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Polysiloxanes substituted with forked mesogens

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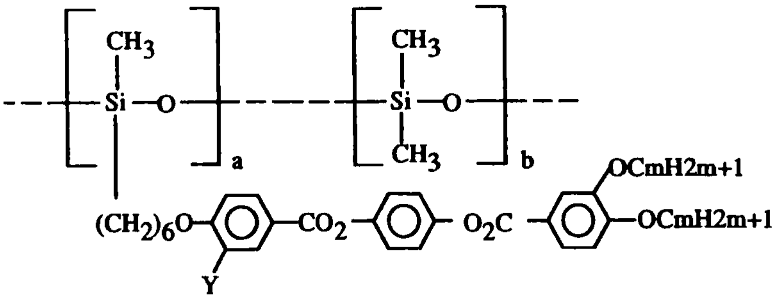
Mesomorphic properties including structural aspects are investigated in a homologous series of forked side chain polymers: the mesogenic units, which are conventionally attached to a polysiloxane backbone via a flexible spacer, possess two long aliphatic tails at their extremities as in forked polycatenar molecules. Several polymers with different proportions, x, of such mesogenic units have been studied. The influence of this parameter is especially interesting on the structure of the mesophases: the layer spacings of the fluid smectics observed at high temperature vary irregularly as a function of x. Microsegregation into sublayers is observed for low values of x while ordered phases with lamellar or/and columnar features appear at low temperatures.

1. Introduction

From rods to discs, from non-polar to polar, most kinds of mesogenic groups have been linked as pendents to a flexible backbone in order to transfer their liquid-crystalline properties to the final polymer [1]. As expected, side rods fixed in a comb-like manner lead preferably to smectic phases (A, C and B) the structures of which are characterized by many subtle changes perceivable in multiple diffractions, additional scatterings and layer spacings incommensurate with the mesogenic group. As expected too, side discs promote columnar phases the structure of which has been little analyzed so far. So, if generally speaking the liquid-crystalline properties are preserved, the specific modifications resulting from the main chain are likely to be found in the structures of the phases and especially in the local order.

In recent years interest has been also focused on mesogens of large size but not polymeric, namely the polycatenars, involving in their chemical structure a rod-shaped core ended by more than one aliphatic chain at least one extremity [2]. Indeed, these compounds have shown great novelty since their polymorphism combines lamellar, columnar and cubic mesophases according to the length, number and positions of the chains. To date the relevant role of these extremities is rather well-known. In this context we describe the synthesis and the characterization of a family of side chain polymers substituted with forked mesogenic groups with the general formula which are denoted by $P_{f,n,Y,m,m,x}$ for short; $a + b = 30$; $x = a/(a + b)$, thus $0 < x \leqslant 1$; $n = 6$ (size of the spacer) for all of the compounds reported in this paper. The statistical character of the copolymers has been evidenced by ^{29}Si NMR experiments [3]. We therefore take special interest in three variable parameters; one is related to the backbone, the proportion of mesogenic units (x) which is known to induce important modifications of the physical properties (e.g. the clearing temperatures and viscosity) and structures [4] and the others related to the side-group namely

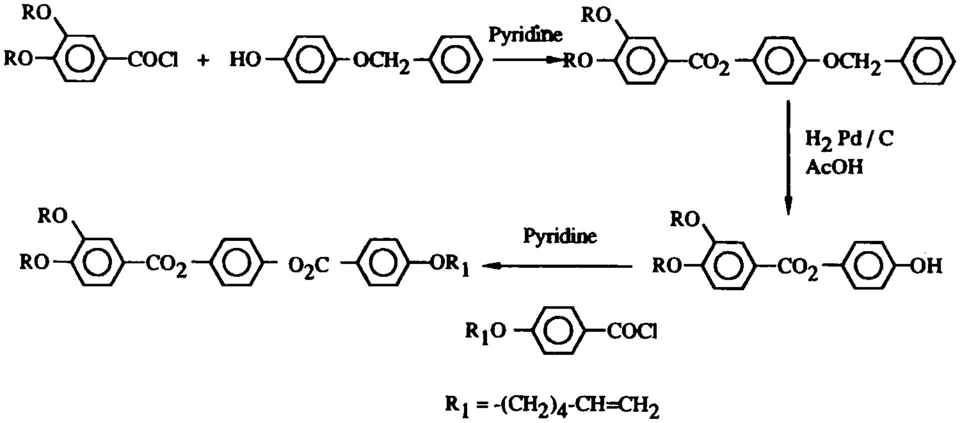


the variation of the length of the alkoxy terminal chains (*m*) and substitution by a hindering group *Y* on the rigid core (i.e. OCH_3 in this work).

In the following we find convenient to use the term dilution to mean that x is reduced by the insertion of additional dimethylsiloxane segments.

2. Synthesis

The synthesis of the vinyl mesogenic moieties is indicated by the reaction scheme



These compounds are only nematic (see table 1). The corresponding polymers are obtained through the classical hydrosilylation reaction in the presence of a platinum catalyst. The mesogenic groups are attached to either a polymethylhydrogenosiloxane chain, thus giving homopolymers [5] ($x = 1$) or copoly(dimethyl-methylhydrogeno)-siloxane chains where two fixation rates of the mesogenic parts are used ($x = 0{\cdot}3$ or $0{\cdot}09$ depending on the number of dimethylsiloxane segments). Their purity was checked using ^1H NMR (270 MHz).

3. Results and discussion

The polymer characterization was achieved by DSC analysis (Perkin–Elmer DSC 7), optical microscopy (Leitz polarizing microscope in conjunction with a Mettler FP 52 heating stage) and low resolution X-ray measurements on powder samples

Table 1. Melting temperatures and liquid-crystalline properties of vinyl compounds.

Vinyl derivative		Polymorphism				
m	Lateral substituent (Y)					
4	H	C	114·3°C	N	117°C	I
5	H	C	108·8°C	N	110°C	I
9	H	C	98°C	N	101·5°C	I
3	OCH_3	C	126·4°C			I
4	OCH_3	C	113°C			I
5	OCH_3	C	112°C			I
9	OCH_3	C	107°C			I

(Guinier camera, $CoK_{\alpha1}$). We specify that except when purposedly performed on samples quenched to room temperature, the thermal X-ray analysis was made upon cooling with long exposure times thus corresponding to annealed samples. The phase behaviour of the polymers as defined by the combination and comparison of these observations is summarized in table 2. We can add to the information reported in this table that no glass transition was detected by DSC down to −40°C whatever the polymer and whatever the scanning rate. This lack is certainly connected to the high degree of lamellar stacking in the case of smectic phases and/or to the formation of ordered mesophases at low temperature as described later.

We discuss first (§3.1) the influence of the proportion of mesogenic groups through the evolution of the liquid-crystalline behaviour of a set of three polymers with identical side groups, namely the $P_{f,6,5,5,x}$ ($x = 1$ §3.1.1, $x = 0{\cdot}3$ §3.1.2, $x = 0{\cdot}09$ §3.1.3.). Generally speaking, the other homologous polymers behave as these reference compounds. However a few modifications resulting from changes in the mesogenic group are discussed in a second section (§3.2).

3.1. *Role of dilution*

3.1.1. $x = 1$ (*homopolymer*)

As frequently observed for polymers of high molecular weight, the textures obtained are uncharacteristic even after long annealing near the clearing temperature (for $P_{f,6,5,5,100\%}$, $M_w = 40\,000$ because of the weight of the mesogenic polycatenar group). This behaviour is the consequence of their high viscosities. Thus in this case the microscopic observations do not provide much assistance in characterizing the phases.

The DSC traces show two first order transitions upon heating and also on cooling (see figure 1, runs (*a*) and (*b*)). We note some modifications of the thermograms according to the thermal history: the low temperature peak is considerably enlarged by annealing (run 1 *c*) and moves significantly from cooling to heating as expected for a crystalline phase while the high temperature one remains almost unchanged. However, the X-ray analysis confirms the existence of two liquid-crystalline states. At both high and low temperature the patterns show three sharp harmonic reflections in the small angle regions, indicating a well-defined lamellar stacking with a layer

Table 2. Liquid-crystalline properties as defined by the combination of microscopic observations, DSC analysis and low resolution X-ray scattering on powder samples.

Polymer ($P_{f6,Y,m,m,x}$)		Dilution		
m	Lateral substituent (Y)	$x = 1$	$x = 0{\cdot}3$	$x = 0{\cdot}09$
4	H	S_2 127°C S_1 159°C I	D_h 86°C S_C 105°C I └[S]┘	$S_{ordered}$ 76°C S_C 85°C I
5	H	S_2 109°C S_1 164°C I	D_h 97°C S_C 105°C I └[S]┘	$S_{ordered}$ 53°C S_C 78°C I
9	H	S 165°C I	D_h 101°C I └[S]—[S_C]┘	$S_{ordered}$ 82°C S_C 85°C I
3	OCH_3	Non-mesomorphic		
4	OCH_3	S 110°C I	S_C 75°C I	S_C 77°C I
5	OCH_3	S 113°C I	S_C 77°C I	S_C 73°C I
9	OCH_3		S_C 88°C I	S_C 74°C I

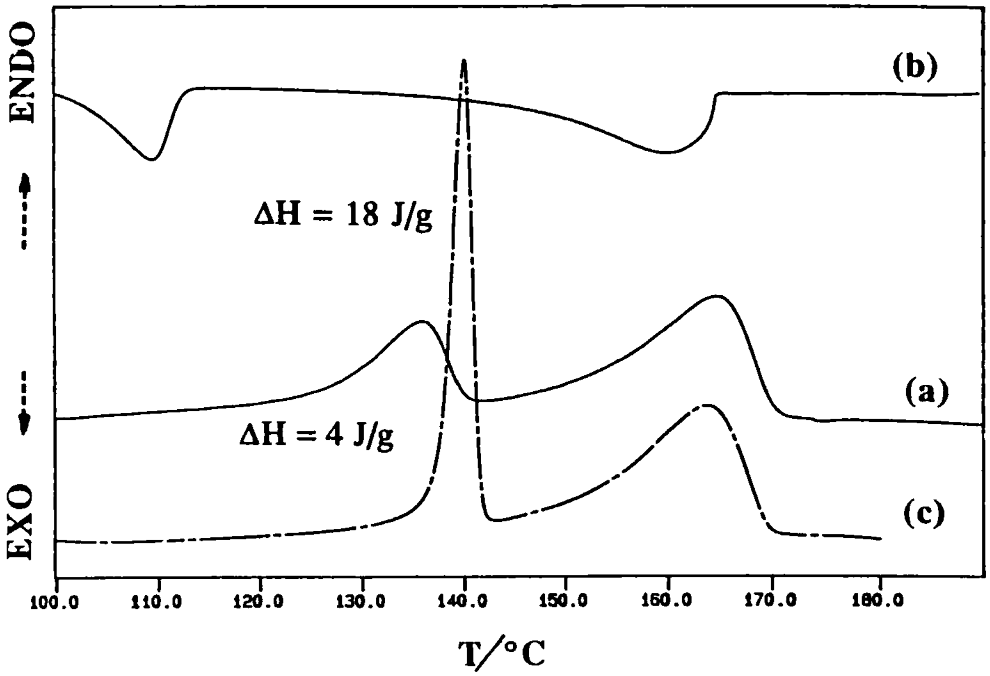
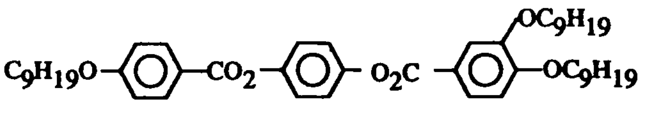


Figure 1. DSC traces for the homopolymer $P_{f,6,H,5,5,100\%}$; (*a*) first run, annealed sample, heating rate 10°C/min, (*b*) cooling rate 5°C/min, (*c*) after annealing, 12 hours at 125°C, heating rate 10°C/min.

spacing larger than the length of the mesogenic side group in its most extended conformation (l = 37 Å) which implies a structure with paired mesogenic groups. At wide angles a diffuse scattering is observed which characterizes in both cases a fluid smectic (either smectic A or smectic C): from a structural point of view the low temperature phase has *no crystalline character at all* although the enthalpy of transition is large and although lengthy annealing is necessary to reach equilibrium. The layer spacing only is modified noticeably between 140°C and 130°C, as shown in figure 2. So, if we assume the high temperature phase to be a smectic A, the decrease of the layer spacing could be the signature of a smectic A–smectic C transition. However, the tilt angle in the latter would remain small which seems unlikely considering the value of the heat of transition. It seems more logical therefore that this change is coupled to a modification of the overlapping in the pairs of side-groups. The other possibility is a transition between two types of smectic C but still with local reorganization.

3.1.2. *x* = *0·3* (*copolymer*)

The first interest of the dilution lies in the lowering of the viscosities which allows easier phase identification [4]. A short annealing near the clearing point is sufficient to obtain characteristic textures; broken fans or schlieren textures strongly suggest a smectic C phase at high temperature. Confirmation is obtained by miscibility experiments which show complete compatibility with the smectic C phase of the saturated monomer [6]



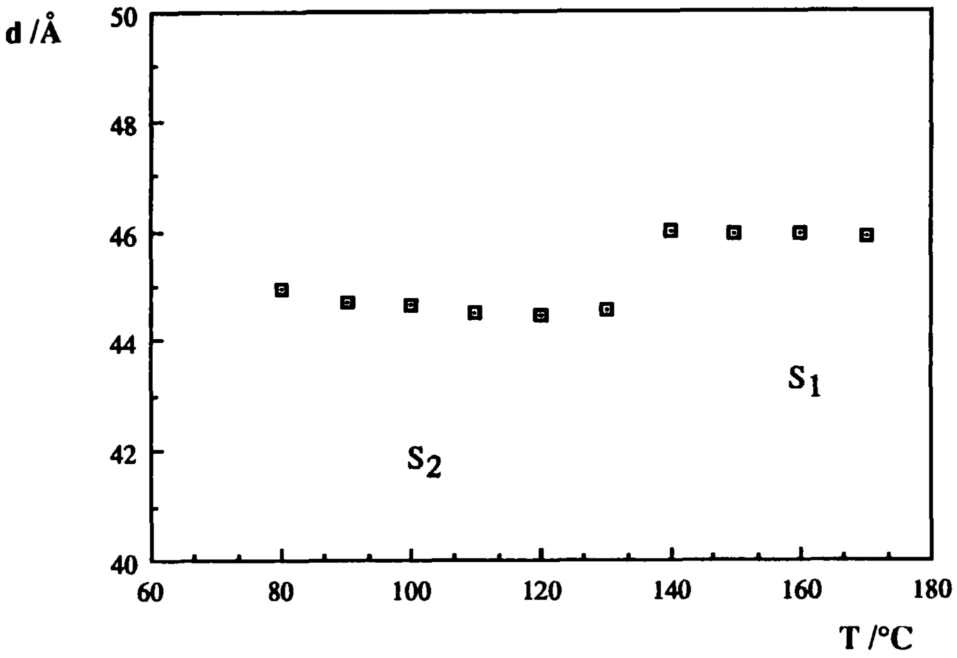


Figure 2. Thermal variation of the layer spacing, *d*, for the homopolymer $P_{f,6,H,5,5,100\%}$.

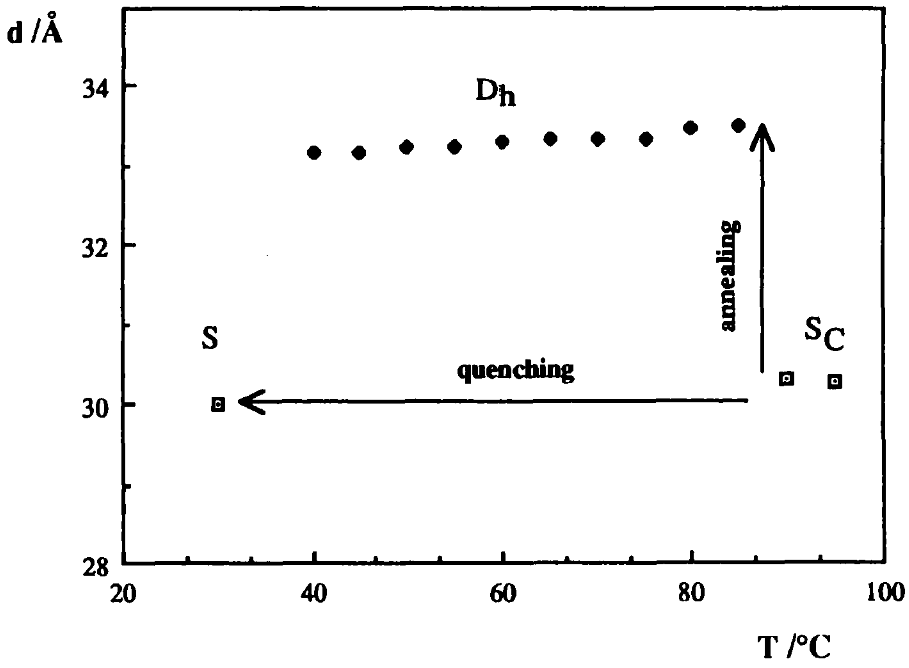


Figure 3. Thermal variation of the layer spacing, *d*, for the copolymer $P_{f,6,H,5,5,30\%}$. The hexagonal lattice parameter, *a*, of the columnar phase is also reported.

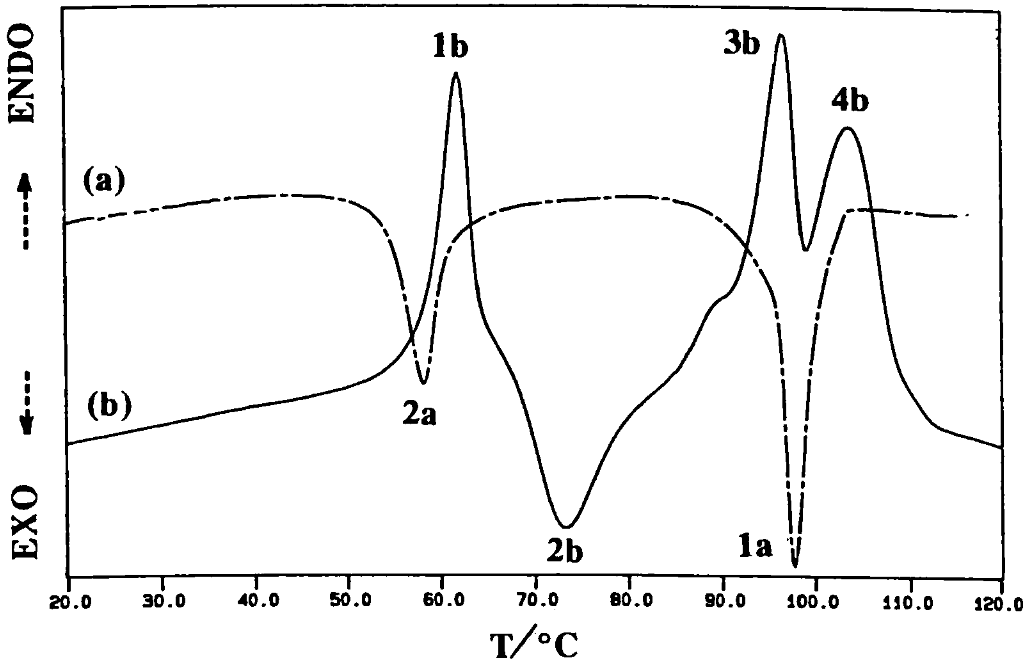


Figure 4. DSC traces for the copolymer $P_{f,6,H,5,5,30\%}$: (*a*) cooling rate 5°C/min, (*b*) heating rate 10°C/min.

Slow cooling of the sample shows a textural modification near 80°C which suggests a change from the smectic C to a bidimensional order at low temperature.

At low temperature two mesophases compete as revealed by the DSC experiments, the traces in figure 4 illustrate this behaviour. Upon cooling two exothermic events are detected: the smectic C–isotropic transition (1 *a*) followed by a second α phase–smectic C transition (2 *a*) (not seen optically with the microscope under rapid cooling). A subsequent heating run shows a reversible endothermic transition from α to the smectic C phase (1 *b*) which spontaneously transforms into a more stable β phase as shown by a large exothermic feature (2 *b*). It appears then as an enantiotropic β to smectic C transition (peak 3 *b*) and eventually the reversible smectic C–isotropic peak (4 *b*). This stable β phase would then be the state observed after slow cooling under the microscope. A heating run from room temperature following annealing at 85°C confirms the disappearance of the sequence $\{1b + 2b\}$. Only the 3 *b* peak remains which allows the measurement of the β phase–smectic C heat of transition as 11 J/g.

The structural analysis confirms these observations. The X-ray patterns at high temperature show only one order of reflection corresponding to a layer spacing of 30 Å. Rapid quenching to room temperature leads to the α phase and induces a few changes in the pattern from the smectic C phase; the layer spacing remains constant but additional $00l$ reflections show up. The most interesting feature is a splitting of the diffuse scattering at large angles; the usual one characterizing the liquid-like order in the layers at 4·5 Å is now accompanied by a more localized one at 4 Å. Short annealing at 75°C gives rise to the stable β phase and the X-ray pattern is strikingly modified; a series of Bragg reflections appear with reciprocal parameters in the ratios 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$. This sequence characterizes a two dimensional hexagonal lattice which could be identified as hexagonal columnar phase D_h with an intercolumnar separation of 33 Å.

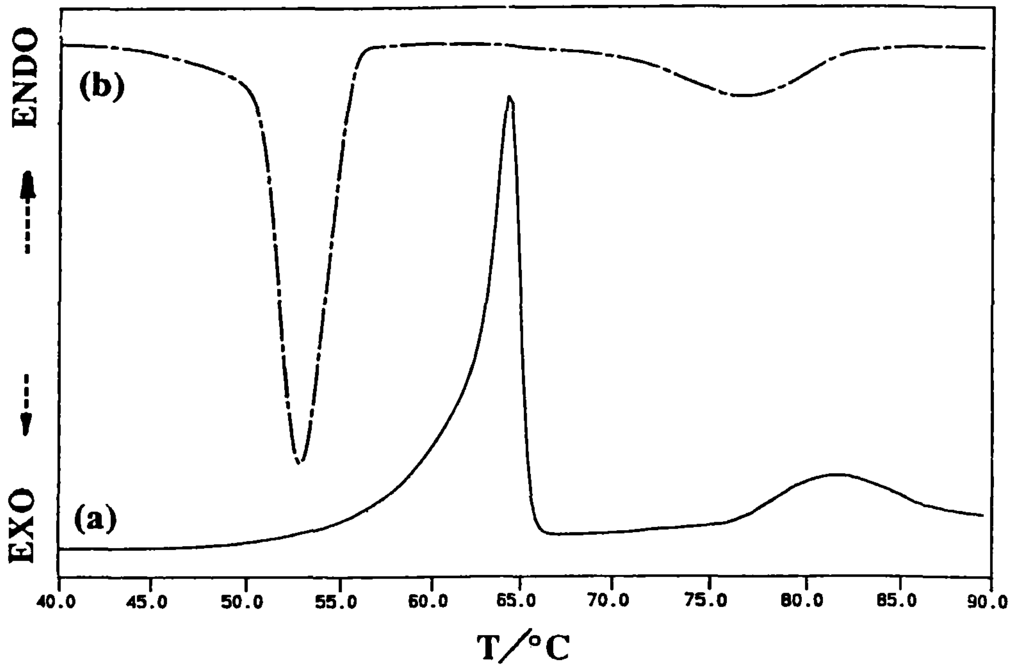


Figure 5. DSC traces for the copolymer $P_{f,6,5,5,9\%}$. (*a*) cooling rate 5°C/min, (*b*) heating rate 10°C/min.

Finally the combination of these results is consistent with the following polymorphism for the $P_{f,6,5,5,30\%}$:

$$\begin{tikzcd}
D_h \arrow[r] & 97^\circ\mathrm{C} \arrow[r] & \text{smectic C} \arrow[r] & 105^\circ\mathrm{C} \arrow[r] & \text{isotropic} \arrow[d] \\
{[S]} \arrow[u] & {[61^\circ\mathrm{C}]} \arrow[l] & \text{smectic C} \arrow[l] & & 100^\circ\mathrm{C} \arrow[ll]
\end{tikzcd}$$

[S] monotropic lamellar phase

This is the first example of a liquid crystal polymer in which a change from liquid lamellae to an hexagonal array is exhibited.

3.1.3. $x = 0{\cdot}09$

For this lowest value of x, the polymers are still liquid-crystalline; the characteristic textures of a smectic C phase are observed at high temperature. At low temperature the thermogram in figure 5 shows a strong first peak (64°C upon heating) which reveals another phase not detected optically. The X-ray analysis gives a layer spacing of 43 to 44 Å ($d \gg L$) in the smectic C phase with only one order of reflection. In the low temperature phase two harmonics at small angles correspond to a layered structure with a periodicity close to the values measured in the smectic C phase (see figure 6). The original feature appear at wide angles; as in a fluid mesophase the diffuse scattering at 4·5 Å still denotes a local liquid-like order while a sharp reflection appears at 3·8 Å. This distance would correspond to the minimum rigid core to rigid core distance in a stack. Taking into account the diluted character of the system, we can imagine the structure of this mesophase as formed from two well-defined sublayers, one contains the melted backbone and the other the mesogenic side groups which develop an in-plane long range unidimensional stacking in a direction parallel

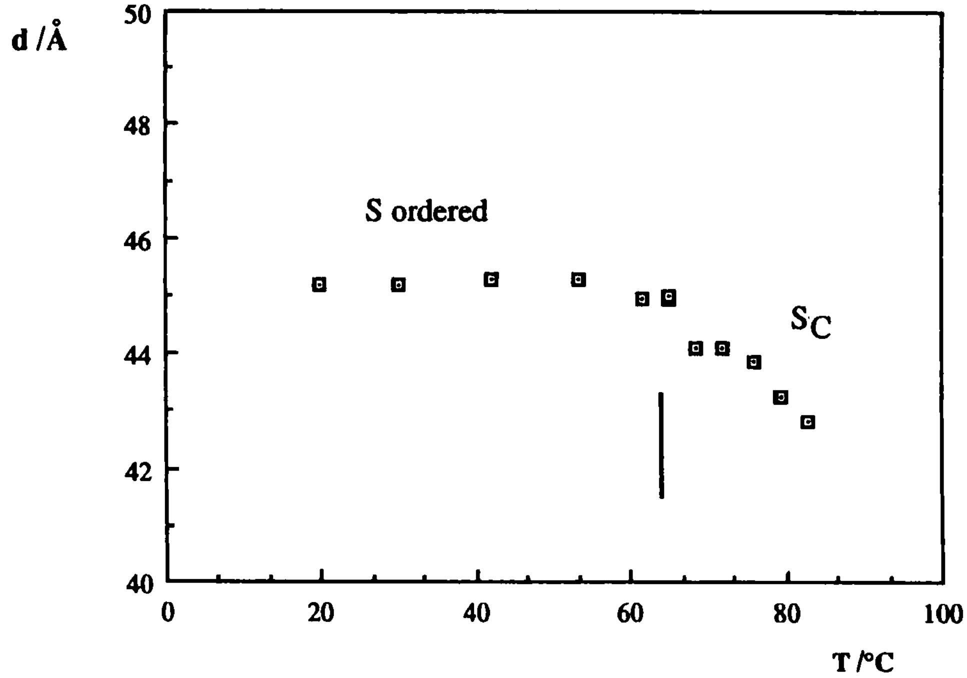


Figure 6. Thermal variation of the layer spacing, *d*, for the copolymer $P_{f,6,5,5,9\%}$.

to the layers. In such a hypothesis, the organization of the mesophase is intermediate between a smectic and a columnar phase and has been described by Davidson and Levelut [7] in a conducting charge transfer complex as a lamello-columnar ordering.

We recall that, for $x = 0{\cdot}3$, the low temperature monotropic phase exhibits a diffuse scattering at 4 Å: it might be a precursor of the long range stacking observed for $x = 0{\cdot}09$.

3.1.4. *Concluding remarks*

To summarize, two effects characterize the role of dilution on the mesomorphic properties of the studied polymers.

(1) The fluid nature of the high temperature smectics is not basically modified by the proportion of mesogenic groups. However their layer spacings vary in an unexpected manner. Larger dilution usually results in thicker layers [8–10] which we interpret as the consequence of microphase separation among the additional dimethylsiloxanes units of the backbone which are repulsed outside the sublayer containing the mesogenic groups [10–13]. This is experimentally consistent with the occurrence of an additional diffuse scattering defining the characteristic distance between two adjacent parts of the siloxane backbone (≈ 8 Å, approximately the thickness of the dimethylsiloxane segments) [8, 9]. This behaviour has been described for smectic A phases and typically from $x = 1$ to $x = 0{\cdot}3$ the swelling of the lamellae ranges between 15 Å and 23 Å depending on the side group and is about 15 Å more from $x = 0{\cdot}3$ to $0{\cdot}09$. Surprisingly, for forked polymers the layer spacing decreases strongly in the first step of dilution then recovers its usual expansion (see table 3). For x varying in the interval $[1, 0{\cdot}3]$ we must then imagine a difference in the type of smectic

Table 3. The layer spacing in the high temperature smectic phase as a function of dilution and tail length. (l is the side group length obtained from stereomodels including the thickness of the backbone.)

		Layer spacing d Å		
Polymer	l Å	$x = 1$	$x = 0{\cdot}3$	$x = 0{\cdot}09$
$P_{f,6,4,4,x}$	38	42	30	46
$P_{f,6,5,5,x}$	39·5	46	30	44
$P_{f,6,9,9,x}$	45	54	31	46

phases (settling or increase of a tilt angle) and/or important modifications of the overlapping of the side groups [9]. In contrast the increase by 14 Å of the layer spacing in the x interval [0·3, 0·09] compares well to the usual value and can be attributed only to the statistical confinement of the siloxane backbone while the packing of the mesogenic parts remains almost unchanged. The scattering at 8 Å is observed for both cases of diluted systems.

(2) The proportion of mesogenic groups strongly modifies the nature of the low temperature states which switch from purely lamellar stackings to hexagonal columnar and eventually to lamello–columnar arrangements. We can add to this analysis of the X-ray patterns that these structural changes resemble the ordered states resulting from microphase separation in diblock copolymers composed of incompatible A and B blocks [14, 15]. In these systems, spherical, cylindrical with hexagonal packing of the cylinders or lamellar morphologies are obtained according to the relative volume fraction of A and B. The lamellar structure is the most stable for a volume fraction of 0·5 and can be changed to other symmetries by varying the proportion in either way [16]. It is thus striking to note that $x = 0{\cdot}09$ corresponds to a volume fraction $\Phi \approx 0{\cdot}45$ in the mesogen and lamellar organization, and that $x = 0{\cdot}30$ corresponds to $\Phi \approx 0{\cdot}75$ in the mesogen and hexagonal organization. This point of view is also sustained by the freezing of a metastable lamellar structure on quenching the sample at $x = 0{\cdot}30$. So, a more careful small angle X-ray scattering study is obviously necessary to investigate whether the organization of the low temperature state is basically imposed by the mesogenic character of the materials or is the consequence of microphase separation.

3.2. *Effects of the modifications in the side group*

3.2.1. *Modifications in the aliphatic chains*

The mesomorphic properties are insensitive to lengthening the two aliphatic chains; the clearing temperatures are almost not affected by this parameter whatever the dilution (see table 2).

In the homopolymers ($x = 1$), for each additional methylene group the layer thickness increases by more than 1·2 Å, i.e. the length of one methylene group; this confirms that bimolecular associations take place among the pendent groups from adjacent chains. In contrast the layer thickness is not affected by the length of the aliphatic chains for diluted systems which proves that the type of association is strongly modified from homo- to diluted polymers. In addition, we can add that some polymers with *three* long terminal chains (and $m = 9$, $Y = H$) have also been synthesized; they are not mesomorphic. This result differs significantly from the conclusions reported by Lin *et al.* [17] on slightly different polymethylsiloxanes fully substituted ($x = 1$) with polycatenar mesogenic groups that the tendency to form liquid-crystalline phases increases with the number of alkoxy substituents.

Finally we note that the thermal stability of the hexagonal columnar phase increases with the length of the aliphatic tail which simultaneously leads to the loss of the enantiotropic character of the smectic C phase for the copolymers $x = 0{\cdot}3$ (see table 2).

3.2.2. *Modifications in the core*

Placing a lateral methoxy group on the phenyl ring next to the spacer lowers the clearing temperatures of the polymers, as is usually observed in mesogens of high and low molecular weight either. The copolymers with reduced proportions of mesogenic groups show only smectic C mesophases without more ordered states at low temperature (see table 2).

In the fluid lamellar mesophase of a fully substituted polymer bearing a lateral methoxy group the layer spacing is systematically larger (+2–3 Å); this can reflect a slight modification of the bimolecular associations discussed previously because of steric hindrance. Moreover for the same exposure time the number of sharp reflections at small angles becomes greater:

$P_{f,6,OCH3,5,5,100\%}$	$d = 48$ Å	five 00*l* reflections with weak 004
$P_{f,6,H,5,5,100\%}$	$d = 46$ Å	three 00*l* reflections

4. Conclusion

The polycatenar architecture of a side group, with both a large rigid core and a large amount of flexible aliphatic tails, is apt to preserve the liquid-crystalline properties when these mesogenic moieties are attached to a polysiloxane backbone. This work confirms the interest of attaching side groups with a high mesogenic potential in a low proportion; the decoupling of the adjacent lamellae is increased by the swelling of a sublayer containing the non-mesogenic backbone when at the same time the ordering of the rods is made easier inside the other sublayer. More or less ordered phases are thus stabilized in these materials with a close packed stacking of the aromatic parts of the rigid cores which deserve additional studies through X-ray scattering and on different systems including, for example, polar mesogens.

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