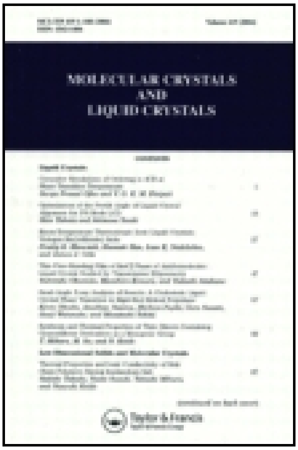

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Effects of Molecular Structure on the Properties of Terminally Cyano-Substituted Side Chain Liquid Crystalline Polysiloxanes

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Effects of Molecular Structure on the Properties of Terminally Cyano-Substituted Side Chain Liquid Crystalline Polysiloxanes[†]

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(*Received August 21, 1984*)

The synthesis and properties of a range of liquid crystalline side chain polysiloxanes are described. The effects of changes in chemical structure, such as lateral substitution, on the properties of these materials are discussed, and comparisons are made with the effects of similar structural changes in low molar mass materials. By selecting suitable side chains for homopolymers and copolymers, room temperature smectic, nematic and cholesteric (chiral nematic) polysiloxanes of positive dielectric anisotropy have been prepared, including the first example of a nematic siloxane homopolymer containing a cyano-group.

INTRODUCTION

Side chain liquid crystalline polysiloxanes are prepared,[1] as in Figure 1, by the interaction, in the presence of an appropriate Pt catalyst, of a mesogenic unit, , containing a terminal double bond, with a suitable poly(methyl hydrogen siloxane).

Polysiloxanes have several advantages over other types of polymer, particularly because of the great flexibility of the backbone, which consequently confers a low glass transition temperature (Tg) upon the polymer. The flexible alkylene spacer is necessary[2] to decouple, to some extent, the motions of the mesogenic moieties and the back-

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[†] Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.

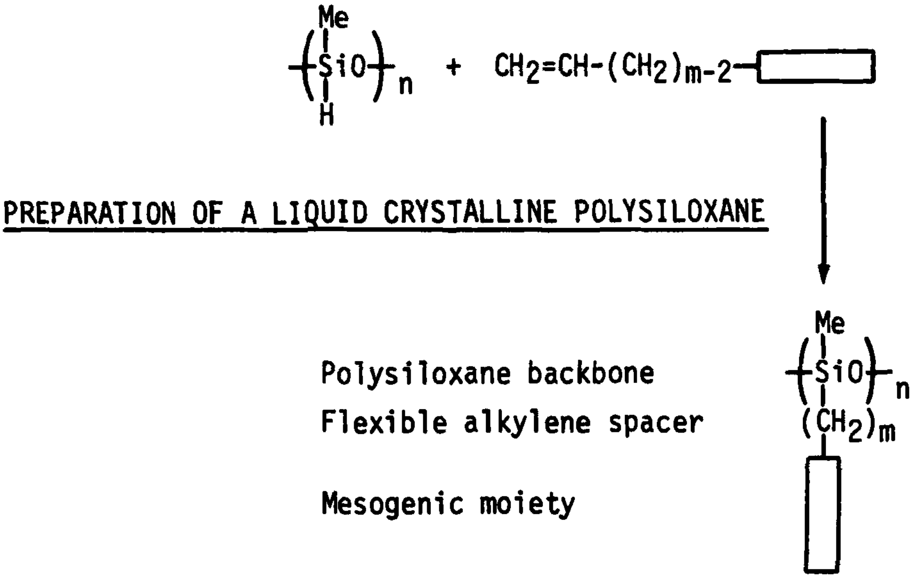
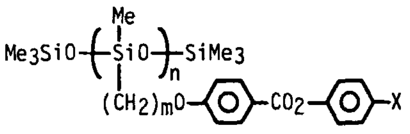


FIGURE 1 Preparative procedure.

bone, thereby allowing the production of a room-temperature mesophase.

Most of the liquid crystalline polysiloxanes which have been produced to date have been based upon the structure given below.



where X = OAlkyl,[1] CO_2Alkyl[3]

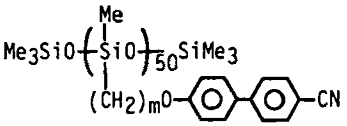
Some copolymers have been produced where $X = NO_2$ or halogen,[4] in order to make materials of positive dielectric anisotropy ($+\Delta\epsilon$), but very few polysiloxanes have been prepared in which the mesogenic moieties contain a terminal cyano-group. This is for two main reasons: (a) if a very reactive platinum catalyst is used in the hydrosilylation reaction (Figure 1), cross-linking occurs due to an addition reaction between the cyano-group and the polymer backbone;[4] (b) cyano-containing polysiloxanes which have been reported[5] have all been smectic, not nematic. Because most of the initial interest in liquid crystalline polymers lay in the production of nematic materials for possible use in electro-optical display devices, this may have discouraged further investigation of such systems.

Results, however, increasingly show that the viscosities, and hence the response times, of most nematic polymers are too high for them to be considered as useful replacements for low molar mass nematic materials in any fast-switching device, such as the twisted nematic device.[4] Attention is, therefore, increasingly being directed towards the use of polymer liquid crystals as durable storage display devices, where information may be stored below *Tg* or in the smectic state, or as a light-reflecting helical cholesteric structure that may be retained 'indefinitely' below *Tg*. Low molar mass smectic *A* devices[6] with a storage capability are already well-established, and it seems likely that LC polymers may be usefully employed in this area, where viscosity is not such an important parameter.

Thus, it seemed to us that a study of LC polysiloxanes with terminally cyano-substituted mesogenic moieties would be useful, especially in view of the fact that, so far, no systematic investigations have been carried out on the effects of changes in chemical structure on the properties of this relatively new type of liquid crystal.

RESULTS AND DISCUSSION

The first materials to be prepared (I) were 4-cyanobiphenyl derivatives, similar to the well-known low molar mass materials[7] (the 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls) which are of great technological importance. Transition temperatures for these polymers and those of the corresponding vinyl precursors, $CH_2 = CH(CH_2)_{m-2}OC_6H_4.C_6H_4CN$, are given in Table I.



(I)

The results given in Table I show some characteristic trends:

1. There is an increase in order of the system on going from vinyl precursor to polymer. This increase in order manifests itself in two ways: (a) the clearing temperatures of the polymers are much higher than those of the monomeric precursors (95° on average); (b) the

TABLE I

Transition temperatures (°C) for vinyl precursors and materials of structure (I), and enthalpies of the S_A-I transitions for the polymers (I)

	Monomer			Polymer			
	m	K-N (I)	N-I	m	Tg	S_A-I	Δ*H* (cal g^{-1})
a	3	80	(79)	3[a]	40	152	1.0
b	4	67.5	(36)	4	28	132.5	0.8
c	5	88	(71)	5[a]	14.5	169.5	1.3
d	6	35	52	6	13.5	165.5	1.3

[a] These materials have been reported by H. Ringsdorf and A. Schneller,[5] who give transition temperatures as *T*g = 32°, S-I = 117°(*m* = 3), and *T*g = 16°, S-I = 152° (*m* = 5).

K-N (I) = crystal to nematic LC (isotropic liquid) transition (melting point)
N-I = nematic to isotropic liquid transition
*T*g = glass transition temperature
S_A-I = smectic *A* to isotropic liquid transition
( ) = monotropic transition
Δ*H* = enthalpy of clearing transition

mesophase exhibited is now the more ordered smectic *A* phase, rather than the nematic phase of the low molar mass precursor.

2. Increasing the length of the flexible spacer lowers *T*g.

3. An 'odd-even' spacer effect operates (an even number of carbon and oxygen atoms in the spacer promotes *higher* clearing points).

The first two trends are well known for LC side chain polymers.[8] The 'odd-even' effect, well known for low molar mass mesogens and LC main chain polymers, has also been reported for side chain polymers,[9] and is presumably due to similar causes; i.e., a spacer containing an even number of (carbon and oxygen) atoms allows the side chains to align normal to the polymer backbone, thus minimising steric interference and promoting the thermodynamic stability and clearing point of the mesophase.

Thus, the materials (I) are characteristic LC side chain polymers, confirming that siloxane homopolymers with side chains of positive $\Delta\epsilon$ tend to be smectic.[4]

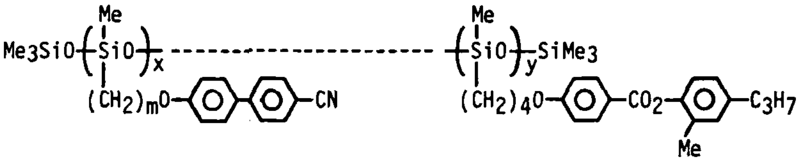
TABLE II

Transition temperatures (*T*g and clearing temperature *T*c) in °C and enthalpies of clearing for materials of structure (II)

	m	*x*	*y*	Phase type	*Tg*	*Tc*	Δ*H* (cal g^{-1})
a	6	25	25	Smectic *A*	4.0	86	0.53
b	5	35	15	Smectic *A*	7.4	151	0.73
c	5	25	25	Smectic *A*	7.4	122	0.80
d	5	16	34	Nematic	4.4	53	0.16

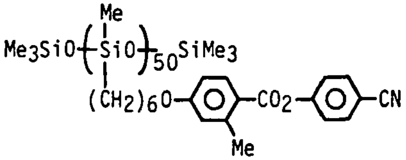
It is well known from studies of low molar mass mesogens[10] that the introduction of a suitable lateral substituent into a molecule may destabilise a smectic phase more than a nematic; if this could be achieved for a LC polysiloxane then it would be possible to produce a nematic material of strongly $+\Delta\epsilon$.

In an attempt to achieve this, we prepared copolymers of structure (II). Transition temperatures for these materials are given in Table II.



(II)

As can be seen from Table II, the 2-methyl-substituted ester gives the polymer a lower *T*g and *T*c and, in sufficiently high concentration, produces a nematic phase. These results show that it is feasible to produce a cyano-substituted nematic polysiloxane. The next logical step was to incorporate the lateral methyl group directly into a terminally cyano-substituted mesogenic unit. This was realised in polymer (III).

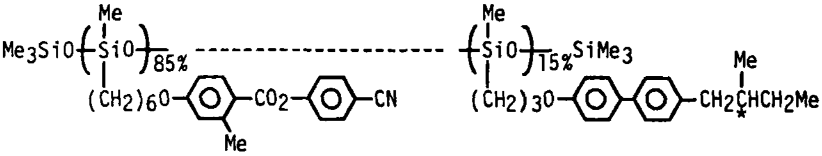


(III)

*T*g = 9°C, N – I = 46°C ($\Delta H = 0.2$ cal g^{-1})

This polymer was the first example of a nematic siloxane homopolymer containing a cyano-group.

Making a copolymer from the vinylic precursor used to prepare polymer (III) and a chiral alkene, resulted in polymer (IV), a room temperature cholesteric polymer which reflects light in the ultraviolet.



*T*g = 5°C, Ch-I = 31°C ($\Delta H = 0.1$ cal g^{-1})

Supporting data relating to polymers (I)–(IV)

Polymers (I)–(IV) were characterised by one or more of the following methods:

(a) *X-ray diffraction.* Results of work carried out by Sutherland *et al.*[11] on two representative polymers are given in Table III.

In the case of polymer (Ic), the layer spacing for the S_A phase is about 1.6 × the length of the mesogenic side chain. This is evidence for antiferroelectric short-range order—the so-called 'antiparallel correlation" effect— giving rise to an interdigitated bilayer structure similar to that of the low molar mass cyanobiphenyls.[12] The results for polymer (IIc), however, show that the layer spacing has decreased to less than 1.2 × the length of the side chain. Thus, the structure of the S_A phase is now much closer to that of a monolayer S_A phase. This effect is also found in mixtures of low molar mass cyanobiphenyls and esters.[13]

(b) *DSC.* For materials (I)–(IV), all the S_A-I transitions have enthalpies in the range 0.5–1.3 $\mathrm{cal\,g^{-1}}$, with a mean value of 0.92 $\mathrm{cal\,g^{-1}}$. The cholesteric and nematic polymers have clearing enthalpies in the range 0.1–0.2 $\mathrm{cal\,g^{-1}}$. Thus the magnitude of ΔH provides useful evidence for mesophase characterisation.

(c) *Polarising microscopy.* All of the materials designated as S_A show a similar behaviour on being cooled from the isotropic liquid. When cooled to a few degrees below T_{S_A-I}, the texture appears as bâtonnets which, on annealing, coalesce to form large, well-formed focal-conic fans against a background of isotropic liquid. Further cooling converts the remaining isotropic liquid into smaller focal-conic fans. The temperature range defining the change from fully isotropic liquid to the fully-formed fan texture varies from about 5°C for the homopolymers to > 10°C for the copolymers. The existence of this biphasic region is probably due to a combination of the high viscosity and the polydispersity of the materials. Low molecular weight mixtures also show a broadening of the various temperature ranges. Apart from the breadth of the transition, the appearance of

TABLE III

X-Ray diffraction data relating to polymers (Ic) and (IIc)

Polymer	Molecular length (Å)	Layer spacing (Å)
(Ic)	18.1	28.7
(IIc)	20.24 (average)	23.8

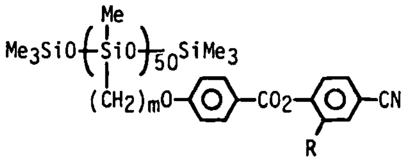
the focal-conic fans is characteristic of low molar mass S_A materials.

In contrast to the S_A materials, the texture of the two nematic polymers appears gradually across the whole field of view, on cooling below T_{N-I}. The natural texture appears to be homogeneous–usually a pale yellow or orange colour of fairly low birefringence. If the sample is viewed near an air-bubble, or if shear strain is applied, a bright, rainbow-like birefringence is observed. Even after annealing for several days, no trace of a fan texture is observable.

The cholesteric mesophase manifests itself similarly to the nematics; the clearing point is close to room temperature and, after being heated, is slow to reverse. The cholesteric phase appears very characteristically, as small, focal-conic fans across most of the field of view, with the rest of the field of view made up of planar *Grandjean* texture which (viewed microscopically) is of a dark blue colour with white disclination walls. This texture is unmistakably cholesteric.

Homologous series

Having established that cyano-substituted polysiloxanes could be obtained as smectic, nematic, or chloesteric materials, we prepared two homologous series (V) to get a more quantitative insight into the effects of lateral substitution and spacer length alternation. Transition temperatures are given in Table IV. As can be seen, the polymers without a lateral substituent (R = H) are all smectic *A* in character, as we would expect. Less predictable is the fact that for $m > 5$, no glass transition is detectable by DSC; instead, we find a well-defined melting peak at a much higher temperature. This phenomenon must be caused by the introduction of the inter-ring ester linkage, as a similar crystalline ordering is not present in the corresponding cyanobiphenylyl polymers (I) up to $m = 6$. Results are more complex for the polymers with laterally-substituted side chains. The homologues with the shortest spacers (Vh) and (Vi) are isotropic. Clearly, the lateral methyl group exerts a more pronounced destabilising effect on the mesophase when the spacer is short (see also the naphthyl polymer (VII)). For $m = 5$ and 6, a nematic mesophase is observed, similar to that of polymer (III),



$\mathrm{Me_3SiO}\left(\mathrm{Si(Me)O}\right)_{50}\mathrm{SiMe_3}$, side chain $\mathrm{(CH_2)_mO{-}C_6H_4{-}CO_2{-}C_6H_3(R){-}CN}$

(V)

TABLE IV

Transition temperatures (°C) for the polymers (V)

No	*m*	R	*Tg*	K-S_A	S_A-I	N-I	Δ*H* (clearing)
a	3	H	29	—	161.5	—	0.48
b	4	H	26	—	150	—	0.43
c	5	H	—	107	183.5	—	0.53
d	6	H	—	55	181.5	—	0.76
e	7	H	—	88	189	—	1.10
f	8	H	—	62	194	—	0.96
g	11	H	—	76	198.5	—	1.50
h	3	Me	40	—	—	—	—
i	4	Me	24	—	—	—	—
j	5	Me	19	—	—	65	0.37
k	6	Me	7	—	—	48	0.22
l	7	Me	9	—	87	—	0.59
m	8	Me	9	—	102	—	0.60
n	11	Me	8	45	131	—	0.95

Other symbols have been defined in Table I

and longer spacers once again give purely S_A phases. In contrast to the unmethylated polymers, all of these materials ((Vh)–(Vn)) have glass transitions; the crystallinity, however, is strongly suppressed, and only for $m = 11$ is a low-temperature melting peak discernible. Thus, the lateral methyl group very effectively inhibits crystalline packing of the side chains–an effect which is also found in low molar mass liquid crystal materials.[10]

Polymers (Vj) and (Vk) have both been classified as nematic on the basis of polarising microscopy studies, i.e., they have textures similar to polymers (IId) and (III), and show no tendency to form focal-conic fans, even on prolonged annealing. The clearing enthalpies of these materials are again lower than those of the smectic *A* polymers, although for polymer (Vj), the enthalpy of clearing, 0.37 cal g^{-1}, is approaching that of a S_A. This polymer has also been examined by X-ray diffraction[14] and has been shown to exhibit some degree of layer structuring. Thus, although polymer (Vj) has been assigned as nematic, it does have some smectic characteristics. It is significant that the spacer contains an even number of (carbon and oxygen) atoms, a factor which allows the side chains to pack parallel with the minimum of interference from the backbone. The existence of short-range smectic-like order in terminally cyano-substituted nematic materials is not of course purely a phenomenon of polymers; it is a well-established feature of the nematic phases of cyano-substituted mesogens of low molar mass.[15]

Behavioural trends for the two series may readily be discerned by plotting graphs of the transition temperatures versus *m* (Figures 2(a) and (b)).

A study of Figure 2(a) reveals an 'odd-even' alternation effect for the S_A-I transition temperatures. As expected, the clearing temperatures for polymers with an even number of (carbon and oxygen) atoms in the spacer lie on the higher curve. As *m* increases, the two curves converge and must be almost coincident by $m = 11$, paralleling the increasing flexibility of the system. As plotted, it is obvious that for $m = 7$ (Ve), the clearing point may be about 3°C low, possibly due to impurities.

It is noticeable that the K-S_A transitions also appear to show an 'odd-even' alternation effect. Again, polymers with an even number of atoms in the spacer lie on the higher curve, which is falling; the lower K-S_A line seems to be rising, and the two lines would appear to coincide by $m = 11$. This sort of alternation effect could not be

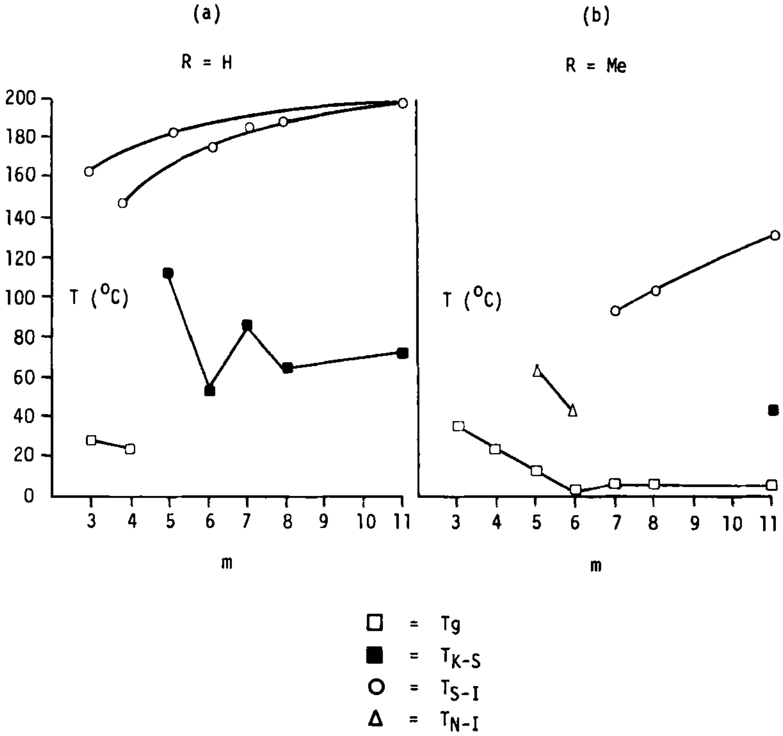


FIGURE 2(a), (b) Graphical representation (transition temperatures versus number of methylene units (*m*) in the-$(CH_2)_m$O- spacer unit) of the data for the polymers (V)—see Table IV.

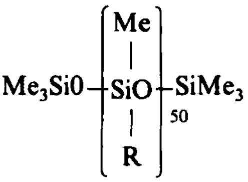
predicted for the melting points of low molar mass materials, but it does seem likely that spacer length in side chain polymers, with its consequent effect on side chain packing, must be a particularly important factor affecting the melting behaviour.

In contrast to Figure 2(a), Figure 2(b) does not reveal alternation behaviour. The two nematic materials are in agreement with our expectation that polymers with 'even' spacers have higher clearing points than those with 'odd' spacers, but no trend is indicated. The S_A-I line is almost linear and does not show an alternation effect. If the line is extrapolated back to $m = 5$, it coincides nicely with the clearing point of polymer (Vj). This fact may be regarded either as supportive evidence for some degree of S_A character for this polymer, or as pure coincidence. Overall, the dominant effect operating in these polymers is the strong drive towards a more ordered system as the spacer length is increased. This is seen on going from the two isotropic polymers, through the two nematics and then the smectics, and finally to a crystalline system. The magnitude of this effect is probably sufficient to mask any additional, small alternation effect.

Perhaps the most significant feature revealed in Figure 2(b) is not a mesophase transition line, but the glass transition line. The glass transition temperature of a LC polymer is dependent on the flexibility of the backbone, which is constant for a given backbone, and the length of the flexible spacer, which changes in a regular way. Thus, as m is steadily increased, we expect to observe a steady decrease in the value of Tg down to some limiting value. This is exactly what is found for $m = 3$–6 and $m = 7$–11; however, the value of Tg 'jumps' on going from $m = 6$ to $m = 7$. This is a significant result because this increase in Tg must reflect an increase in the ordering of the side chains, i.e., a change from a nematic order to a smectic order, in agreement with the microscopic observations. Thus, a close inspection of the Tg values for a homologous series may provide an indirect method of evaluating mesophase type in side chain polymers.

Other structural alterations

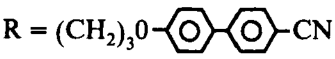
Starting with the basic structure given below, a number of simple modifications can be made.

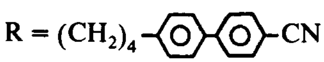


$$\mathrm{Me_3SiO}\left[\begin{array}{c}\mathrm{Me}\\ |\\ \mathrm{SiO}\\ |\\ \mathrm{R}\end{array}\right]_{50}\mathrm{SiMe_3}$$

By altering one structural feature at a time, we can get some idea of the importance of any particular structural unit in the production of a polymer mesophase.

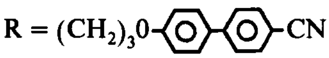
(a) *Alteration of the spacer: alkoxy → alkyl.* All of the LC polysiloxanes so far reported have contained a flexible alkylene spacer linked, via an oxygen atom, to the mesogenic core. It is of interest to see the effect of replacing this oxygen with a methylene group; this was done by preparing polymer (VI).

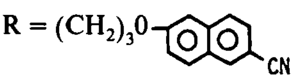
(Ia)  $Tg = 40°$, S_A-I = 152°

(VI)  $Tg = 12°$, S_A-I = 130°

A comparison with (Ia) shows that changing O to CH_2 next to the biphenylyl unit greatly increases the flexibility of the polymer, giving rise to a much lower glass transition temperature. The polymer is also less mesogenic, however, and the clearing temperature is lowered. This is consistent with the behaviour of similar low molar mass mesogens.[7] Thus, the flexible spacer cannot be regarded simply as an 'inert' structure used to decouple the motions of backbone and mesogenic moieties; its chemical nature can have a significant influence on mesophase range and thermal stability.

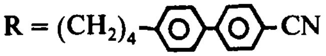
(b) *Alteration of the mesogenic unit: 4, 4′-biphenylyl → 2, 6-naphthyl.*

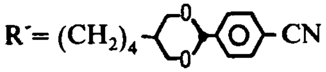
(Ia)  $Tg = 40°$, S_A-I = 152°

(VII)  $Tg = 31°$, No mesophase

Changing the 4, 4′-biphenylyl unit to 2, 6-naphthyl completely destroys the mesophase. This is a very drastic change (> 120°), brought about by only a slight broadening and shortening of the molecule. The glass transition temperature is slightly lowered, probably because of the greater flexibility of the *isotropic* side chains. We have already seen that, for polymers of structure (V), the twisting and broadening caused by the introduction of a lateral methyl group has a disastrous effect on mesophase thermal stability, *especially for polymers with short spacers*. Thus the fact that polymer (VII) does not have a mesophase is not so surprising as it might at first appear. By analogy with the two homologous series (V), we would expect liquid crystallinity to occur only for longer spacer lengths.

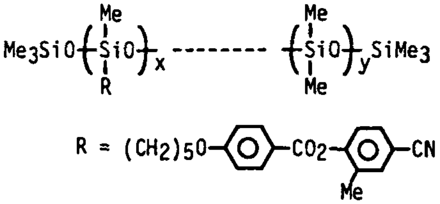
(c) *Alteration of the mesogenic unit: phenyl → trans-1, 3-dioxanyl.*

(VI)

$Tg = 12°, S_A\text{-}I = 130°$

(VIII)

$Tg = 21°, S_A\text{-}I = 167°$

This change substantially raises the clearing point compared with polymer (VI), and this is consistent with the behaviour of low molar mass mesogens.[16] Tg is also raised, but less sharply.

(d) *Alteration of the backbone.* Here, the backbone is 'diluted' with dimethylsiloxane units, through formation of a copolymer of the structure below.



(Vj) $x = 50, \quad y = 0 \qquad Tg = 19°, \quad N\text{-}I = 65°$

(IX) $x = 29, \quad y = 21 \qquad Tg = 15°, \quad N\text{-}I = 56.5°$

This change makes the polymer more flexible, thus lowering Tg. The clearing point is also slightly lowered. This is consistent with results for other polymers derived from similar backbones with different side groups.[5,17]

EXPERIMENTAL

Synthetic work

All of the polymers were prepared by the interaction of the appropriate mesogenic terminal alkenes with poly(methyl hydrogen siloxane), in accordance with Figure 1. A 10% molar excess of alkene : Si-H was employed. The reaction was carried out using dry toluene solutions at 60°, completion of reaction being indicated by the disappearance of the Si-H absorption (i.r.). Chloroplatinic acid (5% w/v in isopropanol; one drop) was used as the catalyst. Repeated precipitation from toluene, chloroform, or DMF, with methanol, was followed by vacuum-drying of the polymers in their isotropic states.

Space considerations do not permit a description to be made of the wide variety of synthetic methods which was used in the preparation of the mesogenic terminal alkenes. All of these precursor alkenes were purified by column chromatography (silica gel/2 : 1 $CHCl_3$: light petroleum (b.p. 40–60°C)) followed by distillation or crystallisation; each product was characterised by n.m.r., mass spectrometry and infra-red spectroscopy, and shown to be pure by t.l.c. and h.p.l.c.

Full experimental details of these procedures will appear in the Ph.D. Thesis of P. A. Gemmell.[20]

Physical measurements

Transition temperatures were measured by polarising optical microscopy (Nikon L-Ke polarising microscope) in conjunction with a Mettler FP52 heated stage and temperature control unit, and by differential scanning calorimetry (Perkin-Elmer DSC-2C). DSC runs were carried out at 10° $\min^{-1}$; Tg values were taken at the midpoint of the transition indicated by DSC, and transition temperatures at the peak maxima given by DSC.

X-ray diffraction work was carried out on selected polymers by Dr. H. H. Sutherland *et al.*[11] of the University of Hull, and by Dr. R. M. Richardson *et al.*[14] of the University of Bristol. Many of the polymers have also been studied[18] by Dr. H. J. Coles and Dr. R. Simon of the University of Manchester who have carried out electro-optical work on electric field–induced turbulence and director reorientation effects with a view to assessing the feasibility of employing the polymers in high-contrast storage displays. Prof. G. Williams of the University of Aberystwyth has also performed dielectric studies on some of the materials.[19]

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