

PART II

Results and Discussion

Part II b

Polysiloxanes

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IIb.1 A brief survey of side chain liquid crystalline polymers with special reference to polysiloxanes

Attainment of a thermotropic mesophase from a side chain liquid crystalline polymer (**SCLCP**) with a flexible backbone containing pendant mesogenic units requires reconciliation of the main chain's tendency to form a statistical random coil conformation and the side groups' tendency to arrange anisotropically. The principle that the motions of both the main chain and the side groups are coupled when the mesogenic groups are directly attached to the flexible backbone is well established. In this case, the conformation of the main chain is disturbed when the side groups adopt an anisotropic arrangement.

In order to balance the competition between the backbone's random-coil conformation and the side groups' alignment, Ringsdorf and co-workers' ^{2,3} predicted that the motion of the polymer main chain must be decoupled from that of the anisotropically orientable mesogenic side groups in the fluid state. As demonstrated schematically in Fig. IIb.1 and explained in Figure IIb.2, decoupling should be achieved when a flexible spacer is inserted between the polymer backbone and the mesogenic side groups. Based on the spacer model, the side groups should be able to self-orient into mesophase even when the main chain adopts a random configuration. Thus, the main chain should do little to hinder the orientation of the mesogenic side groups, *i.e.* for a given mesogen and spacer, the nature of the polymer backbone should, theoretically, not affect the type of mesophase formed and its thermal stability. However, it is found that the polymer backbone does in fact affect both aspects of the mesomorphic behaviour of **SCLCP** which will be discussed later.

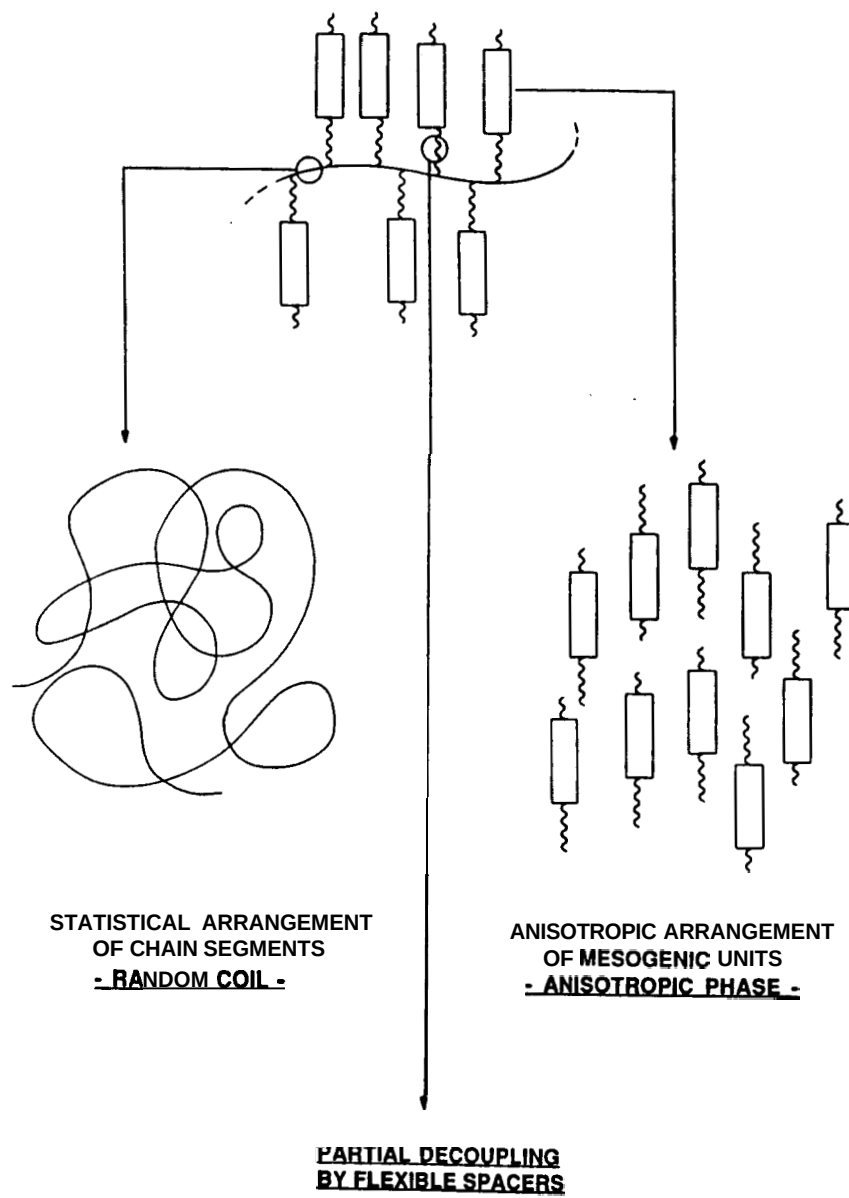


Fig.IIb.1

LINKAGE OF THE HESOGENIC SIDE CHAIN
TO THE MAIN CHAIN

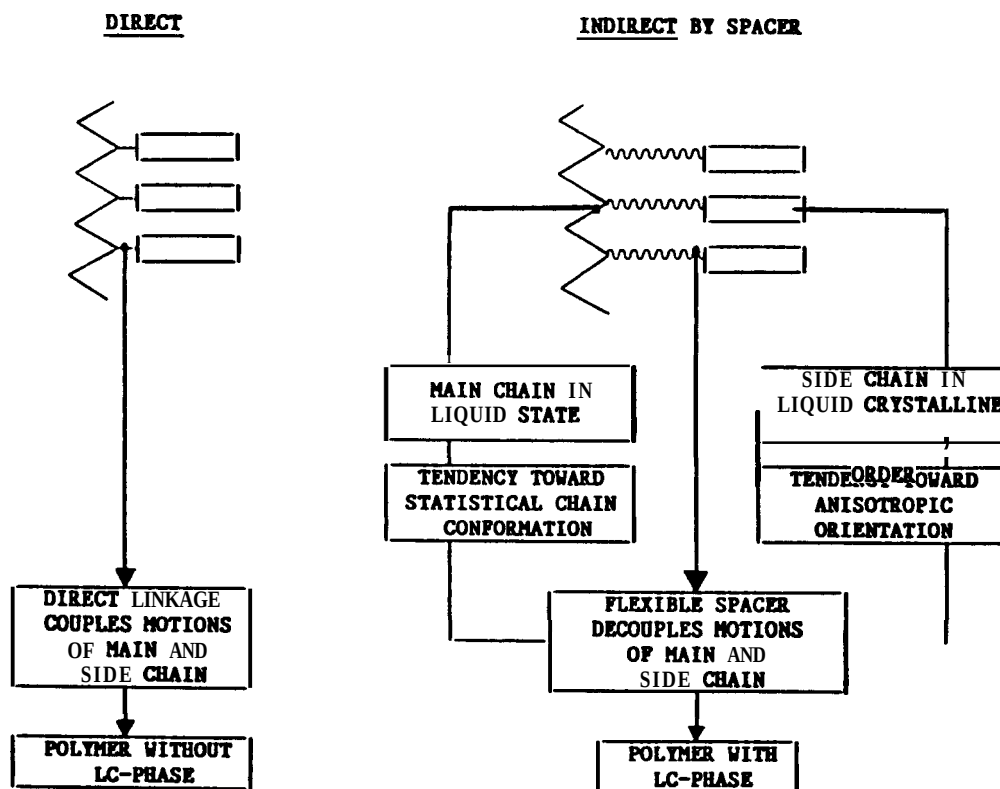


Fig.IIb.2

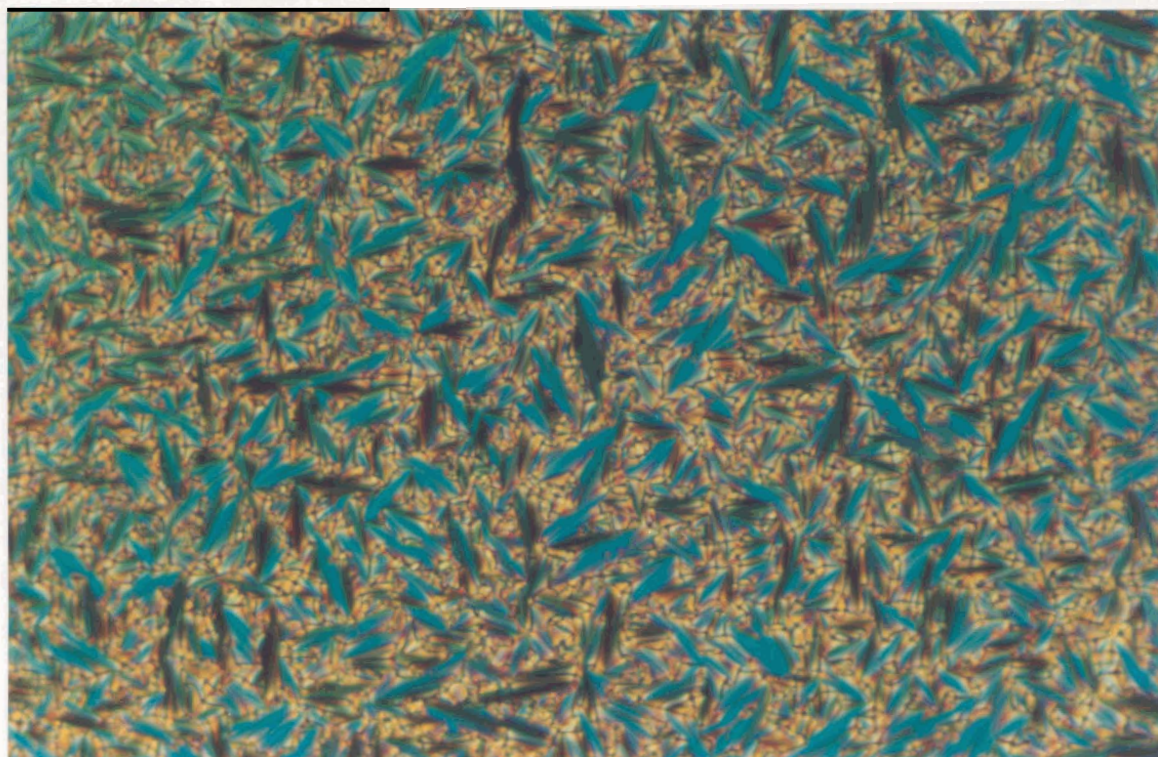


Plate IIb.1 Photomicrograph of sample (KP-4) showing Smectic A phase.

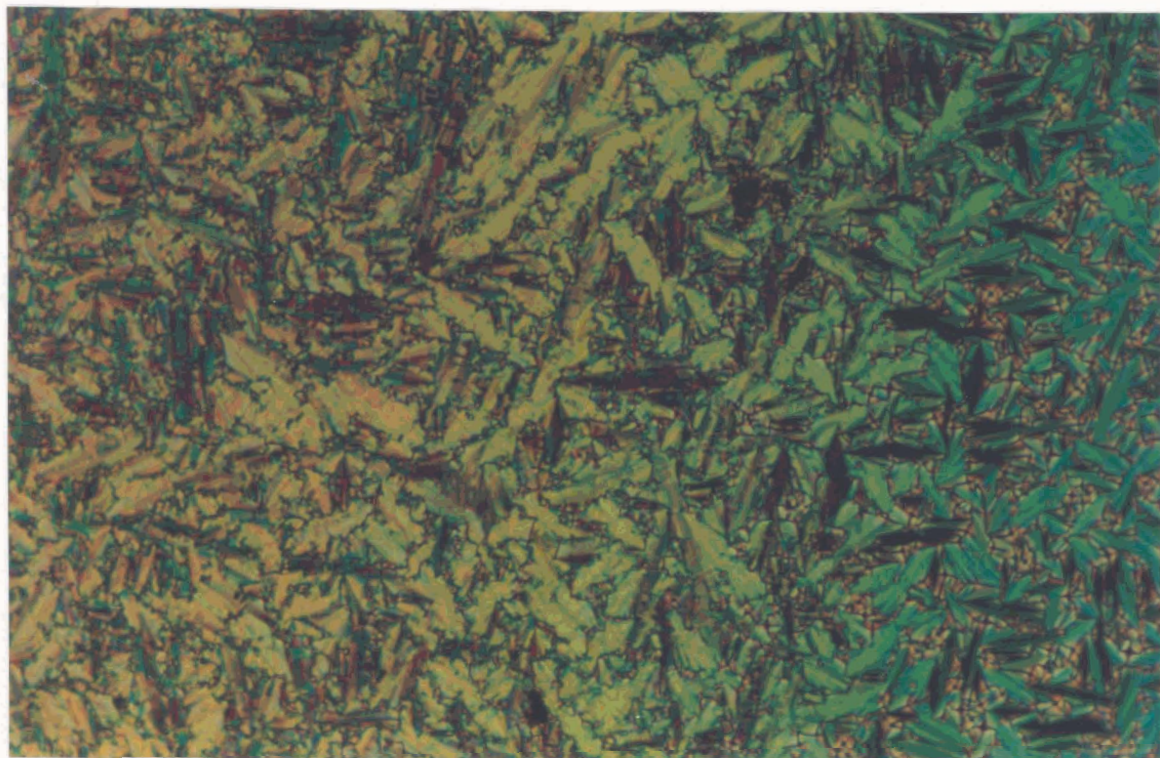


Plate IIb.2 Photomicrograph of sample (KP-4) showing Smectic C* phase.

Ever since the time the spacer concept was proposed, SCLCPs have been routinely synthesised. Subsequent experiments performed by Ringsdorf *et al.*⁴ and Spiess,⁵ demonstrated that although a spacer helps to decouple the mesogenic groups from the main chain, and that decoupling becomes more effective with increasing spacer length, decoupling is nevertheless incomplete. At least part of the backbone and spacer is anisotropically oriented along with the mesogen.

The spacer causes a dynamic coupling of the motions of the main chain and side groups. Consequently, the most accurate visualisation of a SCLCP is the interaction of two semi independent thermodynamic sub-systems through the flexible spacer. Thus, a section of the spacer plasticises the main chain while another section of the spacer stabilises the mesogenic units.⁶

One general conclusion that seems to emerge from the available literature is concerning the influence of the polymer backbone on the mesophase formation by the SCLCPs. In most cases, the nature of the least ordered mesophase exhibited by the polymer with a given mesogenic unit is dictated primarily by the nature of the polymer backbone. The broadest thermal range of mesogenicity is exhibited by polymers containing most flexible backbone, namely polysiloxanes. The enhanced mesophase thermal stability and the increased isotropisation temperature of polymers with flexible backbones can be associated with a high degree of freedom available to the side groups. Logic is that, the conformation of a more flexible backbone can be easily disturbed and subsequently the side groups can adopt a higher degree of order compared to those of a more rigid backbone. But, this can also be related to the miscibility of polymer backbone and the side chains.

However, the existence of a single-phase-morphology (after complete miscibility of the main chain and side chain) of the system in side chain liquid crystalline polymers has little chance of more than a partial decoupling of the side chain and main chain motions. This is because a microphase separated SCLCP should contain microdomains exclusively of polymer backbones, and microdomains exclusively of side groups. Such a system would not only resemble a fine dispersion of an immiscible low-molar-mass liquid crystal in an amorphous polymer, but should also exhibit two glass transition temperatures (T_g) provided the side groups do not crystallise separately; one T_g due to the independent motion of the main chain, and the other due to the cooperative motion of the side groups. The cooperative motion of the side groups would therefore be independent of the main chain.

Lipatov,⁷ Tsukruk,⁸ and Krigbaum⁹ first suggested that smectic SCLCPs might have a microphase structure with clusters of mesogenic side groups embedded in a continuous phase formed by the polymeric backbone. The first examples of side chain liquid crystalline copolysiloxanes containing combined main chain and side chain spacers according to Fig. IIb.2, were synthesised by Ringsdorf and Schneller¹⁰ by the hydrosilylation of poly(methyl-co-dimethylsiloxane). In this case, the main chain spacer was an (oligodimethylsiloxane) of the 'block' copolymers while the side chain was paraffinic.

Percec *et al.*^{11,12,13,14} have reported a large variety of copolysiloxanes with different molecular masses and compositions containing mesogenic side groups and long spacers which exhibit two T_g temperatures by DSC. They assigned the lower glass transition temperatures to the independent motions of the main chain, and the higher glass transition temperatures to the co-operative (but independent from the main

chain) motions of the side groups, implying substantial decoupling between the main chain and side chain motions in SCLCPs, as proposed earlier.

I Ib.1.1 Structural types (homo- and copolymers)

SCLCPs may also be of different types as determined by the nature of the backbone. Copolymers are possible by either using two or more different pendant groups on a homopolymer backbone or a backbone which is itself copolymeric in composition and has one or more than one type of pendant groups. These possibilities for SCLC polysiloxanes are summarised in Fig. I Ib.3, where R_1 , R_2 represent the mesogenic side chains. The structures for the copolymers are intended to represent statistical systems, although block copolymers can also be conceived. Typical values for n , $x+y$, and $x+y+z$ would range from 30 to 120.

Achievement of ordering of the side chains is also affected by the flexibility of the backbone itself. In this respect, polysiloxanes are particularly good, as they have a backbone of alternating silicon and oxygen atoms. Although the Si-O bond is strong (bond dissociation energy = 452 kJmol^{-1} , as compared to 226 kJmol^{-1} for Si-Si and 333 kJmol^{-1} for Si-C), accounting for the high thermal stability of poly(organosilanes),¹⁵ the rotational potential energy of the Si-O bond is low. As a result of this, and the low intermolecular forces due to the shielding effect of the organic groups on the backbone, conformational changes in the backbone may occur easily, assisted by the possibility for wide variations in the Si-O-Si bond angle. These effects are much greater than those for the backbones of hydrocarbon polymers. Comparing polymers with different backbones, varying in DP and polydispersity, SCLC polysiloxanes have lower T_g values and lower mesophase transition temperatures than their

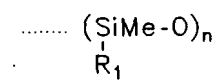
acrylate/methacrylate counterparts. This suggests that ordering of the side chains by the more flexible siloxane backbone is not very good. Data from Finkelmann and Rehage,¹⁶ illustrate this point well in relation to T_{N-I} values (Table IIb.1).

Further evidence for the greater flexibility of the O-Si-O unit comes from LMM systems of structure shown in Fig. IIb.4,¹⁷ where, X = AL {alkyl = $-(CH_2)_5-$ }; EO (ethyleneoxide = $-(CH_2)_2O(CH_2)_2-$); DS (dimethylsilyl = $-CH_2 SiMe_2CH_2 -$). The T_{N-I} falls in the order AL > EO > DS. This may be interpreted as a failure of the O-Si-O unit to propagate effectively a linear structure from one half of the molecule to the other.

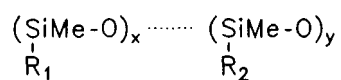
As it turns out, the lower mesophase transition temperatures for polysiloxanes are not in fact disadvantageous, as these values can be corrected upwards by a suitable choice of mesogenic side chains. The lower T_i values are, however, an advantage if we require the polymer to be liquid crystalline at room temperature, as for example with cholesteric polysiloxanes needed to monitor temperatures at or below ambient.

After it became clear that SCLCPs were no competitors to LMMLC materials in applications for fast switching electro-optical displays, because of their very slow response times, attention switched to their applications as materials into which information could be written and then stored. This can be done effectively by writing data at a temperature above T_g and storing the data at temperatures below T_g (in the glassy state). This requires polymers with T_i above ambient temperatures. In this situation, the choice may be for an acrylate polymer. However, there are strong advocates for smectic polysiloxanes.^{18,19} Using these, the data may be stored in the viscous smectic state, with T_i below room temperature. This has been done very successfully by McArdle *et al.*²⁰

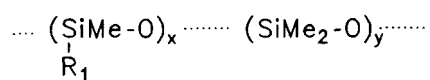
Homopolymer



SC copolymers



Backbone copolymers



Backbone/side chain copolymers

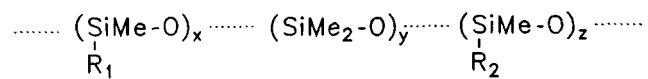


Fig.IIb.3

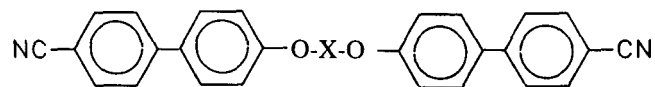


Fig.IIb.4

Tab.IIb.1

Polymer-	T_g (K)	T_{N-I} (K)
$\begin{array}{c} -CH_2-CMe- \\ \\ CO_2R \end{array}$	369	394
$\begin{array}{c} -CH_2-CH- \\ \\ CO_2R \end{array}$	320	350
$\begin{array}{c} -O-SiMe- \\ \\ CH_2R \end{array}$	276	334
$R = -(CH_2)_2O-\text{C}_6\text{H}_4-CO_2-\text{C}_6\text{H}_4-OMe$		

The prospects for SCLC polysiloxanes that are mesogenic at ambient temperatures in the area of applications are very good. Moreover, from the standpoint of studies of the physical properties of polymeric liquid crystalline phases, there is definite merit in the ability to conduct measurements at ambient temperatures.

SCLC polysiloxanes therefore remain an area of strong research activity, and the discovery by Ringsdorf et *al.*,²¹ that copolymers derived from a poly (hydrogenmethyl-dimethylsiloxane) had glass transitions well below those of their homopolymeric counterparts with the same mesogenic side chains, and indeed well below 0°C, was one of very great interest. The extent of the effects is shown by a comparison of the S-I values for a constant spacer length, say eleven C-atoms. The data shows diminishing smectic thermal stability as the population of mesogenic groups becomes smaller and the backbone becomes correspondingly more flexible, *i.e.*, less influenced by the mesogenic ordering processes.

IIb.2 Methods of synthesis

IIb.2.1 General aspects

SCLC polysiloxanes are usually prepared by a polymer modification process, commencing with a preformed polymer backbone which contains reactive functional groups (Si-H) to which the mesogenic side groups are appended. During the reaction, monitoring is carried out to ensure complete reaction of the Si-H functions with the terminal alkene which is to constitute the mesogenic side chain. The scheme, shown in Fig. IIb.5, is known as hydrosilylation.

The preformed backbone may be chosen to produce a homopolymer, *i.e.* every Si atom carries a reactive H atom and all the alkene molecules are the same, or a

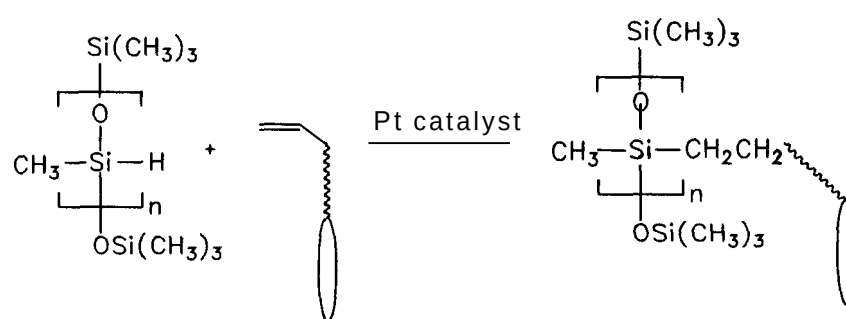


Fig.IIb.5 The hydrosilylation reaction to give a SCLCP

backbone copolymer, in which case the backbone has a statistical distribution of -SiH(Me)-O- and SiMe₂-O- groups in a particular ratio.

It was originally suggested,²² that for a nematic polymer, the transition temperatures would rise only slightly above a DP of 10. Stevens *et al.*²³ proposed a similar critical DP value for polymers with smectic transitions, and this view was further supported by Apfel *et al.*²⁴ This has tended to condition the workers to the view that, within limits, DP of the polysiloxane is not important. But, the reproducibility of results may be affected by the following factors which can be overcome and may have been less than fully appreciated in the past, are:

- (i) Retention of excess of the alkene in the polymer.
- (ii) The danger of cross linking involving side chain substituents such as CN.
- (iii) For side chain copolymers, the need to demonstrate that the ratio of the side groups is in fact the same as the stoichiometric ratio of reactant alkenes. With bulky side chains, this may not be so, and side chain ratios can be affected by reaction conditions.

Factors (i), (ii) and (iii) clearly affect product reproducibility, which is vital if the properties of these polymers are to be correlated with structure and they are to play a role in sophisticated applications. The nature of the cross-linking noted above is not clear ; it could involve interaction between Si-H groups, or hydrosilylation at the cyano-group²⁵ or Pt catalysed cleavage of Si-C bonds²⁶ or a complex reaction.²⁷

Iib.2.1 Types of catalyst

The hydrosilylation reaction *i.e.* the addition of a silane to an alkene, is a reaction of importance in organo-silicon chemistry. It may proceed **thermally**,²⁸ by irradiation,²⁹ or by **catalysts**.^{30,31} Many kinds of catalysts have been tried and studied. Of these, the most extensively explored, and that used originally by Finkelmann and by Ringsdorf in their pioneering studies of side chain polysiloxanes, is hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$) in propan-2-ol. From a range of catalysts including Pt on carbon and RuCl_3 , hexachloroplatinic acid was chosen as highly effective for the preparation of n-pentylsilanes from pent-1-ene.³²

Other catalysts for hydrosilylation have been sought and used, and some are sold commercially. Some ten different catalysts (including $\text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$) and those derived from Pd, Pt, or Rh, for example $[\text{PtCl}_2(\text{PPh}_3)_2]$, $[\text{Pd}(\text{PPh}_3)_4]$, $[\text{RhCl}(\text{PPh}_3)_3]$ are presently available commercially. A further catalyst of interest is dichloro(*endo*-dicyclopentadiene)Pt(II) and its Pd(II) analogue. This catalyst was used by Apfel *et al.*³³ for the production of high temperature mesomorphic polysiloxane solvents for glc stationary phases.

It seems that generalisations cannot yet be made about the reaction mechanisms involved under diverse conditions and with different catalysts of different age, and that more research is needed. In the present work we have used fresh Spier's catalyst for all our polymerisation reactions.

IIb.3 Synthesis and characterisation of side chain liquid crystalline siloxane polymers

All the polymers synthesised were mesomorphic and showed the chiral smectic phases. The general synthetic scheme for the polymers is shown in Fig. IIb.5. A typical hydrosilylation procedure consisted of refluxing the monomer in dry toluene at 80°C for forty-eight hours, with the poly(hydrogenmethylsiloxane) in the presence of a catalyst, hexachloroplatinic acid dissolved in propan-2-ol.

Monitoring the progress of the reaction is important. This was done by periodically checking of the reaction mixture by IR-spectra. Any strong peak at 2180 cm^{-1} would indicate the presence of free Si-H group (Figs. IIb.8 and IIb.9). The complete elimination of hydrogen from the free Si-H group was achieved by adding additional catalyst and monomer and continued refluxing. This ensured at least 95-97% completion of reaction as indicated by NMR spectra (Figs. IIb.10, IIb.11 and IIb.12).

Purification was carried out by first washing the polymer with water to remove any trace of the catalyst and then reprecipitating the polymer from a suitable solvent system viz. dichloromethane or tetrahydrofuran, by pouring the solution into methanol. Further, filtration through a micro-filter ensured white to cream-white polymer.

Copolymers containing different percentages of monomers H-9 and N-9 were also synthesised by following a procedure similar to that described above.

The mesophase textures were observed under a polarising microscope equipped with a heating stage. The transition temperatures and the enthalpy of transitions were determined by DSC. The accurate measurement of transition temperatures by optical polarising microscopy was not possible. Hence, the DSC data was used for all purposes.

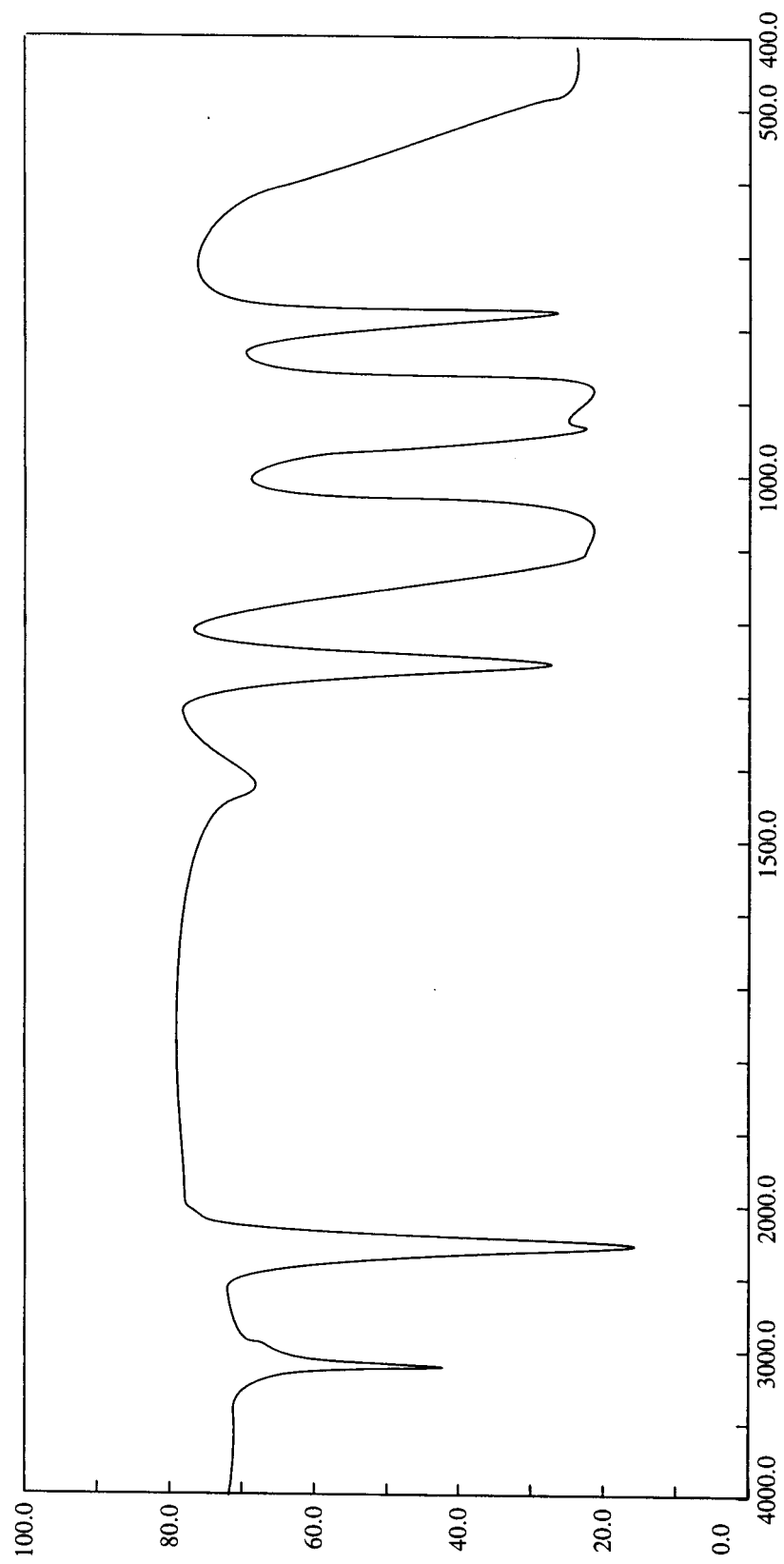


Fig.IIb.8 IR of pure siloxane

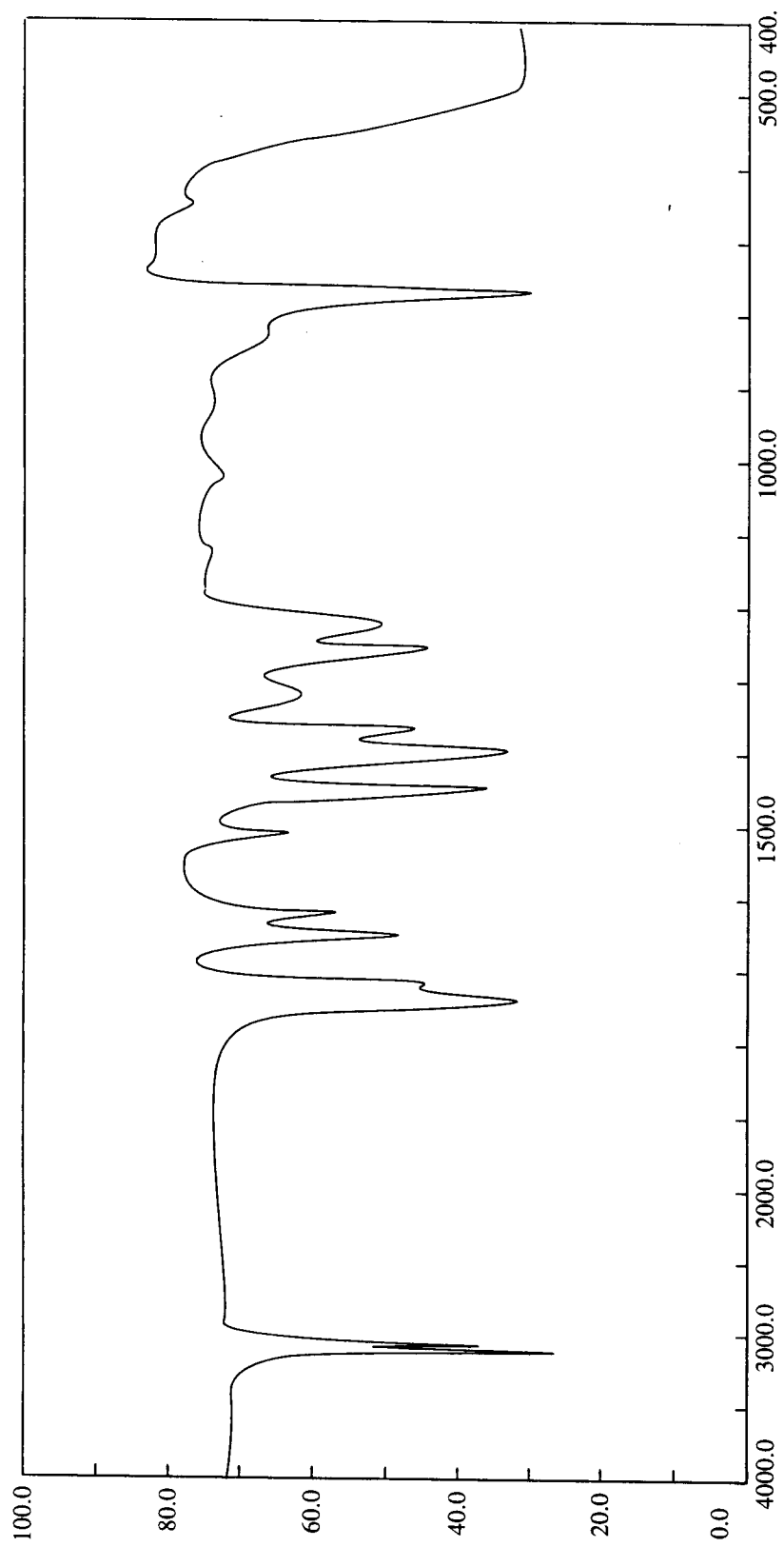


Fig.IIb.9 IR of polysiloxane NP-8

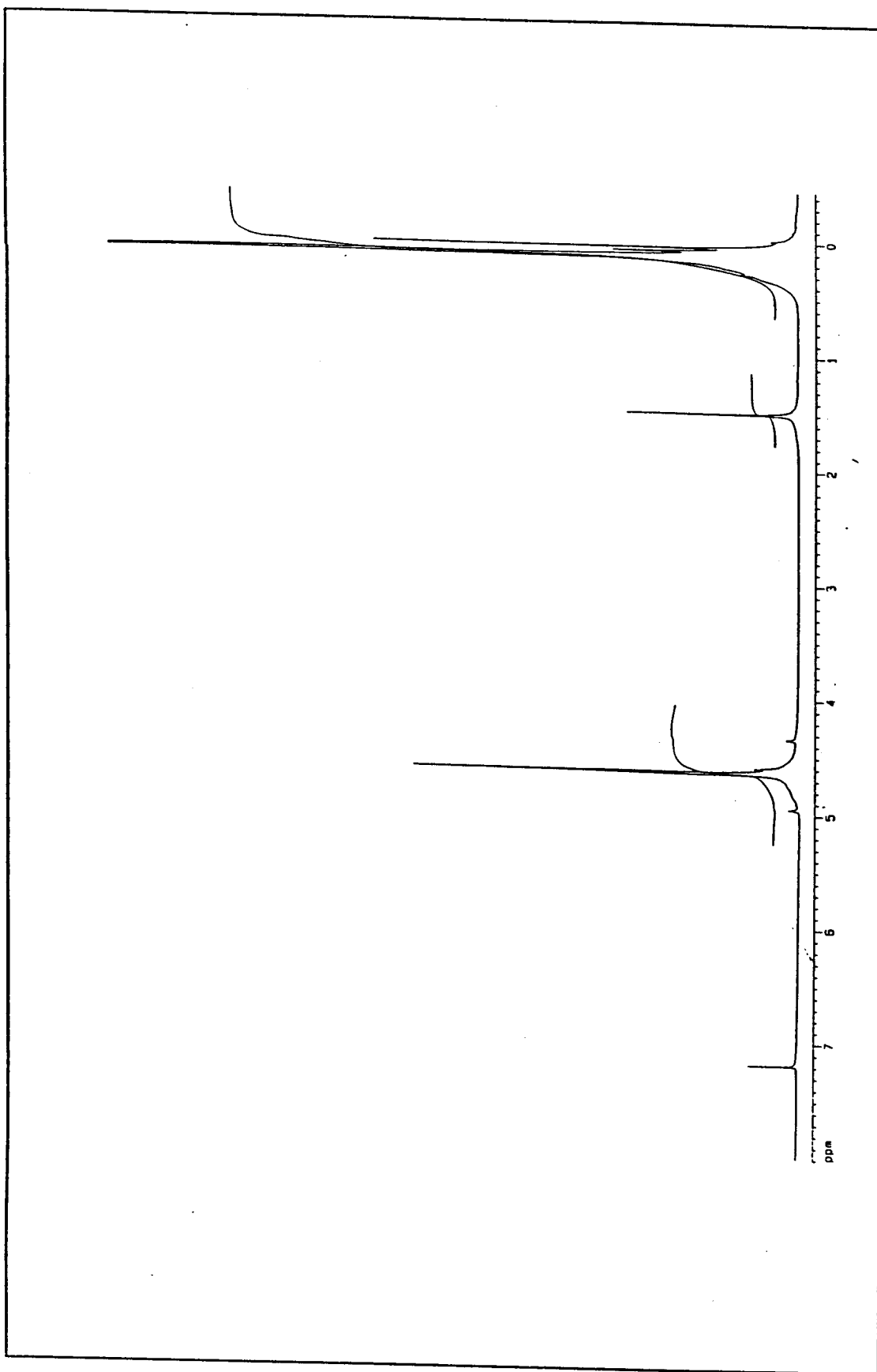


Fig. IIb.10

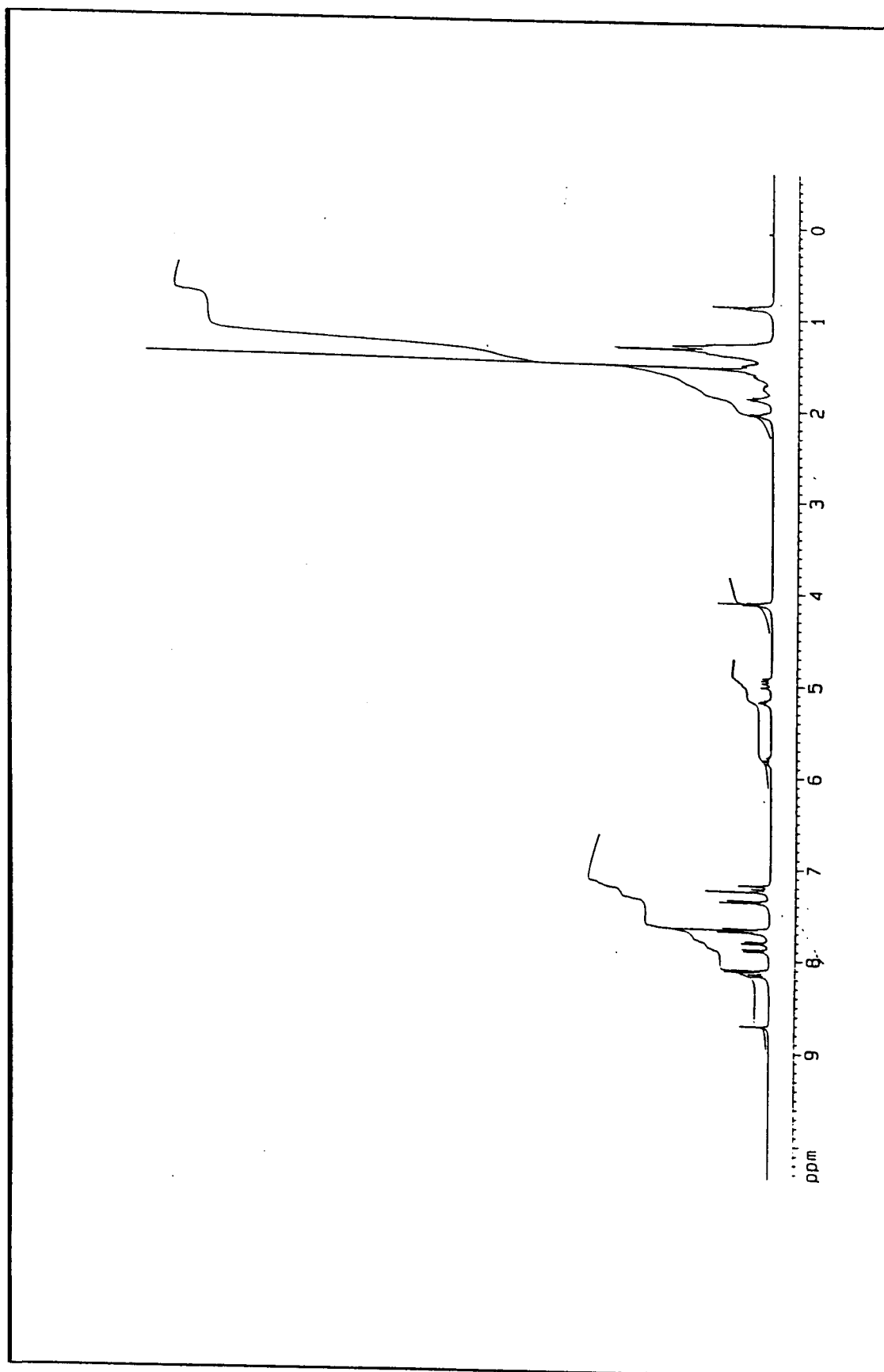


Fig. IIb.11

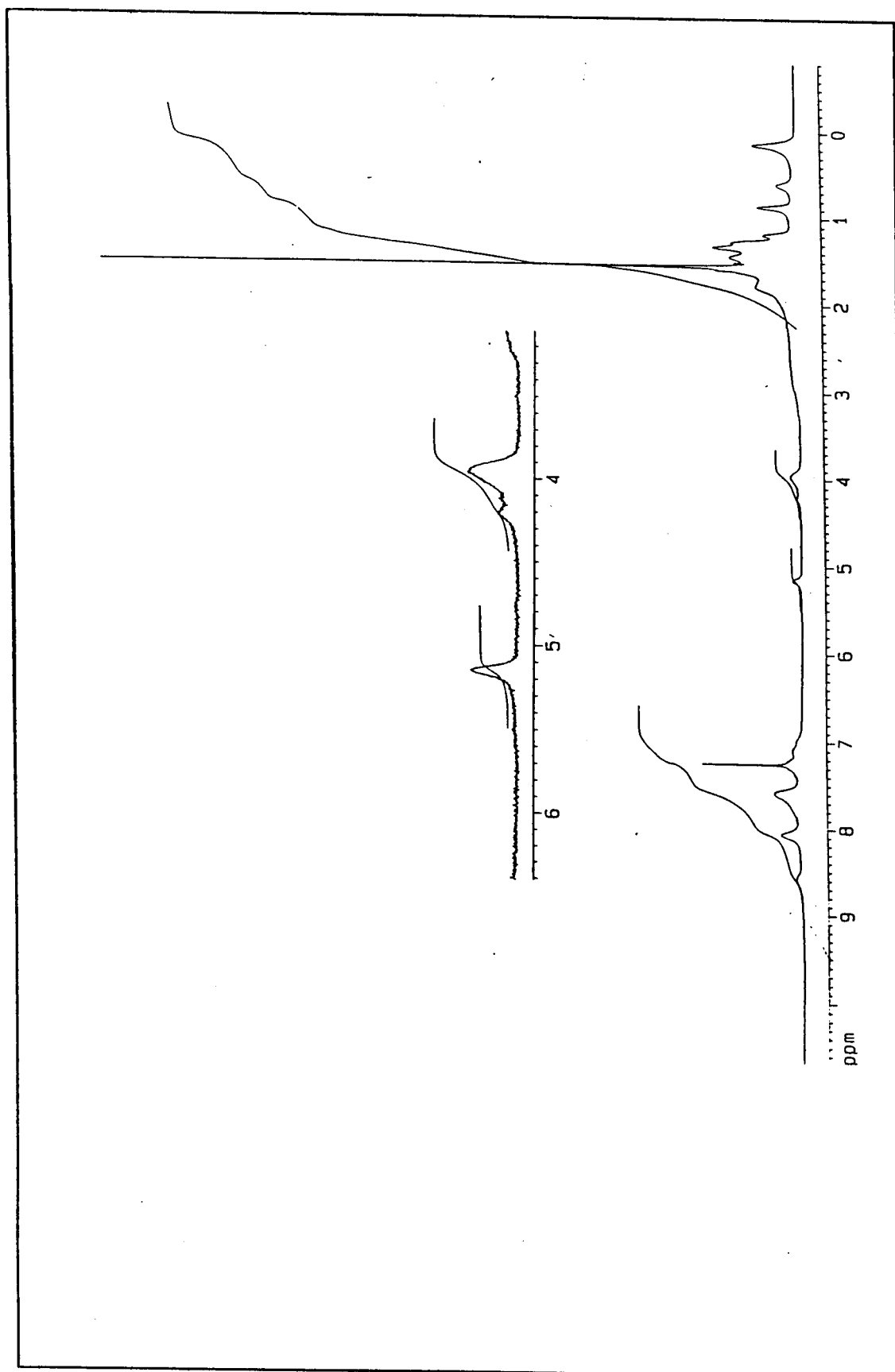


Fig.IIb.12

Gel permeation chromatography (GPC) showed a fairly mono dispersed polymer as shown in Figs. **Ib.13** and **Ib.14**. The molecular weight was in the region of 17,000 - 24,000. This also indicated about 97% completion of the hydrosilylation reaction.

Studying phase transitions of polymers proved to be more arduous than those of their corresponding monomers and low molar mass liquid crystals in general. This is because mesophase formation is difficult due to the high viscosity of the polymers. Typically, an hour or more of annealing was required for unambiguously identifying the mesophase formed. This period, perhaps allows time for the anisotropic cohesive forces between the mesogenic units to overcome the viscous forces and align themselves. It has been reported that there is a direct relationship between the T_g of the polymer backbone and the ease of phase formation.

On cooling the isotropic liquid of polymers, the focal-conic texture of a S_A phase was observed. The ferroelectric phase appears with a striated fan shaped texture. As the temperature was decreased further, the ferroelectric phase structure gets frozen into glass below the T_g . This frozen structure remained unchanged for a week. The plates **Ib.1** and **Ib.2** show the photomicrographs of smectic **A** (annealed at 200°C for one hour) and the ferroelectric S_{C^*} phase (annealed at 100°C for one hour) obtained for polymer KP-4.

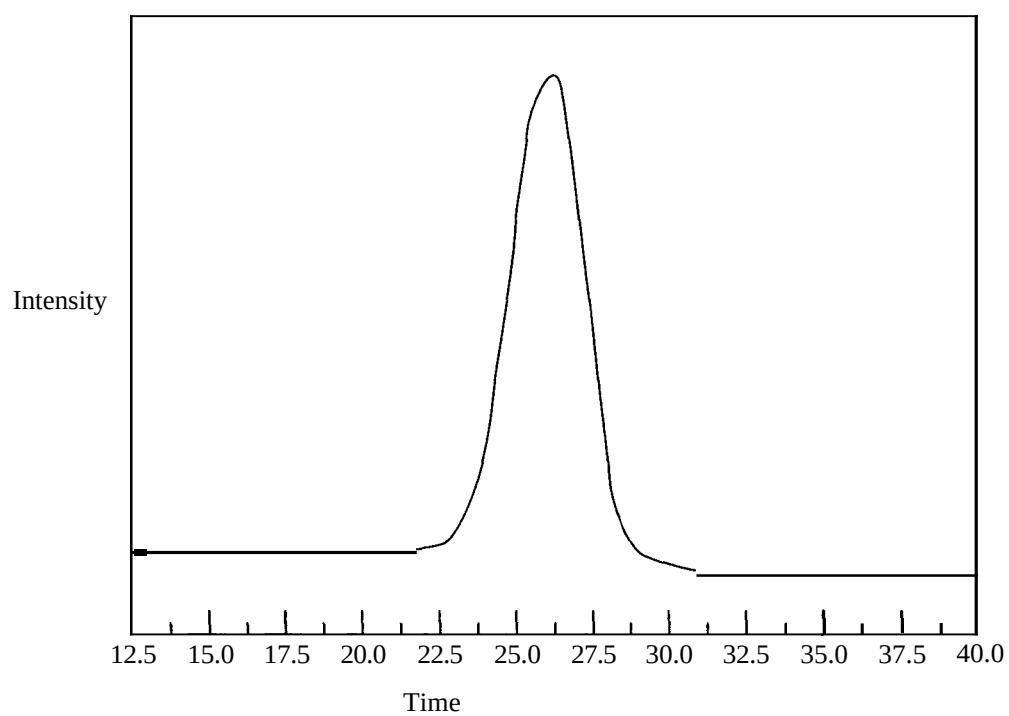


Fig.IIb.13 GPC trace of polymer SP4.

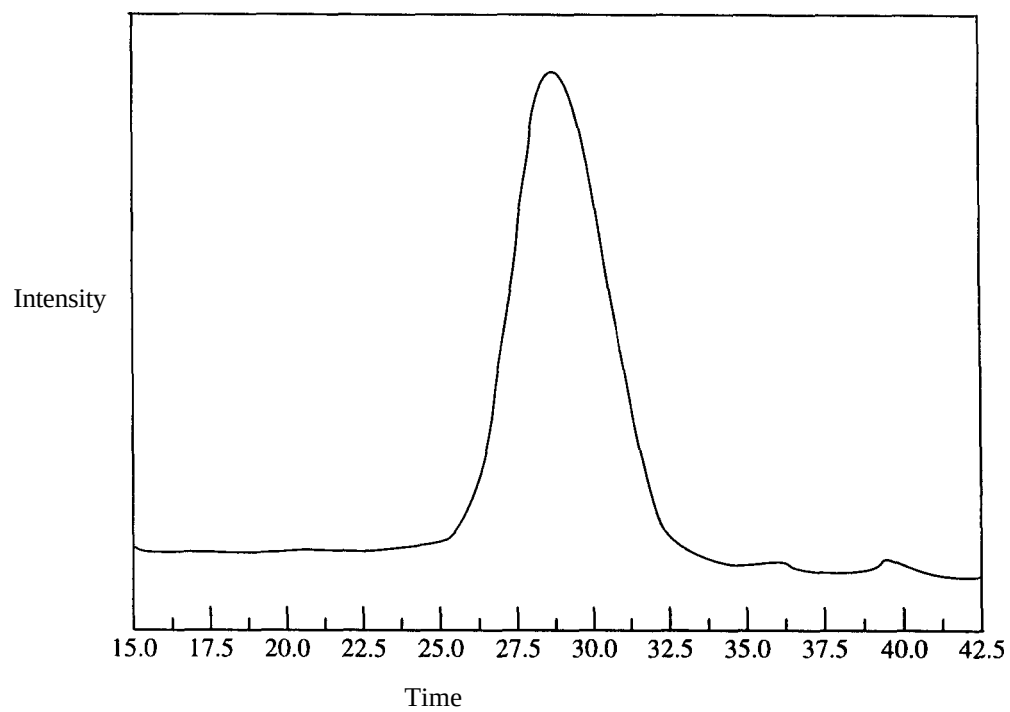


Fig.IIb.14 GPC trace of polymer SP8.

I Ib.3.1 Ferroelectric liquid crystalline siloxane polymers

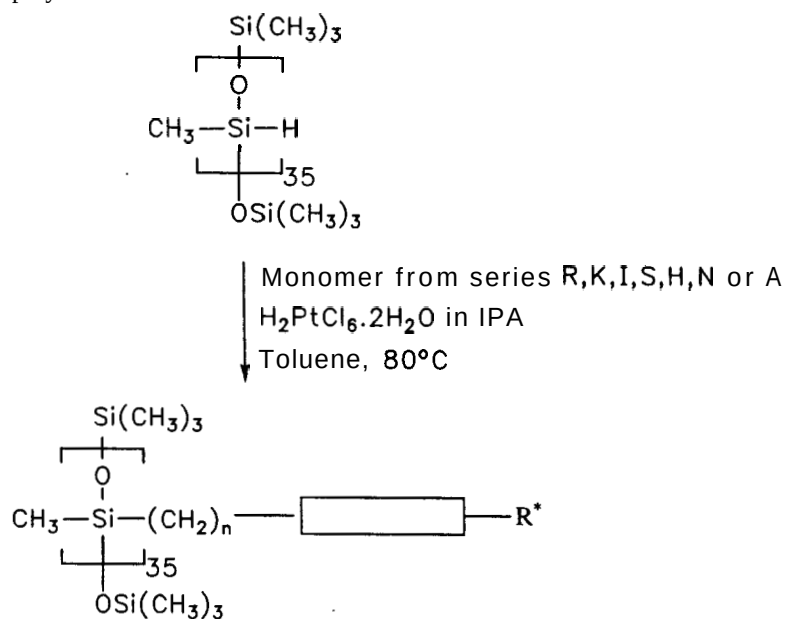
LMMLCs exhibiting S_C^* phase have been widely studied because of their ferroelectric properties^{34,35} and their very fast response times towards an applied field. This makes them particularly suitable for electro-optic applications.³⁶ LCP exhibiting S_C^* phases have been studied quite recently and a number of them have shown ferroelectric properties.³⁷ In this case ferroelectric LCPs can be obtained which combine the properties of polymers (a glassy state in which the ferroelectric structure may be frozen, the capacity of making films, specific mechanical properties, etc.) with the ferroelectric properties observed in the LMMLCs. So the study of these seems promising. However, the polymeric nature of materials is likely to raise its transition temperatures and response times. These properties are unfavourable for materials exhibiting interesting ferroelectric properties at room temperature, which are often needed for applications.

One of the aims of this work was to prepare ferroelectric SCLCPs with broad S_C^* temperature ranges preferably at or close to room temperature and with fast switching times. This could be achieved by combining the following two important features :

- (a) Partial fixation of mesogenic groups on the polymer backbones using co-polymerisation techniques. This dilution of the mesogenic groups on the polymer backbone lowers the transition temperatures and the viscosities of the polymers.³⁸
- (b) Polar mesogenic side chains with one or two asymmetric carbon atoms. This kind of chiral moiety provides high polarisation values and short switching times.^{39,40,41}

The general formula of the polysiloxanes synthesised is given below (Fig. I Ib.15).

Scheme for polymers



Scheme for copolymers

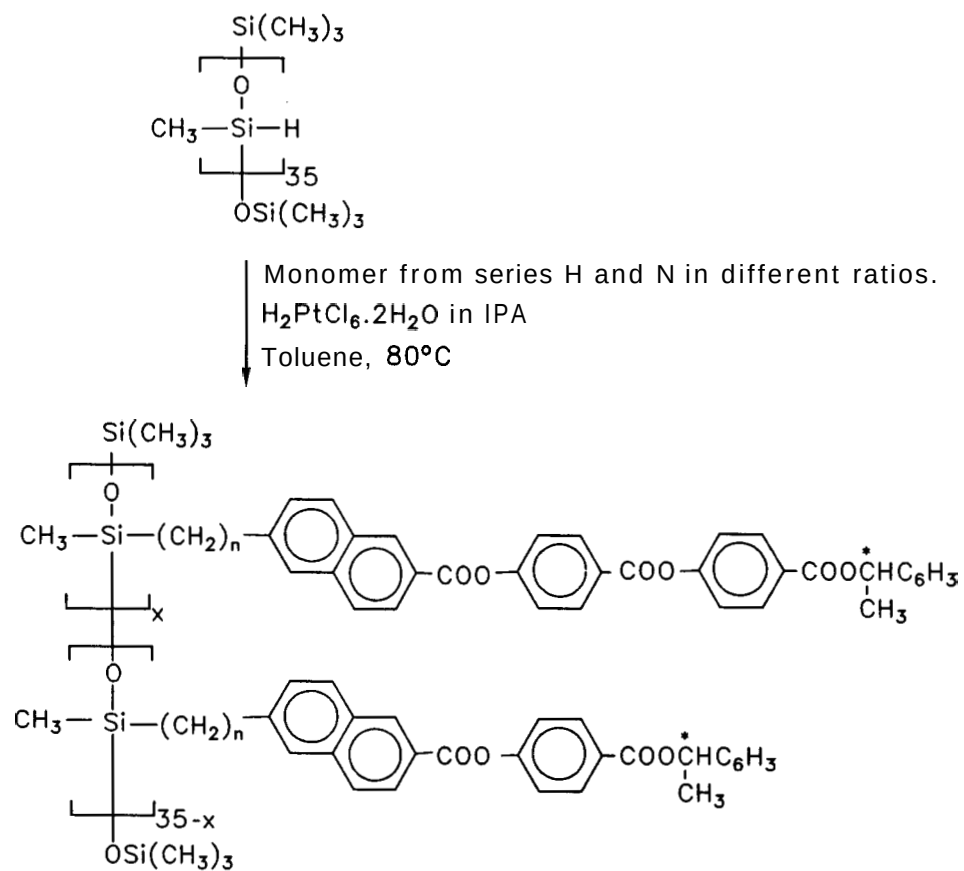


Fig.IIb.15

IIb.4 Discussion

The first ferroelectric side chain liquid crystalline polymer was reported by Shibaev *et al.*, in 1984.⁴² Since then several structural modifications have been attempted for obtaining S_C^* phase in a side chain polymer.⁴³ A ferroelectric SCLCP is generally comprised of four constituents:

(i) Spacer

Besides polymethylene, oligo-oxyethylene spacers also have been used and these also seem to favour the formation of S_C^* phase. These represent a new class of crown ethers and also have applications in solvent free polymer electrolytes.^{44,45}

(ii) Polymer backbone,

(iii) Mesogenic core,

(iv) Chiral end group on the mesogenic unit.

In this work a more systematic investigation is presented regarding the influence of these four components on the possibility of obtaining a ferroelectric SCLCP.

The following tables (Table IIb.2 to IIb.4) summarise the thermal transitions of seven series of polysiloxanes containing the chiral mesogen.

IIb.4.1 Influence of spacer on phase transitions

The aliphatic spacers contain six, ten and eleven methylene units respectively. All of them display an illustrative example of variation of spacer length on the formation of the S_C^* phase. These examples indicate that short spacers are not favourable for the formation of S_C^* phase. A similar observation was made by Chain-

Tab.IIb.1 : Transition temperatures (°C) and enthalpies[#] (Jg⁻¹) of polymers.

Polymer	T _g	S _C *	S _A	I
RP-4	48	.	198.70	236.10 3.92
RP-8	58	.	213.50	256.70 4.55
RP-9	63	.	221.50	258.50 5.64
KP-4	55	.	156.90	188.10 3.96
KP-8	50	.	190.30	214.70 4.24
KP-9	38	.	199.30	216.90 5.55
IP-4	71	.	223.30	256.40 5.62
IP-8	62	.	214.40	251.40 4.36
IP-9	56	.	198.80	244.70 6.23

Table IIb.2 : Transition temperatures (°C) and enthalpies (Jg⁻¹) of polymers.

Polymer	T_{g1}	T_{g2}	S_C*	S_A	I
HP-4	2.20	-	-		44.30 5.21
HP-8	-5.40	-		39.20	89.30 4.89
HP-9	-6.10	4.60		93.20	109.90 5.78
SP-4	-	26		78.50	97.60 4.66
SP-8	-	34		140.50	161.70 6.46
SP-9	-	51		142.80	164.30 6.51

Enthalpies for the S_C*- S_A could not be measured. Enthalpies for S_A-I represents the combined enthalpies for both.

Tab.IIb.3: Transition temperatures (°C) and enthalpies (Jg⁻¹) of polymers.

Polymer	T_{g1}	T_{g2}	S_C[*]	S_A		I
NP-4	-2.20	12.20		54.60	190.60	
					5.20	
NP-8	-5.30	4.50	.	71.20	234.80	.
					8.13	
NP-9	-5.90	-1.50	.	94.10	235.30	.
					9.21	
AP-4	-3.00	17.90	.	107.20	198.80	.
					5.20	
AP-8	-5.20	9.20	.	63.40	223.00	.
					8.42	
AP-9	-5.90	6.70	.	128.90	229.50	.
					8.22	

Enthalpies for the S_C^{*}- S_A could not be measured. Enthalpies for S_A-I represents the combined enthalpies for both.

Tab.IIb.4: Transition temperatures (°C) and enthalpies (Jg⁻¹) of polymers.

Polymer	T_{g1}	T_{g2}	S_C*	S_A	I
M-00	-6.10	4.60		93.20	109.90 5.78
M-25	2.40	-			148.20 6.61
M-50	-3.10	-	.		174.10 8.83
M-75	-8.40	1.70	.		201.80 8.54
M-100	-5.30	4.80	.	71.20	. 234.80 8.13

Enthalpies for the S_C*- S_A could not be measured. Enthalpies for S_A-I represents the combined enthalpies for both.

Shu *et al.*⁴⁶ All the polymers reveal an enantiotropic S_A and S_{C^*} phases, but the thermal ranges in case of the longer spacers are wider and it show a very well stabilised ferroelectric phase. As opposed to Chain-Shu's observation, these polymers do not exhibit a S_B phase. This may be primarily due to the difference in the core structure. They have used biphenyl core in place of naphthalene moiety in our system. The phase characterisation was done using both optical microscopy and temperature dependent X-ray diffraction studies wherever it was possible. The fact remained that the longer spacer favoured the formation of a stabilised S_{C^*} phase. The Fig.IIb.15a, depicts a representative DSC curve of polymer HP-9. It presents two glass transitions temperatures at $-6.1\text{ }^{\circ}\text{C}$ and $4.6\text{ }^{\circ}\text{C}$ and an S_A -I phase transition at $93.2\text{ }^{\circ}\text{C}$. As was discussed earlier, the glass transition at lower temperature can be attributed to independent motion of polysiloxane backbone, while the one at higher temperature to the cooperative motion of the side group mesogens. Such phenomena has been reported.⁴⁷ Many other polymers synthesised also show similar behaviour as can be seen from the transition temperature tables. (Tab. IIb.3 and IIb.4).

IIb.4.2 Influence of polymer backbone on phase transitions

The influence of polymer backbone on the formation of a S_{C^*} phase was examined. A comparison of the mesomorphic properties of compounds prepared by us with those prepared and reported in literature⁴¹ shows that the polymer backbone can not only affect the thermal stability of the mesophases formed but the nature of the mesophases as well. Furthermore, a flexible polymer backbone seems to have a tendency toward having a lower T_g and a wider mesomorphic range. The most

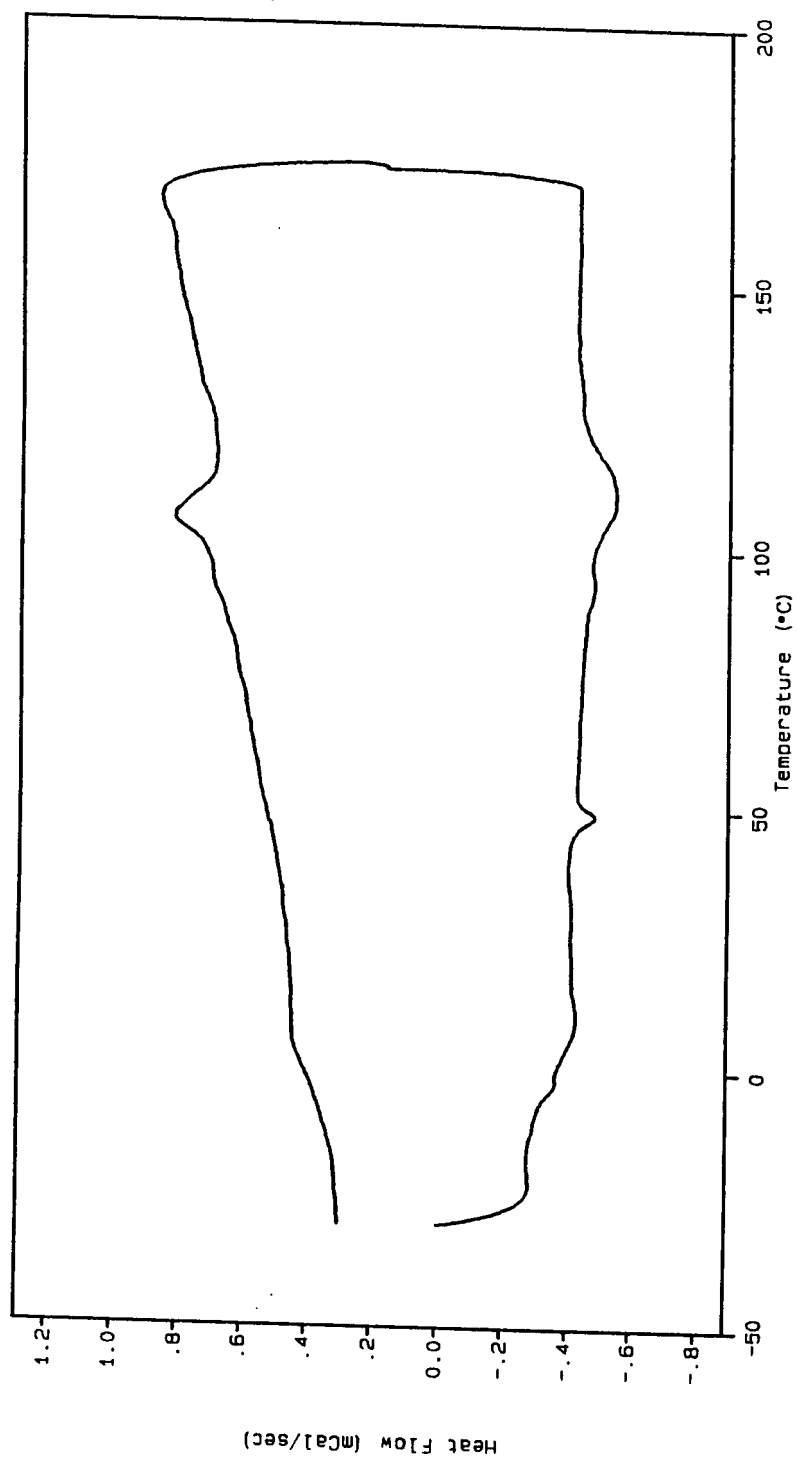


Fig.IIb.15a

important tendency is that the flexible polymer backbone also leads to a wider temperature range of the ferroelectric phase.

IIb.4.3 Influence of mesogenic core on the phase transition

In order to study the influence of core on the phase transition, we compare the phase transition temperatures and the nature of the phases of our polymers with those reported by others. We have varied the core to a large extent as can be seen from the structures shown below (Fig. IIb.16). From Tabs. 2, 3 and 4 it is clear that, introduction of a phenyl group into the core increases the transition temperatures.

IIb.4.4 Naphthalene containing polymers

The geometry of naphthalene unit is such that it has many of the structural features associated with the phenylene ring used in the mesogenic component of liquid crystalline compounds. Very few liquid crystalline materials, however, have been prepared that incorporate the naphthalene residue either in the polymer or in the LMM mesogens outside those appearing in the patent literature. There are a number of ways in which naphthalene moiety can be introduced into the linear mesogenic structure, because of the eight possible sites for substitution as shown below (Fig. IIb.17).

In direct analogy with the phenylene group, 1, 4-substitution would produce *para* functional groups with an aromatic ring as side chain, while both 1, 5 and 2, 6-substitution would give parallel but slightly offset structures. Compounds with functional groups in the 2, 6-positions have been used to a greater extent than the others in liquid crystalline material structures and are believed to lead to 'frustrated' chain packing in the solid state thereby resulting in reduced melting temperatures.⁴⁹

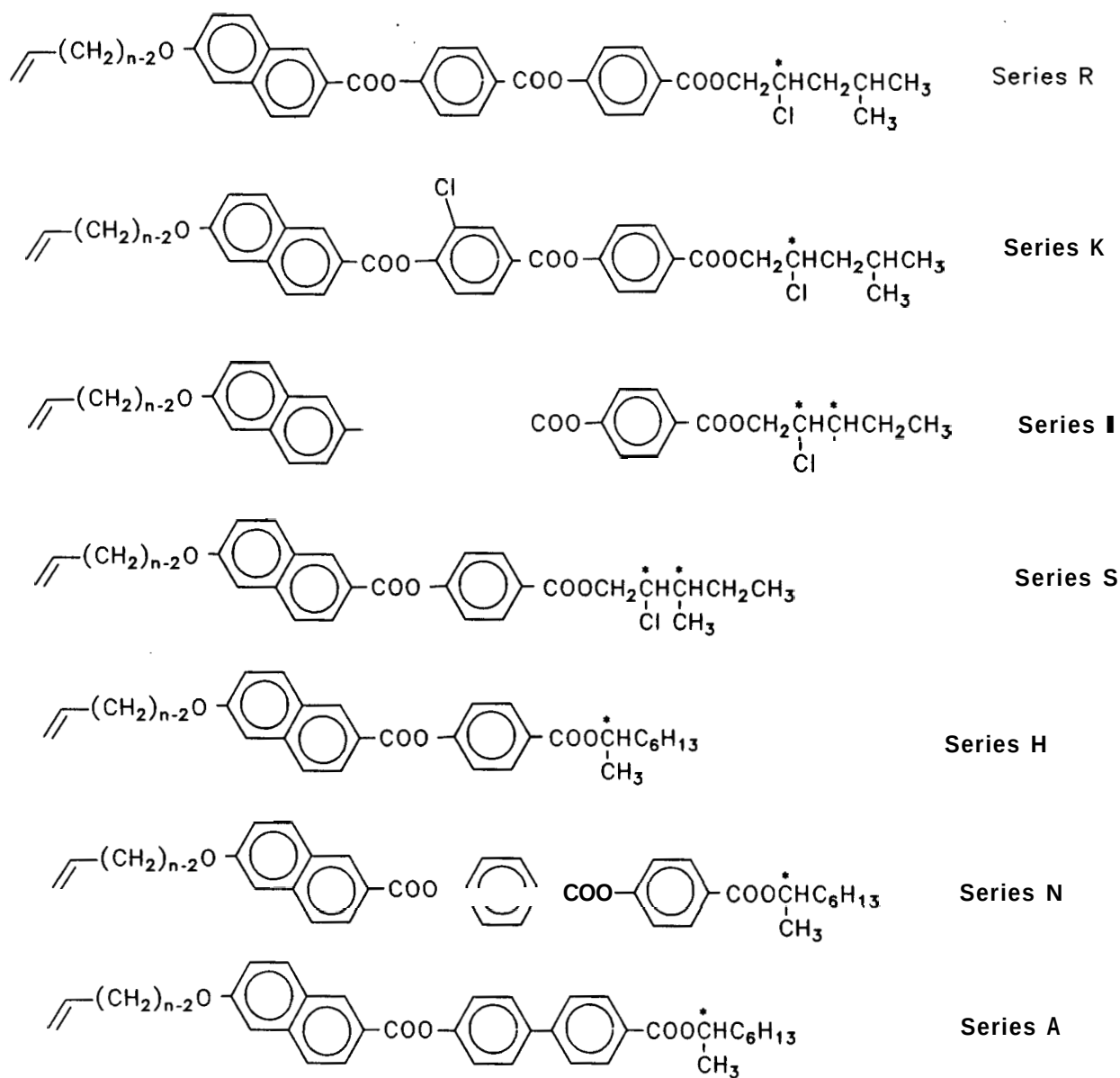


Fig.IIb.16

Recently, the use of naphthalene moiety in liquid crystalline materials has become more common mainly because of the industrial research into liquid crystalline polymers with wholly aromatic structures. Several review articles have recently summarized the available literature, more so in the case of patent literature. Most of them are main chain polymers. Side chain polymers containing naphthalene moiety have not been investigated in detail.^{50,51,52}

IIb.5 Physical studies

IIb.5.1 Measurement of spontaneous polarisation and tilt angle

A typical oscilloscope trace for polymer HP-9 at $T = 122^{\circ}\text{C}$ (S_{C^*} phase) showing the polarisation current peaks is given in Fig. IIb.18.

The temperature dependence of the spontaneous polarisation was determined for some of the polymers and some values are collected for a given reduced temperature of $T_c - T = 10^{\circ}\text{C}$. The highest P_s value that we have measured is 47nCcm^{-2} at 98°C for the polymer SP-9. Looking at the general temperature dependence of polarisation for polymers (Fig. IIb.19), it reaches a maximum value at a particular temperature and then decreases on lowering the temperature. No measurements could be made below this critical temperature although a bistable switching could be observed at even lower temperatures. This is because the switching times were large and the polarisation peak broadens out making it difficult to measure the peak area accurately. The temperatures (T_c) given in Fig. IIb.19 are those obtained from DSC measurements. This is because the S_{C^*} - S_A phase transition could not be detected accurately under the optical polarising microscope.

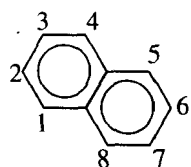


Fig.IIb.17 Eight possible places of substitution in naphthalene core.

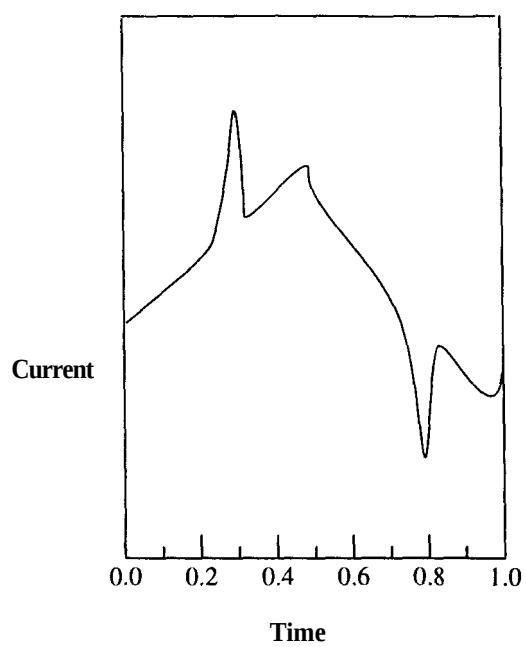
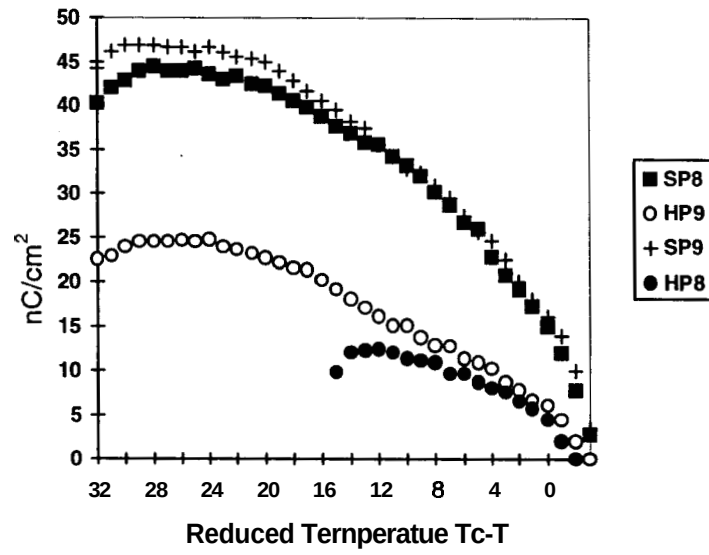
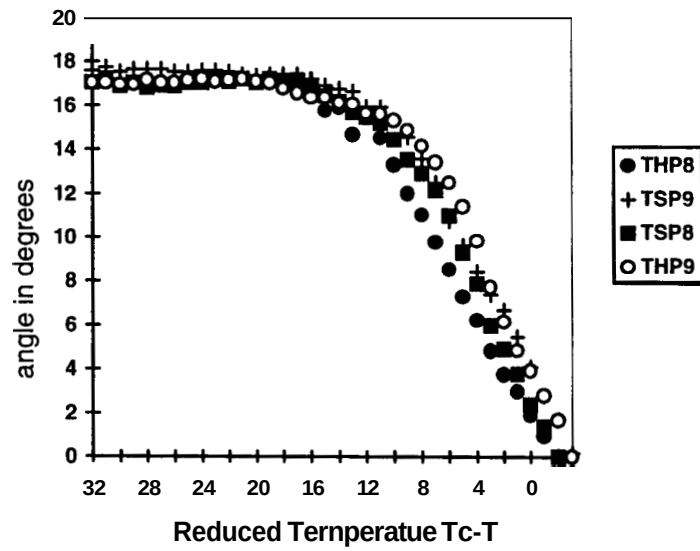


Fig.IIb.18 Current versus time trace for determination of spontaneous polarisation.

Spontaneous Polarisation for Polymers



Tilt angle variation for Polymers



A spill-over of both polarisation and tilt angle could be observed a little into the smectic A phase. This could be interpreted as electroclinic effect, but since the applied voltages were relatively low, it does not explain the small spill-over satisfactorily. A plausible explanation could be the coexistence of S_{C^*} and S_A phases for a small range of temperature.

The following trends could be generalised for the two sets of polymers *viz.* SP and HP studied. The tilt angle for all the polymers increases monotonously until about 16°C below the S_{C^*} - S_A phase transition and saturates beyond this temperature. An increase in spontaneous polarisation was observed with the lowering of temperature, as was expected. Below a certain temperature, which depends on individual polymer, the P_s tends to decrease. This may be explained as due to the increase of the viscosity of the polymer medium, restricting the switching of the polarisation in effect decreasing the net value measured. Such effects have been reported before.⁵⁴ The SP set of polymers have a larger polarisation value as compared to the HP set. This can be interpreted as due to the presence of the chloro group at the chiral centre which has a strong dipole. Similar effects of strong polar groups at the chiral centre have been observed⁵⁴ and are confirmed here. Another general trend is that the longer spacer containing polymer has a larger polarisation value and a larger tilt angle, which have also been reported for low molar mass compounds.⁵⁵

Iib.5.2 Results from X-ray studies

The synthesised polymers were subjected to X-ray diffraction analysis. The temperature dependent X-ray diffraction patterns were obtained for powder samples of most of the polysiloxanes. The diffraction pattern for polymer SP-8, which is typical

for all the investigated systems is shown in Fig. IIb.20. In the S_{C^*} phase ($T = 122^\circ\text{C}$), the pattern is dominated in the small angle region by well-pronounced Bragg peak, indicating a well organised smectic layer structure. In the wide angle region, only a broad diffuse halo was observed, which is characteristic of a fluid like packing of the mesogens within each smectic layer of the S_{C^*} phase. Calculating the tilt angle (θ) from x-ray measurements yields only 70% of the value determined from optical measurements. This may be due to a change in the extent of interdigitation of the side chain and the zig-zag arrangement of the mesogenic unit. In the S_A phase the layer spacings are slightly increased $\approx 1.3\text{-}1.5 \text{ \AA}$ in comparison with those of S_{C^*} phase.

Another interesting observation is that the layer spacing of the polymer (35.21 $\text{\AA}$) in the smectic **A** phase is more than the layer spacing observed for a pure monomer in its smectic **A** phase (33.16 $\text{\AA}$). This indicates that either:

- (i) Some amount of interdigitation takes place increasing the layer spacing, (in which case a large increase would be expected. But, as the increase is not substantial the interdigitation can be safely ruled out);
- (ii) It can be assumed that there is a net non-zero contribution of the polymer backbone to the layer spacing, in which case the increase in the layer spacing would not be significant (Fig. IIb.21). This seems a plausible explanation to the observed phenomenon.



Fig.IIb.18

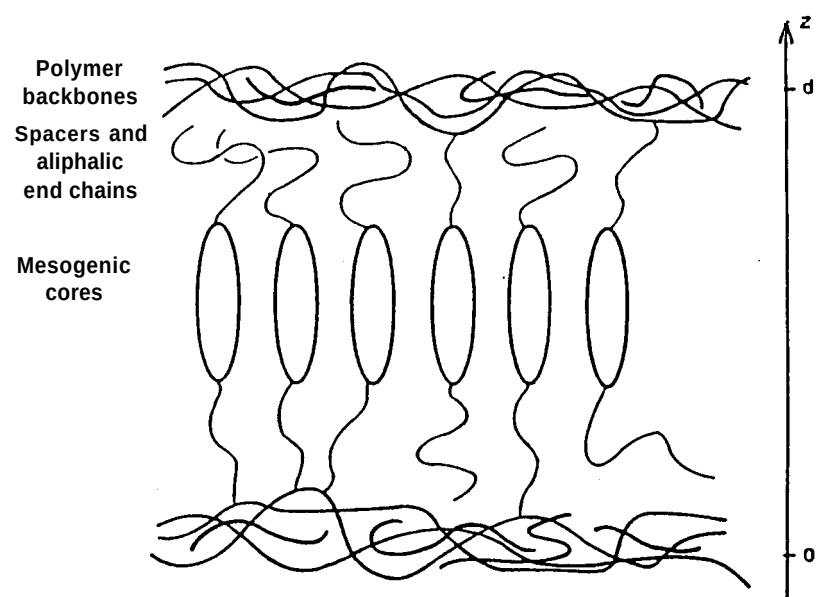


Fig.IIb.21

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