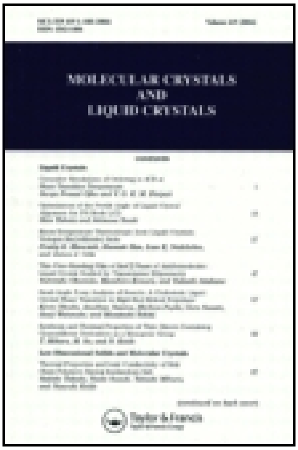

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Synthesis and Properties of Some Liquid Crystal Polysiloxanes with Laterally or Terminally Attached Side Chains

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Synthesis and Properties of Some Liquid Crystal Polysiloxanes with Laterally or Terminally Attached Side Chains

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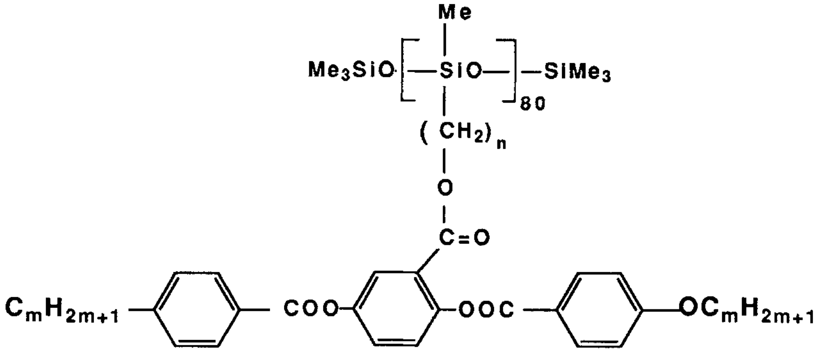
A series of polysiloxanes having laterally-attached mesogenic side chains and involving variations in spacer length and the nature of the two end groups are reported. The terminally-attached analogues of some of these polymers are also reported. Optical microscopy and differential scanning calorimetry were used to establish the mesomorphic properties. An explanation is proposed for the low T_{N-I} values observed for the polymers with laterally attached side chains.

1. INTRODUCTION

Hessel and Finkelmann[1] were the first to prepare and examine liquid crystal polymers of the polyacrylate type with the mesogenic side chains appended laterally to the backbone. Keller *et al.*[2] have reported four polysiloxanes with similarly appended side chains. These polymers were of structure



where m = 4 and 6 for each of n = 4 and 10.

Like the polyacrylates,[1] the polymers were purely nematic. In three of the four cases, the T_{N-I} values were just 4–6°C higher than those of the vinylic side chain precursors; in one case (n = 4, m = 6) the polymer's T_{N-I} was 1°C lower.

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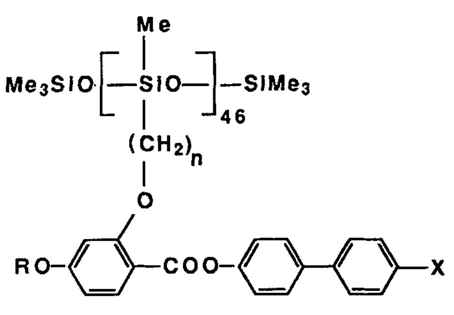
In view of the pronounced nematic tendencies of these polymers, we wished to extend the small number of known polysiloxanes of this type using a different mesogenic group in which the spacer attachment is more off-set than central and terminal substitution of an unsymmetrical kind is achieved more readily.

The polymer system chosen (**1**) has enabled us to monitor the effects of variation in spacer length and terminal substitution on the liquid crystal properties. Some early results have been published,[3,4] but a much more complete account is now given.



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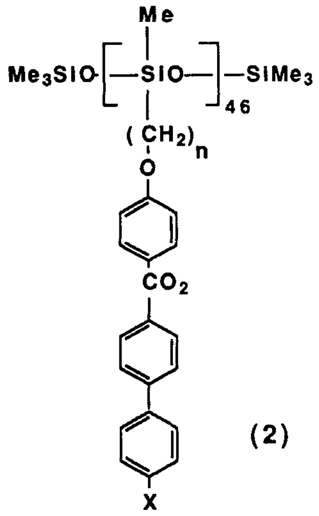

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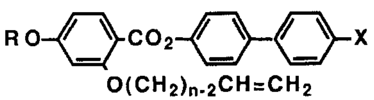
Two series of terminally-attached analogues (**2**) of the lateral systems have also been prepared in order to have some comparison between the effects of lateral and terminal attachment.

2. RESULTS

The vinylic side chain precursors (**3**) to the laterally-attached polymers were synthesized as described earlier,[3] and those (**4**) used for terminal attachment by standard procedures.



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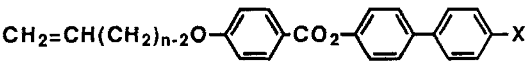

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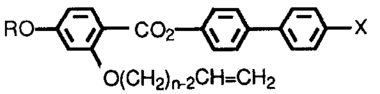
The polymers **1** and **2** were prepared by the well known hydrosilylation procedure using either hexachloroplatinic acid dihydrate in isopropanol[5] or, for the most part, platinum divinyltetramethyldisiloxane complex (PVMS) as catalyst. In all cases poly(hydrogenmethylsiloxane) (PHMS) backbone obtained from Wacker Chemie, Munchen, FRG, (DP = 46 ± 3, $M_w/M_n = 2.3$) was used. A 10% molar excess

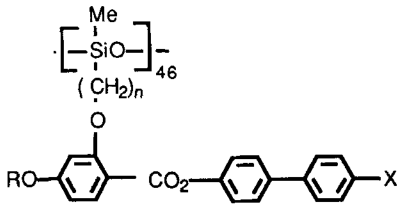
TABLE I

Transition Temperatures (°C) for the polymers (**1**)* and their vinylic side chain precursors (**3**)

Alkene



Polymer



R	X	n	No		No	Tg	K-I	K-N	N-I	$\Delta T_{(N\text{-}I)}$**
CH_3	OC_9H_{19}	5	**3a**	K 99.3 I	**1a**		110.2			
C_5H_{11}	OC_9H_{19}	5	**3b**	K 71.3 (N 69.3) I	**1b**	11.2			54.6	−14.7
C_8H_{17}	C_3H_7	5	**3c**	K 53.5 (N 50.6) I	**1c**	8.5			31.7	−18.9
C_8H_{17}	$C_{10}H_{21}$	5	**3d**	K 51.1 (N 47.6) I	**1d**	1.7			33.9	−13.7
C_8H_{17}	OC_5H_{11}	5	**3e**	K 75.2 (N 71.8) I	**1e**	9.3			65.5	−6.3
C_8H_{17}	OC_9H_{19}	5	**3f**	K 54.0 N 74.3 I	**1f**	4.8			58.0	−16.3
C_8H_{17}	$OC_{11}H_{23}$	5	**3g**	K 52.6 N 72.5 I	**1g**	9.5			60.5	−12.0
C_8H_{17}	$CH_2CH(CH_3)$-C_2H_5	5	**3h**	K 49.7 (N* 30.0) I	**1h**	8.9				
C_8H_{17}	$C_{10}H_{21}$	8	**3i**	K 41.9 (N 40.7) I	**1i**	−9.3			32.3	−8.4
C_8H_{17}	OC_9H_{19}	8	**3j**	K 44.5 N 64.5 I	**1j**	−2.1			66.8	+2.3
C_8H_{17}	C_3H_7	11	**3k**	K 41.5 I	**1k**	16.2		36	45.3	(>+3.8)
C_8H_{17}	$C_{10}H_{21}$	11	**3l**	K 41.1 (N 39.7) I	**1l**	10.7			31.5	−8.2
C_8H_{17}	OC_5H_{11}	11	**3m**	K 46.0 K' 64.2 (N 56.1) I	**1m**	8.3			57.1	+1.0
C_8H_{17}	OC_8H_{17}	11	**3n**	K 44.3 N 63.1 I	**1n**	−3.4			41.0	−22.1
C_8H_{17}	OC_9H_{19}	11	**3o**	K 45.6 N 62.7 I	**1o**			40.4	54.4	−8.3
C_8H_{17}‡	$OC_{11}H_{23}$	11	**3p**	K 42.0 N 61.7 I	**1p**	−1.5			59.2	−2.5
C_8H_{17}‡	$CO_2CH(CH_3)$-CO_2Et	11	**3q**	K 40.7 (S-27.3 S_C*-8.6 S_A 16.9) I	**1q**	13				
$C_{10}H_{21}$	$CO_2CH(CH_3)$-CO_2Et	11	**3r**	K 32.7 (S-23.1 S_C* 0.1 S_A 18.8) I	**1r**	14				
$C_{10}H_{21}$	$C_{10}H_{21}$	11	**3s**	K 49.1 (N 44.2) I	**1s**	3.0			37.3	−6.9

‡ The uncharacterised phase may be a highly ordered smectic phase, but the low temperature at which the phase occurs made confirmation difficult.

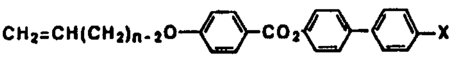
* GPC gave $M_w/M_n = 2.3 \pm 0.3$; $\Delta H(N\text{-}I) = 0.25 \pm 0.12$ cg-1.

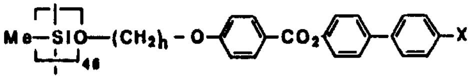
** $\Delta T_{(N\text{-}I)} = T_{N\text{-}I}$ (polymer)-$T_{N\text{-}I}$ (alkene)/°C.

TABLE II

Transition temperatures (°C) for the polymers (**2**)* and their vinylic side chain precursors (**4**)

Alkene **Polymer**





X	n	No		No	
OC_9H_{19}‡	3	**4a**	K 126.6 N 204.5 I	**2a**	K 129 S 205 S_A 254 I
OC_9H_{19}	6	**4b**	K_1 100.2 K_2 129.2 S_C 145.0 N 184.5 I	**2b**	K 121 S_C 240 I
OC_9H_{19}	11	**4c**	K 112.0 S_C 158.4 N 173.7 I	**2c**	K 133.4 S_C 237.5 I
$C_{10}H_{21}$‡	3	**4d**	K 106.2 N 182.9 I	**2d**	K 111 S 202 N 235 I
$C_{10}H_{21}$	6	**4e**	K_1 65 K_2 74.4 K_3 86.5 (S_B 79.3) S_C 126.8 N 163.2 I	**2e**	K 127 S_C 238 I
$C_{10}H_{21}$‡	11	**4f**	K 58.0 S_B 98.7 S_C 147.0 S_A 150.6 N 157.6 I	**2f**	K 90.4 S 120.0 S_C 218.9

‡ The nature of the lower temperature smectic phase has yet to be confirmed.
* GPC gave $\overline{M}_w/\overline{M}_n = 2.3 \pm 0.2$.

of alkene was employed. Purification of the polymers (**1**) was effected by precipitation of the polymers from dichloromethane solution with methanol and subsequent centrifugation, a process which was repeated until side chain precursors could not be detected by tlc. The pure polymers were dried *in vacuo* in the isotropic state.

In the case of the polymers (**2**), purification was effected by continuous soxhlet extraction with ethyl acetate, until the side chain precursors could not be detected in the insoluble polymers by tlc. The pure polymers were dried *in vacuo* at 150°C.

The thermal properties of the polymers were determined by optical microscopy and differential scanning calorimetry, and the results are summarized in Tables I and II.

3. DISCUSSION

A novel general result is immediately obvious from the data in Table I. The $T_{N\text{-}I}$ values for 12 of the 15 liquid crystal polymers with laterally attached side groups are lower than those for the corresponding vinylic precursors. $\Delta T_{N\text{-}I}$ ranges from -22.1°C to $+2.3$°C. The isotropic nature of the remaining three other polymers **1h**, **1q** and **1r** also show that decreases in mesogenicity occur from precursor to polymer. Apart from the one small decrease (1°C) in $T_{N\text{-}I}$ noted by Keller *et al.*,[2] this result is quite exceptional, side chain polymers usually having higher clearing temperatures than their side chain precursors.

An unsubstituted flexible polymer backbone (e.g., PHMS) will tend to form a statistical, random coil. In a side chain liquid crystal polymer (SCLCP), the spacer helps to decouple the motions of the mesogenic side groups from those of the main polymer backbone. However, decoupling is never complete, and part of the spacer is anisotropically ordered with the more rigid mesogenic side group. Therefore the spacer can allow some dynamic coupling of the motions of the main polymer backbone and the side groups. As such, the tendency of the side groups to arrange anisotropically will affect the backbone conformation, leading to a loss of entropy.

Zhou *et al.*[6] have proposed a "mesogen-jacketed" type structure (Figure 1) for a laterally attached SCLCP (Figure 1).

Some evidence for this arrangement was found in X-ray diffraction patterns of drawn fibers of laterally-attached polyacrylates,[7] where the side groups were observed to align parallel to the draw direction, implying that the polymer backbone and mesogenic groups are capable of adopting a parallel arrangement.

If this is the case, then the nematic phase of a laterally-attached SCLCP is analogous (Figure 2) to the prolate N_{III} model[8,9] proposed by Wang and Warner for the nematic phase of a *terminally*-attached SCLCP, as opposed to their oblate N_I model or the other prolate model (N_{II}). According to the prolate model, the polymer backbone is stretched out towards being a rod by the aligning field in the nematic phase, thus losing more entropy than it would in the N_I model. In extreme instances, in the N_{III} case, the polymer backbone is restricted to one dimension, whereas in the N_I case it is free to lie in two dimensions. Thus there is a greater rise in the entropic contribution, -TS, to the free energy, ΔF, in the N_{III} phase compared to that in the N_I model. This rise in energy may resist the nematic ordering of the side chains and so reduce the N-I transition temperatures, i.e., diminish the thermal stability of the nematic phase. If these arguments are applied to laterally attached SCLCPs with the structure shown in Figure 1, it is possible to explain why laterally-attached SCLCPs do not show the significant rises in $T_{N\text{-}I}$ on going from side chain precursor to polymer that are normal for terminally-attached SCLCPs.

Moreover, in the laterally-attached polymers (**1**), the spacer connection to the

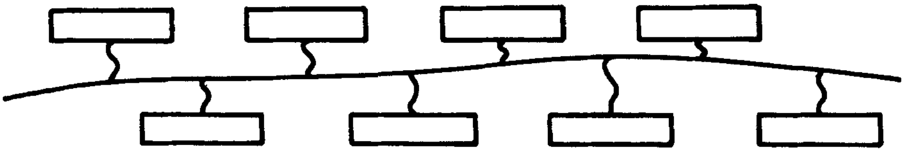


FIGURE 1 "Mesogen-jacketed" model[6] for a laterally attached SCLCP.

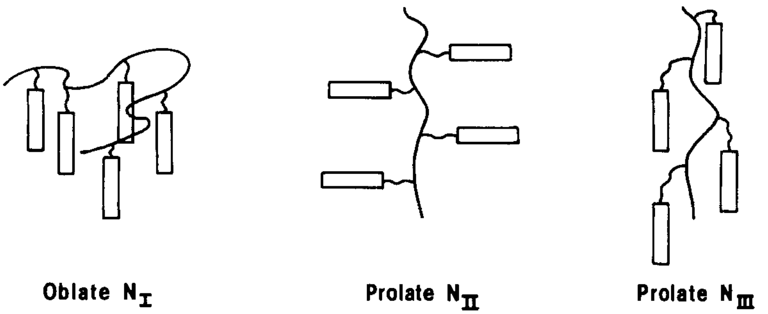


FIGURE 2 Oblate and prolate models[8,9] for terminally attached SCLCP.

mesogen is more off-center than in those polymers previously prepared by Keller *et al.*[2] This off-center position, based on mechanical arguments, will presumably result in greater coupling between the motions of the side groups and the polymer backbone compared with the coupling involved when the spacer is in a position closer to the center of the mesogenic core.

This factor, coupled with a prolate N_{III} arrangement of the polymer backbone and side groups, would tend to decrease nematic thermal stability, and hence explain the general reductions in $T_{N\text{-}I}$ values observed on passing from alkene to polymer compared with the slight increases found in general by Keller *et al.*[2] As mentioned later in more detail, these arguments are supported by the fact that larger $T_{N\text{-}I}$ decreases in Table 1 are in general associated with shorter spacer lengths.

The "jacketed" arrangement of mesogenic groups around the polymer backbone would also explain the marked lack of smectic properties in laterally attached SCLCPs, despite in some instances, long alkyl chains being present at both ends of the mesogenic group e.g., in the alkenes **3g** and **3p**. There is a total of 20 atoms (not counting the hydrogen atoms) in the chains of the two end groups RO and X.

The effects of variation in molecular structure on the alkenes (**3**) and polymers (**1**) are depicted in Figures 3–6. Figures 3 and 4 illustrate the effects of different groups X present in the biphenyl moiety on the transition temperatures of the alkenes and polymers with spacer length n = 5, respectively. For both alkenes and polymers, the replacement of an n-alkyl group by an n-alkoxy group results in an increase in the nematic thermal stability (about 25–30°C).

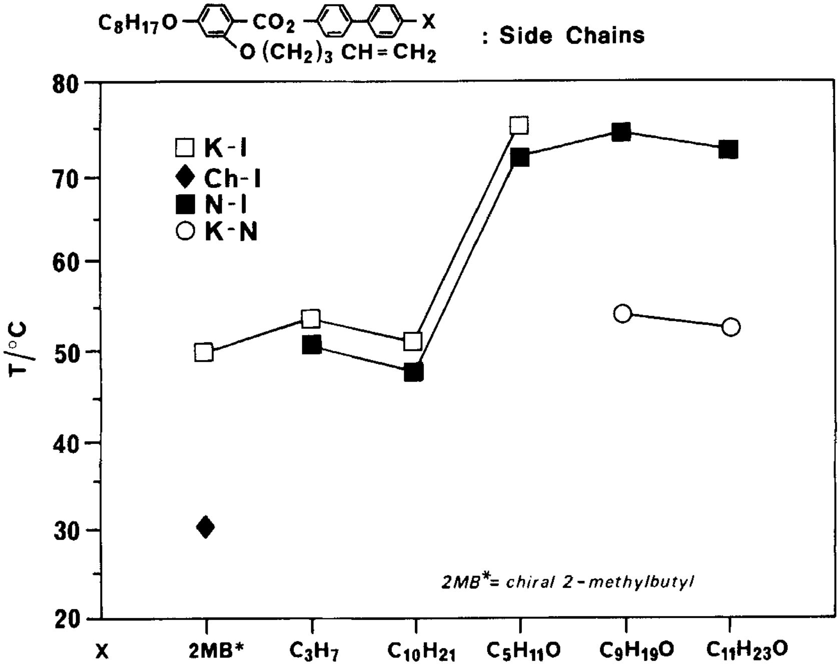


FIGURE 3 Effects of the terminal group X on the transition temperatures of alkenes.

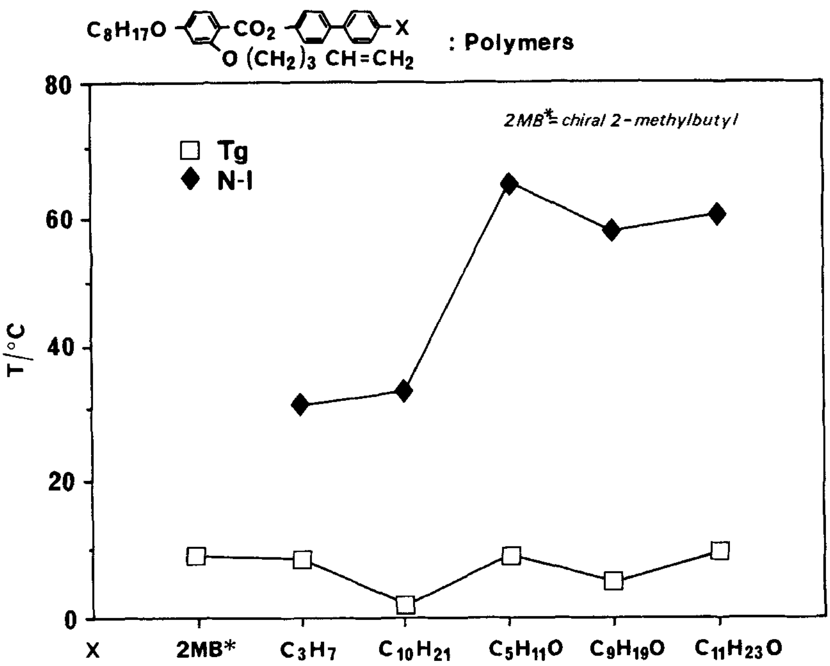


FIGURE 4 Effects of the terminal group X on the transition temperatures of SCLCP.

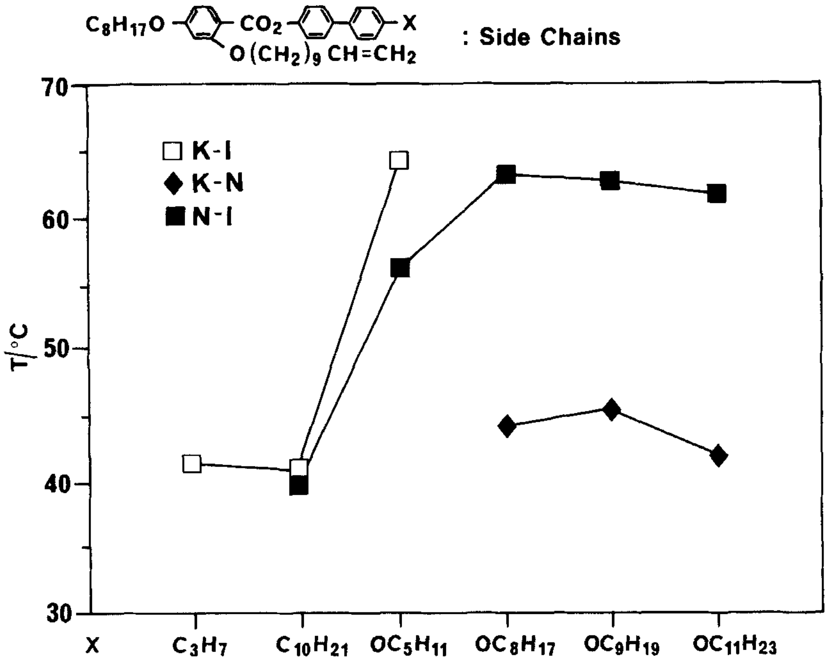


FIGURE 5 Effects of the terminal group X on the transition temperatures of alkenes.

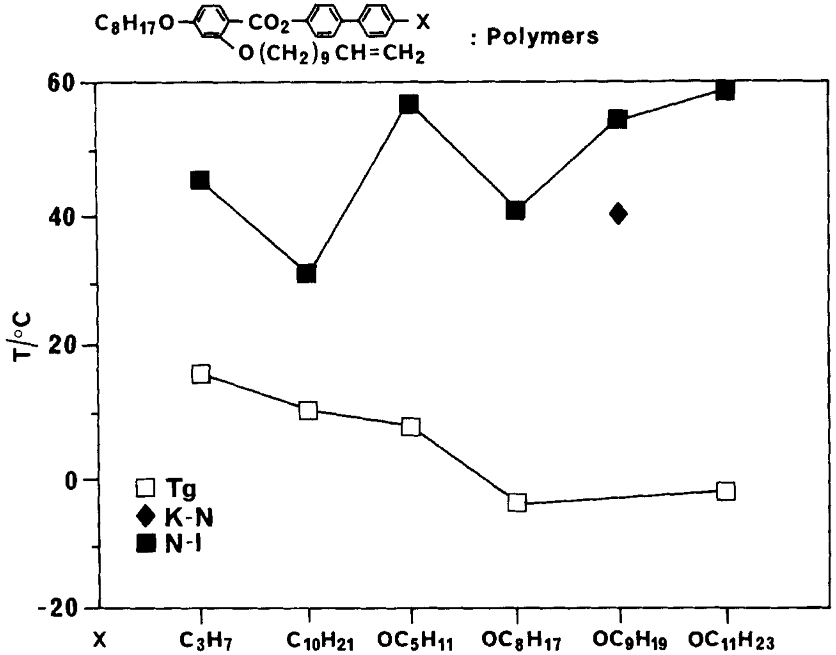


FIGURE 6 Effects of the terminal group X on the transition temperatures of SCLCP.

Tg values for the polymers are not so affected and remain at about the same low level (0–10°C). As a result all the polymers with X = n-alkyl or n-alkoxy exhibit enantiotropic nematic phases. As can be seen in Figure 3, the m.p.s. of the side chain precursors are subject to much wider fluctuations, and for x = n-alkyl or n-alkoxy, only with the higher alkoxy homologues ($C_9H_{19}O$ and $C_{11}H_{23}O$) are enantiotropic nematic phases observed.

The chiral 2-methylbutyl group (2MB*) gives a monotropic cholesteric phase in the alkene (3h). $T_{N^*\text{-}I}$ is low (30°C) as a consequence of the chain branching, and not surprisingly this group does not give a mesomorphic polymer (1h).

The corresponding results for spacer length n = 11 are depicted in Figures 5 and 6. Similar trends emerge, with an alkoxy substituent again promoting greater nematic thermal stability than an alkyl substituent. However, the differences in $T_{N\text{-}I}$ values between the alkenes and the polymers are not as marked as those with the shorter spacer, and although the Tg values of the polymers do not fluctuate as markedly as the m.p.s. of the alkenes, they do vary a little more than those for the 5-spacer polymers.

When the chiral ethyl carbolactate group [X = $CO_2CH(CH_3)CO_2CH_2CH_3$] was substituted as X on the biphenyl ring, the alkenes (3q, r) did not exhibit chiral nematic properties. Instead, the alkenes gave monotropic smectic phases (I $\rightarrow S_A \rightarrow S_C^* \rightarrow$ S) at temperatures well below the melting point. As a consequence of the general decrease in clearing temperatures from alkene to polymer, the corresponding polymers (1q, r) were not liquid crystalline (isotropic glasses).

The effect of variation in the length of the alkyl chain in the terminal phenyl ring is illustrated by alkenes (**3a**, b, f) where X = OC_9H_{19} and (**3i**, s) where X = $C_{10}H_{21}$, and the polymers (**1a**, b, f) and (**1i**, s). Increasing the length of the alkyl chain leads to similar increases (about 5°C) in T_{N-I} values in both alkenes and polymers, and to decreases in Tg values in the case of the polymers. With a methoxy group no liquid crystal phases are observed in either alkene (**3a**) or polymer (**1a**).

The effect of spacer length (n = 5, 8, 11) was investigated in two instances: R = C_8H_{17}, X = OC_9H_{19} (**3f**, j, o and **1f**, j, o) and R = C_8H_{17}, X = $C_{10}H_{21}$ (**3d**, i, l and **1d**, i, l). For all of the alkenes there is a reduction in T_{N-I} value as the spacer length is increased, with the larger reduction being observed from n = 5 to n = 8. This decrease in T_{N-I} value is presumably due to increased interference of the spacer group in the nematic ordering. The T_{N-I} values for the polymers are given in Table III.

The overall trend is a slight *decrease* in T_{N-I} as the spacer length is increased. Keller *et al.*[2] also found a reduction in T_{N-I} on going from spacer length n = 4 to n = 10. This result is at variance with the normal trends for terminally-attached SCLCPs where isotropization temperatures tend first to decrease and then to increase with increasing spacer length, usually with a concomitant odd-even effect.[10] Increasing the spacer length leads to greater decoupling between the motions of the polymer backbone and the side groups. As such, the polymer backbone will be less restricted by the nematic ordering of the side chains. In laterally-attached SCLCPs, this may result in the "mesogen-jacketed" type structure breaking down (particularly on increasing temperature, when entropy factors become more important), and being replaced by an oblate N_I type structure, with the laterally-attached mesogens possibly behaving as "quasi-terminal pendents" (Figure 7). The

TABLE III

The effect of spacer length, n, on T_{N-I} values (°C) of the polymers

	X = OC_9H_{19}			X = $C_{10}H_{21}$	
No.	n	T_{N-I}	No.	n	T_{N-I}
1f	5	58.0	**1d**	5	33.9
1j	8	66.8	**1i**	8	32.3
1o	11	54.4	**1l**	11	31.5

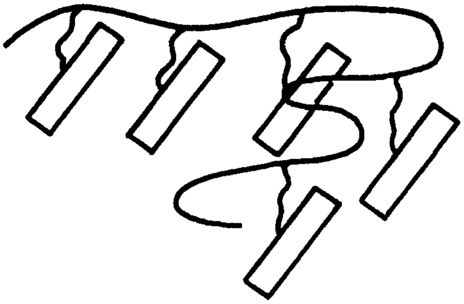
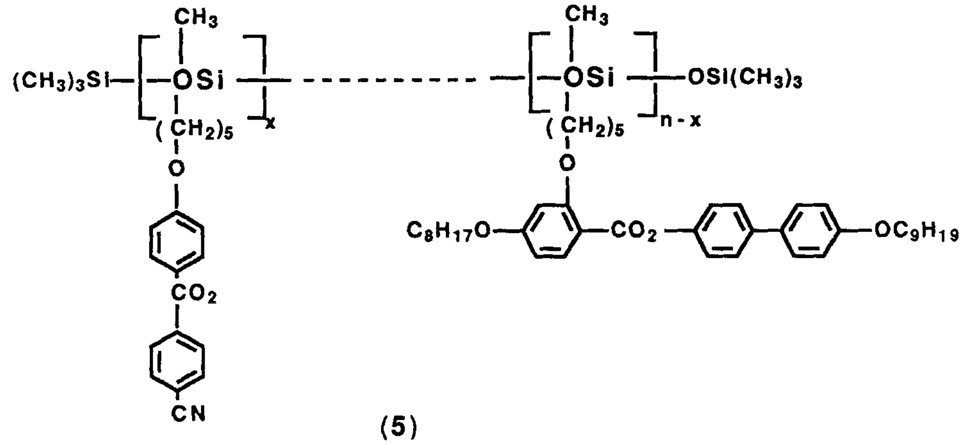


FIGURE 7 Oblate (N_I) model for a SCLCP with the laterally attached mesogenic groups behaving as "quasi-terminal pendents."

consequent distortion to the nematic field will develop a large nematic elastic energy, resulting in a lowering of the nematic-isotropic transition temperature.

This quasi-terminal behavior may also be a feature of statistical copolymers containing both laterally and terminally attached mesogenic side groups.



(5)

In particular in the copolymer series (5), as x is varied, the thermal properties[11] of the siloxane copolymers change in the manner shown in Figure 8.

In the lateral nematic homopolymer the mesogenic groups may cause a prolate N_{III} arrangement of the backbone of the type depicted in Figure 2 to be adopted. As terminally attached mesogenic groups are introduced they can take up a similar arrangement around the prolate backbone, without overly affecting the nematic order, so explaining the reasonable constancy in $T_{N\text{-}I}$—Figure 8. N_{III} was conceived as having the spacer in a state of strain, because of the dominance of the nematic

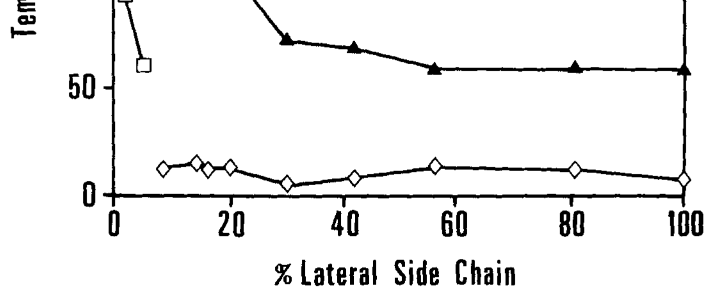


FIGURE 8 Changes in transition temperatures and mesophase type as the percentage of laterally attached mesogenic groups is increased in the statistical side-chain copolymer (5).

coupling—backbone to side chain. Here however, the backbone is polysiloxane (about as flexible and non-nematic as you can get), and this nematic coupling is presumably absent. If therefore the spacers are bent round, it must either be (*a*) because they want to be or (*b*) because the laterally attached side chains couple nematically to the terminally attached and force them to be in the N_{III} state. Effect (*a*) would presumably generate odd:even effects and (*b*) would give a sensitivity to x in (**5**).

Conversely, in the terminal smectic homopolymer, the polymer backbone is likely to tend towards an oblate conformation, since the mesogenic sidechains are confined in layers, and the backbone, being firmly attached to them, will be drawn into the planes between layers, although entropic relief might be obtained *via* 'layer hops.' As laterally-attached mesogenic groups are introduced into this arrangement, they are at first likely to behave as quasi-terminals as depicted in Figure 7; nevertheless they will significantly disrupt the smectic ordering and lead first to sharp drops in transition temperatures (Figure 8), and then to the abrupt phase change from smectic to nematic, with the latter phase being likely to be initially of the oblate N_I type.

Eventually as more lateral mesogenic groups are included in the copolymer, a switch must occur from oblate N_I to prolate N_{III}. This is illustrated schematically in Figure 9.

Further support for this hypothesis may come from the dielectric studies carried out by D. G. McDonnell at R.S.R.E. (Malvern, England) on the statistical copolymer (**6**) with 75% terminally attached side chains. A change in the sign of the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel}\text{-}\varepsilon_{\perp}$, from negative to positive occurs as the temperature is increased.

An explanation for this may be that at low temperatures the copolymer adopts a prolate arrangement as depicted in Figure 9—but as the temperature is increased and the entropic contribution to the free energy of the system becomes more important, the polymer changes to the more entropically favorable oblate arrangement.

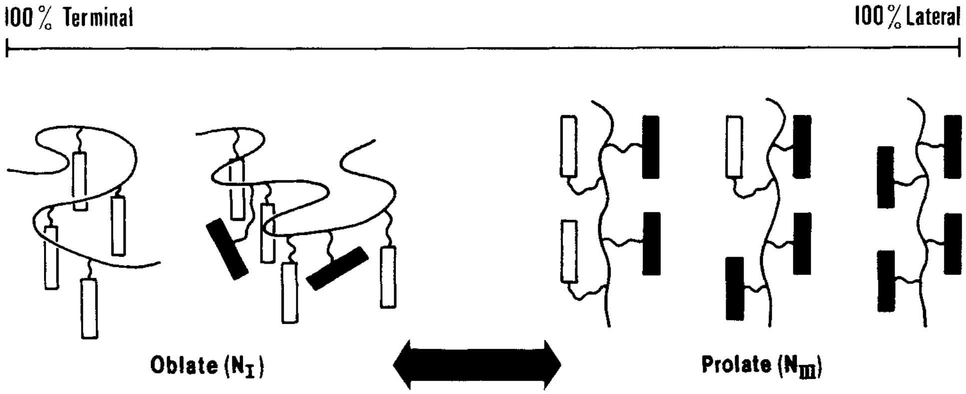
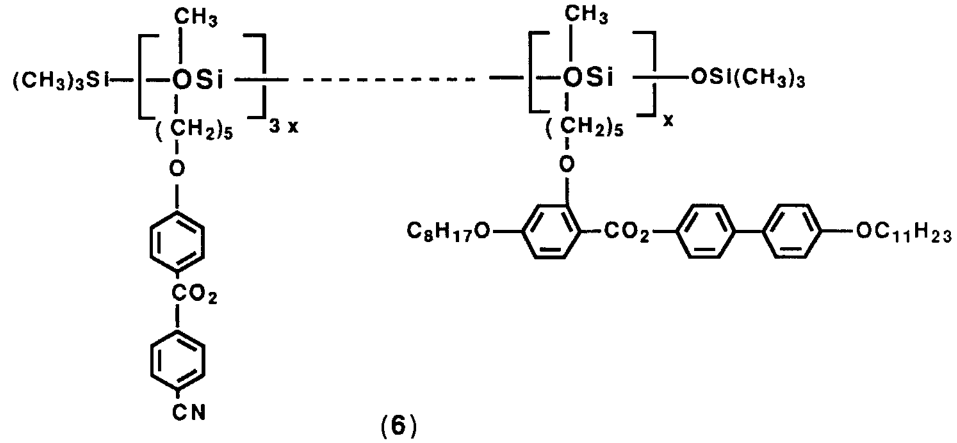


FIGURE 9 Proposed change from the oblate (N_I) to the prolate (N_{III}) model as the percentage of laterally attached mesogenic groups is increased in the statistical side-chain copolymer (**5**).



(6)

The terminally-attached polymeric analogues (**2** a–f) of some of the laterally-attached species illustrate (Table II) the dramatic effects of changing the point of attachment to the polymer backbone. The relevant alkenes (**4** a–f) have much higher melting and clearing points, and for n = 6 and 11 have smectic phases. In the alkenes (**3** b–p, s), the lateral alkyl chain precludes smectic ordering and causes reductions in transition temperatures. The polymers (**2** a–f), in direct contrast to their laterally-attached nematic analogues, are all crystalline, with high melting points and clearing points, and are predominantly smectic materials.

Within the series, the following trends are observed. For both alkenes and polymers, members of the —OC_9H_{19} series (**2**, **4** a–c) have higher melting and clearing points than the corresponding members of the —$C_{10}H_{21}$ series (**2**, **4** d–f). Increasing the spacer length n results in lower clearing points and more pronounced smectic character in both alkene series (**4** a–c, d–f). The latter is also true of the polymers in that only 2d ($C_{10}H_{21}$, n = 3) has a nematic phase. One final point is that both alkenes and polymers tend to give mainly tilted smectic phases (S_C), phase identification at present having been confined to optical microscopy.

4. EXPERIMENTAL

All alkene precursors were synthesized by standard procedures, and were purified by column chromatography and subsequent recrystallization. Their structures were confirmed by infra-red spectroscopy (Perkin-Elmer 783), nuclear magnetic resonance (Jeol JNMGX-270 MH_3, fourier transform spectrometer) and mass spectrometry (Finnegan MAT 1620).

Polydispersity (M_w/M_n) values for the polymers were determined relative to polystyrene standards by gel permeation chromatography (Gel Mix, THF, Polymer Laboratories, Church Stretton, Shropshire, UK). Transition temperatures were measured by differential scanning calorimetry (Perkin-Elmer DSC-2C with data station) and optical microscopy (Olympus BDSP 753 polarizing microscope) in conjunction with a Mettler FP52 heating stage and temperature control unit.

5. CONCLUSIONS

Dramatic differences in properties between analogous laterally- and terminally-attached SCLCPs were observed, both in phase type and transition temperatures. Wang and Warner's model for nematic ordering in SCLCPs may offer a helpful explanation of these effects. Supporting evidence for the application of this model was provided by thermal and dielectric data on laterally- and terminally-attached copolymers. Structural changes in both lateral and terminal polymers considered in this paper tend to influence transition temperatures according to the same empirical rules as those applicable to low molar mass LC systems.

Dielectric studies on these materials are currently being undertaken by Prof. G. Williams at the University of Swansea and will be discussed in a forthcoming publication.

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