Polymers with rigid anisotropic side groups: 2. Synthesis and properties of some side chain acrylate and methacrylate liquid crystal polymers containing the 4′-alkylbiphenyl-4-yl moiety

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(*Received 24 September 1984*)

A number of acrylate and methacrylate side chain polymers in which the mesogenic moiety is either a 4′-n-pentyl- or 4′-(2-methylbutyl)-biphenyl-4-yl group have been synthesized. A systematic investigation into the effect on the thermal properties of the acrylate polymers containing the n-pentylbiphenylyl moiety, by changing the size of the flexible spacer group, has revealed large differences in the smectic thermal stability of these polymers with respect to whether the flexible spacer group contains an even or odd number of methylene groups. An explanation is given as to why this alternation effect was observed. X-ray diffraction has shown the smectic phase to be S_A in type with a near perfect bilayered structure for the polyacrylates, but a more disordered bilayered structure for the methacrylates. Two of the acrylate polymers exhibit a second smectic phase which has not yet been identified.

(Keywords: liquid crystal; side chain polymers; mesogenic moiety)

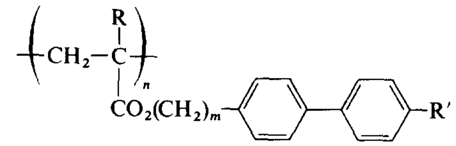
INTRODUCTION

In the first paper of this series[1] we described the synthesis of a number of acrylate and methacrylate side chain polymers in which the mesogenic group (either a 4′-n-pentyl- or 4′-cyano-biphenyl-4-yl group) was directly linked to the polymer backbone. X-ray diffraction studies on these polymers showed that they are crystalline and that the polymer backbone lies in essentially parallel planes, with the anisotropic side groups lying perpendicular to the polymer backbone in smectic-like layers.

It is well known that for side chain polymers, the motions of the polymer backbone towards a statistical distribution of conformations can be decoupled from the anisotropic orientational motions of the mesogenic side groups, by introducing a flexible spacer group which links the mesogenic side group to the polymer backbone[1,2]. In this present paper, we have investigated the effect of lengthening the flexible spacer group upon the liquid crystal behaviour of the polymer. Even though similar work of this type has been done before, it has not been carried out in a systematic fashion by studying all possible spacer lengths from say 1 to 6 for a given system. In our attempt to correct this, we have found some very interesting results.

RESULTS AND DISCUSSION

In our present investigation, we have synthesized a number of polymers of structure (I).


(I)

R = CH_3, hydrogen
R′ = n-C_5H_{11}, $CH_3CH_2\overset{*}{C}H(CH_3)CH_2-$
m = 1→6

We have prepared six acrylate polymers of structure (I), where R = hydrogen, R′ = n-C_5H_{11}, and $m = 1 \rightarrow 6$, and one methacrylate polymer, where R = CH_3, R′ = n-C_5H_{11}, and $m = 2$. In addition, two polymers, one acrylate and the other a methacrylate, were prepared where R′ = $CH_3CH_2CH(CH_3)CH_2$ and $m = 2$. The transition temperatures for the monomers and polymers were measured either by differential scanning calorimetry (d.s.c.) (polymers) or by using a Mettler hot stage in conjunction with a polarizing microscope (monomers); these are listed in *Table 1*. In the case of the monomers, no liquid crystal behaviour was observed; monomers 7 and 8 were waxy in appearance and monomers 6 and 9 had very low melting points. On polymerization, all the resulting polymers gave smectic phases, polymers 6 and 9 exhibiting a smectic–smectic transition. From X-ray diffraction data (see later), the smectic to isotropic liquid transition was established as a S_A–I transition. This increase in the order of a system on polymerization is typical of side chain polymers[3].

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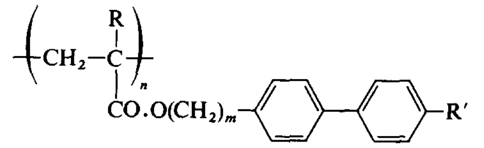
Table 1 Thermal properties of the monomers and polymers



	R	*m*	R′	Monomer	Polymer		
				C–I (°C)	g (°C)	S–S_A (°C)	S_A–I (°C)
1	H	1	n–C_5H_{11}–	62	67	–	130 (decomp)
2	H	2	n–C_5H_{11}–	48	65	–	192
3	CH_3	2	n–C_5H_{11}–	61	–	–	97
4	H	2	$CH_3CH_2CH(CH_3)CH_2$–	Liquid	–	–	159
5	CH_3	2	$CH_3CH_2CH(CH_3)CH_2$–	Liquid	62	–	–
6	H	3	n–C_5H_{11}–	22	69	90	124
7	H	4	n–C_5H_{11}–	Wax	–	–	129
8	H	5	n–C_5H_{11}–	Wax	66	–	93
9	H	6	n–C_5H_{11}–	22	–	102	110

C = crystal
I = isotropic liquid
g = glass—later work suggests that entrained MeOH may have caused some of these d.s.c. transitions
S = smectic

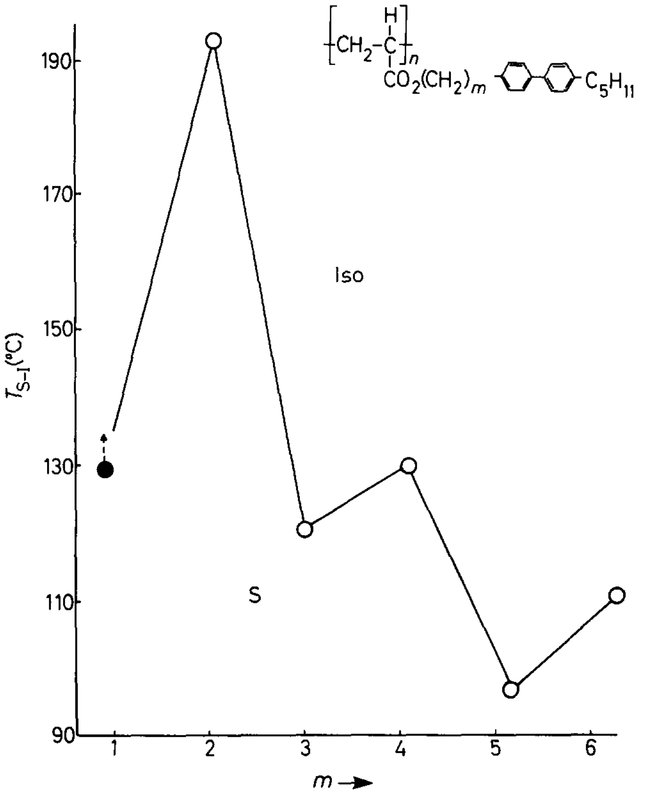


Figure 1 Plot of the transition temperatures against the number of methylene groups in the spacer moiety for the acrylate polymers. ○ = S_A–I; ● = S_A–I with decomposition

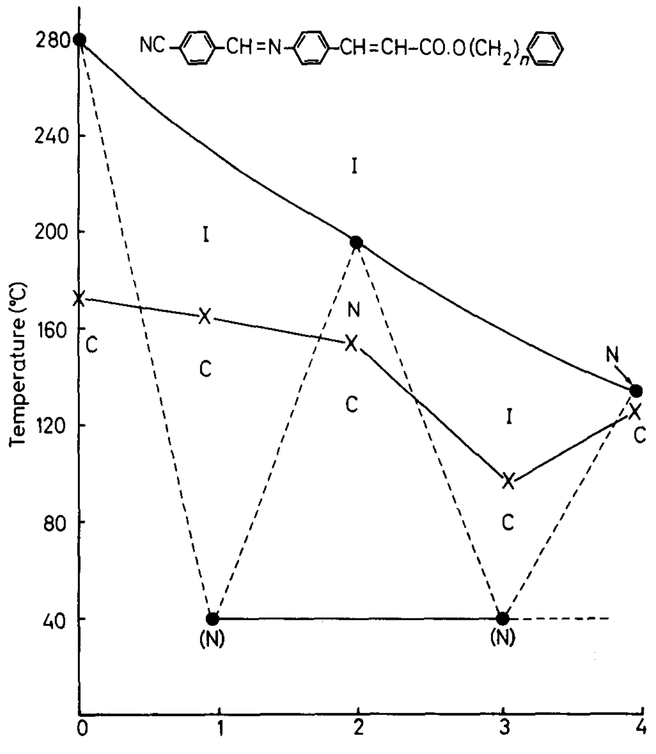


Figure 2 Plot of the transition temperatures against the number of methylene groups in the arylalkyl moiety for the ω-phenylalkyl 4-*p*-cyanobenzylideneaminocinnamates. X = C–N or I; ● = N–I. This figure shows the extremely large alternation in the nematic to isotropic transition temperatures as the methylene spacer changes from an even to an odd number of carbon atoms, i.e. the nematic order in the system is very sensitive to any deviations from molecular linearity (see also *Figure 3*)

A plot of the transition temperatures against the number of methylene groups in the flexible spacer moiety for the acrylate polymers with a pentyl terminal group is given in *Figure 1*. This plot shows the very large differences in the T_{S_A-I} values depending on whether the flexible spacer contains an even or odd number of methylene groups. It is impossible to assess whether this type of behaviour should be common to all side chain liquid crystal polymers, because such a systematic investigation has not been carried out before. However, in low molar mass liquid crystals, this kind of behaviour is well known, a good example being provided by the ω-phenylalkyl 4-*p*-cyanobenzylidene-aminocinnamates[4]. A plot of the T_{N-I} values against the number of methylene groups in the arylalkyl group for these compounds is given in *Figure 2*. This clearly shows a very large decrease in T_{N-I} value as the

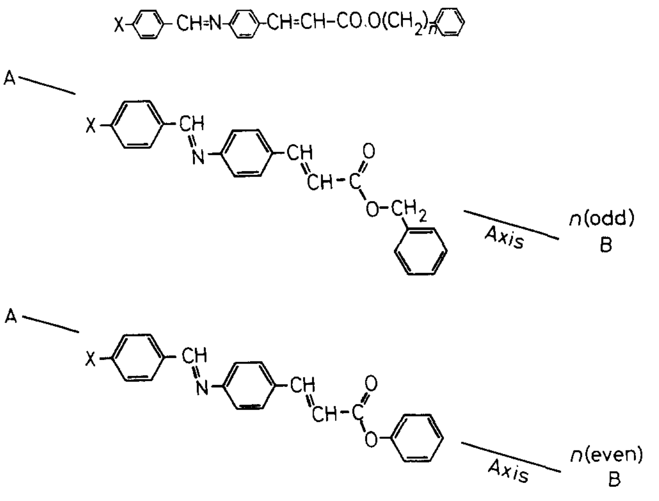


Figure 3 Zig-zag conformations for the ω-phenylalkyl 4-*p*-cyanobenzylideneaminocinnamates

number of methylene groups in the arylalkyl moiety is alternated between odd and even. One possible reason for this could be the change in orientation of the terminal benzene ring with respect to the rest of the molecule. This idea is illustrated in *Figure 3*. When the number of methylene groups in the arylalkyl moiety is odd (top diagram in *Figure 3*), then the benzene ring is 'off-axis' and this makes it difficult for the molecules to pack neatly in the parallel arrangement needed for a liquid crystal phase. This effect, coupled with the decrease in anisotropy of the molecular polarizability associated with the 'off-axis' orientation of the benzene ring, greatly decreases the $T_{N\text{-}I}$ value of the homologues where n is odd. However, when n is even, the benzene ring is 'on-axis' and strongly enhances the anisotropy of the molecular polarizability. This effect, coupled with the fact that the molecule is more linear when the benzene ring is 'on-axis', greatly increases the $T_{N\text{-}I}$ value for the homologues when n is even.

These explanations are supported by the damping of the alternation effect as the alkylene chain is extended, i.e., the aligning/disaligning influence of the ω-phenyl group would not differ significantly for an odd or even number of methylene groups if the alkylene chain were of infinite length.

This reasoning about the alternation effects for the cinnamates can also be applied to side chain liquid crystal polymers. In these polymers, the greatest stability of the smectic mesophase should be obtained when the mesogenic moieties are perpendicular to the local director of the polymer backbone, i.e., when the side chains are most effectively separated from the backbone and able to adopt an anisotropic layer-like arrangement without interference. Thus, any deviation from this perpendicular orientation of the mesogenic side groups with respect to the polymer backbone, may cause a decrease in the smectic thermal stability of the system. Thus, when m is even (*cf.* the value of n in the cinnamates), we observe the higher $T_{S_A\text{-}I}$ values, which decrease rapidly when m becomes odd because the orientation of the mesogenic side groups with respect to the polymer backbone is less than perfect.

The alternation sense for the low molar mass cinnamate esters and the current polymers of the side chain type is therefore the same. Moreover, it is the same as that for main chain polymers with varying spacer lengths (now an integral part of the backbone) between the mesogenic core units. This is not surprising, since in all three cases, the alkylene chain is functioning, when it is even, either to promote the linearity of the system and assist parallel packing (cinnamate esters and main chain polymers) or simply to facilitate parallel packing of the side chains (in the polymers discussed in this paper).

It should be noted, however, that for a *terminal* alkyl group ($-C_nH_{2n+1}$) the situation is at first sight different. Thus, in low molar mass liquid crystal systems, we always find that for such a terminal n-alkyl chain the odd members of the series, i.e., homologues having an odd *total* number of carbon atoms in the n-alkyl chain, always have the higher mesophase thermal stability[5,6]. However, the spacer group in a polymer is made up only of methylene groups, and a fair comparison between the two situations can only be made on the basis of the number of *methylene groups* in either the spacer or the n-alkyl chain, i.e., the methyl group of a terminal alkyl chain is not part of the spacer. Put in another way, the terminal methyl group of the n-alkyl chain may be regarded as equivalent to the ester moiety which joins the mesogenic polymer side group via the spacer to the polymer backbone (*Figure 4*). Therefore if for both the polymer and low molar mass systems we now compare equivalent situations, i.e., the length of the 'methylene bridge' between the benzene ring and the polymer backbone and between the benzene ring and the terminal methyl group, the difference vanishes and as in the case depicted in *Figure 4*, the 'methylene bridges' containing four methylene groups, give rise to the higher mesophase thermal stabilities for both systems.

This comparison of data for polymer and low molar mass systems seems to be a useful one since, for the latter type of system, over the years, many systematic investigations have been carried out, giving a vast library of information. This information can now be usefully applied in the relatively new area of liquid crystal polymers to reveal points of similarity and difference.

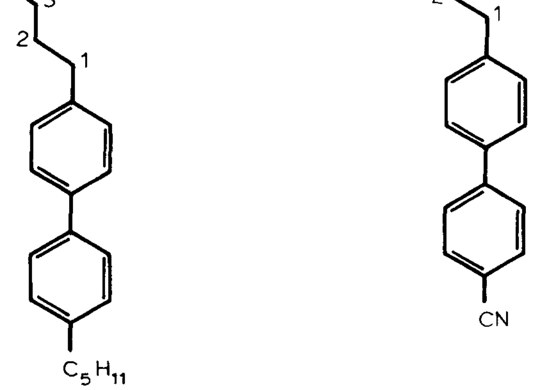


Figure 4 Comparison between the conformation of the terminal n-alkyl group in low molar mass liquid crystal systems with that found for the spacer group in liquid crystal side chain polymers

Table 2 X-ray diffraction results for the acrylate and methacrylate polymers

Polymer number (from *Table 1*)	X-ray diffraction data: Inner ring 2θ	d_1 (Å)	Outer ring 2θ	d_2 (Å)	Caclulated length of anisotropic unit d (Å)
1	3.32	33.3	24.22	4.61	16.7
2	2.93	37.8	24.22	4.61	18.7
3	3.22	34.4	24.07	4.64	18.7
4	3.18	34.8	22.22	5.01	17.2
5	3.57	31.0	22.10	5.05	17.2
6	2.89	38.3	24.30	4.54	18.8
7	2.79	39.8	24.58	4.55	20.5
8	2.97	44.2	29.30	4.52	20.8
9	2.86	45.9	28.80	4.59	22.5

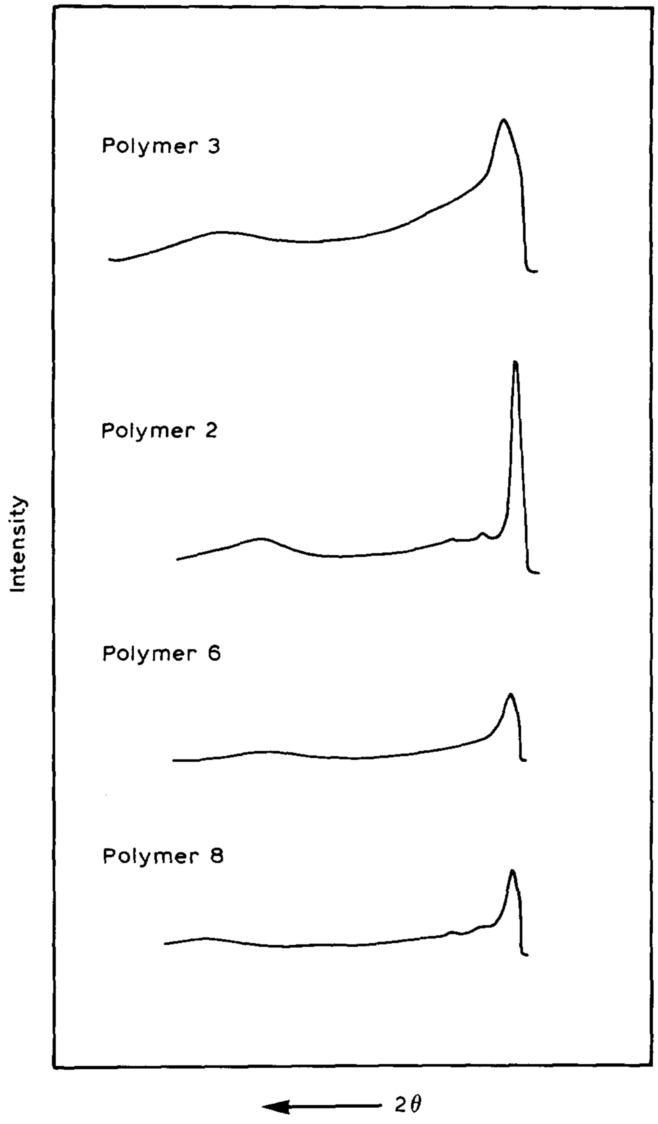


Figure 5 X-ray densitometer patterns for a selected number of acrylate and methacrylate polymers

Finally, with regard to transition temperatures for the polymers, it should be pointed out that the much lower $T_{S\text{-}I}$ values for polymers **4** and **5** compared with those for polymers **2** and **3** respectively, are consistent with the observed effects of terminal chain branching on transition temperatures in low molar mass systems. The methacrylate polymers also have lower $T_{S\text{-}I}$ values than the corresponding acrylates.

X-ray diffraction studies

The X-ray studies were very similar to those outlined in our first paper[1], and the data for the polymers cited in this paper are given in *Table 2*. A number of selected X-ray densitometer patterns are given in *Figure 5*. The results from this study show that the inter-chain spacings for the acrylate and methacrylate polymers containing a flexible spacer group are very similar to those given for the acrylate and methacrylate polymers having no spacer[1]. In the case of the acrylate polymers [see *Figure 6*(*a*)], the end-to-end inter-chain spacing (d_1) corresponds approximately to twice the length of the mesogenic side group, and fits very well with the model of Magagnini[7]. In contrast, the end-to-end inter-chain spacing for the methacrylate polymers corresponds to a distance (d_1) less than twice the lengths of the mesogenic side group. This gives rise to two possible models for the side chain ordering:

(i) a tilted smectic-like ordering [*Figure 6*(*b*)];
(ii) an overlapping of side chains within the ordered smectic-like array [*Figure 6*(*c*)].

The X-ray diffraction patterns for the two methacrylate polymers, where $R' = n\text{-}C_5H_{11}-$ and $CH_3CH_2CH(CH_3)CH_2-$, and $n = 2$, in structure (**I**) were very similar. This suggests that the structure for the methacrylate polymers is probably better depicted by the model in *Figure 6*(*b*), since the overlapping arrangement [*Figure 6*(*c*)] would be significantly hindered by the bulky 2-methylbutyl group. The arrangement given in *Figure 6*(*b*) will accommodate, to some extent, the bulky 2-methylbutyl moiety, giving rise to similar X-ray diffraction patterns for both these polymers.

It should be noted that optical microscopy of the smectic phase of the two methacrylate polymers does not in fact reveal any tilted (smectic C) characteristics. Therefore the model proposed for the tilted packing in *Figure 6*(*b*) is one in which the tilt direction would average to zero over a number of layers, i.e., the system would have S_A-like properties.

A more detailed X-ray diffraction examination has been carried out on polymer **2** (see *Table 2*) to identify the smectic phase. From this investigation, the mesophase is smectic A in type, with a layer spacing corresponding to twice the length of the mesogenic side group.

This X-ray diffraction work was carried out by Dr R. Richardson, School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS.

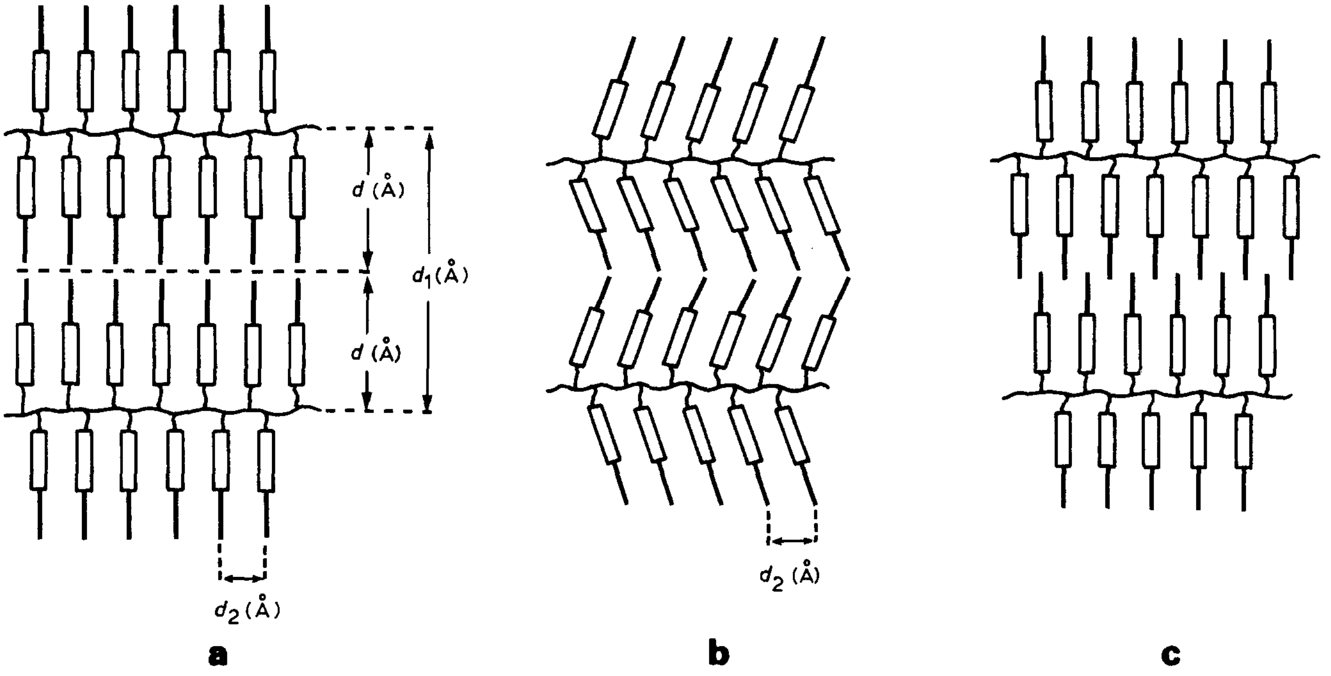


Figure 6 Schematic representations of ordering in (a) the acrylate polymers, (b) the tilted smectic-like and (c) the overlapping arrangement of the methacrylate polymers

EXPERIMENTAL

All values for T_g and other transition temperatures were measured using the following techniques.

(1) a Mettler FP5 hot stage and control unit, in conjunction with a Nikon LKE polarizing microscope;

(2) a Perkin-Elmer Differential Scanning Calorimeter 2C with Data Station.

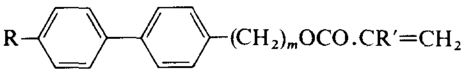
The structures of all compounds and synthetic intermediates were confirmed by a combination of the following techniques:

(1) infra-red spectra (KBr disc) were recorded using a Perkin-Elmer 457 Grating Infrared Spectrometer;

(2) low resolution ^1H n.m.r. spectra were recorded using a Jeol JNM-PMX60 n.m.r. Spectrometer (internal standard: tetramethylsilane; solvent: $CDCl_3$);

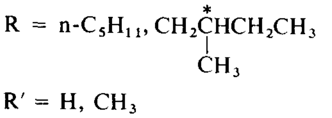
(3) low resolution mass spectra were recorded using an A.E.I. MS902 Mass Spectrometer.

The following scheme represents the reaction pathway used to prepare the compounds of structure **(II)**.



(II)

where



$R = n\text{-}C_5H_{11}, CH_2\underset{CH_3}{\underset{|}{\overset{*}{C}}}HCH_2CH_3$

$R' = H, CH_3$

$m = 1 \rightarrow 6$

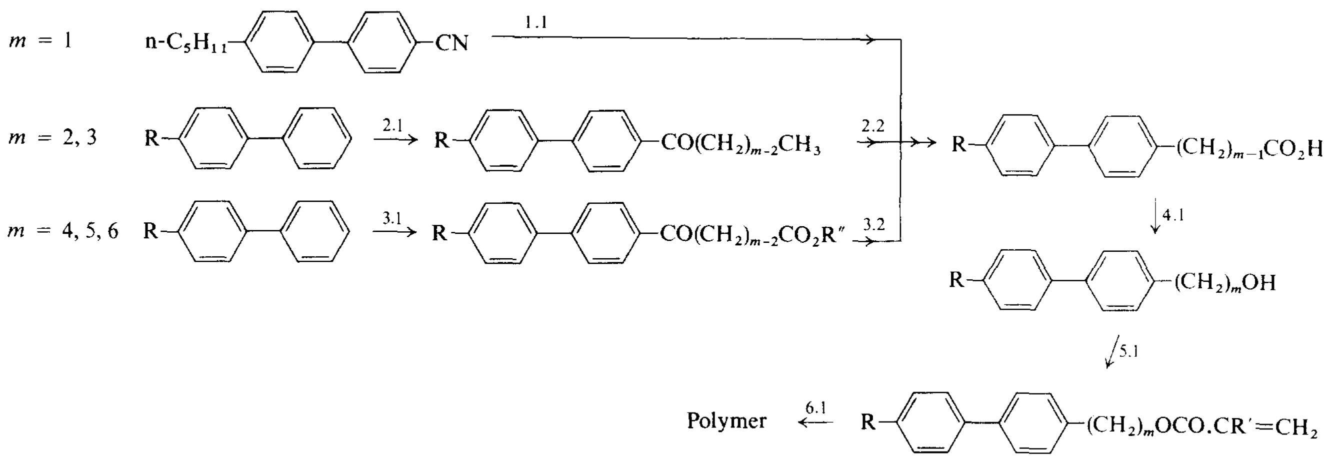
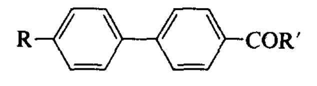
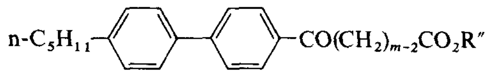


Table 3 Melting points for compounds of structure



R	R′	M pt (°C)
C_5H_{11}	CH_3	76
C_5H_{11}	CH_3CH_2	117
$CH_2\underset{CH_3}{\overset{*}{C}}HCH_2CH_3$	CH_3	60

Table 4 Melting points for compounds of structure



m	R″	M pt (°C)
4	H	176
5	CH_3	92
6	CH_3	96

1.1 Hydrolysis of 4′-cyano-4-pentylbiphenyl

A mixture of 4′-cyano-4-n-pentylbiphenyl (8.0 g, 0.032 mole), glacial acetic acid (80 cm^3), and 50% w/v sulphuric acid (80 cm^3) was boiled under reflux for 20 h. The solution was allowed to cool and the precipitate was filtered off, washed with water and crystallized from ethanol. The product was obtained as a white crystalline solid, mp 175.5°, (lit.[8] 176°).

2.1 Preparation of 4-n-alkyl-4′-n-alkanoylbiphenyls

The 4-alkylbiphenyls were acylated by a standard Friedel–Crafts reaction[9], using the appropriate acid chloride and aluminium chloride, with dry nitrobenzene as solvent. Melting points are given in *Table 3*.

2.2 Willgerodt/Kindler reaction

This reaction was carried out by a standard method[10]. The product from 2.1 was heated at the boiling point with sulphur and morpholine for 7 h and the resulting crude thiomorpholide was hydrolysed in ethanolic potassium hydroxide solution. Purification was effected by reprecipitation from aqueous sodium hydrogen carbonate and crystallization from glacial acetic acid or ethanol. Melting points are given in *Table 5*.

3.1 Friedel–Crafts acylation

This reaction was carried out by a standard method[9]. The 4-n-pentylbiphenyl was acylated with succinic anhydride ($R''=H$) or with the appropriate half ester acid chloride, in 1,1,2,2-tetrachloroethane solution, with aluminium chloride as catalyst. The products were crystallized from ethanol. Melting points are given in *Table 4*.

3.2 Huang–Minlon reduction

A mixture of the product from 3.1 (0.1 mole), potassium hydroxide (0.4 mole), and hydrazine hydrate (1.0 mole) was dissolved, with heating and vigorous stirring, in diethylene glycol (400 cm^3). The reaction mixture was then heated to 125°C and maintained at that temperature for 2½ h. Water and hydrazine hydrate were then distilled out until the internal temperature reached 205°C. This temperature was maintained for 6 h, whereupon the solution was allowed to cool and poured into water (1000 cm^3). The mixture was strongly acidified and repeatedly shaken with ether. The combined extracts were washed with water (2×200 cm^3) and dried over magnesium sulphate. The ether was removed under reduced pressure and the product crystallized from ethanol. Melting points are given in *Table 5*.

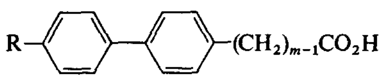
4.1 Reduction of carboxylic acids

The acids shown in *Table 5* were first converted into the corresponding acid chlorides by heating under reflux with an excess of thionyl chloride. The resulting acid chlorides were then reduced by a standard lithium aluminium hydride reduction in diethyl ether solution[11]. The crude products were crystallized from hexane. Their melting points are given in *Table 6*.

5.1 Preparation of esters

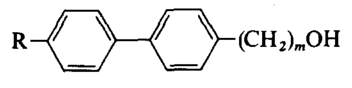
To a stirred solution of the alcohol (*Table 6*) (0.01 mole) and dry triethylamine (2 cm^3), in dry dichloromethane (25 cm^3), at 15°C, was added dropwise a solution of (meth)acryloyl chloride (2 cm^3) in dry dichloromethane (10 cm^3). After addition was complete, the solution was stirred for 4 h and poured into 2M hydrochloric acid. The organic layer was separated and washed successively with 2M hydrochloric acid and water (2×50 cm^3). After drying over magnesium sulphate, the solvent was removed at room temperature under reduced pressure.

Table 5 Melting points for compounds of structure



R	*m*	M pt (°C)
C_5H_{11}	1	175.5
C_5H_{11}	2	120
C_5H_{11}	3	114
C_5H_{11}	4	112
C_5H_{11}	5	139
C_5H_{11}	6	120
$CH_2\underset{CH_3}{\overset{*}{C}}HCH_2CH_3$	2	115

Table 6 Melting points for compounds of structure



	m	M pt (°C)
C_5H_{11}	1	103.5
C_5H_{11}	2	110
C_5H_{11}	3	87
C_5H_{11}	4	91
C_5H_{11}	5	85
C_5H_{11}	6	82
$CH_2\underset{CH_3}{\overset{*}{C}}HCH_2CH_3$	2	73

The crude products were purified by chromatography on silica gel, using chloroform as the eluant. All products gave single spots by t.l.c. The solvent was removed under reduced pressure. Owing to the extreme sensitivity of the monomers to thermal polymerization, recrystallization was not attempted. Some monomers, therefore, remained as waxes or liquids at room temperature. Melting points are given in *Table 1*.

6.1 Polymerization

All the monomers prepared in ester preparation section above were prepared as described previously[1].

CONCLUSION

The systematic investigation of the effect of lengthening the flexible spacer group upon the smectic thermal stability of the acrylate polymers **(I)** has shown that there is a large alternation effect in the $T_{S_A\text{-I}}$ values depending on the number of methylene groups in the spacer. Higher $T_{S_A\text{-I}}$ values are observed for the even numbers of methylene groups. By comparing this effect with a known and comparable example in low molar mass liquid crystal systems, it can be concluded that the large alternation effect is due to changes in the relative spatial distribution of the backbone and the side chain.

This does not contravene the general rule for low molar mass systems concerning the effect of the length of a *terminal* n-alkyl group upon the mesophase thermal stability, provided that the same basis for comparison— the number of methylene groups— is used for all systems.

X-ray diffraction studies show that the phases involved are smectic A phases. The layered structure in polymers with a methacrylate backbone is less perfect than that found in the polymers with an acrylate backbone, these having either an overlapping arrangement or a tilted layer structure.

The second smectic phase in polymers **6** and **9** has not yet been identified.

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