conference papers

Aspects of side-chain liquid-crystal polymers, especially polysiloxanes, in relation to their potential for speciality applications

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Interest in side-chain liquid-crystal polymers for speciality applications, e.g. in data storage systems, in piezo-, pyro- and ferroelectric devices and in systems requiring non-linear optical characteristics, is increasing steadily. The most popular polymers under study are those of the side-chain polyacrylate, polymethacrylate and polysiloxane types, and reference will be made to the potential of these systems for applications.

The work here described centres, however, upon homopolymers and copolymers of the polysiloxane kind. Particular emphasis is placed upon the requirement that, for applications as sophisticated as those noted above, the production of polymers with highly consistent properties is essential, and that if structure–property correlations are to be of assistance in working towards best polymer types, these must be derived from comparisons made between polymers with consistent $\overline{DP}$ and $\bar{M}_w/\bar{M}_n$.

The main areas covered are: (i) the reproducible batch synthesis of side-chain polysiloxanes by the hydrosilylation process; (ii) the importance of establishing structure–property correlations for side-chain polymers and some relevant examples; (iii) Langmuir–Blodgett side-chain polysiloxanes; (iv) polysiloxanes with side-chains linked laterally to the backbone.

(Keywords: liquid crystal; side-chain polymers; polysiloxanes; mesogenic group)

INTRODUCTION

Side-chain liquid-crystal polymers (SCLCP)[1] incorporate a fairly flexible polymer backbone to which are attached lateral groups that are mesogenic, i.e. possessed of a structure that is compatible with the production of thermotropic liquid-crystal properties in low-molar-mass systems[2]. An important prerequisite is that the mesogenic group should be linked to the backbone via a flexible spacer unit, commonly for example $(CH_2)_n$, where $n > 3$.

Types of mesogenic group (side-chain)

(i) *Calamitic groups*: rod- or lath-shaped groups attached to the flexible spacer by the ends of the rods or at a position along the sides of the rods.

(ii) *Discotic groups*: disc-shaped mesogenic groups attached at their edges to the flexible spacer and pendent to the backbone.

(iii) *Amphiphilic groups*: mesogenic groups structurally related to amphiphiles such as soaps, which form micellar lyotropic liquid-crystal phases with a solvent such as water; the mesogenic groups therefore terminate in a polar, hydrophilic function such as CO_2H or CH_2OH, and are attached to the flexible spacer at the terminus of the apolar, hydrophobic part of the amphiphile.

Because the flexible spacer decouples the motions of the mesogenic group from the backbone, the mesogenic groups are relatively free to assume orientationally ordered states similar to those adopted in equivalent low-molar-mass systems. Consequently we find long-range orientational ordering of the following types for the different classes of mesogenic side-chain in LC polymers.

Types of structural ordering of side-chains

(i) *Calamitic groups.* These may be arranged as a statistically parallel alignment of rods with no positional order of the molecular centres, as in low-molar-mass (LMM) nematics, or a statistically parallel alignment of rods with the molecular centres of gravity distributed in density planes, giving a smectic lamellar arrangement of the side-chains. As in LMM smectics, there exist all the possibilities for smectic polymorphism[3] arising from different tilt and packing arrangements in the layers. Finally, if the rod-shaped side-chains are chiral, the nematic type arrangement can adopt a helicoidal structure analogous to that of LMM cholesterics, bestowing on the polymer thermochromic characteristics. Chiral versions of the tilted lamellar smectic (S) phases are also possible, e.g. chiral S_C polymeric phases which may exhibit ferroelectric and pyroelectric properties.

(ii) *Discotic groups.* The discs may pack, without ordering of their centres, with their planes parallel, like a random scattering of pennies on a tray. This gives a nematic discotic arrangement (N_D). Alternatively, the discs may stack up in columns; the arrangement in a

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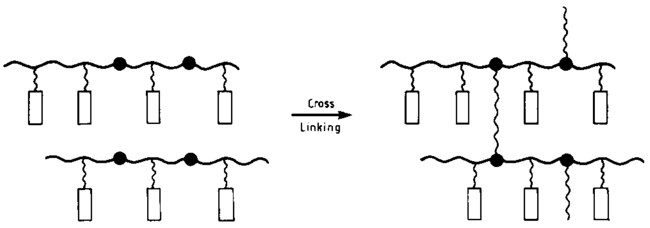


Figure 1 Formation of an elastomer network by crosslinking of partly mesogenated polymer chains, in which the full circles represent unused reactive sites

column may be regularly or irregularly spaced, and the columns themselves may be packed in tilted or untilted and differently ordered ways (e.g. hexagonal). There is therefore ample scope for polymorphism amongst these discotic columnar phases[4].

(iii) *Amphiphilic groups*. Amphiphilic side-chains may arrange themselves into a variety of micelles with associated solvent, as in LMM lyotropic liquid crystals[5]. Also amphiphilic side-chain polymers may be laid down as monolayers on water surfaces, and then, by dipping methods, transferred onto solid substrates and built up into Langmuir–Blodgett multilayers.

Elastomers

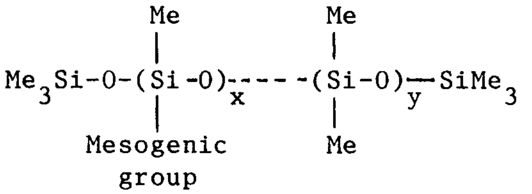
The above possibilities have also been extended by Finkelmann to include elastomers[6]. As shown in *Figure 1*, if reactive sites are left unoccupied in a partly mesogenated SCLCP, and these are then used, by means of a suitable reagent, to crosslink backbones via a flexible spacer, a liquid-crystal elastomer or rubber is formed.

Such three-dimensional elastomeric networks give macroscopic alignment of the side-chains in response to stretching, just as low-molar-mass liquid-crystal materials respond to external electrical/magnetic fields. Finkelmann has recently drawn attention[7] to a further valuable property of such elastomers. If a die with a raised or embossed pattern is pressed onto the top surface of a volume of elastomer in which the mesogenic side-chains are aligned orthogonally to that surface, local distortions of the director occur. These distortions, in the embossed pattern, may be locked into the elastomer by cooling below T_g. The distortions in fact form a pattern of light conducting pathways (of micrometre dimensions) that are visible microscopically, and this clearly has implications for use in elements for integrated circuits.

DIVERSITY OF STRUCTURAL POSSIBILITIES FOR SIDE-CHAIN LIQUID-CRYSTAL POLYMERS

If the backbone carries mesogenic side-chains all of which have identical structures, then the polymer is a side-chain *homopolymer*. However, side-chain *copolymers* can be made in which the side-chains may have two or more different structures selected from the wide variety of possibilities presented by any one of the mesogenic group types ((i)–(iii) above) or a combination of these. In the case of calamitic groups, we may also have some groups terminally attached and some laterally attached to the backbone[8]. The spectrum of copolymer side-chain types is widened still further by the possibility that some of the side-chain sites are filled by non-mesogenic groups, a technique that may be used to tune the properties of SCLCP to desired levels.

The latter situation is particularly commonly encountered in SCLCP (I) formed from a statistical poly(hydrogenmethyldimethylsiloxane) backbone where only a proportion of the silicon sites carries the mesogenic groups, and the other silicons carry methyl groups:

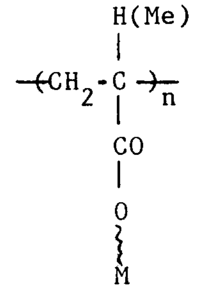


$$\mathrm{Me_3Si{-}O{-}(\underset{\text{Mesogenic group}}{\overset{Me}{Si}}{-}O)_x{-}{-}{-}{-}{-}(\underset{Me}{\overset{Me}{Si}}{-}O)_y{-}SiMe_3} \qquad \text{(I)}$$

A polymer like (I) is however often referred to as a backbone copolymer.

To the great panoply of structural possibilities arising from the above considerations of the side-chains in LCP must of course be added the structural modifications that can be achieved through using different backbones. The backbones in common use in SCLCP are shown in the structures below, where M is an appropriate mesogenic group.

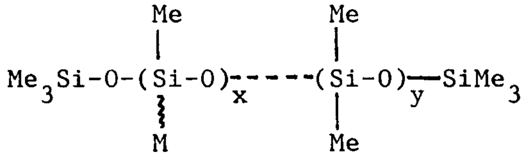
(1) *Polyacrylate* (*methacrylate*)



$$\mathrm{{-}\!\left(CH_2{-}\underset{\underset{\underset{\underset{M}{\wr}}{O}}{|}}{\underset{CO}{\underset{|}{\overset{\overset{H(Me)}{|}}{C}}}}\right)_n}$$

T_g often > room temp.

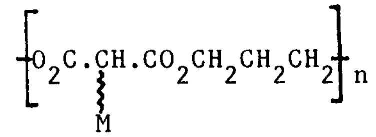
(2) *Polysiloxane*



$$\mathrm{Me_3Si{-}O{-}(\underset{M}{\overset{Me}{Si}}{-}O)_x{-}{-}{-}{-}{-}(\underset{Me}{\overset{Me}{Si}}{-}O)_y{-}SiMe_3}$$

T_g often < room temp.; $y=0$ (homopolymer).

(3) *Malonate/diol*. For example



$$\left[\mathrm{O_2C.\underset{M}{CH}.CO_2CH_2CH_2CH_2}\right]_n$$

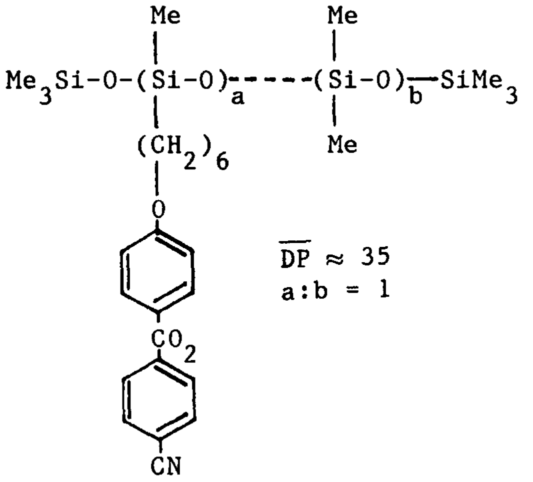
SCLCP derived from mesogenically substituted malonic esters and diols were first studied by Reck and Ringsdorf[9] and recently Zentel *et al.*[10] have adapted such systems, through crosslinking, to give elastomers which are said to have chiral S_C phases (S_C^*).

This great variety of structural types of SCLCP has created much interest—both academic and commercial. The reasons are several: (a) they provide very novel materials for physical study; (b) there is a desire to establish structure–property relationships; (c) the potential of the materials for applications, e.g. in the field of optics or electro-optics, is of interest. Reason (c) has indeed provided a strong driving force for research in the field of LCP, and currently, for instance, there is strong activity concentrated on the quest for SCP incorporating specialized dyes for use in optical data storage and retrieval systems with grey scale and a capability, when desired, for selective or bulk erasure.

SOME POTENTIAL APPLICATIONS OF SIDE-CHAIN POLYMERS

A laser-addressed data storage device[11]

Using the polymer:



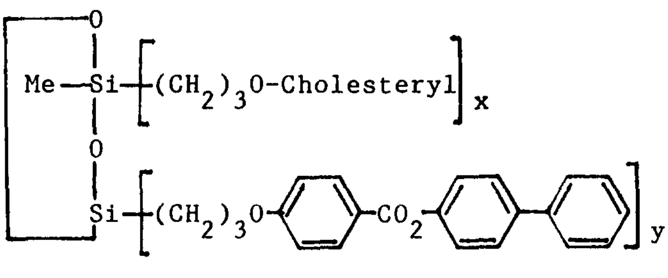
$\overline{DP} \approx 35$
a:b = 1

and through initial experimental evaluation, it was established that at 60°C, using laser pulses of $300\ \mu$s or less, write and selective erasure times were <1 ms; bulk erasure required 1–2 min. Demonstration was made of the polymer in an analogue optical data store with an unoptimized sensitivity of $12\ \mathrm{nJ}\ \mu\mathrm{m}^{-2}$ at 24°C with light of $\lambda = 632.8$ nm. The device was used to portray the fine details of an area of an Ordnance Survey Map.

Fixed-wavelength filters or reflectors

Finkelmann first demonstrated that a cholesteric SCLCP could be heated above T_g, to a temperature at which it was selectively reflecting a desired wavelength of light, and then quenched below T_g, thereby locking in both the helical structure of the cholesteric mesophase and the required optical characteristics[12]. This technique makes possible the production of cast films or coatings with defined optical properties preselected by temperature. The structural helicity and the light-reflecting characteristics of the polymer can also be controlled by the chirality of the side-chains, the incorporation of non-chiral or racemic side-chains, the ratio of non-chiral to racemic side-chains, etc.

In a related area, Eberle, Miller and Kreuzer[13] announced recently the use of mesogenated poly(hydrogenmethylcyclosiloxanes), for example, of structure (II):

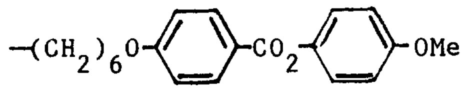


where x + y = 5 (II)

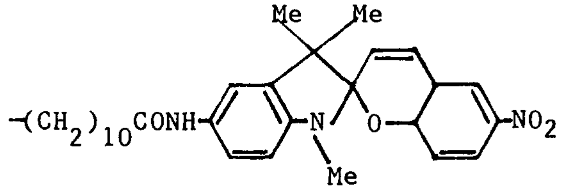
These materials give good pliable coatings on paper which reflect beautiful iridescent colours, varying with viewing angle. By the addition of pigments, it was demonstrated that the colour vs. viewing angle dependence could be reversed from blue to red with decreasing angle.

Photochromic polymers

Cabrera, Kongrauz and Ringsdorf[14] have studied polysiloxane side-chain copolymers incorporating the mesogenic group:



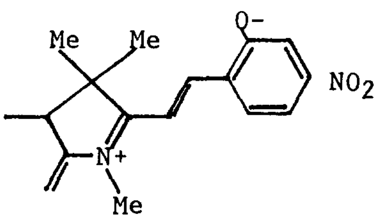
and the spiropyran moiety:



where $T_g \simeq 10$°C and T_{Cl} depended upon [spiropyran].

A photochromic effect arises from the interconversion:

Spiropyran ⇌ Merocyanine



(BLUE)

A pale pink (at room temperature) cast film becomes yellow (spiropyran) on irradiation with light of $\lambda > 500$ nm and then deep red on irradiation with light of $\lambda = 365$ nm. Aggregation effects involving dimerization of the merocyanine moieties and crosslinking of the macromolecules explain the deep-red colour. Further developments of this work were presented at a recent conference in Freiburg[15], and such systems obviously have possibilities for novel applications in imaging technology.

REPRODUCIBLE PRODUCTION OF SIDE-CHAIN POLYMERS

For such sophisticated uses, it is obviously essential that reproducible techniques of preparation are employed, so that batch variations do not influence important physical parameters such as transition temperatures, viscosity, dielectric properties, electro-optical responses, elastic constants, etc.

Structural variations quite apart, it is known that T_g and T_{CI} are affected by $\overline{DP}$ and $\bar{M}_w/\bar{M}_n = \gamma$, the polydispersity of the polymer. These are always potential variables for polymers, and we simply do not yet have the evidence to say whether $\overline{DP}$ and γ also affect some of the other important parameters mentioned above.

Other possible variables that will be mentioned later relate to copolymers, and questions such as the following:

(a) In a side-chain copolymer, is the ratio of the different side-chains really the same as that of the initial feedstock of reactants?

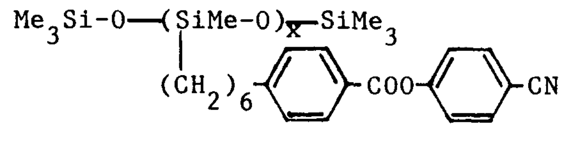
(b) In a side-chain copolymer or a polymer involving a proportion of $-SiMe_2O-$ groups, is the distribution of mesogenic side-chains or of $-SiMe(mesogen)O-$ and $-SiMe_2O-$ groups truly statistical?

Polysiloxanes

On the subject of reproducibility of product, let us first discuss SCLC polysiloxanes, which are normally prepared from a preformed poly(hydrogensiloxane) backbone (homo- or copolymer) and a terminal alkene carrying the mesogenic function, in the presence of an appropriate platinum catalyst[16], e.g. $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol (IPA), or divinyltetramethyldisiloxane platinum, or endocyclopentadiene platinum.

It has been claimed that while the thermal transitions (T_g, T_{CI}, etc.) of the polymers rise sharply with $\overline{DP}$ for low $\overline{DP}$ (up to 10), thereafter the transition temperatures level off. This implies that, other than for relatively low oligomers, $\overline{DP}$ is not an important factor in relation to polymer reproducibility.

The results in *Table 1* for the polymer (III):



(III)

prepared from samples of poly(hydrogenmethylsiloxane) backbone that had been obtained by careful fractionation by gel permeation chromatography[17] cast doubt on these claims, and show that, at least in the case in question, transition temperatures increase up to $\overline{DP} \approx 100$ at approximately constant $\bar{M}_w/\bar{M}_n$ values. This latter point is important, because changes in $\bar{M}_w/\bar{M}_n$ from 1.9 to 1.25 have been found to cause increases in T_g and T_{CI} by $\sim 5°C$.

Table 1 Effect on transition temperatures of polymer (III) of increasing $\overline{DP}$

Backbone		SC polymer		
$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ (g mol^{-1})[a]	$\overline{DP}$	T_g (°C)	T_{CI} (°C)
1.15	1760	30	2	128
1.15	3460	55	9	137
1.06	5200	84	13	142
1.12	6580	107	14	145

[a] G.p.c. data

Table 2 Effect of number of precipitations on the transition temperatures for polymer (IV)

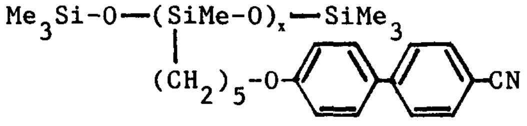
After three precipitations			After 8–10 precipitations			Differences		
T_g (°C)	T_{S-I}[a] (°C)	P_W[b] (°C)	T_g (°C)	T_{S-I} (°C)	P_W (°C)	ΔT_g (°C)	ΔT_{S-I} (°C)	ΔP_W (°C)
8	156	24	15	164	17	7	8	−7
7	155	23	15	161	15	8	6	−8
6	154	26	16	163	16	10	9	−10
10	160	22	16	167	14	6	7	−8
8	154	31	16	162	19	8	8	−12
13	163	24	16	168	21	3	5	−3

[a] T_{S-I} = Smectic–isotropic transition temperature
[b] P_W = Baseline peak width from d.s.c.

Careful control of $\overline{DP}$ and $\bar{M}_w/\bar{M}_n$ are therefore essential if reproducible polymers are required. Now, in the field of SCLC polysiloxanes, we are usually tied to the commercial availability of the preformed backbone. In the case of poly(hydrogenmethylsiloxane) (PHMS), available materials often have $\overline{DP} < 100$, and in the case of copolymer polysiloxane backbones, $\overline{DP}$ values can be quite low (see later). It is essential therefore that, in a continuing programme of work designed to give reproducible polymers, preformed backbone should be monitored for $\overline{DP}$ and $\bar{M}_w/\bar{M}_n$, and if need be purified or fractionated.

In these circumstances, techniques for controlled ring opening of poly(cyclosiloxanes), followed by anionic polymerization, seem eminently worthy of study as a source of narrow, low-polydispersity and controlled, high-$\overline{DP}$ open-chain SCLC polysiloxanes. Semlyen and his coworkers[18] at York have developed techniques for obtaining pure fractions of poly(cyclosiloxanes) with up to about 20 silicons in the ring.

As we have demonstrated[19], complete removal from the polymer of the side-chain precursor (the alkene) is also a most significant factor if reproducible products are to be obtained. This is shown by the results in *Table 2* for the polymer (IV):



(IV)

prepared from PHMS backbone of $\overline{DP} = 46 \pm 3$ and $\bar{M}_w/\bar{M}_n = 2.3$. The procedure for removal of alkene involves a number of precipitations which are carried out quite rapidly with a 5:1 ratio of the precipitating solvent (MeOH or $MeOH/Et_2O$) to polymer solution in CH_2Cl_2. The procedure is therefore different from that used when a polymer is being fractionated, and in one instance where we have studied this carefully, there is no evidence that the removal of alkene causes any change in $\overline{DP}$ or $\bar{M}_w/\bar{M}_n$ of the polymer.

With reference to *Table 2*, the results listed under three precipitations (the number often regarded by workers as sufficient) are for six batches of the same polymer from separate preparations. As can be seen, T_g and T_{S-I} are variable, and the peak width indicates that the clearing transition is associated with a fairly broad biphasic region indicating the possible presence of alkene, a fact that was confirmed in all cases by thin-layer chromatography (t.l.c.). After 8–10 precipitations, no alkene was detectable and the T_g values are now almost constant, and 3–10°C higher. The T_{S-I} values are also improved; they are higher (5–9°C) and narrower in distribution. The peak widths are also narrower, i.e. the biphasic gap has been narrowed through removal of alkene. The use of an adequate number of precipitations, until alkene can no longer be detected by t.l.c., is therefore strongly recommended.

Acrylates/methacrylates

Polymerization of mesogenically substituted acrylate/methacrylate monomers usually involves a radical procedure—the easy method of choice.

For methacrylates this gives high $\overline{DP}$ values, which may mean that the polymers relate to the flat portion of the $\overline{DP}$ vs. property curve, but the polydispersity is usually high, and chain branching is a possibility.

For acrylates, lower $\overline{DP}$ values result because of chain transfer processes.

Recent developments by Reetz[20] at Marburg and elsewhere are interesting, however, in that methods have been obtained for polymerization of acrylates/methacrylates at room temperature using metal-free carbon nucleophiles—tetrabutylammonium malonates (V)—as initiators:

$$\mathrm{RC(CO_2Et)_2\ NBu^n_4} \qquad \mathrm{(V)}$$

The initiators are stable, and the molar mass of the polymer is controlled precisely by the ratio of initiator to monomer. Controlled values of $\overline{DP}$ up to 20000 have been reported with $\bar{M}_w/\bar{M}_n$ values $\leqslant 1.3$. A significant feature is that the resultant polymer is 'living', and addition of a different monomer and more initiator starts the process again, making the preparation of controlled block copolymers possible.

Such methods would appear to provide a route to SCLC polyacrylates and methacrylates with defined $\overline{DP}$ up to around 150, and narrow polydispersity, just the features needed to achieve reproducible polymers.

Monodisperse polyacrylic acid and its derivatives can of course be obtained and interacted with suitably functionalized mesogenic moieties to obtain SCLCP, e.g. poly(acryloyl chloride) with a mesogenic alkanol or sodium polyacrylate with mesogenic alkyl bromide. If such methods are used, care must be taken that all available reactive sites have in fact reacted with the functionalized mesogen. This is of course also an important factor in preparing SCLC polysiloxanes, where care must be taken to monitor the reaction of the preformed backbone with the alkene until no free Si–H groups can be detected by infra-red spectroscopy[19].

SOME DEVELOPMENTS USING POLYSILOXANES OF A CONTROLLED NATURE

The polymers studied in the Liquid Crystal Group at Hull University are considered to be of a consistent, reproducible quality. In the hydrosilylation process, routine monitoring for total reaction of Si–H sites is carried out, and all polymers are purified until side-chain precursor (alkene) cannot be detected by t.l.c. As a further safeguard, a constant source of preformed backbone, monitored for consistency of $\overline{DP}$ and polydispersity, and purified if necessary, is used. Use of g.p.c. fractionated preformed backbone may be desirable, but would severely limit the amounts and number of polymers that could be studied. We therefore compromise by using the backbones (quality and sources) detailed in *Table 3*.

Table 3 Physical parameters relevant to different prepolymer backbones

$\mathrm{Me_3Si{-}O{-}(SiMeH{-}O)_n{-}SiMe_3}$ (homopolymer)

	G.p.c.			^{1}H n.m.r.	
Source	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\overline{DP}$
Dow[a]	9950	3100	3.2	2560	40±3
Wacker	8050	3500	2.3	2920	46±3

[a] Dow 1107 purified by six methanol precipitations

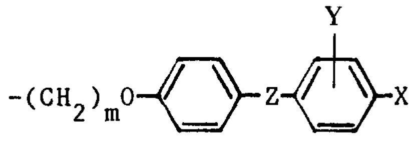
$\mathrm{Me_3Si{-}O{-}(SiMeH{-}O)_x{-}{-}{-}{-}(SiMe_2{-}O)_y{-}SiMe_3}$ (copolymer)

	G.p.c.			^{1}H n.m.r.		
Source	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\overline{DP}$	x/y
Petrarch (PS1.22.5)	2400	1300	1.9	1100	1312[b]	1:1.1

[b] About 26 silicons in the backbone

When the SCP are made from such backbones, there are further factors to be considered. For example, was the copolymer preformed backbone statistical in its distribution of the $-\mathrm{SiMe_2}-$ and $-\mathrm{SiMeH}-$ groups? This should be checked[17] by ^{29}Si n.m.r. Also, if more than one side-chain is attached to a homopolymer backbone, is the distribution of these along the backbone statistical, and is the ratio of the side-chains really determined by the ratio of alkenes used in the hydrosilylation process? Assumptions about the latter point do not allow for different rates of attack by alkenes of different steric bulk and reactivity, and the fact that the alkenes are present in 10 mol% excess.

Using such backbones, many SCLCP have been made with side-chains of the generalized form (VI):



(VI)

where m = 3 - 11
Z = COO. OOC, single bond, etc.
Y = H, Me, F, etc.
X = CN, O-Alkyl, etc.

Establishment of structure–property relationships

A reason for synthesizing a range of SCLCP of consistent and reproducible quality is to establish reliable trends in the properties of the polymers with change in spacer length, molecular structure of the mesogenic side-chains, etc.

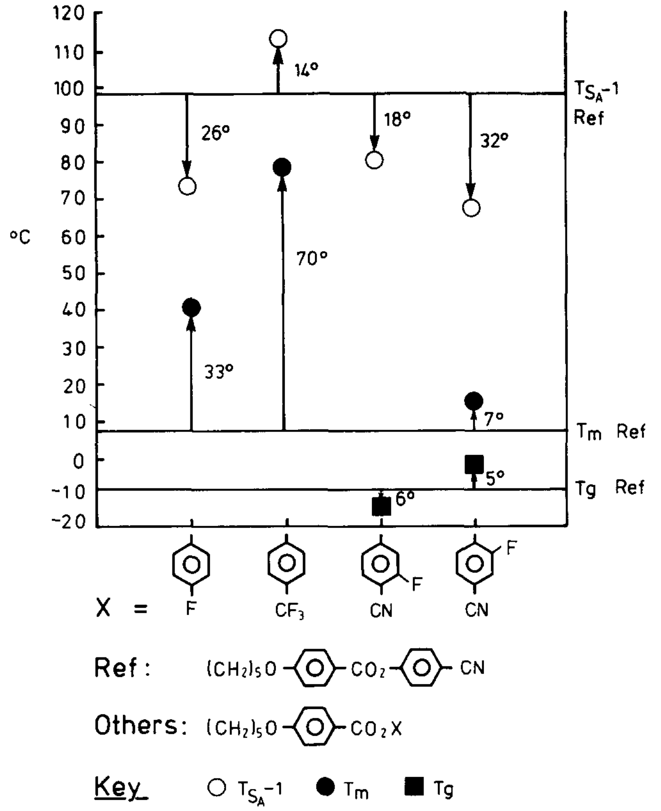


Figure 2 Representation of changes in the transition temperatures of a SCLCP (copolymer backbone) arising from the structural changes indicated

These trends can be examined through SCLCP made from either homopolymer or copolymer backbones (see *Table 3*). No differences in the phase *behaviour* have been observed as between homopolymer- and copolymer-derived systems. The only difference is that all transition temperatures (T_g, T_m, T_{S-I}, etc.) are moved to *much* lower values in the copolymers, as originally found by Ringsdorf *et al.*[21].

The results in *Figure 2* are illustrative of just one simple example of structure–property correlation studies, in this case on the role of fluoro-substituents on the behaviour of the polymers[22]. The data in *Figure 2* relate to polymers derived from the copolymer backbone (Petrarch PS1.22.5) given in *Table 3*.

In *Figure 2*, the horizontal lines represent the T_{S_A-I}, T_m and T_g values of the *reference* polymer with the cyanophenyl benzoate ester side-chain shown. The arrows represent the changes where relevant in these transition temperatures consequent upon the structural changes in X.

In summary, these changes are:

(i) an increase in T_m and a decrease in T_{S_A-I} on changing CN to F;

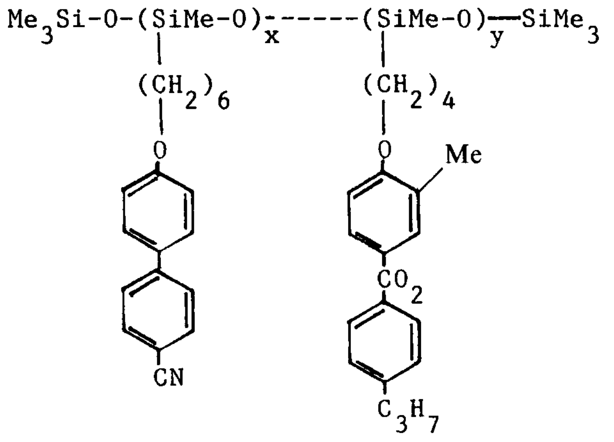
(ii) a strong increase in T_m and an increase in T_{S_A-I} on changing CN to CF_3;

(iii) decreases in T_{S_A-I} on introducing a lateral fluoro-substituent into the cyanophenyl ring in either the 3- or 2-position, and minor changes in T_g and/or T_m.

The above changes in T_{S_A-I} are all in line with the effects of making the same structural changes in low-molar-mass (LMM) systems. Interestingly, however, in such systems, the effect of 3-fluoro is more marked than that of 2-fluoro, the reverse of the effect in these polymers. This may be a consequence of changes in the antiparallel pairwise correlations of cyano-terminated groups in polymers relative to LMM systems.

As mentioned already, this is just one example of such a property–structure correlation study, but the establishment of such relationships is essential if we are to be guided in the choice and synthesis of polymers with tailored properties for applications. Such relationships have already been useful in various ways.

The design of nematic polymers containing terminal cyano groups. Such polymers are important because of their strong positive dielectric anisotropy (Δε), but very often the polymers are smectic. It has however been demonstrated[23] that lateral methyl groups strongly depress smectic properties in LMM systems. Application of this information to polymers has allowed the preparation of the copolymer (VII):



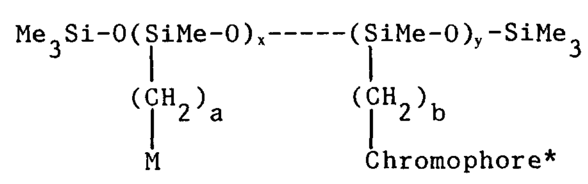
(where x + y ≈ 50)

(VII)

which at $y/x \approx 7/1$ is purely nematic and has a positive value of Δε.

The design of chiral S_C polymers. These are very important because of their ferroelectric/pyroelectric properties.

The synthesis of polymers with dichroic side-chains[24].



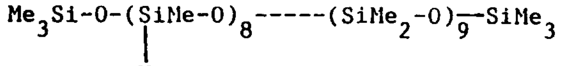
$$\mathrm{Me_3Si\text{-}O(}\underset{\substack{|\\(CH_2)_a\\|\\M}}{\mathrm{SiMe}}\mathrm{\text{-}O)_x\text{-----}(}\underset{\substack{|\\(CH_2)_b\\|\\Chromophore^*}}{\mathrm{SiMe}}\mathrm{\text{-}O)_y\text{-}SiMe_3}$$

*e.g. a moiety with the structure of an azo dye, a stilbene, or an anthraquinone.

Here the choice of the 'diluting' group M is very important both to minimize the steric interactions of the sometimes bulky chromophoric functions (which can inhibit total reaction with Si–H groups) and to improve solubility, preventing possible precipitation of the polymer at a stage when only a fraction of the Si–H sites has reacted with the chromophoric alkene.

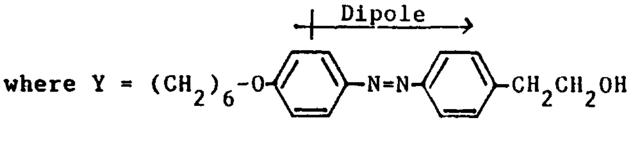
Polymeric Langmuir–Blodgett (LB) systems

In the context of LB systems with non-linear optical characteristics, the idea was conceived[25] of a polymer of general structure (VIII) in which the mesogenic side-chain Y would terminate in a hydrophilic group. This work was done under a collaborative programme with Plessey (Caswell) and others supported by a JOERS/SERC grant.

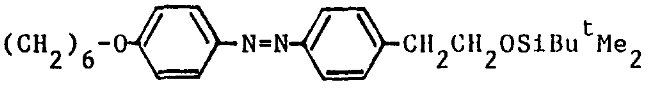


$Me_3Si\text{-}O\text{-}(\underset{Y}{SiMe}\text{-}O)_8\text{-----}(SiMe_2\text{-}O)_9\text{—}SiMe_3$

(VIII)



Use of hydrophilic terminal groups in Y leads to problems in the hydrosilylation reaction, and it was necessary to prepare the polymer with Y as:

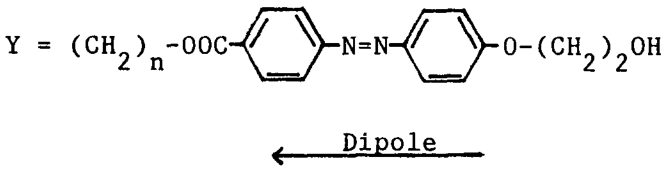


from the alkene in which the -OH group is protected by the t-butyldimethylsilyl group. Treatment of the protected side-chain polymer with boron trifluoride etherate in CH_2Cl_2 then liberated the -OH group giving the polymer (VIII), in which the resultant dipole lies along the long axis of the side-chain with the positive charge on the oxygen next to the flexible spacer and the negative charge on the phenyl ring carrying the $-CH_2CH_2OH$ group.

Polymer (VIII) can be deposited as a very stable monolayer ($\pi_c = 38\ mN\ m^{-1}$) giving wave-guiding with an attenuation of $\approx 10\ dB\ cm^{-1}$. Multilayer stacks of >200 layers can readily be achieved by normal dipping procedures. In the monolayer, the OH groups are at the subphase (H_2O). However, in the multilayer stack, the layer distribution is Y-type, such that the axial, side-chain dipoles cancel in each pair of layers, giving no net macroscopic dipole.

The second harmonic generation (SHG) observed for the deposited monolayer does not therefore occur in the multilayer stack which has centrosymmetry of the bilayers because of the Y-type stacking.

In an attempt to overcome this problem a similar polymer with the side-chain shown below was made:



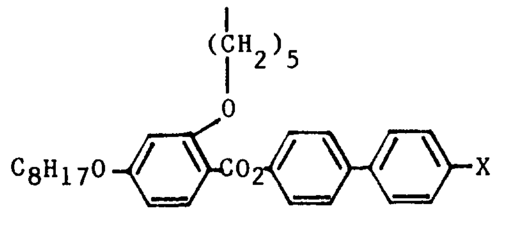
wherein the conjugative interactions lead to a net dipole directed from the polar end-group, along the side-chain axis, towards the backbone. Again good monolayers were produced.

Alternating layers of the two polymers in Y-type deposition should therefore give non-centrosymmetry, dipole reinforcement and an enhanced SHG relative to that of the monolayer of polymer (VIII). Whether this is so has yet to be established.

Polysiloxanes with laterally attached side-chains

SCLCP with calamitic mesogenic groups attached laterally to the backbone via a flexible spacer have been known for some little time[8].

Our experiments in this area, like those of Keller *et al.*[26], have been on polysiloxanes (derived from Wacker backbone—*Table 3*) with the side-chains of structure (IX):

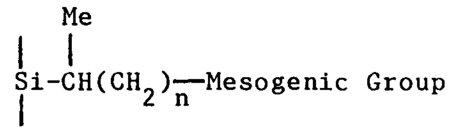


(IX)

where X = alkyl, alkoxy or cyano.

The polymers were made[27] by the hydrosilylation procedure using either $H_2PtCl_6 \cdot 6H_2O$ in IPA or divinyltetramethyldisiloxane platinum catalyst (Petrarch).

At this point, it is noted that anomalous addition[28] of the Si–H to the alkene in the hydrosilylation reaction has not been found to be a problem with chloroplatinic acid catalyst when the side-chains are attached by their *termini* to the backbone. With the *laterally* attached side-chains, anomalous addition, i.e. giving:



$\overset{|}{\underset{|}{Si}}\text{-}\overset{Me}{\overset{|}{C}}H(CH_2)_n\text{—Mesogenic Group}$

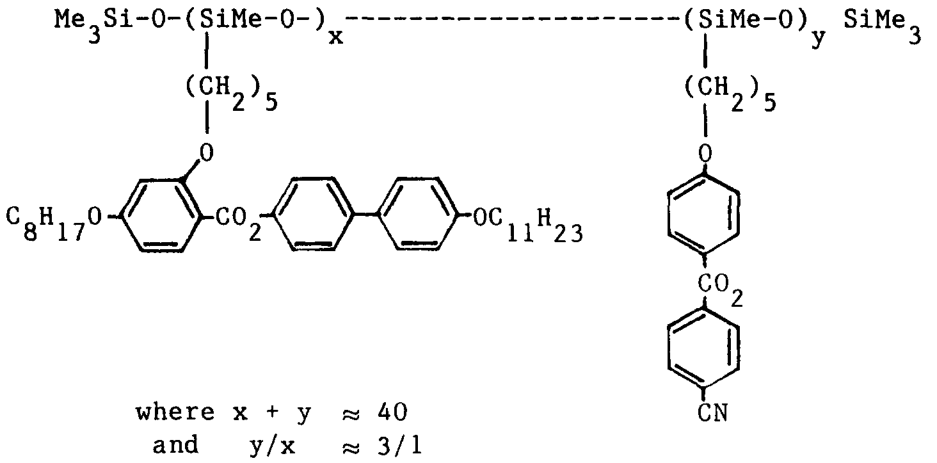
has been observed (by ^1H n.m.r.) in some cases with chloroplatinic acid, but apparently not with the Petrarch catalyst.

The polymers with side-chains (IX) are consistently nematic, even with X = CN or long-chain alkyl or alkoxy, and have low T_g values (0 to ~ 20°C). As would be anticipated they are also optically biaxial.

The strong nematic tendencies, or, conversely, the smectic depressing tendencies stemming from these laterally attached side-chains, seemed to be a factor that could be used to produce SCLCP with some at least of the side-chains attached by their termini and carrying terminal cyano groups, so that *nematic* polymers of strong positive $\Delta\varepsilon$ might be obtained.

Copolymers were made of general structure (X): The homopolymers with $x = 0$ and $y = 0$ are smectic ($T_{S_A\text{-}I} = 184$°C) and nematic ($T_{N\text{-}I} = 58$°C) respectively. With only 25% of laterally attached side-chains, the purely smectic polymer with $x = 0$ becomes a purely nematic copolymer ($T_{N\text{-}I} = 96.7$°C). The $\Delta\varepsilon$ value will be strongly positive because 75% of the side-chains are cyano-terminated.

Mixed lateral/terminal side-chain polymers therefore provide a further valuable device for tuning the properties of SCLCP to have desired physical characteristics and parameters.



where x + y ≈ 40
and y/x ≈ 3/1

(X)

CONCLUSIONS

It is hoped that this review demonstrates that the synthesis of side-chain liquid-crystal polymers with controlled and reproducible properties is an important objective in order both that reliable molecular structure–property correlations can be developed and that the full potential of such polymers, in all their structural diversity, for speciality applications can be established with reliability.

ACKNOWLEDGEMENTS

Several aspects of the work in this review were carried out in the School of Chemistry of the University of Hull with support, which is gratefully acknowledged, from the Science and Engineering Research Council (M. S. White, J. S. Hill and a CASE studentship to G. Nestor) and the Ministry of Defence (M. S. K. Lee).

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