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## Liquid Crystals

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### Phase behaviour of liquid-crystalline copoly(dimethyl-methylhydrogeno)siloxanes substituted with long polar side groups

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## Phase behaviour of liquid-crystalline copoly(dimethyl-methylhydrogeno)siloxanes substituted with long polar side groups

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The liquid-crystalline properties and structural characteristics of copoly(dimethyl-methylhydrogeno)siloxanes substituted with different proportions of long mesogenic cyano groups are investigated. Comparison is made with the phase behaviour of the chemically related low molecular weight molecules. Some of the unusual features of the polymorphism of these polar compounds are preserved. The compatibility of these copolymers with their low molar mass parents is tested through the study of binary phase diagrams.

### 1. Introduction

It is now well-known that polar low molecular weight mesogens show a singular liquid-crystalline behaviour compared to non-polar ones. This difference appears mainly in the smectic A state and is evidenced experimentally by the measurement of the layer spacings: in non-polar low molar mass mesogens this parameter ( $d$ ) is generally commensurate with the length of the molecule in the all trans conformation ( $L$ ), i.e. the ratio  $d/L = 1$ , in polar low molecular weight mesogens  $d$  is generally incommensurate with  $L$ , i.e.  $1 < d/L < 2$ . Consequently different kinds of smectic A phases have been defined according to the value of this ratio, respectively  $S_{A1}$  (monolayer),  $S_{Ad}$  (partially bilayer),  $S_{A2}$  (bilayer) [1]. Now, this structural difference is not readily made for liquid-crystalline side chain polymers: most often the layer thickness in the smectic A phase differs from the length of the repeat unit whatever its nature, polar or non polar [2]. However it is likely that a difference still exists between polar and non-polar associated systems at least from a local point of view. For example, an anomaly is observed in the evolution of the layer spacings in the  $S_A$  phases of copolymers combining various proportions of a polar side group and a non-polar one [3]. Mixing a polar low molar mass mesogen to a non-polar liquid crystal polymer may also lead to strong non-ideal behaviour with induced bilayered phases and  $S_{Ad}$ - $S_{A2}$  transitions [4].

So far the extension of the  $S_A$  polymorphism of polar low molecular weight liquid crystals and its derived phenomena (such as nematic reentrance) to polymer systems are far from completion; only a few examples of reentrant nematic phases and of sequences of  $S_A$  phases have been reported [5-8]. From these early works it appears that, as for low molar mass liquid crystals, the most promising way of investigating the peculiar phase behaviour of polar liquid crystal polymers is the elaboration of macromolecules bearing long mesogenic groups comprising three aromatic rings

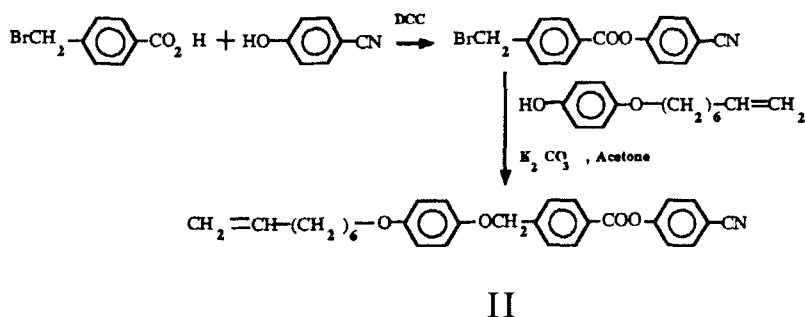
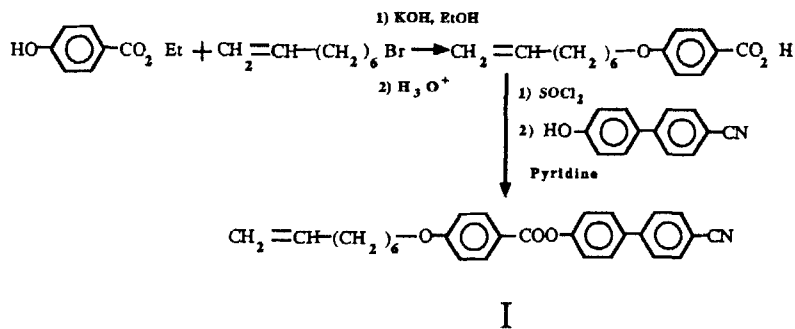
instead of two as in the materials commonly studied. However a major difficulty occurs regarding the characterization of their liquid-crystalline properties. The polymerization of a liquid-crystalline moiety (or its attachment to a backbone) generally results in a large increase of the clearing point of the final polymer. This effect is more drastic with long polar groups which already have higher transition temperatures. In order to lower these values we can choose more flexible side groups including, e.g.,  $-\text{CH}_2-\text{CH}_2-$  or  $-\text{CH}_2-\text{O}-$  linkages between two phenyl rings [5–8]. However, the viscosity still remains very large and for these reasons it is much more difficult to obtain reliable textures for microscopic observation or to obtain orientated samples with an external field for X-ray analysis.

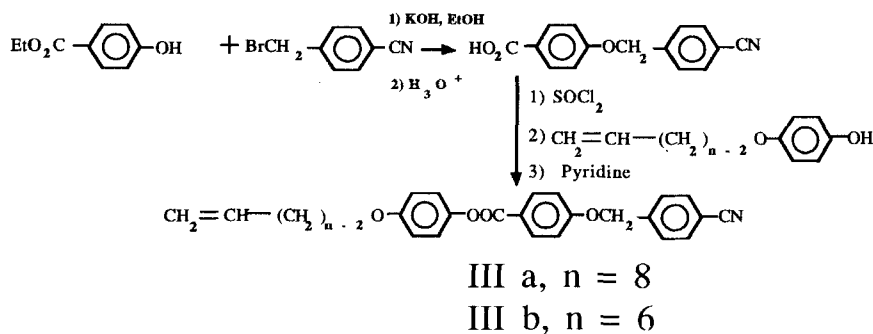
In this paper we present the properties of liquid-crystalline polymers in which cyano mesogens chosen for their polymorphism are fixed on a copoly(dimethylmethylhydrogeno)siloxane: the attachment of the mesogenic groups occurs only on the methylhydrogeno sites. The experimental conditions are greatly improved by this partial fixation and permit easier comparison with the behaviour of low molecular weight polar mesogens especially through the analysis of binary phase diagrams.

## 2. Experimental

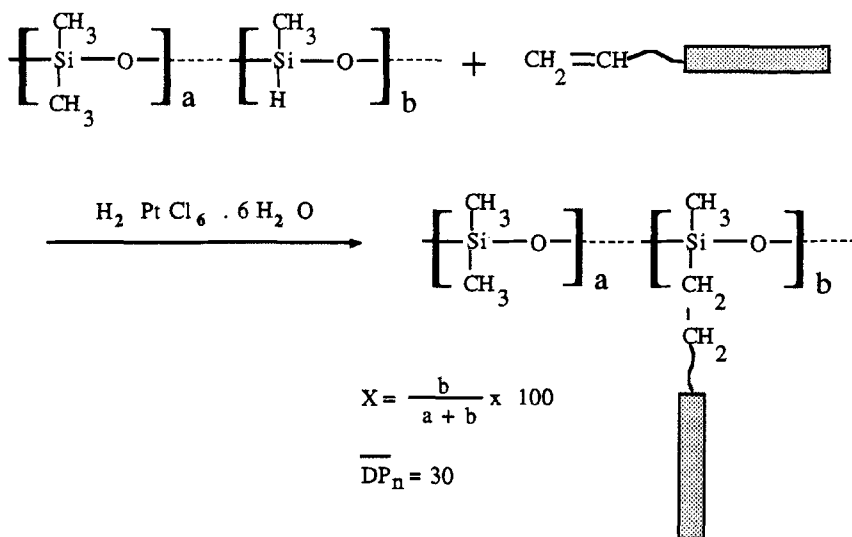
### 2.1. Synthesis

All of the vinyl derivatives were prepared by standard methods, namely





All of these compounds were purified by chromatography on silica gel with toluene as the eluent, then recrystallized in absolute ethanol and dried under vacuum. The corresponding polymers are obtained through the classical hydrosilylation reaction [2] using statistical copoly(dimethyl-methylhydrogeno)siloxanes (from PETRARCH) with variable content in the methylhydrogeno moiety. They were precipitated several times in methanol or purified by GPC with toluene as the eluent. The purity of the polymers was checked using  $^1\text{H}$  N.M.R. (270 MHz).



## 2.2. Results

The liquid-crystalline properties of the polymers were characterized from microscopic observation on a heating stage with polarized light, combined with DSC and small angle X-ray diffraction.

The polymorphism of the polymers is reported in the table together with these of the vinyl derivatives and of the low molar mass molecules (LMW) which have been chosen as model compounds for the side-groups. These compounds have been selected taking into account the peculiar interest of their sequences of mesophases as observed in the table. LMW I has a reentrant nematic phase. LMW II has a smectic C phase which is rather unusual for a molecule with a cyano polar head group. LMW III *a* and *b* belong to a family of polar mesogens in which a  $S_{A1}$  phase and (for *b*) a bidimensional fluid phase of  $S_C$  type appear.

Polymorphism and transition temperatures. [xx] indicates monotropic transitions.  
C: crystalline phase.

Type	Low molecular weight mesogen	Vinyl derivative	Polymer X = 30	Polymer X = 9
I	C 97°C N <sub>re</sub> 120°C S <sub>Ad</sub> 201°C N 240°C I {9}	C 84°C N 233°C I	S <sub>Ad</sub> 260°C I	S <sub>Ad</sub> 170°C I
II	C 114°C → S <sub>Ad</sub> 151°C N 155°C I S <sub>C</sub> [110°C] {10}	C 77°C → N 147°C I S <sub>C</sub> [67°C] S <sub>A</sub> [74°C]	S <sub>ordered</sub> 60°C S <sub>Ad</sub> 171°C I	
IIIa	C 115°C → S <sub>A1</sub> 122°C N 167°C I S <sub>C</sub> [111°C] {11}	C 107°C → N 169°C I S <sub>A</sub> [91°C]	S <sub>C</sub> 115°C S <sub>Ad</sub> 200°C I	S <sub>ordered</sub> 75°C S <sub>Ad</sub> 125°C I
IIIb	C 115°C S <sub>A1</sub> 116°C N 171°C I {11}	C 124°C N 185°C I	S <sub>ordered</sub> 90°C S <sub>Ad</sub> 205°C I	S <sub>ordered</sub> 85°C S <sub>Ad</sub> 140°C I



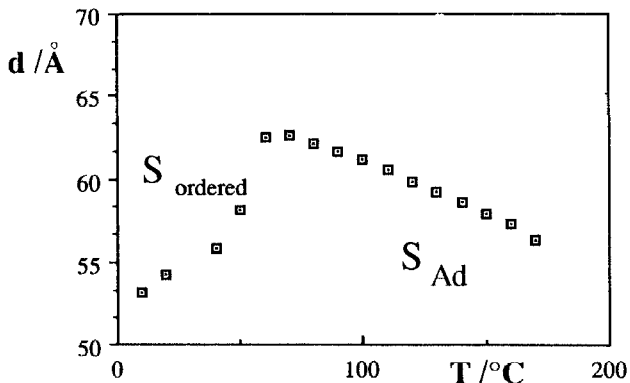


Figure 2. Layer spacing versus temperature in the system of type II ( $X = 30$ );  $l = 33.5 \text{ \AA}$ .

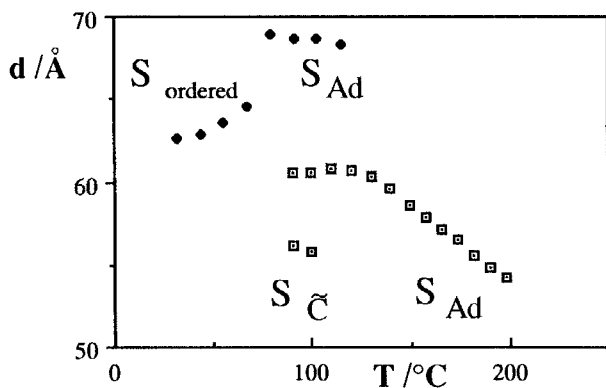


Figure 3. Layer spacing versus temperature in the two systems of type IIIa with different rates of fixation ( $X = 9$  (♦) and  $30$  (□));  $l = 36 \text{ \AA}$ .

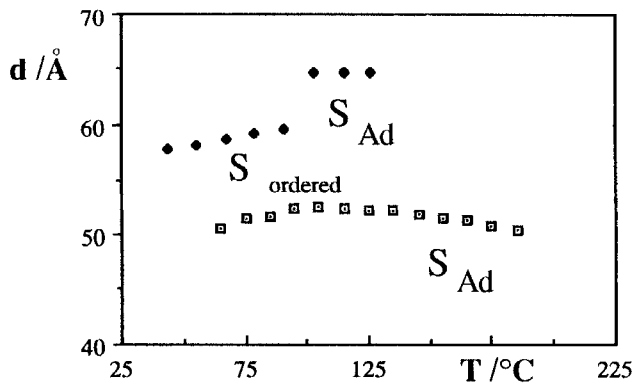


Figure 4. Layer spacing versus temperature in the two systems of type IIIb with different rates of fixation ( $X = 9$  (♦) and  $30$  (□));  $l = 33.5 \text{ \AA}$ .

figure 5). The same variation of  $X$  in [12] results in an increase of  $23.5 \text{ \AA}$ . We would expect the same variation of the thickness of the layers if it results from the main chain alone. It turns out in fact that the swelling of the lamellae depends on the nature of the side-group. The diffuse scattering reported by Diele *et al.* [12], corresponding

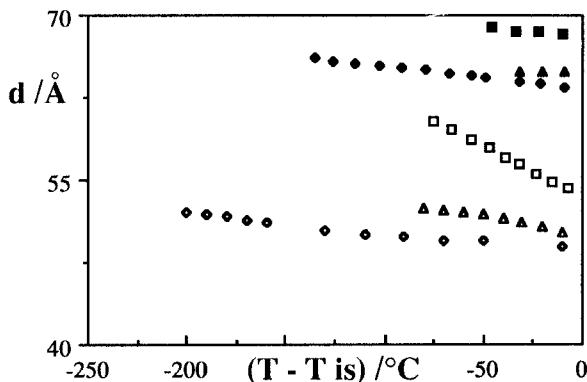


Figure 5. Comparison of the difference in layer spacings between  $X = 30$  and  $X = 9$  using a shifted temperature scale from the isotropic phase. I  $X = 9$  ( $\blacklozenge$ ) and  $30$  ( $\diamond$ ); IIIa  $X = 9$  ( $\blacksquare$ ) and  $30$  ( $\square$ ) and IIIb  $X = 9$  ( $\blacktriangle$ ) and  $30$  ( $\triangle$ ).

approximately to a distance of  $8 \text{ \AA}$  and assumed to be the characteristic size for the width of the dimethylsiloxane parts of the backbone, is also observed, peculiarly, in the samples richer in dimethylsiloxane units ( $X = 9$ ).

Figure 3 shows the change from  $S_{Ad}$  to  $S_C$  for the polymer IIIa: the signature of the bidimensional phase is given by the occurrence of a second Bragg reflection  $\bar{1}1$  corresponding to a wavevector incommensurate with the component of the Bragg reflection  $01$  which proceeds from the  $S_{Ad}$  phase.

The structures of the smectic phases which appear at low temperature in polymers II and IIIb cannot be characterized definitely from the powder patterns. However, more located diffuse scatterings at wide angles indicate more ordered layers with tilting of the molecules since the layer thickness decreases in both cases at the transition (see figures 2 and 4).

#### 2.4. Phase diagrams with low molecular weight compounds

To compare the phase behaviour of the polymers and of the corresponding low molecular weight compounds, we have studied their binary phase diagrams through the observation of contact samples (the use of the contact method is reliable because of the reasonable viscosity of the polymers).

The isomorphism of the  $S_{Ad}$  phase of polymers I ( $X = 30$ ) and II ( $X = 30$ ) with the  $S_{Ad}$  phases of low molar mass mesogens I and II is shown in figures 6 and 7. In contrast we note that no continuous  $S_A$  domain is observed in the phase diagram of figure 8 on combining the polymer IIIa ( $X = 30$ ) and the LMW IIIa; however neither is a  $S_{Ad}$ - $S_{A1}$  line of transition obtained. This phase diagram is especially interesting for it shows complete miscibility between the  $S_C$  phases of the two compounds and proves through the similar nature of the phases that the polymorphism of polar low molecular weight mesogens can actually be preserved in high molecular weight systems.

Using the compounds with the lowest degree of attachment ( $X = 9$ ) it turns out that the polymer and its low molar mass analogue are no longer miscible: a miscibility gap extends far beyond the clearing temperature (see figure 9). We have already observed miscibility gaps in mixtures of liquid-crystalline polymers and low molar mass solvents but only with homopolysiloxanes rich in mesogenic parts ( $X = 100$ )



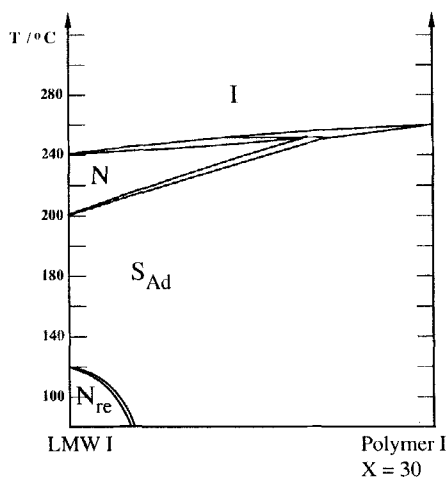


Figure 6. Binary isobaric phase diagram: contact method between the polymer (on the right) and its corresponding low molecular weight mesogen.

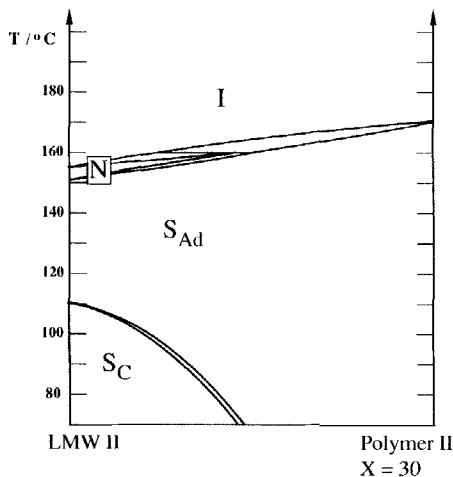


Figure 7. Binary isobaric phase diagram: contact method between the polymer (on the right) and its corresponding low molecular weight mesogen.

[13] and we have shown that partial attachment readily improves the miscibility [4]. Indeed a bare polydimethylsiloxane, not liquid-crystalline of course, is completely incompatible with any classic liquid-crystalline compound: it could be expected that polymers with very low content in mesogenic side groups should also become immiscible. However it is the first time that a miscibility gap is found at low  $X$  since for  $X = 9$  and non-polar mesogenic side groups we still observe total miscibility in the isotropic phase even though the liquid-crystalline properties are already ruled out in these materials [14]. We show in addition that with long polar side groups the loss of miscibility occurs prior to the loss of the smectic character.

### 3. Conclusion

It is clear from these studies that partial attachment of mesogenic groups on a polysiloxane backbone is especially valuable in the investigation of the polymorphism

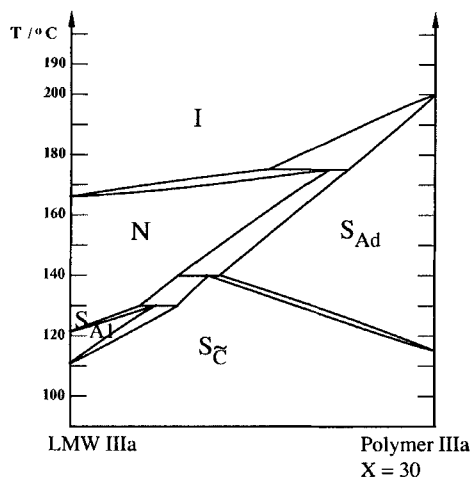


Figure 8. Binary isobaric phase diagram: contact method between the polymer (on the right) and its corresponding low molecular weight mesogen.

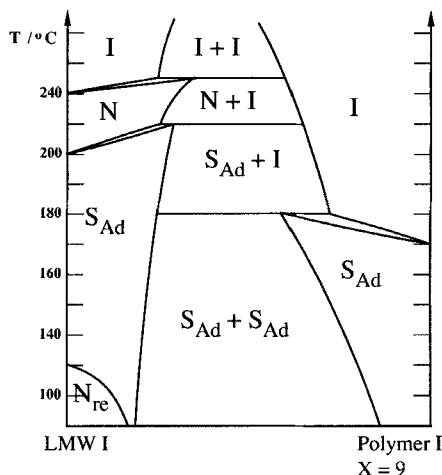


Figure 9. Binary isobaric phase diagram: contact method between the polymer (on the right) and its corresponding low molecular weight mesogen.

of polar polymers since the comparison with low molecular weight model compounds becomes possible. The main interest of this comparative study regards the polymorphism of the polar liquid crystals: some characteristic features are preserved such as the existence of a bidimensional  $S_C$  phase. In contrast, the partial fixation of cyano side groups on polysiloxane backbones results in the loss of part of the rich phase behaviour observed in the low molar mass compounds such as the nematic phase and the reentrance which disappear in polymer I and the  $S_C$  phase which is eliminated for polymer II. From another point of view the low values of  $T_g$  ( $< -40^\circ\text{C}$ ) in these materials and their poor tendency to crystallize, allow us to observe ordered smectic phases at low temperatures which are not usually observed in low molecular weight systems owing to the better stability of their crystal phases. Another interest of these polar polymers lies in their ability to remain liquid crystalline for very low contents in mesogenic moieties, lower than the non-polar ones. This strong mesogenic potential

of the long cyano groups permits us to provide evidence for the amphipatic nature of these polymers which combine two immiscible moieties: at low degree of attachment the liquid-crystalline polymers and the low molecular weight liquid crystals are completely miscible in the smectic A phase but at low  $X$  the incompatibility of the polysiloxane part with the low molecular weight mesogens prevails although the content in side groups is nevertheless sufficient to keep the polymer liquid crystalline.

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