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Synthesis and characterization of two isomeric liquid crystal series with reactive double bonds

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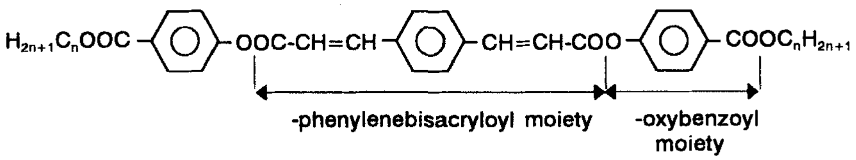
Two series of potentially cross-linkable liquid crystal materials derived from *p*-phenylenebisacrylic (series I, *n*(P.FB.P), $n = 2$–10) and *p*-hydroxycinnamic acid (series II, *n*(HC.T.HC), $n = 2$–10) have been synthesized and their thermal and mesomorphic properties studied. All these compounds show enantiotropic mesomorphism over a wide range of temperatures. Compounds with short terminal chains are nematic and when the terminal chain length is increased they show smectic polymorphism-smectic A and C. Most of the compounds are thermally stable over their mesophase ranges.

1. Introduction

The photoreaction process in liquid crystals has been a subject of research over the last few years. Different objectives can be achieved using this method: anisotropic calamitic and discotic networks [1–4], main chain and side chain cross-linked polymers [5–9], elastomers [10–12], topochemical reactions [13], generation of phase transitions [14], reversible optical effects [15–17], etc. The cinnamoyl group has often been used as a reactive unit included in mesogenic molecules [4, 5, 10, 13], even in basic studies of liquid crystal photoreactions [18, 19]. In this field our group is interested in the synthesis of self-reinforced polymers as engineering materials. For this purpose we use complex monomers including the cinnamoyl group in different positions [20–23]. In some cases we use low molecular weight compounds.

This paper deals with the synthesis and characterization of two series of potentially photopolymerizable mesogenic compounds, whose basic structure is centro-symmetric with cinnamoyl moieties as photoreactive groups. The double bonds in series I come from *p*-phenylenebisacrylic acid, so that the reactive groups are very close to the molecular centre. The double bonds in series II bonds come from *p*-hydroxycinnamic acid and are located in the external part of the mesogenic core.



Series I, n(P.FB.P), n=2-10

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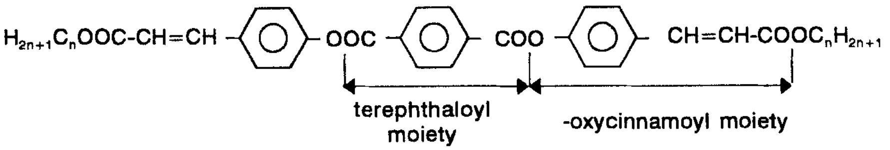


Series II, n(HC.T.HC), n=2-10

These compounds are to be studied with reference to their thermal stability and mesomorphic properties, in order to determine the influence of the position of the double bonds on the mesomorphic ordering. This study will enable us to choose the most interesting candidates for further studies of liquid crystal photoreactions.

2. Experimental

2.1. *Synthesis*

2.1.1. *Synthesis of diacids*

2.1.1.1. *4,4′-p-(Phenylenediacryloxyloxy)dibenzoic acid (P.FB.P diacid)*

To a solution of 28·2 g (0·2 mol) of *p*-hydroxybenzoic acid in 200 ml of 2M NaOH, vigorously stirred, a solution of 25·5 g (0·1 mol) of *p*-phenylenediacryloyl chloride in 180 ml of 1,4-dioxan was added all at once. After stirring for 1 h, the white precipitate was collected, washed with water, 1M HCl and then acetone, and vacuum dried to yield 42 g (85 per cent) of 4,4′-(*p*-phenylenediacryloyloxy)dibenzoic acid.

2.1.1.2. *4,4′-(Terephthaloyldioxy)dicinnamic acid (HC.T.HC diacid)*

To a solution of 32·4 g (0·2 mol) of *p*-hydroxycinnamic acid, a solution of 20·3 g (0·1 mol) of terphethaloyl chloride was added all at once. After stirring for 1 h, the white precipitate was collected, washed with water, 1M HCl and then acetone, and vacuum dried to yield 34·6 g (70 per cent) of 4,4′-(terephthaloyldioxy)dicinnamic acid.

2.1.2. *Synthesis of diacid chlorides*

P.FB.P and HC.T.HC diacids were heated under reflux with thionyl chloride and a catalytic amount of pyridine for 5 h. The solids were filtered off from hot mixtures and recrystallized from toluene to yield 4,4′-(*p*-phenylenediacryloyloxy)dibenzoyl chloride (DC.P.FB.P) (55 per cent) and 4,4′-(terephthaloyldioxy)dicinnamoyl chloride (DC.HC.T.HC) (50 per cent).

2.1.3. *Synthesis of diester derivatives*

Two different methods were used to obtain the diester derivatives dependent upon their terminal chain length. The syntheses are described in general form below.

Method 1

A solution of 2 mmol of DC.P.FB.P or DC.HC.T.HC in 50 ml of 1,4-dioxan, 25 ml of pyridine and 25 ml of the aliphatic alcohol was heated with stirring at 100°C for 3 h. The cooled solution was poured into hexane. The white precipitate was collected and purified.

Method 2

A 5 mmol mixture of DC.P.FB.P or DC.HC.T.HC and 15 mmol of the aliphatic alcohol in 15 ml of diphenyl ether was introduced into a condensation tube and dry

Table 1. Reaction data, elemental analyses and infrared data for series I and series II.

		Reaction data			Elemental analysis				IR/cm^{-1}		
					C/per cent		H/per cent				
Structure	n†	Method of synthesis‡	T/°C	Yield/ per cent	Found	Calculated	Found	Calculated	C=O st§	C=C st§	=CH δ oop‖
n(P.FB.P) (Series I)	2	1	100	35	70·04	70·08	5·06	5·14	1721,1707	1632	973
	3	1	100	45	70·71	70·85	5·86	5·51	1718,1713	1626	976
	4	1	100	50	70·79	71·58	6·01	5·96	1720,1709	1626	971
	5	2	150	40	72·14	72·24	6·65	6·35	1718,1708	1626	971
	6	2	150	50	72·15	72·84	6·94	6·71	1718,1710	1625	970
	7	2	200	50	73·22	73·39	6·68	7·03	1720,1707	1625	970
	8	2	200	50	73·29	73·90	7·68	7·33	1719,1709	1626	971
	9	2	200	60	74·72	74·37	8·01	7·61	1719,1708	1626	970
	10	2	200	45	75·57	74·80	8·27	7·86	1722,1708	1626	970
n(HC.T.HC) (Series II)	2	1	100	35	69·63	70·08	4·96	5·14	1729,1704	1634	987
	3	1	100	35	71·20	70·85	5·80	5·51	1725,1708	1641	980
	4	2	150	35	72·27	71·58	6·18	5·96	1741,1708,1698	1639	987
	5	2	150	35	72·71	72·24	6·67	6·35	1742,1729,1715,1708	1637	992
	6	2	150	60	73·64	72·84	7·02	6·71	1729,1714	1641	982
	7	2	200	60	74·05	73·39	7·37	7·03	1732,1719	1642	982
	8	2	200	65	74·20	73·90	7·71	7·33	1728,1708	1641	982
	9	2	200	50	75·07	74·37	8·00	7·61	1732,1719	1643	981
	10	2	200	65	75·51	74·80	8·18	7·86	1730,1719	1641	980

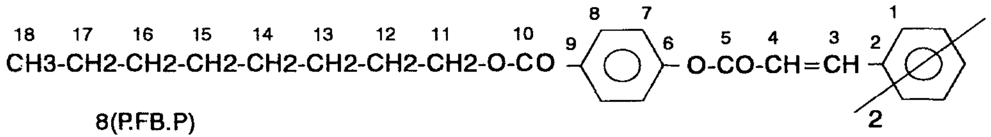
† Number of carbons in alkyl group of the terminal ester chain.

‡ Method 1: condensation in 1,4-dioxan/pyridine; method 2: high temperature procedure—see Experimental section.

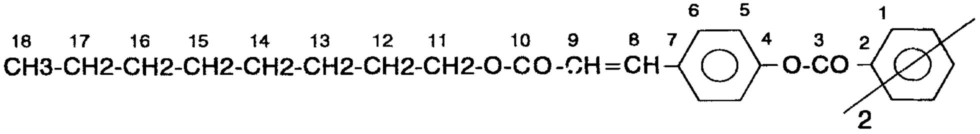
§ Stretching.

‖ Out of plane vibration.

Table 2. ^{1}H, ^{13}C NMR and UV–visible spectroscopic data for the compounds dioctyl 4,4′-(phenylenediacryloyloxy)dibenzoate (8(P.FB.P)) and diocty 4,4′-terephthaloyldioxy)dicinnamate (8(HC.T.HC)).



8(P.FB.P)



8(HC.T.HC)

(*a*) ^{1}H NMR data (CDCl$_3$).

	δ/ppm and multiplicities†												J/Hz			
	H_1	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{11}	H_{12}	H_{13-17}	H_{18}	J_{3-4}	J_{7-8}	J_{11-12}	J_{17-18}
8(P.FB.P)	7·64 s	7·87 d	6·67 d	—	—	7·24 d	8·10 d	—	4·30 t	1·60–1·80 m	1·20–1·50 m	0·87 t	16·1	8·8	6·6	6·6
8(HC.T.HC)	8·32 s	—	—	7·27 d	7·61 d	—	7·68 d	6·43 d	4·19 t	1·60–1·80 m	1·20–1·50 m	0·87 t	J_{8-9} 15·9	J_{5-6} 8·6	J_{11-12} 6·6	J_{17-18} 6·6

† s, singlet; d, double; t, triplet; m, multiplet.

(*b*) ^{13}C NMR data ($CDCl_3$).

	δ/ppm																	
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}
8(P.FB.P)	128·9	136·2	145·7	118·3	165·9	154·3	121·5	131·1	128·2	164·5	65·3	28·7	26·0	29·1	29·2	31·8	22·6	14·0
					a					a		b		b	b			
8(HC.T.HC)	130·4	133·8	166·9	152·0	122·1	129·3	132·6	143·2	118·8	163·9	64·8	28·7	26·0	29·2	29·1	31·8	22·6	14·1
	c	d	e			c	d			e		f		f	f			

a, b, c, d, e, f: these signals could be exchanged.

(*c*) UV-visible data (CH_2Cl_2).

	λ_1/nm (log ε)	λ_2/nm (log ε)
8(P.FB.P)	232(4·84)	329(5·04) 342^{sh}
8(HC.T.HC)	226·3(4·42)	283·5(4·80) 302^{sh}

nitrogen was bubbled through at room temperature for 30 min. The mixture was then heated to 150 or 200°C (see table 1) for 30 min. Toluene (P.FB.P series) or hexane (HC.T.HC series) was used as precipitant. The white solids were collected and purified.

The crude diesters were purified by recrystallization from toluene and column chromatography on silica gel using dichloromethane as eluent; then they were recrystallized again. *n*(P.FB.P) compounds and 2(HC.T.HC) were recrystallized from toluene and the *n*(HC.T.HC) compounds from toluene/hexane.

The method of synthesis used in each case (1 or 2), the reaction temperature and the yield after purification of the *n*(P.FB.P) and *n*(HC.T.HC) diesters are given in table 1.

2.2. *Characterization of the compounds*

All the compounds were characterized by elemental analysis and FTIR spectroscopy. In table 1 reaction data, elemental analysis results and fundamental IR bands, corresponding to C=O bonds (stretching) C=C bonds (stretching), and –C–H (bending) for the diester derivatives are gathered.

Due to the fact that the UV–visible and the ^{1}H and 13C NMR spectra of analogous compounds within each series are very similar, we have included spectroscopic data only for the octyl derivatives, as representative examples (see table 2). All the results in tables 1 and 2 are in good agreement with the proposed structures.

2.3. *Techniques*

FTIR spectra were recorded using a Perkin–Elmer 1725X spectrometer, and elemental analyses were carried out with a Perkin–Elmer 240C microanalyser. UV–vis spectra were recorded using a Milton Roy Spectronic 3000 Array and dichloromethane solutions. ^{13}C and ^{1}H NMR spectra were obtained with a Varian XL-200 instrument using $CDCI_3$ solutions.

Transition characteristics and mesophase textures of the diesters were studied by means of a Reichert–Jung Thermogalen HT 240 polarizing microscope with a heating stage and a temperature control unit.

DSC measurements were performed with a Perkin–Elmer DSC-7 at a heating rate of 10°C min^{-1} under nitrogen. The apparatus was calibrated with indium (m.p. 156·6°C, heat of fusion 28·42 J g^{-1}) and tin (m.p. 231·9°C, heat of fusion 60·40 J g^{-1}). Transition temperatures were read at the peak onsets. Thermogravimetric analyses were carried out using a Perkin–Elmer TGA-7 at 10°C min^{-1} under nitrogen.

3. Results and discussion

3.1. *Synthesis*

We have synthesized the P.FB.P and HC.T.HC diacids in a single step reaction, avoiding protection and deprotection procedures for the functional groups. The synthesis of these compounds has been published using the interfacial condensation method [20, 22]. In this work we have modified this method, replacing chloroform with 1,4-dioxan for the diacid chloride solutions in order to avoid chloroform/water mixtures which complicate and prolong precipitate processing.

The high temperature diacid chloride-aliphatic alcohol condensation reaction in solvents with high boiling point [29] was a suitable method for preparing the diesters when using aliphatic alcohols with more than four carbon atoms. The temperature of the original synthesis (200°C) was decreased (to 150°C) for *n*-butanol in the P.FB.P series, and *n*-pentanol and *n*-hexanol in the HC.T.HC series in order to avoid evaporation of aliphatic alcohol before reaction.

Using ethanol, *n*-propanol and *n*-butanol in this method for the P.FB.P series was not successful even at low temperatures (150°C). For this reason we tried out various solvents and chose condensation Method 1, using 1,4-dioxan/pyridine [22] at 100°C.

3.2. *Structural characterization*

Spectroscopic data made it possible to obtain some structural information about the compounds, for example, the ^{1}H NMR spectra and the IR wave number of the –C–H vibration confirm the *E*-conformation of the double bond in both structures (coupling constant 16 Hz and IR wavenumber of the =C–H vibration 970–980 cm^{-1}).

In some cases, the IR spectroscopic data show more than two carbonyl bands—4(HC.T.HC) and 5(HC.T.HC). This behaviour may be due to the fact that the HC.T.HC unit might exit in the s-*cis*- and s-*trans*-conformations simultaneously. On the other hand, the rest of the compounds show only two carbonyl bands, probably due to the energetically more favourable *s*-*cis*-conformation (see figure 1) in accordance with MNDO calculations [24] and X-ray crystallographic data [25, 26].

The UV-visible spectra of the homologous compounds of the series synthesized are very different. The *p*-phenylenebisacrylic acid derivatives (series I) show a bathochromic shift and a hyperchromic effect in relation to the *p*-hydroxycinnamic acid derivatives (series II) (see figure 2). These results indicate a major extension of conjugation in the first case and probably a more planar structure. These results could suggest greater intermolecular interactions for the *n*(P.FB.P) diesters compared to the *n*(HC.T.HC) diesters and explain the higher melting points for the former series.

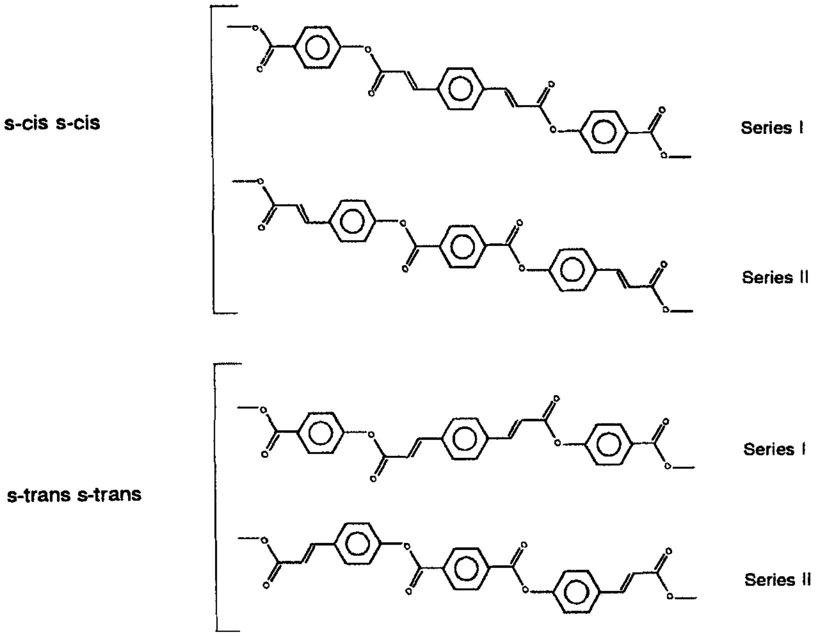


Figure 1. Most stable conformations of the two mesogenic units in series I and series II.

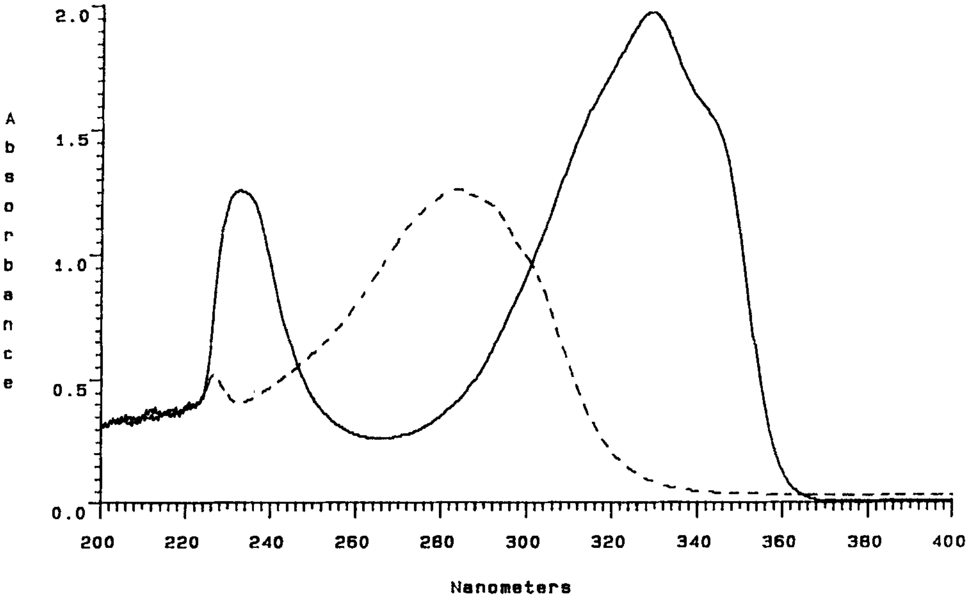


Figure 2. UV-visible spectra of octyloxycarbonyl derivatives in CH_2Cl_2: 8(P.FB.P), $c = 1{\cdot}8 \times 10^{-5}$ M (——); 8(HC.T.HC), $c = 2{\cdot}0 \times 10^{-5}$ M(- - -).

3.3. *Thermal and mesomorphic behaviour*

All the compounds show mesomorphic behaviour. The type of mesophase, transition temperatures and enthalpy values for the different transitions for series I (*n*(P.FB.P)) and series II (*n*(HC.T.HC)) are summarized in tables 3 and 4, respectively.

In spite of their high clearing temperatures, most of the diesters were thermally stable during the DSC measurements over the temperature ranges scanned (from 20°C to 30°C after their clearing points). For this reason, the data gathered in tables 3 and 4 correspond to the second heating scan. Only 2(P.FB.P), 3(P.FB.P) and 2(HC.T.HC) decompose partially in the isotropic state, and the DSC data for these materials correspond to the first heating scan.

Thermogravimetric studies of the octyloxycarbonyl derivatives were carried out under a nitrogen atmosphere with a heating rate of 10°C min^{-1}. The onset values of the decomposition curves (TG curves) are 368°C for series I and 387°C for series II. The peaks of the first TG derivative are at 391°C for 8(P.FB.P) and 410°C for 8(HC.T.HC). Weight loss is not detected at lower temperatures. Most of the synthesized diesters exhibit crystalline polmorphism, which was detected by DSC. In many cases these transitions are reproducible (tables 3 and 4).

The compounds in series I and series II show the typical mesomorphic behaviour of calamitic liquid crystals: nematic for the members with shorter terminal chains and smectic when the terminal chain length is increased [30]. The odd–even effect is observed for the nematic–isotropic transitions (see figures 3 and 4). Both series show smectic polymorphism–smectic A and C.

The nematic mesophase was identified by its characteristic marbled texture. It is noted that the nematic mesophase exhibits large homeotropic areas on heating and cooling. The S_A mesophase shows homeotropic and focalconic textures on heating and

Table 3. Temperature (°C) and associated enthalpy values (kJ mol^{-1}, lower line, in brackets) of transitions determined for *n*(P.FB.P) compounds (series I).

n†	C		C′		C″		S_C		S_A		NI		I
2	●	191·3 (62·6)									●	314·9	●
3	●	214·4 (60·6)									●	297·9 (2·0)	●
4	●	40·8 (1·7)	●			197·3 (54·1)	●	(185)§	●	207‡	●	262·3 (1·1)	●
5	●	117·5 (3·8)	●			173·8 (47·0)	●	190‡	●	230·3 (0·7)	●	254·7 (0·7)	●
6	●	54·4 (12·0)	●			168·9 (60·0)	●	201·7 (0·2)	●	225·2 (1·1)	●	238·2 (1·1)	●
7	●	163·1 (59·1)					●	209·2 (0·2)	●	228·8 (1·1)	●	233·5 (1·1)	●
8	●	45·7¶ (23·9)	●	52·0¶ (23·9)	●	159·1 (54·8)	●	212·2 (0·2)	●	225·6¶ (6·7)	●	226·3¶ (6·7)	●
9	●	162·0 (50·8)					●	212·6 (2·2)	●	220·0 (5·3)			●
10	●	102·3 (13·2)	●			156·8 (51·3)	●	210·7 (0·5)	●	214·3 (5·2)			●

†Number of carbons in alkyl group of the ester terminal chain, *n* = 2, 3 first scan data; *n* = 4–10 second scan data.

‡ Microscopic data.

§ Monotropic transition, microscopic data.

¶ Temperatures correspond to maximum of two overlapped peaks. Enthalpy corresponds to the total area under both peaks.

Table 4. Temperatures (°C) and associated enthalpy values (kJ mol^{-1}, lower line in brackets) for transitions determined in *n*(HC.T.HC) compounds (series II).

n†	C		C′		C″		S_C		S_A		N		I
2	●	170·1 (5·8)	●	190·0 (40·0)					●	229·6 (0·7)	●	311‡	●
3	●	113·0 (1·2)	●	134·4 (31·9)					●	253·4 (0·8)	●	302·7 (0·8)	●
4	●	109·7 (33·3)					●	(96)§	●	253·4 (1·6)	●	269·2 (0·8)	●
5	●	112·8 (36·6)					●	(100)§	●	252·9 (2·2)	●	259·4 (0·9)	●
6	●	45·6 (3·8)	●	108·6 (35·9)			●	170‡	●	244·9 (5·2)			●
7	●	108·5 (38·1)					●	190‡	●	237·8 (5·8)			●
8	●	45·7 (10·2)	●	96·6 (1·1)	●	108·2 (35·6)	●	201‡	●	230·9 (6·0)			●
9	●	65·5 (12·7)	●	106·9 (40·6)			●	200‡	●	225·7 (6·5)			●
10	●	76·7 (21·7)	●	99·6	●	108·3 (40·2)	●	204·1 (0·3)	●	220·1 (0·3)			●

† Number of carbons in the alkyl group of the terminal ester chain, *n* = 2 first scan data; *n* = 3–10 second scan data.

‡ Microscopic data.

§ Monotropic transition, microscopic data.

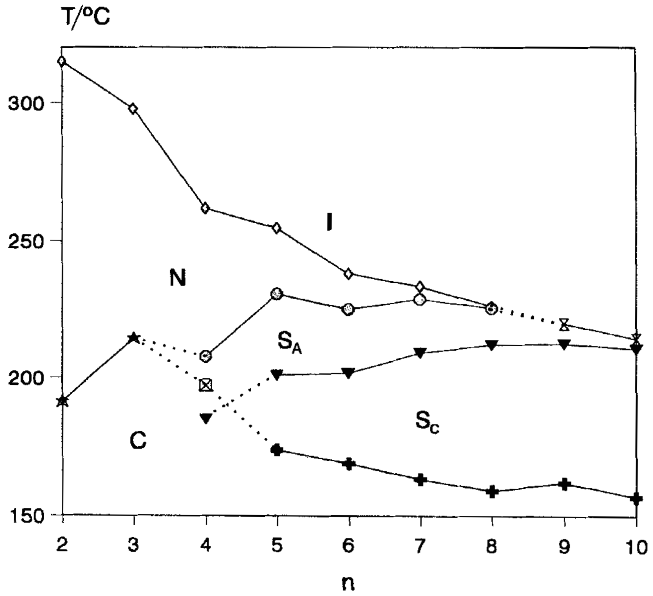


Figure 3. Transition temperatures as a function of alkyl chain length for the *n*(P.FB.P) (series I): C–S_C (✚); C–S_A (☒); C–N(☆); S_C—S_A (▼); S_A—N (●); S_A—I (⧖); N–I (◆).

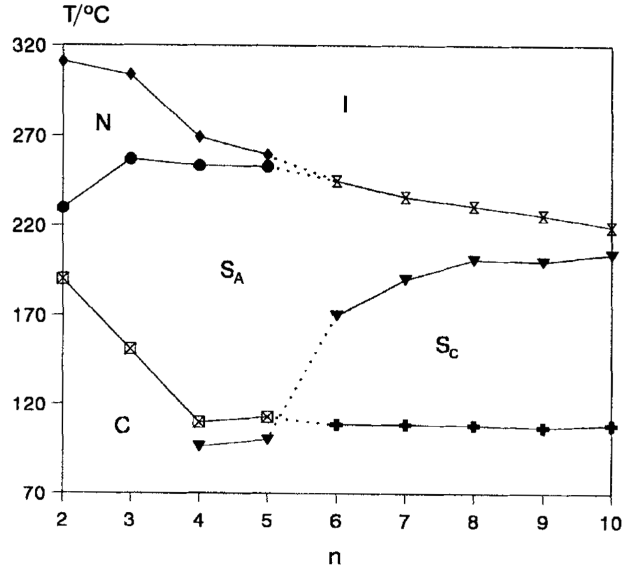


Figure 4. Transition temperatures as function of alkyl chain length for the *n*(HC.T.HC) (series II); C–S_C (✚); C–S_A (☒); S_C—S_A (▼); S_A—N (●); S_A—I (⧖); N–I (◆).

cooling. The S_C mesophases were clearly identified on cooling by their broken focal-conic texture, if this came from a similar S_A texture or by their schlieren texture when this came from a homeotropic texture of this proceeding phase.

The 4,4′-(terephathaloyl)dicinnamoyl and 4,4′-phenylenediacryloyloxydibenzoyl moieties show a high mesogenic capability, for the diester derivatives of both series exhibit wide range enantiotropic mesomorphism which must be due to their structural characteristics. The most likely conformations (*s-cis* and *s-trans-*, see figure 1) enable high electronic conjugation and are planar, both vary favourable for mesomorphism.

Homologous compounds within each series show similar isotropic transition temperatures. The compounds in series II exhibit lower melting temperatures than the compounds in series I, so, that the *p*-hydroxycinnamic acid derivatives show wider enatiotropic mesomorphic ranges. The UV-vis data indicate that the electronic conjugation and therefore the planarity for the *n*(P.FB.P) molecules are greater than that for the homologous *n*(HC.T.HC) compounds. This could explain the higher melting temperatures of the compounds in the former series—see tables 3 and 4.

4. Conclusions

All the compounds in the two series exhibit wide range mesomorphism, homologous compounds of both series having very similar clearing points. On the other hand, the melting points are significantly different. These results could be due to structural factors. The position of the double bond, inside (series I) or outside (series II) the central core has a decisive influence.

Most of the compounds exhibit thermally stable mesophases. It is therefore possible to choose homologous compounds from both series as candidates for photopolymerization studies to be effected using different mesophases (N, S_A, S_C) and at different temperatures.

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