Liquid crystal side chain polysiloxanes containing various proportions of non-mesogenic units

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Recent studies have established that side chain polymeric liquid crystals composed of mesogenic and non-mesogenic side groups keep their liquid-crystalline properties even for a low proportion of mesogens. We show that the detailed structures of three kinds of new diluted liquid crystal polysiloxanes depend on the nature of the co-substituent as well as on the proportion of the silicon sites occupied by the mesogenic groups. Mixtures of these systems with low molar mass liquid crystals were also investigated in terms of compatibility and/or stabilization of smectic A phases.

1. Introduction

A polysiloxane chain bearing a mesogenic group on each repeat unit readily shows liquid-crystalline properties. Recently, interest has been focused on the partial fixation of liquid-crystalline side groups on the polymer chain which leads to an increase in the amount of the non-mesogenic moiety: the first studies have shown that the mesophases are preserved even for a low content of mesogenic groups [1–14]. Apart from their basic liquid-crystalline behaviour it is found that the structural and miscibility properties of these compounds are strongly modified. From these points of view, such polysiloxanes can be pictured as a combination of two amphipatic moieties (since the bare backbone is totally immiscible with any classical low molecular mass liquid crystal) which could induce microphase separations in the bulk [7, 8, 11] and phase separations [14–17] in liquid-crystalline solutions as the proportion of both parts is modified.

This work presents a systematic study of the effect of the proportion of fixed mesogenic groups and of the nature of the additional non-mesogenic siloxane segments. The liquid-crystalline and structural properties as well as the behaviour of solutions in a low molar mass liquid-crystalline solvent have been investigated.

2. Materials

The mesogenic groups were obtained via a classical scheme previously described [18]. These mesogenic moieties were then attached to the backbone following an hydrosilylation reaction [19]. Three kinds of backbone were used

(i) one is a homopolymethylhydrogenosiloxane from Petrarch Systems Inc. (series 1). Partially substituted polymers were then obtained by using the appropriate amount of mesogenic groups and adding a catalyst poison (1,2-bis(diphenylphosphino)ether) when the hydrosilylation reaction is achieved

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[20]. The hydrosilylation reaction is performed in toluene under dry nitrogen ($60°C$, 20 hours, $[H_2PtCl_6.6H_2O]$ as catalyst). Then an excess of about 100 per cent of solid poison relative to the catalyst was added and the mixture was kept for 2 h at $60°C$. The polymer was precipitated in methanol and purified twice, dissolving in tetrahydrofuran and reprecipitating in methanol.

  (ii) two are statistical copolymers with various ratios either of methylhydrosiloxane and dimethylhydrosiloxane units from Petrarch (series **2**) or of methylhydrosiloxane and methylphenylsiloxane units from Petrarch (series **3**). In the latter two cases all of the Si–H functions are substituted.

The final products have the following general form
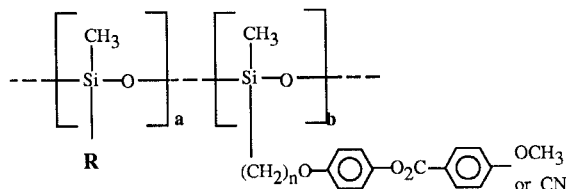
where

$$R = H\ (1),\ CH_3\ (2),\ Phenyl\ (3).$$

$$n = 3 \rightarrow 10.$$

$$a + b = 30\text{--}35,\ series\ (1)\ and\ (2).$$

$$a + b = 10\text{--}13,\ series\ (3).$$

The proportion, X, of mesogenic groups is defined as

$$X = \frac{b}{a+b} \quad (9 \text{ per cent} \leqslant X \leqslant 100 \text{ per cent}).$$

So, the polymers are labelled $P^R_{n,1,X}$ (the index 1 refers to the constant methoxy tail) or $P^R_{n,CN,X}$. The final products were purified by GPC (toluene as eluent). The value of X was checked using ^1H NMR (270 MHz).

3. Characterization of the sequence distribution in copolymers

As reported by Gray *et al.* [21], the distribution of the units in the commercial copolymers can be analysed by ^{29}Si NMR (see figure 1). The spectrum is complex owing to the effects of tacticity [22]. These effects are clearly evidenced in the homopolymer: each type of silicon gives a strong triplet with a 1–2–1 distribution of the intensities (see figure 2). These features combined with those coming from the end groups make the full assignment of the spectrum quite impossible. However, a triad structure is readily visible in the dimethylsiloxane (D) and methylhydrogenosiloxanes (D′) regions corresponding to different chemical environments of the silicon atoms. A rough indexing has been realized (according to [21]) and by comparison with different copolymers synthesized in our laboratory (see figure 3). The contribution of the various sequences has been evaluated in each region (the comparison between different regions is made impossible by the lack of data for the relaxation time). The ratios of the measured intensities agree with a statistical distribution of the different triad sequences in the copolymer as shown in table 1. Due to this random distribution, the proportion of silicon sites occupied by a mesogenic group (X) is the reliable parameter with which to describe a copolymer.
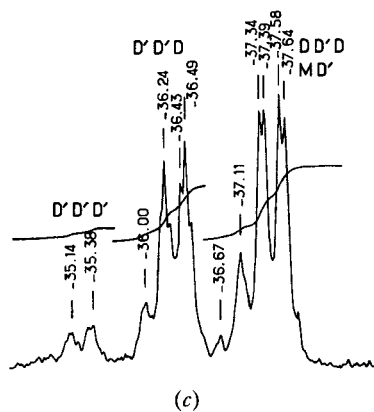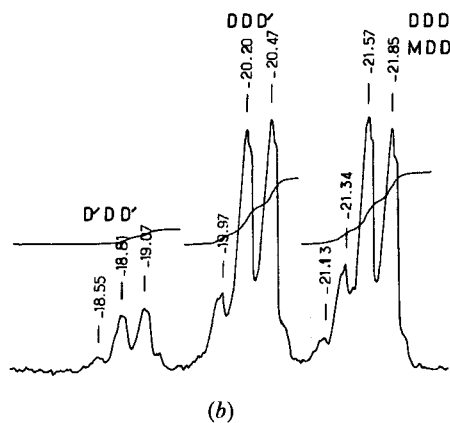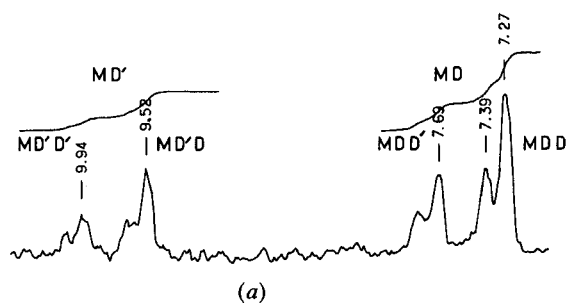
Figure 1. 39·76 MHz ^{29}Si-$\{^1$H$\}$ spectrum of a copolymer with average composition $M_2D_{21}D'_9$ (M: end group, D: dimethylsiloxane, D': methylhydrogenosiloxane). (a) Region M; (b) region D; (c) region D'.

Table 1. Ratios of the different triad sequences (D: dimethylsiloxane unit; D': methyl-hydrogenosiloxane unit) measured by ^{29}Si NMR or calculated using a statistical distribution in a copolymer with 70 per cent of D units and 30 per cent of D' units.

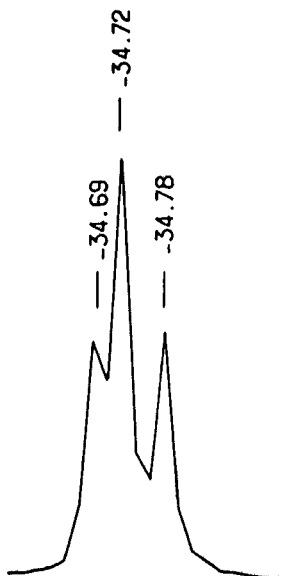|		Measured (per cent)	Calculated (per cent)
	DDD	45	49
Region D	DDD'	45	42
	D'DD'	10	9
	D'D'D'	10	9
Region D'	D'D'D	40	42
	DD'D	50	49

Figure 2. 39·76 MHz ^{29}Si-$\{^{1}$H$\}$ spectrum (centre of the D' region) of the homopolymethyl-hydrogenosiloxane (series 1) showing the fine structure connected to tacticity effects.
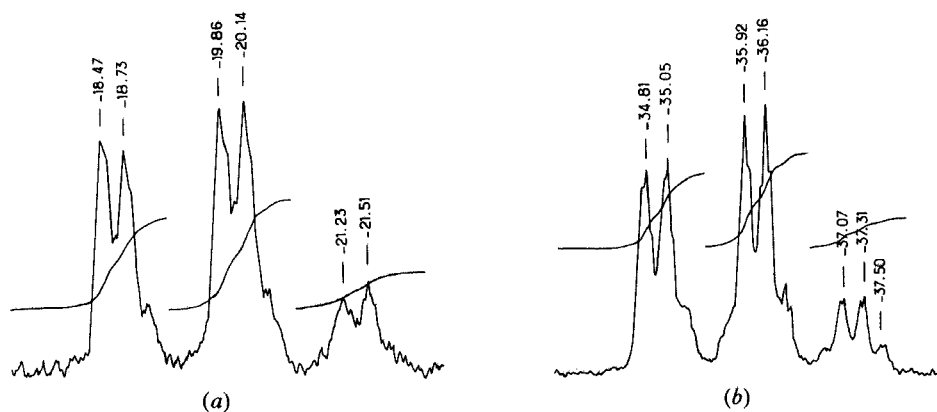

(a)   (b)

Figure 3. 39·76 MHz ^{29}Si-$\{^{1}$H$\}$ spectrum of a copolymer of average composition $M_2D_{28}D'_{52}$. (a) Region D; (b) region D'.

4. Liquid-crystalline and structural properties

The characterizations were achieved through microscopic observations with a Leitz polarizing microscope equipped with a Mettler FP 52 hot stage and thermal analysis on a Perkin–Elmer DSC 7. They were complemented by X-ray diffraction experiments on powder samples using monochromatic $Co-K_{\alpha 1}$ radiation.

We now describe the influence of two parameters on the liquid-crystalline and structural properties namely the dilution X and the nature of the cosubstituent R. The clearing point decreases gradually with decreasing X (as usually observed [1–14, 23] (see figures 4 and 5). In the series (1) and (2), $n = 4$, the nematic phase disappears first. No sample with the lowest X (9 per cent) shows mesomorphic properties down to the glassy state. With partial substitution the nature of all the smectic A phases remain partially bilayer (S_{Ad}); the layer spacings are larger than the length of the mesogenic group. In addition, as figure 6 shows, in partially substituted polymers as well as the corresponding homopolymers [18, 24] an increment of one in n makes d increase by more than the 1·2Å value expected for one methylene group added in the spacer. The continuity in the phase behaviour of partially substituted and fully substituted polymers is also demonstrated by the evolution of the clearing temperatures which vary in a parallel way as a function of the spacer length n (see figure 7). These similarities are consistent with comparable organization of the mesogenic groups inside the layers for the different values of X. The evolution of the layer spacing in the smectic A phase as a function of X shows an increase of d with X decreasing from 100 per cent to 30 per cent (see figure 6) which seems natural if we consider this effect as the result of a simple swelling of the sublayer containing the backbone by the extra siloxane units not substituted by mesogenic groups. However as we already have remarked in [25] the nature of the side group plays a significant role on the magnitude of this effect.

Dealing with the influence of the cosubstituent R the results in figures 4 and 5 show that there is only little difference in the mesomorphic behaviour of copolymers with H or CH_3 (series 1 and 2); the smectic A phase is slightly more depressed with the larger substituent. A more hindering substituent, i.e. a phenyl (series 3), has a more drastic effect since no polymer with a short spacer ($n < 8$) exhibits a mesophase down to the glassy state although the proportion of mesogenic groups (50 per cent) appears high enough to preserve the liquid-crystalline character. However, the polymer $P^{Phenyl}_{8, 1, 50\,per\,cent}$ is nematic at low temperatures ($T_{NI} = 14°C$). It is worth comparing this result to the mesomorphism of the fully substituted homopolymer $P_{8, 1, 100\,per\,cent}$ which

T /°C

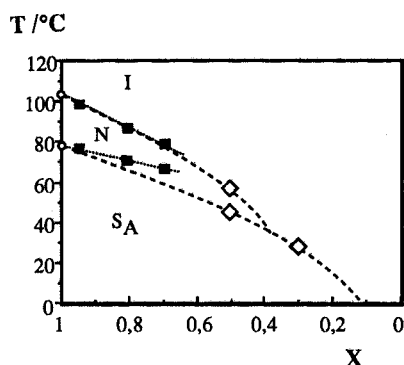Figure 4. Transition temperatures as a function of X for $P^{CH_3}_{4, 1, X}$ and $P^{H}_{4, 1, X}$ ($\Diamond$, $R = CH_3$; ■, $R = H$).

T /°C
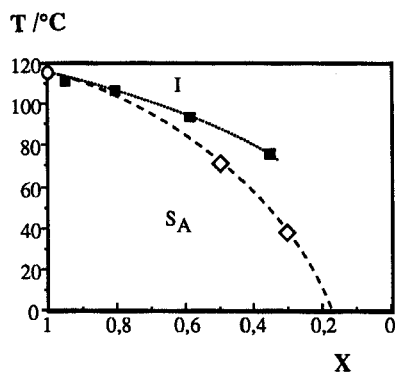
Figure 5.   Transition temperatures as a function of X for $P_{6,1,X}^{CH_3}$ and $P_{6,1,X}^{H}$ ($\Diamond$, $R = CH_3$; $\blacksquare$, $R = H$).

d / Å
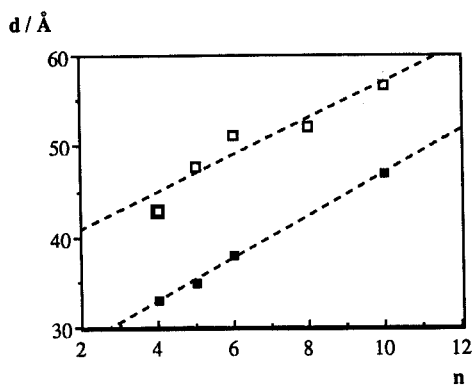
Figure 6.   Layer spacing in the S_A phase as a function of spacer length n in fully substituted polymers $P_{n,1,100\,per\,cent}$ and in partially substituted polymers $P_{n,1,30\,per\,cent}^{CH_3}$ ($\blacksquare$, $P_{n,1,100\,per\,cent}$), $d = (23\cdot6 + 2\cdot35n)$ Å; $\square$, $P_{n,1,30\,per\,cent}$), $d = (36\cdot8 + 2\cdot00n)$ Å).

T /°C

Figure 7.   Clearing temperatures as a function of spacer length n in fully substituted polymers $P_{n,1,100\,per\,cent}$ and in partially substituted polymers $P_{n,1,30\,per\,cent}^{CH_3}$ ($\blacksquare$, $X = 1$; $\blacktriangle$, $X = 0\cdot3$).

has no nematic phase but only a smectic A phase ($T_{S_AI} = 127°C$). In this case, the trend observed for the two other series in which a lower quantity of mesogenic side groups favours 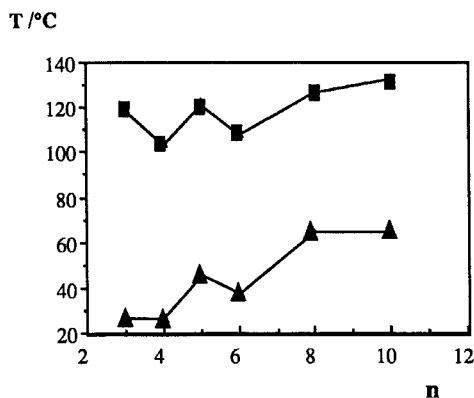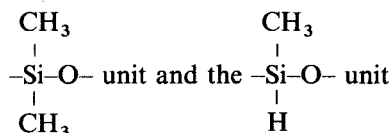the smectic state is completely reversed. Nevertheless we have to be careful because in series **3** the degree of polymerization is weaker.

From a structural point of view, the layer spacings in the smectic A phases of the partially substituted polymers seem strongly dependent on the nature of the non-mesogenic co-substituent. In the compounds of series $P^H_{6,1,X}$ the increase in d is only 3·5 Å for X varying from 100 per cent to 30 per cent. The same variation of X in the series $P^{CH_3}_{6,1,X}$ results in an enhancement of 13·2 Å. Since the

$$
\begin{array}{cc}
CH_3 & CH_3 \\
| & | \\
-Si-O- \text{ unit and the } & -Si-O- \text{ unit} \\
| & | \\
CH_3 & H
\end{array}
$$

are not very different this result seems surprising. It suggests that the expansion of the non-mesogenic sublayer could be dependent on the flexibility of the co-substituent (CH_3 or H) and questions the limit of the validity of a model of microphase separation into two independent sublayers with simple swelling of the non-mesogenic one.

5. Properties of solutions

Generally speaking the solutions of fully substituted ($X = 100$ per cent) side chain polymers in a low molar mass nematic solvent are remarkable through the existence of gaps of miscibility [14–17] which can be characterized by a critical temperature at the consolute point T_C, and the enhancement or induction of S_A phases [13, 17] which can be characterized by their maximum temperature in the phase diagram $T_{S_{Ad}}$ (see figure 8). The contact method was used to determine these two temperatures in numerous binary systems with little consumption of the compounds. Two low molar mass liquid crystals were used here to test and compare the solubilities of the polymers. One is non-polar with long aliphatic chains which is likely to induce phase separation

$$C_9H_{19}O-\langle O \rangle-CO_2-\langle OO \rangle-OC_7H_{15}$$
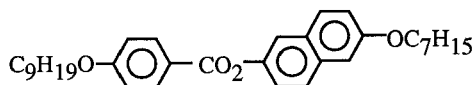
The second is a polar cyanobiphenyl from BDH Ltd. (6OCB)

$$C_6H_{13}O-\langle O \rangle-\langle O \rangle-CN$$
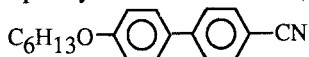
Two examples of the evolutions of T_C and T_{S_A} as a function of X are reported in tables 2 and 4 for the copolymers $P^H_{6,1,X}$ and $P^{CH_3}_{6,1,X}$ mixed in these solvents: they are typical of the qualitative evolution of these parameters versus the proportion of mesogenic groups in the polymer.

Table 2. $P^H_{6,1,X}$ in the non-polar solvent.

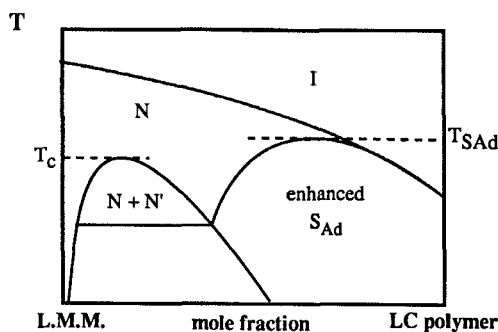| $P^H_{6,1,X}$ X	100 per cent	80 per cent	56 per cent	35 per cent	0 per cent
$T_C/°C$	117	115	—	—	No miscibility
		Partial miscibility	Miscibility		
$T_{S_{Ad}}/°C$	125	122	112	113	
$T_{S_{Ad}l}/°C$ (pure polymer)	116	107	95	75	

Figure 8.   Typical phase diagram for a liquid crystal polymer–low molar liquid crystal system. Two types of non-ideal behaviour can be observed: phase separation and/or induced smectic phase.

In a non-polar solvent a gap of miscibility and/or induced S_A phase is likely to be observed (see table 2). The temperature of the consolute point T_C decreases with decreasing X, which signifies an increased solubility of the polymer, and no phase separation is observed for X lower than 50 per cent. Of course the liquid-crystalline solvent is not miscible at all in the silicon oil corresponding to $X = 0$.

The effect of lowering X on the miscibility properties is peculiarly drastic with polymers with polar side groups even though they are much less soluble than polymers with non-polar side groups in a non-polar solvent ($P_{5,CN,100\,percent}$ is not miscible in the isotropic phase whereas no phase separation is observed with $P_{5,CN,30\,percent}^{CH_3}$ (see table 3)).

Table 3. $P_{5,CN,X}^{CH_3}$ in the non-polar solvent.

X	100 per cent	30 per cent
$T_C/^\circ C$	$\gg 200$	Miscibility

The second temperature $T_{S_{Ad}}$ is surprisingly insensitive to X while the temperature of transition, $T_{S_{Ad}I}$, of the polymer is significantly lowered (see table 2). We can observe that this temperature is also little dependent on modifications in the side group such as the length n of the spacer (see table 4) by comparison with the strong effects on the miscibility.

Table 4. $P_{n,1,30\,percent}^{CH_3}$ in the non-polar solvent.

$P_{n,1,30\,percent}^{CH_3}$ n	3	4	5	6	8	10
$T_C/^\circ C$	150	121	119	117	Miscibility	Miscibility
$T_{S_{Ad}}/^\circ C$	104	102	114	113	120	121
$T_{S_{Ad}I}/^\circ C$ (pure polymer)	28	27	46	38	65	65

In the polar solvent the investigated polymers show complete miscibility. In addition the evolution of $T_{S_{Ad}}$ with X is more marked than in the non-polar solvent (see table 5).

The new feature of the phase behaviour is a textural change which occurs at a lower temperature in the S_{Ad} domain: it results from the induction of an additional S_{A2} phase (see figure 9) [13]. Both $T_{S_{Ad}}$ and $T_{S_{A2}}$ temperatures decrease with decreasing X (see table 5). Again a regular evolution of $T_{S_{Ad}}$ is observed versus the length of the spacer of the side group (see table 6).

In the bulk, making homogeneous mixtures is quite impossible with fully substituted polymers owing to their high viscosity. But a lower proportion of mesogenic groups decreases this viscosity (see figure 10) and a more complete study of the solutions is then possible. Especially for binary systems with a polar solvent different temperature–concentration phase diagrams have been investigated [13]. Therefore, assignment of the induced S_{A2} has been achieved by X-ray analysis. Finally table 6 shows that $T_{S_{A2}l}$ is weakly altered by a modification of the side group.

Table 5. $P_{6,1,X}^{H}$ in the polar solvent.

$P_{6,1,X}^{H}$ X	100 per cent	80 per cent	56 per cent	35 per cent	0 per cent
		Miscibility			No miscibility
$T_{S_{Ad}}/°C$	—	115	108	96	
$T_{S_{Ad}l}/°C$ (pure polymer)	116	107	95	75	
$T_{S_{A2}}/°C$	103	99	93·5	88	

Table 6. $P_{n,1,30\,per\,cent}^{CH_3}$ in the polar solvent.

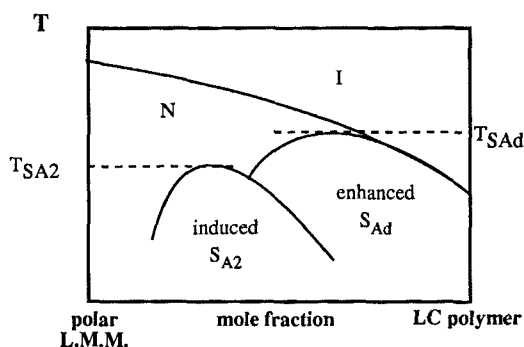| $P_{n,1,30\,per\,cent}^{CH_3}$ n	3	4	5	6	8	10
$T_{S_{Ad}}/°C$	74	72	91	86	105	106
$T_{S_{A2}}/°C$	69	65	76	68	78	78

Figure 9.   Schematic phase diagram for a liquid crystal polymer–polar low molar mass liquid crystal system: S_{Ad} enhancement ($T_{S_{Ad}}$) and induced bilayer smectic A ($T_{S_{A2}}$).
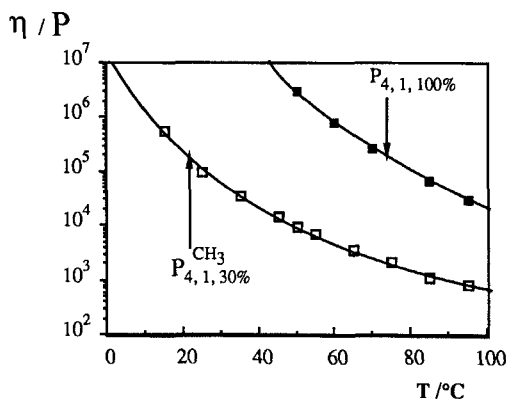
Figure 10. Apparent viscosity as a function of temperature in fully substituted polymers
($X = 100$ per cent) and in partially substituted polymers ($X = 30$ per cent).

6. Concluding remarks

Partial fixation, i.e. partial substitution of mesogenic groups at the silicon sites,
preserves the mesogenic character even though more than half the sites (on average) are
not occupied by a mesogenic group. However, we must take into account the nature of
the co-substituent which results in large modifications of the liquid-crystalline
properties ($R = $ phenyl) or of the structural properties ($R = H/R = CH_3$). Partial fixation
offers significant advantages for the investigation of phase diagrams combining
polymers and low molar mass liquid crystals. These partially substituted polymers
mixed with low molar mass solvents have a strong tendency to stabilize lamellar
phases. The viscosity of the polymer is decreased (see figure 10) resulting in better
diffusion of the low molar mass liquid crystal and as a consequence in easier miscibility
investigations. The compatibility of the two components is favoured. Nevertheless a
limit exists since the bare backbone ($X = 0$ per cent) is immiscible in a low molar mass
solvent and a demixing can occur again for low X values [25].

References

[1] SHIBAEV, V. P., FREIDZON, Y. S., and PLATE, N. A., 1978, *Vysokomolek. Soedin* A, **20**, 82.
[2] RINGSDORF, H., and SCHNELLER, A., 1981, *Br. Polym. J.*, **13**, 43.
[3] FINKELMANN, H., KOCK, H. J., and REHAGE, G., 1981, *Makromolek. Chem. rap. Commun.*, **2**,
      317.
[4] RINGSDORF, H., and SCHNELLER, A., 1982, *Makromolek. Chem. rap. Commun.*, **3**, 557.
[5] ENGEL, M., HISGEN, B., KELLER, R., KREUDER, W., RECK, B., RINGSDORF, H.,
      SCHMIDT, H. W., and TSCHIRNER, P., 1985, *Pure appl. Chem.*, **57**, 1009.
[6] HSU, C. S., and PERCEC, V., 1987, *Polym. Bull.*, **18**, 91.
[7] DIELE, S., OELSNER, S., KUSCHEL, F., HISGEN, B., RINGSDORF, H., and ZENTEL, R., 1987,
      Makromolek. Chem., **188**, 1993.
[8] DIELE, S., OELSNER, S., KUSCHEL, F., HISGEN, B., and RINGSDORF, H., 1988, *Molec. Crystals
      liq. Crystals*, **155**, 399.
[9] GEMMELL, P. A., GRAY, G. W., and LACEY, D., 1985, *Molec. Crystals liq. Crystals*, **122**, 205.
[10] SUTHERLAND, H. H., ALI-ADIB, Z., GASGOUS, B., and NESTOR, G., 1988, *Molec. Crystals liq.
      Crystals*, **155**, 327.
[11] WESTPHAL, S., DIELE, S., MÄDICKE, A., KUSCHEL, F., SCHEIM, U., RÜHLMANN, K., HISGEN, B.,
      and RINGSDORF, H., 1988, *Makromolek. Chem. rap. Commun.*, **9**, 489.
[12] DE MARIGNAN, G., TEYSSIE, D., BOILEAU, S., MALTHÊTE, J., and NOEL, C., 1988, *Polymer*, **29**,
      1318.

[13] HARDOUIN, F., SIGAUD, G., KELLER, P., RICHARD, H., NGUYEN HUU TINH, MAUZAC, M., and ACHARD, M. F., 1988, *Liq. Crystals*, **5**, 463.
[14] RINGSDORF, H., SCHMIDT, H. W., and SCHNELLER, A., 1982, *Makromolek. Chem., rap. Commun.*, **3**, 745.
[15] CASAGRANDE, C., VEYSSIE, M., and FINKELMANN, H., 1982, *J. Phys.*, **43**, L-371.
[16] SIGAUD, G., ACHARD, M. F., HARDOUIN, F., MAUZAC, M., RICHARD, H., and GASPAROUX, H., 1987, *Macromolecules*, **20**, 578.
[17] ACHARD, M. F., SIGAUD, G., KELLER, P., and HARDOUIN, F., 1988, *Makromolek. Chem.*, **189**, 2159.
[18] MAUZAC, M., HARDOUIN, F., RICHARD, H., ACHARD, M. F., SIGAUD, G., and GASPAROUX, H., 1986, *Eur. Polym. J.*, **22**, 137.
[19] FINKELMANN, H., and REHAGE, G., 1980, *Makromolek. Chem. rap. Commun.*, **1**, 31.
[20] LEMAITRE, E., 1983, Thesis, Lille.
[21] GRAY, G. W., HAWTHORNE, W. D., LACEY, D., WHITE, M. S., and SEMLYEN, J. A., 1989, *Liq. Crystals*, **6**, 503.
[22] HARRIS, R. K., and KIMBER, B., 1975, *J. appl. Spectrosc. Rev.*, **10**, 117.
[23] ACHARD, M. F., NGUYEN, H. T., RICHARD, H., MAUZAC, M., and HARDOUIN, F., 1990, *Liq. Crystals*, **8**, 533.
[24] ACHARD, M. F., HARDOUIN, F., SIGAUD, G., and MAUZAC, M., 1986, *Liq. Crystals*, **1**, 203.
[25] NGUYEN, H. T., ACHARD. M. F., HARDOUIN, F., MAUZAC, M., RICHARD, H., and SIGAUD, G., 1990, *Liq. Crystals*, **7**, 385.