Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Side chain liquid crystal polysiloxanes and their low T_g copolymer analogues

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To cite this Article Nestor, G. , Gray, G. W. , Lacey, D. and Toyne, K. J.(1989) 'Side chain liquid crystal polysiloxanes and their low T_g copolymer analogues', Liquid Crystals, 6: 2, 137 — 150
To link to this Article: DOI: 10.1080/02678298908033209
URL: http://dx.doi.org/10.1080/02678298908033209

LIQUID CRYSTALS, 1989, VOL. 6, NO. 2, 137–150

Side chain liquid crystal polysiloxanes and their low T_g copolymer analogues

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(*Received 23 January 1989; accepted 27 February 1989*)

A number of side-chain liquid crystal homopolymers derived from poly(hydrogenmethylsiloxane) and their copolymeric analogues with the same mesogenic side chains appended to a poly(hydrogenmethyldimethylsiloxane) backbone have been prepared. The homo and copolymers exhibit the same mesophase types, but markedly different T_g values, mesophase transition temperatures and isotropisation enthalpies. These differences are interpreted in terms of the relative $\overline{\mathrm{DP}}$ values and flexibilities of the backbones for the homo and copolymers.

1. Introduction

The past decade has seen much activity in the synthesis and study of liquid crystal side-chain polymers [1, 2, 3]. From a theoretical standpoint, side-chain liquid crystal polymers are interesting because they must combine the anisotropy and fluidity of liquid crystals with the disorder associated with the melted conformation of the polymer backbone. This seemingly incompatible situation gives rise to interesting questions concerning the competing influences of the two antagonistic tendencies, (i) of the backbone to be randomly coiled, and (ii) of the side chains to be ordered. Technologically side-chain liquid crystal polymers are becoming of interest for a number of applications, e.g., as stationary phases for high resolution gas chromatography [4, 5, 6], as selective optical filters/reflectors [7], as dopants for low molar mass liquid crystals to alter the thermal, visco-elastic, and dielectric properties of the bulk materials, hopefully to improve multiplexing capability and performance of electro-optic displays [8], and possibly as materials for use as electro-optic data storage media [8, 9, 10].

In this paper we report the synthesis and characterization of two series of side-chain liquid crystal polysiloxanes, which were produced as part of a programme to establish structure/property relations, with particular reference to their use as electro-optic data storage media. The side-chain polysiloxanes synthesized were based on two different polysiloxane backbones: poly(hydrogenmethylsiloxane) (PHMS, DOW DC 1107) homopolymer and poly(hydrogenmethyldimethylsiloxane) copolymer [P(HM/DM)S, Petrarch PS 122.5] (see table 1). These backbones were separately combined with each of six different alkenes which constituted the mesogenic side chains. The polymers are represented by structures (I) and (II) (see figure 1).

Polymers of type (I) are typical of many reported in the literature [1, 2, 3, 11, 12, 13], and it is of interest to compare polymers IE and IF with those reported by Stevens *et al.* [11]. The agreement between the two sets of results is particularly good, especially when we consider the many contributory reasons advanced to explain the

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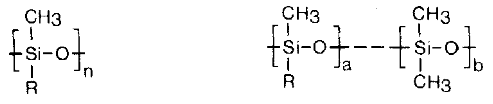

(I)
Homopolymer.

(II)
Statistically random copolymer.
(a:b = 1:1·17)

where *R* is one of the mesogenic side chains.

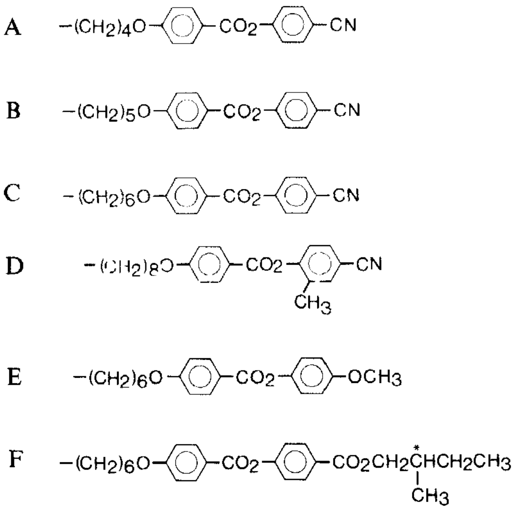

Figure 1. Structures of liquid crystal polysiloxanes ((I) and (II)).

Table 1. Specifications for poly(hydrogensiloxane)s.

	GPC‡			^{1}H N.M.R.§		
Source	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	DP	Polymers prepared
Dow DC 1107	9950	3100	3·2	2560	40 ± 3	I A–F
Petrarch PS122·5†	2400	1300	1·9	1100	13 ± 2	II A–F

† Ratio -SiHMeO-:-SiMe$_2$O = 1:1·17.

‡ GPC analysis was carried out using toluene solutions on PL gel; 30 cm column 10 μm packing (10^3–10^5 Å), ambient temperature, flow rate 1 ml min^{-1}. Calibration was based on a third order polynomial expression to give polystyrene equivalent molecular weights.

§ End group analytical values obtained by N.M.R. spectroscopy represent an average of five integrations.

poor comparisons that have arisen in other instances between different preparations of side-chain liquid crystal polymers of the same structure [12].

The main purpose of this paper is however to report the synthesis of the copolymers (II), and to make comparisons of their properties with those of type (I). Some interesting work of a similar nature was earlier carried out by Ringsdorf and Schneller [13]. These workers were primarily concerned with studying the effects upon properties of varying the ratio **a**:**b** (see figure 1), and showed that a decrease in **a** relative to **b** resulted in a lowering of the glass transition temperature (T_g) and the clearing temperature (T_c) of the mesophase of a given polymer. Other examples of the use of P(HM/DM)S as the backbone in liquid crystal polymers have been briefly reported [5, 14], and Finkelmann, Kock and Rehage [15] have also described the synthesis of a type (II) liquid crystal polymer comparable with polymer IIE. The disagreement between the results reported for IIE in this study and those recorded by Finkelmann *et al.* can probably be attributed to the difference in the average degree of polymerization ($\overline{DP}$) of the two P(HM/DM)S copolymer backbones used, 13 and 120 respectively. Similar effects have also been demonstrated for PHMS-derived liquid crystal polymers [11].

Realizing the significance of these early studies, particularly those of Ringsdorf and Schneller, we have kept the ratio of **a** : **b** constant and varied the mesogenic side chains (*R*). By synthesizing these copolymers with a diluted content of mesogenic side chains we hoped to achieve some desired changes in the properties of the liquid crystal polymers, e.g., viscosity, T_g, phase types, transition temperatures, and crystalline tendencies, resulting in better materials for practical applications in data storage devices [10].

3. Experimental section

The alkenes used in this study were prepared by published standard methods [13, 22, 23]. IR and ^{1}H N.M.R. spectra were run on a Perkin Elmer 58OB infrared spectrophotometer and a Jeol JNM-G × 270 N.M.R. spectrometer, respectively. The liquid crystal polysiloxanes (I) were prepared by a poly(hydrosilylation) reaction between the PHMS backbone and an appropriate alkene as reported previously [12]. When P(HM/DM)S backbone [0·6 g, 4·5 mmol (Si–H)] was used to produce the copolymers (II), the same procedure was followed, based on the molar content of Si–H in the copolymer backbone, and employing 60 ml of toluene as the reaction solvent. Each liquid crystal polymer was synthesized twice to ensure that the results were reproducible.

The polymers were characterized by differential scanning calorimetry (D.S.C.), using heating and cooling rates of 10°C min^{-1}, polarizing optical microscopy, and thermo-optical analysis (TOA), again as detailed previously [12]. Any crystallization effects were studied by repeating the thermo-optical and D.S.C. analyses after the samples of the liquid crystal polymer used for the original D.S.C. and optical microscopy experiments had been stored at ambient temperature (approximately 20°C) for 28 days. No preheating of these samples was, of course, carried out.

The degree of polymerization ($\overline{DP}$) and the ratio weight to number average molecular weight $\bar{M}_w/\bar{M}_n$ of the liquid crystal polysiloxanes have been assumed to be the same as those for the PHMS or P(HM/DM)S prepolymer used.

4. Results and discussion

The results (i) of the thermal and optical analysis of the liquid crystal polysiloxanes (I) and (II) are summarized in tables 2 and 4 respectively, and (ii) of the 28 day crystallinity studies in tables 3 and 5, respectively. The quantitative differences between the initial analytical results for liquid crystal polymers of types (I) (see table 2) and (II) (see table 4) are recorded in table 6, and illustrated by figures 2 and 3 (the latter specifically for polymers IC and IIC).

Table 2. Thermal data for polymers of structure (I).

Polymer	T_g/°C	T_m/°C	$T_{SN/I}$/°C§	T_{NI}/°C	PW/°C	ΔC_p/ J g^{-1} K at T_g	ΔH_{T_m}/ J g^{-1}, ΔS_{T_m}/ J K^{-1} g^{-1} 10^{-3}	$\Delta H_{SN/I}$/ J g^{-1}, $\Delta S_{SN/I}$/ J K^{-1} g^{-1} 10^{-3}	ΔH_{NI}/ J g^{-1}, ΔS_{NI}/ J K^{-1} g^{-1} 10^{-3}
IA	26	—	136	—	11	0·3	—, —	1·9, 4·7	—, —
IB	—	84	170	—	24	—	12·9, 36·2	3·3, 7·5	—, —
IC	18	[40]	167	—	15	0·1	7·4, 23·6	3·6, 8·1	—, —
ID	5	—	95	—	9	0·2	—, —	2·9, 7·8	—, —
IE	6	—	[40]	106	13	0·2	—, —	0·2, 0·7	2·1, 5·6
IF	−9	75	75#	—	19	0·2	†	†	—, —

PW Baseline peak width of clearing transition from D.S.C.
[ ] Metastable phase.
§ Smectic phases are S_A except # which is believed to be chiral S_C (S_C^*).
† Values unavailable due to coincidence of transitions.

Table 3. Thermal data from 28 day crystallinity studies of polymers of structure (I).

Polymer	T_g/°C	T_{m_A}/°C	T_m/°C	$T_{SN/I}$/°C§	T_{NI}/°C	PW/°C	ΔC_p/ J K g^{-1} at T_g	$\Delta H_{T_{m_A}}$/ J g^{-1}, $\Delta S_{T_{m_A}}$/ J K^{-1} g^{-1} 10^{-3}	ΔH_{T_m}/ J g^{-1}, ΔS_{T_m}/ J K^{-1} g^{-1} 10^{-3}	$\Delta H_{SN/I}$/ J g^{-1}, $\Delta S_{SN/I}$/ J K^{-1} g^{-1} 10^{-3}	ΔH_{NI}/ J g^{-1}, ΔS_{NI}/ J K^{-1} g^{-1} 10^{-3}
IA	23	—	—	135	—	11	0·3	—, —	—, —	1·8, 4·4	—, —
IB	—	{49}	84	170	—	20	—	2·3, 7·1	11·5, 32·2	3·4, 7·7	—, —
IC	—	{45}	—	168	—	15	—	15·8, 49·7	—, —	3·5, 8·0	—, —
ID	5	—	—	95	—	9	0·2	—, —	—, —	2·9, 7·8	—, —
IE	7	{50}	—	—	106	10	0·1	11·5, 35·6	—, —	—, —	1·9, 5·1
IF	−9	—	75	75#	—	19	0·2	—, —	†	†	—, —

PW Baseline peak width of clearing transition from D.S.C.
{ } Melt temperature for a crystalline phase which appears after annealing.
§ Smectic phases are S_A except # which is believed to be S_C^*.
T_{m_A} Transition involving a crystalline phase consequent upon annealing.
† Values not available due to coincidence of transitions.

Table 4. Thermal data for polymers of structure (II).

Polymer	T_g/°C	T_m/°C	$T_{SN/I}$/°C§	T_{NI}/°C	PW/°C	ΔC_p/ J K^{-1} g^{-1} at T_g	ΔH_{T_m}/ J g^{-1}, ΔS_{T_m}/ J K^{-1} g^{-1} 10^{-3}	$\Delta H_{SN/I}$/ J g^{-1}, $\Delta S_{SN/I}$/ J K^{-1} g^{-1} 10^{-3}	ΔH_{NI}/ J g^{-1}, ΔS_{NI}/ J K^{-1} g^{-1} 10^{-3}
IIA	−9	—	72	—	18	0·2	—, —	2·7, 7·9	—, —
IIB	−9	6	98	—	19	0·1	0·8, 2·9	4·6, 12·5	—, —
IIC	−10	[1]	100	—	22	0·1	0·5, 1·7	4·5, 12·1	—, —
IID	−16	—	57	—	14	0·3	—, —	3·8, 11·4	—, —
IIE	−14	—	26	54	10	0·2	—, —	0·3, 1·0	1·2, 3·5
IIF	−25	—	31	—	17	0·1	—, —	3·9, 12·9	—, —

PW Baseline peak width of clearing transition from D.S.C.
[ ] Metastable phase.
§ Smectic phases are S_A.

Table 5. Thermal data from 28 day crystallinity studies of polymers of structure (II).

Polymer	T_g/°C	T_{m_A}/°C	T_m/°C	$T_{SN/I}$/°C§	T_{NI}/°C	PW/°C	ΔC_p/ J K g^{-1} at T_g	ΔH_{T_m}/ J g^{-1}, ΔS_{T_m}/ J K^{-1} g^{-1} 10^{-3}	$\Delta H_{T_{m_A}}$/ J g^{-1}, $\Delta S_{T_{m_A}}$/ J K^{-1} g^{-1} 10^{-3}	$\Delta H_{SN/I}$/ J g^{-1}, $\Delta S_{SN/I}$/ J K^{-1} g^{-1} 10^{-3}	ΔH_{NI}/ J g^{-1}, ΔS_{NI}/ J K^{-1} g^{-1} 10^{-3}
IIA	−5	—	—	70	—	19	0·2	—, —	—, —	3·1, 9·0	—, —
IIB	−9	6	—	98	—	24	0·1	1·1, 4·1	—, —	4·6, 12·3	—, —
IIC	—	—	{47}	102	—	23	—	—, —	13·3, 41·4	4·5, 12·0	—, —
IID	−16	—	—	57	—	12	0·2	—, —	—, —	3·7, 11·2	—, —
IIE	−14	—	—	26	54	10	0·2	—, —	—, —	0·3, 1·1	1·4, 4·2
IIF	−22	—	{37}	31	—	17	0·2	—, —	†	†	—, —

PW Baseline peak width of clearing transition from D.S.C.
{ } Melt temperature for a crystalline phase which appears after annealing.
T_{m_A} Transition involving a crystalline phase consequent upon annealing.
† Values not available due to overlap of transitions.
§ Smectic phases are S_A.

Table 6. Differences in thermal data for polymers of structures (I) and (II) (Δ' = data from table 2 minus table 4).

Polymer side chain	$\Delta' T_g$/°C	$\Delta' T_m$/°C	$\Delta' T_{SN/I}$/°C	$\Delta' T_{NI}$/°C	$\Delta'(\Delta H_{T_m})$/ J g^{-1}, $\Delta'(\Delta S_{T_m})$/ J K^{-1} g^{-1} 10^{-3}	$\Delta'(\Delta H_{SN/I})$/ J g^{-1}, $\Delta'(\Delta S_{SN/I})$/ J K^{-1} g^{-1} 10^{-3}	$\Delta'(\Delta H_{NI})$/ J g^{-1}, $\Delta'(\Delta S_{NI})$/ J K^{-1} g^{-1} 10^{-3}
A	35	—	64	—	—, —	−0·8, −3·2	—, —
B	—	78	72	—	12·1, 33·3	−1·3, −5·0	—, —
C	28	39	67	—	6·9, 21·9	−0·9, −4·0	—, —
D	21	—	38	—	—, —	−0·9, −3·6	—, —
E	20	—	14	52	—, —	−0·1, −0·3	0·9, 2·1
F	34	—	44	—	—, —	†	—, —

† Values unavailable due to coincidence of transitions.

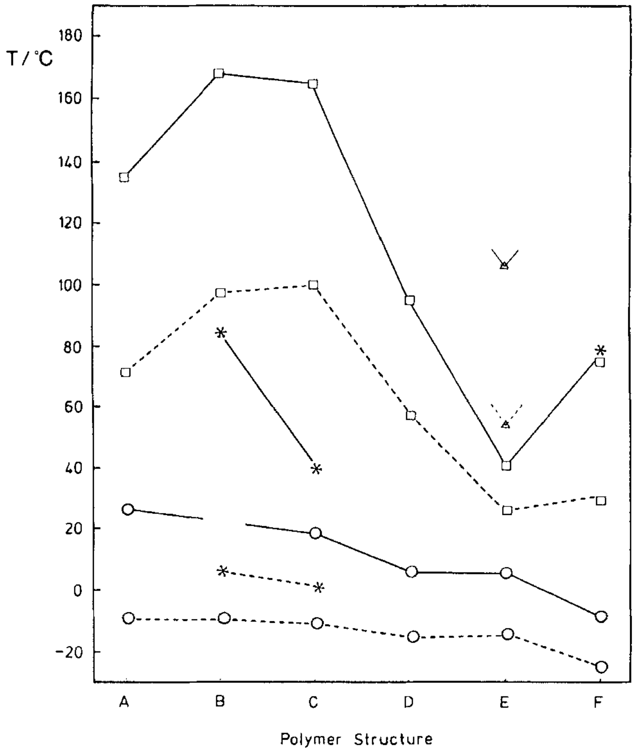

Figure 2. Representation of thermal data for polymers of structures (I) and (II). Solid lines denote type I liquid crystal polymers and broken lines, type II liquid crystal polymers. △, denote T_{NI}; □, $T_{SN/I}$; *, T_m; and ○, T_g.

Some photomicrographs of the textures typical for liquid-crystalline polysiloxanes are given in figures 4–9. Figure 4 shows a typical nematic texture obtained when a thin film of polymer IE was cooled from 108°C to 100°C and then annealed for 30 min. Figure 5 shows the nematic texture of polymer IIE at 46°C, after the sample had been cooled from the isotropic liquid and annealed for 5 minutes. Figures 6–9 are examples of smectic textures. Figure 6 shows a typical smectic A focal conic texture obtained by cooling polymer IC to 160°C and annealing for 5 hours. When this polymer is cooled further to 23°C, it passes through a crystallization transition, and the S_A focal conic textures becomes broken (see figure 7). Figure 8 shows the grainy S_A texture of polymer IC which is obtained on flash cooling the isotropic melt of the polymer; this texture in fact consists of very small focal conic fans. Figure 9 shows the semi-crystalline smectic C* texture of polymer IF obtained by cooling the sample from the isotropic liquid and annealing for 60 hours at 65°C.

When studying the results obtained for these two series of liquid crystal polymers and drawing comparisons between them, four effects are noticed. First, when using the P(HM/DM)S prepolymer, the T_g values are reduced by between 20°C and 38°C, depending on which particular side chain is considered. However, the observed T_g values still do not remotely approach that of poly(dimethylsiloxane) (PDMS), which has a T_g of -123°C [16]. This is obviously due to the dominant ordering effect of the mesogenic side chains (R). The reduction in T_g does however support the assumption that the backbone in the copolymers (II) is more flexible than that in the

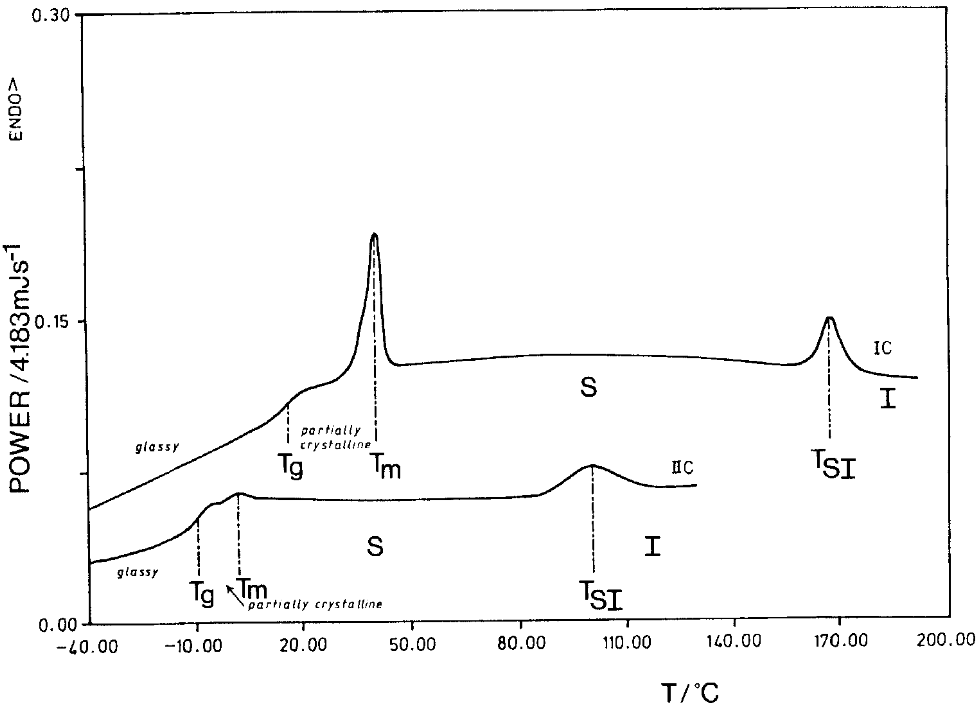

Figure 3. D.S.C. thermograms for liquid-crystalline polymers IC and IIC (see tables 2 and 4 respectively) showing the difference in thermal characteristics between the homopolymer and the copolymer.

homopolymers (I), a supposition that is also corroborated by the lower apparent bulk viscosities of type II polymers and the greater speeds with which they develop well defined optical microscopic textures.

Secondly, when considering the phase types and mesophase transition temperatures for liquid crystal polymers of types (I) and (II), it can be seen from tables 2 and 4 and from figure 2, that whereas the phase types are generally unchanged, the transition temperatures are reduced, e.g., by as much as 72°C for T_{SI} for polymers IB and IIB.

Thirdly, it is interesting to examine the enthalpy (ΔH) and entropy (ΔS) values for the polymers, where it can be seen that the ΔH and ΔS values of the smectic to nematic or isotropic transitions are *larger* for the copolymers (II) than for the homopolymers (I) (hence the negative values in column 7 of table 6). However, the converse is found for the nematic to isotropic transitions of polymers IE and IIE, the only two of the polymers for which this comparison may be made. The significance of these observations will be considered shortly.

Finally, the crystalline tendencies of each liquid crystal polymer have been appraised by studying any changes which occurred in the original D.S.C. and TOA samples after storage for 28 days at ambient temperature. The extent of these tendencies can be assessed by considering the size (ΔH) and sharpness of any melting transitions, and by the reductions in the step values (ΔC_p) of the glass transitions of the polymers which occur as the glassy fraction of the sample is reduced as any crystallization proceeds. As can be seen by studying all of the results, it is generally evident that liquid crystal polymers of type (II) have fewer crystalline tendencies than those of type (I). Taking some specific examples, it is noted that an additional melting transition is observed for polymer IB after 28 days, whereas polymer IIB does not exhibit this effect. Furthermore, polymer IC is particularly susceptible to crystallization (see figure 10), whilst polymer IIC seems to be slightly less affected. Finally, polymer IE is affected to such an extent that the smectic phase is only metastable [17], and is subsequently eliminated by the crystallization process; this is not observed for polymer IIE, which remains essentially unchanged.

In attempting to explain the results and effects observed, several factors have to be taken into account. It must first be remembered that, in general, there is a conflict between the drive towards maximization of the internal entropy of a semi-flexible main chain (backbone) and the minimization of the energy of any liquid crystal system. Secondly, when considering the present results, two additional factors must be considered; these are (*a*) the increased flexibility of the polysiloxane backbone of type (II) polymers; and (*b*) the smaller degree of polymerization ($\overline{\mathrm{DP}}$) of type (II) polymers compared with those of type (I). With these points in mind, from the results of this study and by careful examination of results already in the literature [15, 18, 19, 20, 21], the following suggestions are now made to explain the effects observed for the liquid crystal polysiloxanes of types (I) and (II).

It is first proposed that the reduction in the degree of polymerization reduces:

(i) the liquid crystal phase order;
(ii) the liquid crystal transition temperatures;
(iii) the crystalline tendencies of these liquid crystal polysiloxanes.

Secondly, it is proposed that the increased backbone flexibility (achieved by diluting the mesogenic content with dimethylsiloxy [$(CH_3)_2SiO$] units) allows the side chains to adopt a higher degree of smectic order; the more flexible backbone is more readily accommodated between the smectic layers and is therefore less disruptive of the smectic order. This offers an explanation of the increased ΔH and ΔS values observed for the smectic–nematic or smectic–isotropic transitions on going from homopolymer to copolymer. Consequently, it must be recognized that the observed decreases in the transition temperatures due to the fall in $\overline{\mathrm{DP}}$ may in fact be smaller than might have been anticipated, because the $\overline{\mathrm{DP}}$ effect is mitigated by the opposing influence of increased side-chain order arising from greater backbone flexibility.

Interestingly, we note that the ΔH and ΔS values for the isotropization transitions from the one available pair of nematic polymers do *not* increase on passing from homopolymer IE to copolymer IIE, implying that the nematic order is not stabilized by the increased backbone flexibility; perhaps the polymer backbone is the dominant consideration in the nematic state where interactions between side chains are weaker than in the smectic state.

This hypothesis concerning backbone flexibility is also in agreement with literature results presented on methacrylate and acrylate side chain liquid crystal polymers [2, 18, 19]. It is more specific than the observation made by Finkelmann [2] on the main chain flexibility of the polymer, and is also different from the explanation used in a previous study [15] to account for the increased smectic stability of some liquid crystal polysiloxane copolymers. Therefore, it seems reasonable to believe that a balance must be obtained between the flexibility of the backbone and the dilution of the mesogenic content in order to produce a good liquid crystal polymer. Further dilution of the mesogenic content appears to result in a weakening of the mesogenic side chain interactions, due presumably to increased spatial separation and backbone

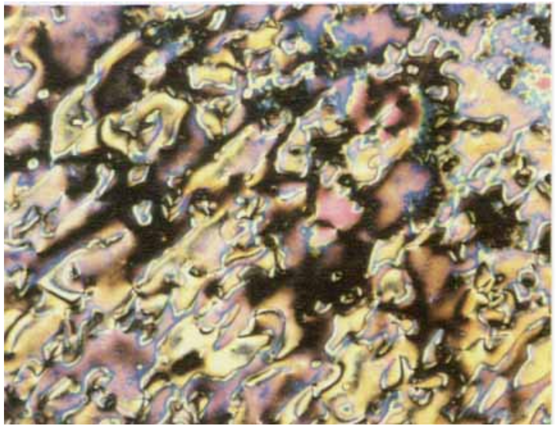

Figure 4. Nematic texture of polymer IE after annealing at 100°C.

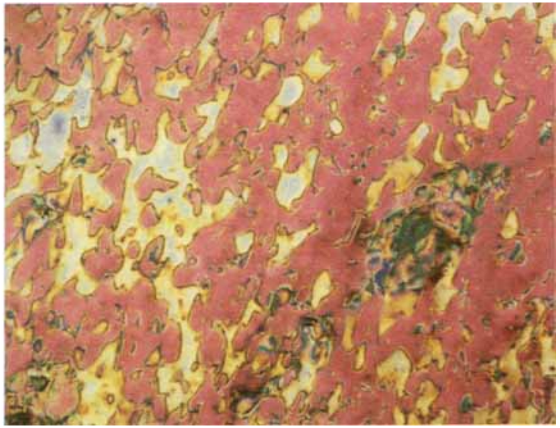

Figure 5. Nematic texture of polymer IIE at 46°C.

Figure 6. Smectic A focal conic fan texture of polymer IC at 160°C.

Figure 7. Broken focal conic fan texture of polymer IC at 23°C (after the sample has undergone a crystallization transition).

Figure 8. Grainy smectic A texture of a sample of polymer IC after flash cooling the isotropic liquid.

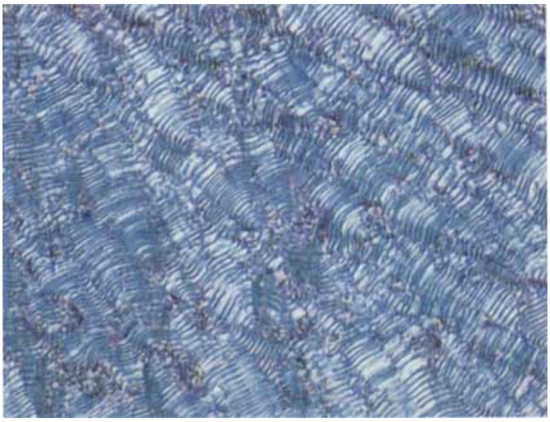

Figure 9. Semicrystalline chiral smectic C* texture of polymer IF at 65°C.

conformational forces, since lower ratios of **a**:**b** give rise to a reduction in the mesophase order and thermal stability for liquid crystal polysiloxanes. It may be fortunate that a favourable balance between all of the factors which can affect such liquid crystal polysiloxanes has been obtained in the copolymers (II). Certainly, these materials are already proving useful as media for electro-optic data storage [10], and similar systems have also proved more useful than homopolymers as stationary phases for high resolution gas chromatography [6].

In figure 11, the full line indicates that when half of the silicon atoms in the backbone carry mesogenic groups, the side chain order is greater than when every silicon (100 per cent mesogen concentration) is mesogenated. Obviously at 0 per cent mesogen concentration, there is no side chain ordering. However, we cannot be sure that the curve has its maximum at 50 per cent mesogen concentration. There may still be room for improvement, e.g., by increasing the mesogen content to 75 per cent, and the dashed line indicates that side chain ordering for such copolymers could peak at > 50 per cent mesogen content. Presumably too, the maximum in side chain ordering would depend upon the nature of the flexible backbone and would be affected by

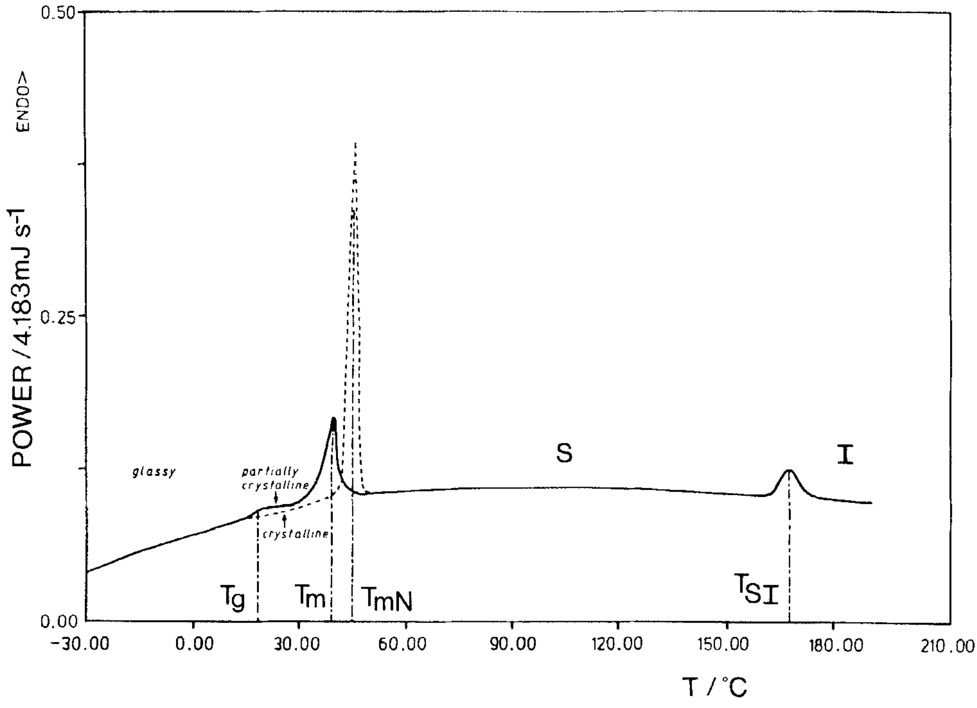

Figure 10. D.S.C. thermograms (initial shown by the solid line and after sample annealing represented by the broken line) for liquid crystal polymer IC.

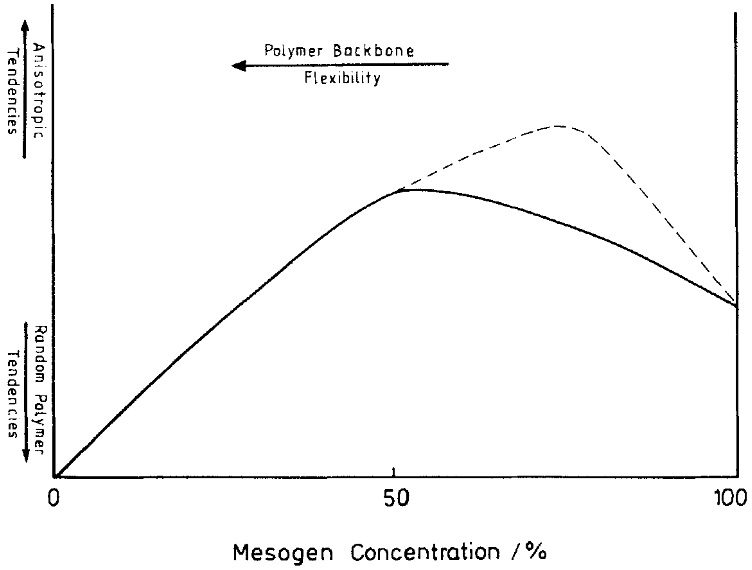

Figure 11. Possible trends in mesogenic side-chain ordering as a function of increasing side-chain content and decreasing backbone flexibility.

changing to a different flexible backbone, e.g., one having ethyl [22] rather than methyl groups on the silicons.

5. Conclusion

Variation of the polysiloxane backbone through dilution of the mesogenic side-chain content with dimethylsiloxy groups has allowed a number of conclusions to be drawn regarding the effects of the degree of polymerization and polymer backbone flexibility on side-chain ordering, as reflected in both the mesophase-isotropic liquid transition temperatures and the enthalpies/entropies of these transitions. The results obtained are supportive of previous conclusions presented in the literature about the effects of degree of polymerization on such liquid crystal polymers.

It would now be interesting to study the effects of structural variants on the polysiloxane backbone by preparing polymers with an increased backbone flexibility, but with the same degree of polymerization, or by variation of the mesogenic content between the 50 and 100 per cent limits employed in this work.

In conclusion, it should be stressed that it is important to consider a combination of all the factors which may influence the behaviour of a side-chain liquid crystal polymer, e.g., DP, backbone flexibility and type, and nature of the mesogenic side chain, for it is clear that a balance has to be obtained between these often antagonistic parameters.

The authors thank the Science and Engineering Research Council for research grants for the purchase of the DSC equipment and for a CASE studentship (to G.N.) with G.E.C., Hirst Research Centre, Wembley and Laser-Scan Laboratories, Cambridge. Acknowledgement is due to Dr M. S. White (previously of these laboratories) for his valued assistance. They also thank Dr R. S. Holding of RAPRA Technology Limited, for the GPC analysis of the polysiloxane backbones, and BDH Limited of Poole, Dorset for the donation of the alkenes needed to produce the liquid crystal polymers of structures D, E and F.

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