermal properties were carried out using a DSC7 Perkin Elmer differential scanning calorimeter and a Stanton Redcroft TG-760 thermal analyser. Optical microscopy experiments were performed with an Olympus BH-2 polarizing microscope equipped with a Linkam THM 600 hot stage. Mass spectra were recorded on a 7070E VG analytical spectrometer. Elemental (CHN) analyses were carried out using a Carlo Erba 1106 elemental analyser equipped with a

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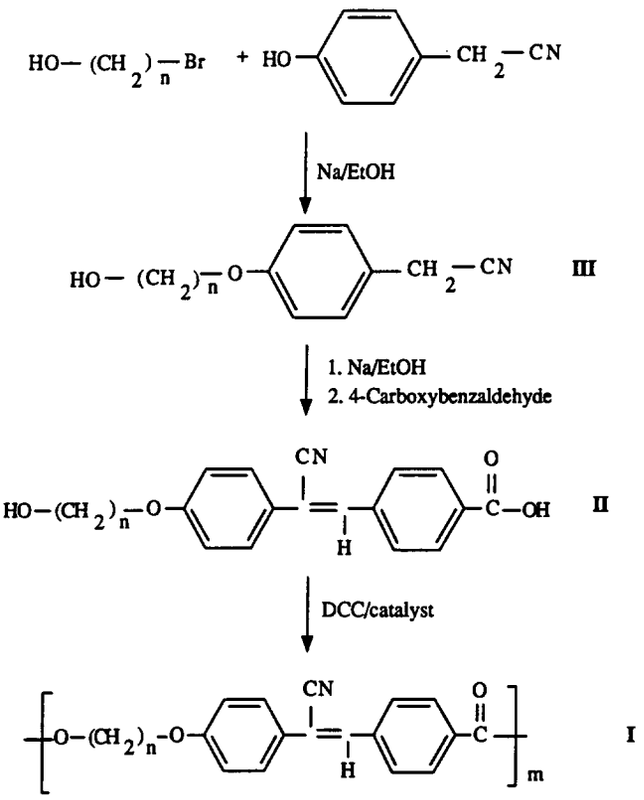
DP110PRC data processor. The purity of compound II was checked by h.p.l.c. using a Perkin Elmer 601 liquid chromatograph equipped with a Perkin Elmer LC55 spectrophotometric detector operating at 254 nm. Experiments were performed at room temperature on an ODS column with tetrahydrofuran (THF) as solvent using a flow rate of 1 $cm^3 min^{-1}$. Molecular weight distribution studies on the polymer I were performed by g.p.c. in THF solution using a VISCOTEK instrument equipped with two mixed columns of PL gel (pore size 10^4 nm; Polymer Laboratories Ltd). Measurements were carried out at room temperature using a flow rate of 1 $cm^3 min^{-1}$. A g.p.c. calibration graph was obtained using a series of polystyrene standards.

Synthesis

The polymers I were synthesized according to *Scheme 1*.



Scheme 1 Monomer and polymer synthesis

General method for the synthesis of III

Sodium metal (0.23 g, 0.01 mol) and dry ethanol (5 cm^3) were mixed in a dry flask (25 cm^3) equipped with double surface condenser. After the sodium had completely dissolved, a solution of 4-hydroxybenzylcyanide (1.33 g, 0.01 mol) in absolute ethanol (5 cm^3) was added with stirring followed by the appropriate ω-bromoalkanol (0.015 mol). Once the addition was complete the reaction mixture was refluxed for 6 h. Ethanol was removed by rotary evaporation, ether (50 cm^3) was added to the residue and the resulting solution was washed with 10% aqueous sodium hydroxide solution (3 × 5 cm^3), aqueous sulfuric acid solution (1 M, 3 × 5 cm^3) and water (3 × 10 cm^3). Evaporation of the dried (magnesium sulfate) ether solution gave the crude product which was purified by chromatography on silica (6 cm × 2 cm^2) using ether/ethyl acetate (7:3) as the eluent to give I as a white crystalline solid. These materials were characterized by a combination of spectroscopic measurements and elemental analysis results (see *Table 1*).

General method for the synthesis of II

4-Carboxybenzaldehyde (2 g, 0.013 mol) was added to a solution of sodium (0.6 g, 0.026 mol) in absolute ethanol (25 cm^3). Compound III (0.013 mol) was added and the resulting mixture was stirred (magnetic follower) under a nitrogen atmosphere for 3 days. The mixture was poured into aqueous hydrochloric acid solution (0.1 M, 200 cm^3) and the solid which precipitated was recovered by filtration, washed with acetone (5 × 50 cm^3) and dried *in vacuo* (20°C/10^{-2} mbar) to give the cyanostilbene hydroxy acid compound II. Some spectroscopic characterization data and elemental analysis results for the monomers made are given in *Table 2*. The purity of these compounds was checked by h.p.l.c.; a single narrow peak was displayed in all cases.

General method for the synthesis of I

A solution of II (0.010 mol), *N,N*-dicyclohexylcarbodiimide (2.06 g, 0.010 mol) and 4-pyrrolidinopyridine (0.015 g, 0.0001 mol) in dried dichloromethane (20 cm^3) was stirred at 50°C for 24 h under a nitrogen atmosphere. The mixture was filtered, washed with methanol (3 × 50 cm^3), ethyl acetate (3 × 50 cm^3) and dried under vacuum (20°C/10^{-2} mbar) to give I as a pale yellow solid. The yields, some spectroscopic parameters, the number average molecular weights and the polydispersities for the polymers synthesized are given in *Table 3*.

RESULTS AND DISCUSSION

Synthesis of compounds III

The general method for the synthesis of III is recorded in detail in the Experimental section. These compounds

Table 1 Characterization data and yields for compounds III

n	ν (CN) (cm^{-1})	ν (OH) (cm^{-1})	^{1}H n.m.r. (ppm)	M^+ (mass spec.)	M.p. (°C)	Yield (%)
3	2246	3419	7.2(d, 2H); 6.9(d, 2H); 4.1(t, 2H); 3.9(t, 2H); 3.7(s, 2H); 2.1(b, 2H)	191	55–56	27
6	2246	3297	7.2(d, 2H); 7(d, 2H); 3.9(t, 2H); 3.6(s, 2H); 3.5(t, 2H); 1.7(b, 8H)	233	49.5	35
7	2249	3383	7.2(d, 2H); 6.9(d, 2H); 4(t, 2H); 3.6(s, 2H); 3.5(t, 2H); 1.5(b, 10)	247	62	90
8	2245	3295	7.3(d, 2H); 7.2(d, 2H); 3.9(t, 2H); 3.8(s, 2H); 3.7(t, 2H); 1.7(b, 12)	261	65	89
9	2245	3328	7.2(d, 2H); 6.8(d, 2H); 3.9(t, 2H); 3.6(s, 2H); 3.5(t, 2H); 1.7(b, 14)	275	74	60
10	2245	3302	7.2(d, 2H); 6.9(d, 2H); 4(t, 2H); 3.7(s, 2H); 3.6(t, 2H); 1.3(b, 16H)	289	75	86
11	2245	3317	7.2(d, 2H); 6.8(d, 2H); 3.9(t, 2H); 3.6(s, 2H); 3.5(t, 2H); 1.7(b, 18H)	303	80	67
12	2245	3285	7.3(d, 2H); 6.9(d, 2H); 4(t, 2H); 3.6(s, 2H); 3.5(t, 2H); 1.3(b, 20)	317	85	59

Table 2 Characterization data for monomers II

n	ν (CN) (cm^{-1})	ν (C=O) (cm^{-1})	^{1}H n.m.r. (ppm)	M^+ (mass spec.)	λ_{max} (nm)	Found (calculated) C (%)	H (%)	N (%)
3	2218	1682	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 6.9(d, 2H); 4.0(t, 2H); 3.6(t, 2H); 1.3(b, 2H)	323	332	71.07(70.56)	5.29 (5.30)	4.33 (4.32)
6	2221	1694	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 6.9(d, 2H); 4.0(t, 2H); 3.6(t, 2H); 1.3(b, 8H)	365	331	72.35(72.30)	6.03 (6.35)	3.63 (3.83)
7	2218	1706	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 7.0(d, 2H); 4.0(t, 2H); 3.7(t, 2H); 1.4(10H)	379	332	72.52(72.80)	6.46 (6.65)	3.31 (3.69)
8	2220	1693	8.2(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.5(s, 1H); 7.0(d, 2H); 4.0(t, 2H); 3.7(t, 2H); 1.3(b, 12H)	393	332	73.18(73.25)	7.02 (6.91)	3.44 (3.56)
9	2221	1692	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 7.0(d, 2H); 4.0(t, 2H); 3.6(t, 2H); 1.3(b, 14H)	407	333	73.99(73.68)	7.39 (7.17)	3.38 (3.43)
10	2215	1705	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 6.9(d, 2H); 4.0(t, 2H); 3.6(t, 2H); 1.3(b, 16H)	421	331	74.40(74.08)	7.60 (7.41)	3.23 (3.32)
11	2221	1690	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 6.9(d, 2H); 4.0(t, 2H); 3.6(t, 2H); 1.3(b, 18H)	435	332	74.48(74.44)	7.76 (7.65)	2.95 (3.20)
12	2219	1693	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 6.9(d, 2H); 4.0(t, 2H); 3.6(t, 2H); 1.3(b, 20H)	449	331	74.00(74.79)	7.64 (7.86)	3.21 (3.11)

Table 3 Characterization data and yields for polymers I

n	ν (CN) (cm^{-1})	ν (C=O) (cm^{-1})	^{1}H n.m.r. (ppm)	Found (calculated) C (%)	H (%)	N (%)	λ_{max} (nm)	Yield (%)	M_n	M_w/M_n
3	2216	1717	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 6.9(d, 2H); 4.6(t, 2H); 4.0(t, 2H); 1.3(b, 2H)	–	–	–	–	62	–	
6	2217	1717	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 6.9(d, 2H); 4.3(t, 2H); 4.0(t, 2H); 1.3(b, 8H)	76.56(76.05)	5.78 (6.09)	3.44 (4.03)	–	63	–	
7	2216	1716	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 7.0(d, 2H); 4.3(t, 2H); 4.0(t, 2H); 1.4(10H)	76.28(76.45)	6.63 (6.41)	4.28 (3.88)	337	56	6500	1.21
8	2218	1718	8.2(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.5(s, 1H); 7.0(d, 2H); 4.3(t, 2H); 4.0(t, 2H); 1.3(b, 12H)	76.18(76.80)	7.00 (6.72)	3.44 (3.73)	336	62	11 000	1.54
9	2215	1717	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 7.0(d, 2H); 4.3(t, 2H); 4.0(t, 2H); 1.3(b, 14H)	77.74(77.12)	7.08 (6.99)	4.18 (3.60)	335	55	3400	1.49
10	2215	1716	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 6.9(d, 2H); 4.3(t, 2H); 4.0(t, 2H); 1.3(b, 16H)	77.88(77.38)	7.35 (7.24)	3.80 (3.47)	338	91	5600	1.57
11	2216	1715	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 6.9(d, 2H); 4.3(t, 2H); 4.0(t, 2H); 1.3(b, 18H)	77.22(77.66)	7.46 (7.40)	3.30 (3.35)	337	54	9650	1.24
12	2216	1715	8.1(d, 2H); 7.9(d, 2H); 7.6(d, 2H); 7.4(s, 1H); 6.9(d, 2H); 4.3(t, 2H); 4.0(t, 2H); 1.3(b, 20H)	77.35(77.92)	7.54 (7.70)	3.16 (3.24)	336	78	4500	2.11

were obtained by the S_N2 reaction of the phenolate ion with the appropriate ω-bromoalkanol (see *Scheme 1*). The highest yields were obtained with 7-bromo-1-heptanol ($n=7$), 8-bromo-1-octanol ($n=8$) and 10-bromo-1-decanol ($n=10$). The lower molecular weight analogues ($n=3$ and $n=6$) gave the lowest product yield which can probably be explained in terms of the formation of cyclic ether by-products favoured for the shorter chain analogues.

The i.r. spectra of compounds III were consistent with the assigned structures. The ν(OH) stretching vibration occurs at lower wavenumbers in compounds containing an even number of aliphatic ($-CH_2-$) moieties ($n=6$, 8, 10, 12) than in their odd-membered analogues (*Table 1*). The bands are broad and typical of hydrogen-bonded –OH bands. The shifts appear to indicate stronger hydrogen bonding interactions in the even series of compounds, possibly a reflection of differences in packing in the solid state.

Synthesis of monomers II, cyanostilbenes

The monomers II were synthesized by the condensation reaction of compound III with 4-carboxybenzaldehyde.

The u.v./vis. spectra of the monomers II are characterized by the presence of a strong band at ~332 nm which may be attributed to the π–π^* absorption of the conjugated, unsymmetrically disubstituted cyanostilbene; the positions of the absorption maxima, λ_{max}, given in *Table 2*, are independent of the length of the aliphatic chain.

The ^1H n.m.r. data are tabulated in *Table 2*. There is no evidence for the presence of more than one isomer in any case. It is believed, but could not be unambiguously proved, that the monomers exist in the more thermodynamically stable *trans* form.

Liquid crystalline transitions of monomers. All monomers exhibited liquid crystallinity. A combination of d.s.c. and optical microscopy investigations demonstrated that the monomer crystals undergo liquid-crystal phase transitions to nematic phases. A typical d.s.c. thermogram is shown in *Figure 1*. The area and position of endotherm A depends on the heating conditions suggesting a crystal–crystal transition. The enthalpy change associated with peak B is of the order of 40 kJ mol^{-1} and marks the crystal to liquid crystal phase transition. The liquid crystal to isotropic phase transition, computed from the area of endotherm C, is characterized by an enthalpy change of ~4.5 kJ mol^{-1}. These values are typical of all the monomers investigated. Evidence for the formation of a nematic phase was obtained by the observation under the polarizing microscope of disclination textures containing both two and four brushes (*Figure 2*).

As expected, the crystalline to LC transition temperatures of the monomers decreased in a regular manner with increasing length of the aliphatic chain. In parallel with the decrease in the crystal to liquid crystal transition temperatures, a similar decrease in the liquid crystal to isotropic liquid transition temperatures was observed (*Table 4*). This relationship is depicted in *Figure 3*.

Table 4 Thermal transitions of the LC polymers and the corresponding monomers[a]

	Monomer		Polymer	
n	T_1	T_2	T_1^*	T_2^*
3	218(nematic)	264(isotropic)	–	–
6	184(nematic)	231(isotropic)	169(nematic)	228(isotropic)
7	168(nematic)	221(isotropic)	127(nematic)	222(isotropic)
8	161(nematic)	212(isotropic)	116(nematic)	214(isotropic)
9	149(nematic)	207(isotropic)	131(nematic)	172(isotropic)
10	148(nematic)	199(isotropic)	95(nematic)	126(isotropic)
11	146(nematic)	196(isotropic)	–	–
12	145(nematic)	191(isotropic)	69(nematic)	181(isotropic)

[a] T_1, crystalline to LC transition (monomer); T_2, LC to isotropic phase transition (monomer); T_1^*, crystalline to LC transition (polymer); T_2^*, LC to isotropic phase transition (polymer)

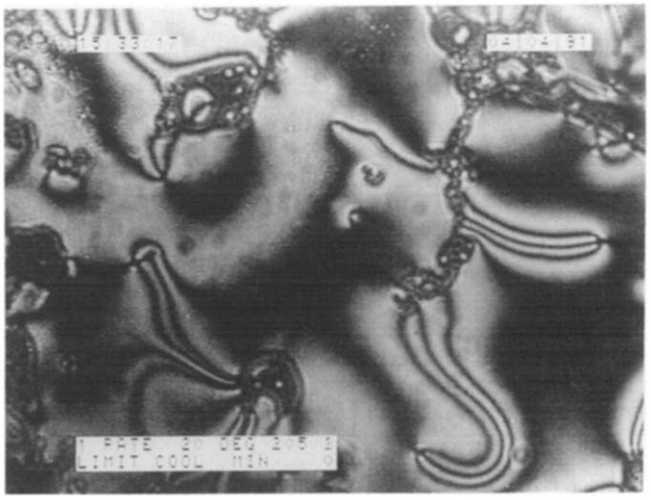


Figure 2 Photomicrograph of C_8 monomer at 205°C showing the existence of a nematic mesophase (× 57)

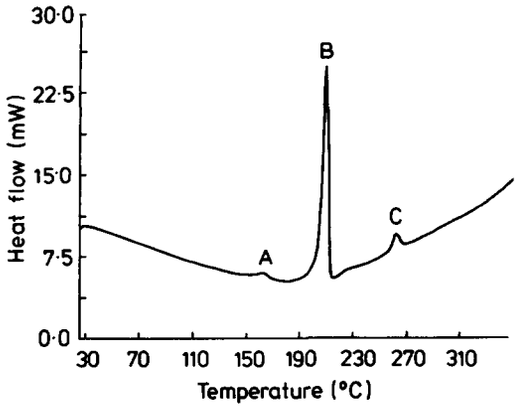


Figure 1 D.s.c. thermogram for C_3 monomer; first heating (heating rate 10°C min^{-1}). For A, B and C, see text

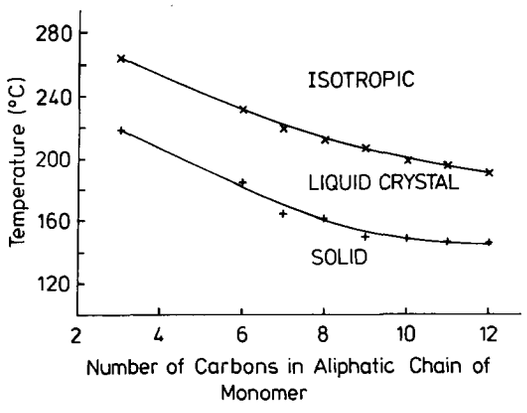


Figure 3 Transition temperatures for the LC monomers as a function of the number of carbon atoms in the aliphatic chain

Synthesis of polymers I

The polymers I were obtained via solution polymerization of II in yields, after purification, ranging from 55 to 91%. The polymer syntheses are recorded in detail in the Experimental section.

I.r. spectroscopy revealed that the carbonyl band of the acid monomers at $\sim 1690\,cm^{-1}$ disappears on polymerization giving place to a new absorption at $\sim 1715\,cm^{-1}$ due to the ester carbonyl. The extensive hydrogen-bonded -OH absorptions between $3600\,cm^{-1}$ and $2400\,cm^{-1}$ in the monomer spectrum are absent in that of the polymer. The bands associated with structural features such as the methylene absorption (2980 to $2850\,cm^{-1}$) and the nitrile stretch ($\sim 2220\,cm^{-1}$) experience only minor shifts which lie within the resolution limits of our instrument. In *Figure 4* a typical monomer spectrum is compared with that of the corresponding polymer.

The major difference between the ^1H n.m.r. spectra of the monomers as compared to those of the polymers

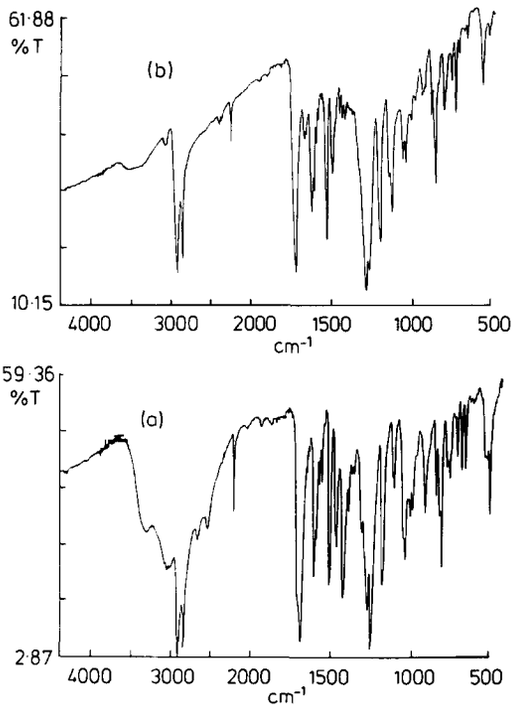


Figure 4 I.r. spectra for (a) C_{11} monomer and (b) C_{11} polymer

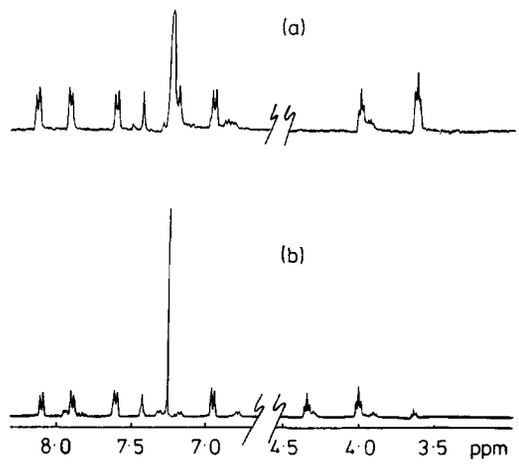


Figure 5 ^1H n.m.r. spectra for (a) C_{11} monomer and (b) C_{11} polymer

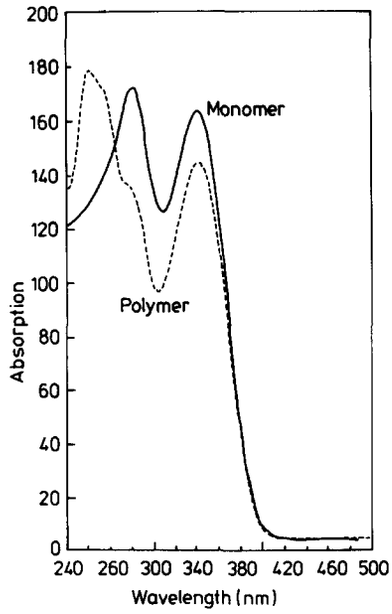


Figure 6 Solution (chloroform) u.v./vis. spectra for C_8 monomer and C_8 polymer

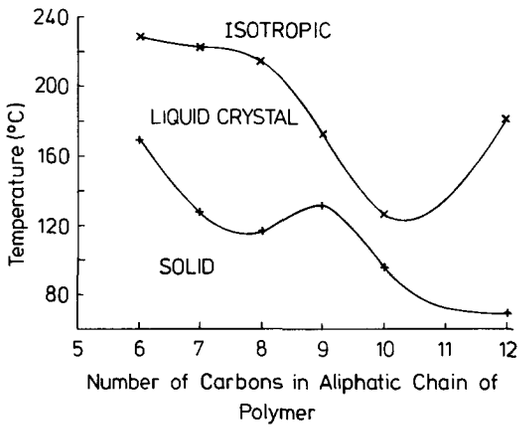


Figure 7 Transition temperatures for the LC polymers as a function of the number of carbon atoms in the aliphatic chain

(*Figure 5*) is the disappearance of the $C\underline{H}_2$–OH resonance at 3.5 ppm and the appearance of a new triplet due to $-CO_2-C\underline{H}_2-$ at 4.3 ppm. Other differences between the monomer and polymer spectra include a 0.3 ppm downfield shift in the position of the Ph–O–$C\underline{H}_2$– resonance and a 0.3 to 0.4 ppm shift in the $-CO_2-CH_2-C\underline{H}_2-$ resonance. All the other spectral features remain unaffected on polymerization. The ^1H n.m.r. data are reproduced in *Table 3*.

Comparison of the u.v./vis. spectra of the polymers with those of the monomers (*Tables 2* and *3*) reveal a slight shift in the position of the absorption maximum which reflects the difference in electron accepting power between the acid and ester groups. The electronic absorption spectrum for a typical monomer and the corresponding polymer is shown in *Figure 6*.

The number average molecular weights and polydispersities of the polymers, as determined by g.p.c. using the VISCOTEC instrument, are given in *Table 3*.

Liquid crystalline transitions of polymers. The thermal behaviour of most of the polymers as determined by

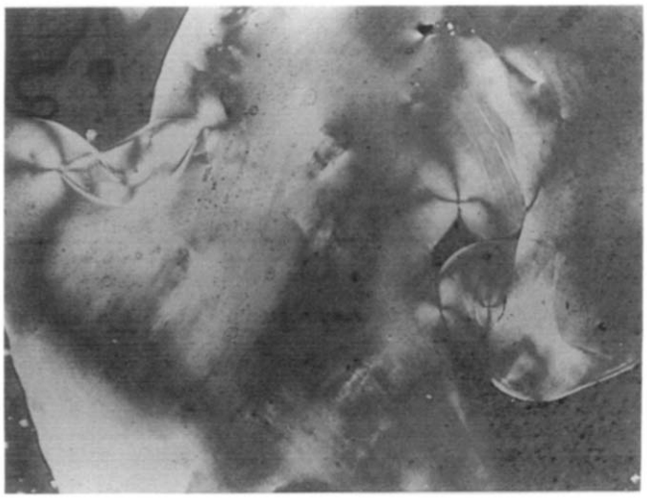


Figure 8 Photomicrograph of C_8 polymer at 138°C (under light pressure) in the heating cycle (× 57)

polarized optical microscopy and d.s.c. is illustrated by:

$$\text{Solid polymer} \xrightarrow{\text{heat}} \text{nematic polymer} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftarrows}} \text{isotropic polymer}$$

Figure 7 shows the mesophase stability range for all the polymers. The exact temperature for each transition is recorded in *Table 4*. In accordance with observations on the monomer samples, the crystal to liquid crystal transition temperatures of the polymers were found to generally decrease with increasing length of the ($-CH_2-$) spacer unit. Examination using polarized optical microscopy showed that most polymers, when quenched from the melt state, displayed coarse, thread-like nematic textures at room temperature. Above the crystal to liquid crystal transition temperature, the majority of polymers exhibited an apparent isotropic texture which was retained until the true clearing transition was reached. When a light pressure or shear was applied to such polymer samples, nematic textures developed; a typical photomicrograph is shown in *Figure 8*. The exception to this behaviour was C_7 polymer which exhibited a highly birefringent texture throughout the mesophase stability range.

The clearing temperatures for the polymers showed a tendency to decrease with increasing length of the spacer up to C_{10}. In polymers with longer spacers the liquid crystal to isotropic transition temperature exhibited an anomalous behaviour in that the C_{12} polymer showed a much higher clearing temperature than the C_{10} analogue and that a sample of the C_{11} polymer (prepared under the same reaction conditions) failed to exhibit LC properties. It is clear from the results summarized in *Table 4* that the thermal behaviour of the polymers depends on the length of the flexible spacers. In this, these unsymmetrically disubstituted stilbene polymers follow the well documented general trends observed with other main-chain LC polymers[21–24].

The failure to observe LC behaviour for the C_{11} polymer was a puzzling anomaly, which will be the subject of a more detailed investigation of the effects of molecular weight and its distribution in these polymers. We are continuing the detailed examination of these phase transitions and properties, particularly optical and non-linear optical behaviour, of this interesting set of materials.

CONCLUSIONS

The synthesis of a new class of main-chain LC polymers with potential second-order non-linear optical properties is reported. In these polymers, the chromophore is part of the backbone and the dipole moments point in the same (head to tail) direction along the polymer chain. The second-order non-linear optical properties of these polymers are currently under investigation.

REFERENCES

1 Flory, P. J. *Proc. R. Soc. London (A)* 1956, **234**, 73
2 de Gennes, P.-G. *CR Seances Acad. Sci.* 1975, **281B**, 101
3 Roviello, A. and Sirigu, A. *J. Polym. Sci., Polym. Lett. Edn* 1975, **13**, 455
4 Ober, C. K., Jin, J.-I. and Lenz, R. W. *Adv. Polym. Sci.* 1984, **59**, 103
5 Shaffer, T. D. and Percec, V. *Makromol. Chem., Rapid Commun.* 1985, **6**, 97
6 Flory, P. J. *Adv. Polym. Sci.* 1984, **59**, 2
7 Chung, T.-S. *Polym. Eng. Sci.* 1986, **26**, 901
8 Blumstein, A., Sivaramakrishman, K., Clough, S. B. and Blumstein, R. B. *Mol. Cryst. Liq. Cryst. Lett.* 1979, **49**, 255
9 Shaffer, T. D. and Percec, V. *J. Polym. Sci., Polym. Lett. Edn* 1985, **23**, 185
10 Iiamura, K., Koido, N., Okta, R. and Takeda, M. *Makromol. Chem.* 1981, **182**, 2563
11 Rovielo, A. and Sirigu, A. *Makromol. Chem.* 1979, **180**, 2543
12 Percec, V., Shaffer, T. D. and Nava, H. *J. Polym. Sci., Polym. Lett. Edn* 1984, **22**, 637
13 Stenger-Smith, J. D., Fischer, J. W., Henry, R. A., Hoover, J. M. and Lindsay, G. A. *Makromol. Chem., Rapid Commun.* 1990, **11**, 141
14 Warner, M. 'Proc. Materials Research Soc. Conf.', Materials Research Society, Boston, 1989, Vol. 134, p. 61
15 Tsibouklis, J., Cresswell, J. P., Feast, W. J., Mukherjee, S. and Petty, M. C. *J. Mol. Electron.* 1990, **6**, 221
16 Cresswell, J. P., Tsibouklis, J., Petty, M. C., Feast, W. J., Carr, N., Goodwin, M. and Lvov, Y. in 'Nonlinear Optical Properties of Organic Materials III' (Ed. G. Khanarian), Proc. SPIE Int. Soc. Opt. Eng., Vol. 1337, SPIE, Washington, 1990, p. 358
17 Tsibouklis, J., Cresswell, J. P., Kalita, N., Pearson, C., Maddaford, P. J., Yarwood, J., Goodwin, M. J., Carr, N., Feast, W. J. and Petty, M. C. *J. Phys. D* 1989, **22**, 1608
18 Tsibouklis, J., Cresswell, J. P., Pearson, C., Petty, M. C. and Feast, W. J. in 'Materials for Non-linear and Electro-Optics' (Ed. M. H. Lyons), Int. Phys. Conf. Ser. No. 103, IoP Publishing Ltd, Bristol, 1989, p. 187
19 Song, Y. P., Yarwood, J., Tsibouklis, J., Feast, W. J., Cresswell, J. P. and Petty, M. C. *Langmuir* 1992, **8**, 257
20 Song, Y. P., Petty, M. C., Yarwood, J., Feast, W. J., Tsibouklis, J. and Mukherjee, S. *Langmuir* 1992, **8**, 262
21 Lenz, R. W. and Jin, J.-I. in 'Liquid Crystals and Ordered Fluids' (Eds A. Griffin and J. Johnson), Plenum Press, New York, 1984, p. 347
22 Griffin, A. C. and Havens, S. J. *J. Polym. Sci., Polym. Phys. Edn* 1981, **19**, 951
23 Strzelecki, L. and van Luyen, D. *Eur. Polym. J.* 1980, **16**, 299
24 Lenz, R. W., Furukawa, A., Bhowmik, P., Garay, R. O. and Majnusz, J. *Polymer* 1991, **32**, 1703