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## Liquid Crystals

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LIQUID CRYSTALS, 1998, VOL. 25, NO. 1, 85–94

# Side-on fixed polysiloxanes and ‘diluted’ copolysiloxanes with nematic and smectic C phases

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The influence of the molecular parameters of side-on fixed liquid crystal polymers (LCP), namely the spacer length, the aliphatic tail length and the proportion of mesogenic groups (‘dilution’ effect), on the mesomorphic, thermodynamic and structural properties of the nematic and smectic C phases has been studied. This shows in particular the stabilization of the SmC phase on increasing the terminal chain lengths. Moreover, this paper provides evidence for an original behaviour in the SmC organization of side-on LCP with a non-monotonous evolution of the thermodynamic and structural properties with the ‘dilution’. Finally, a comparison with side-end LCP can be established : the question of the participation of the polymer backbone in the smectic organization in side-on LCP is raised.

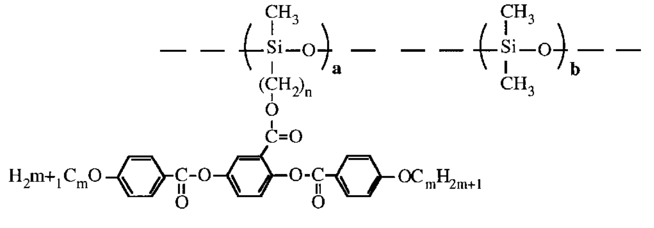
## 1. Introduction

In liquid crystalline polymers (LCP), the tendency of polymer chains to maximize their entropy is counter-balanced by orientational ordering effects resulting from anisotropic interactions between mesogenic units. In this sense, the structure and the thermodynamic properties of LCP are governed by this competition and strongly depend on the molecular architecture. In particular, side group LCP present basically two classes depending upon whether the mesogenic groups are attached terminally (side-end fixed) or laterally (side-on fixed) to the polymer backbone via a flexible spacer. The mesomorphic features of these two families are directly connected with the mode of fixation of the mesogenic cores to the polymer chain. In side-end LCP, the nature of the mesophases is generally changed on varying the length of the spacer and of the terminal groups and these polymers exhibit the same wealth of smectic polymorphism as do low molar mass liquid crystals [1]. On the contrary, in side-on LCP the nematic phase is usually favoured [2–12], as for main chain polymers, and changes in the chemical constitution of the mesogenic groups do not easily modify this tendency. In addition to distinctive mesomorphic properties, the conformation of the backbone essentially differs from side-end to side-on LCP [13]. Indeed SANS experiments reveal for side-end LCP which exhibit a nematic–smectic A sequence a weak anisotropy of the backbone in the nematic phase and, induced by the SmA structure, a more significant anisotropy, with an oblate shape with respect to the director [14–19]. Unlike side-end fixed LCP, the side-on fixed mesogenic polymers exhibit in the nematic phase a large prolate anisotropy of the polymer conformation with a jacketed arrangement of the mesogenic groups around the polymer backbone [20–26]. This prolate extension of the polymer chain imposed by the mesogens is a function of the spacer length [23], of the aliphatic terminal tail length [26] and also of the proportion of the mesogenic groups laterally fixed on the polymer chain [25].

The aim of this paper is to study the influence of these three molecular parameters (namely spacer length, aliphatic tail length and proportion of mesogenic side groups) on the mesomorphic, thermodynamic and structural properties of a series of side-on fixed LCP. Note that we recently observed the occurrence of a smectic C phase in some polymers of the same series [27]. In this work, the evolution of the nematic–smectic C polymorphism versus the molecular parameters is systemically explored. In particular, the influence of the proportion of mesogenic side pendents on the smectic C structure is studied. For the first time, a comparison of the effect of ‘dilution’ on side-on and side-end LCP can be made.

## 2. Results and discussion

The polymers under study have the following general formula:



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$\mathrm{P}_{n,m,m}X$ for short, with $X = a/(a+b)$: therefore $X = 1$ corresponds to the homopolymers and $0 < X < 1$ to copolymers (or 'diluted polymers'). The spacer length $n$ was varied from 4 to 11, the length $m$ of the external aliphatic tails from 1 to 12. The synthesis of these side-on liquid crystalline polysiloxanes has already been described [7]: the vinyl derivative corresponding to the side group is fixed via a classical hydrosilylation reaction either on a commercial polymethylhydrogenosiloxane chain or on home-made poly(hydrogenmethylsiloxane-co-dimethylsiloxane) chains [25]. Concerning the latter, particular effort has been given to preparing well defined copolymer chains with comparable $DP_n$. To this end, the classical mode of preparation [25] has been optimized using mixtures in convenient proportions of two commercial polyhydrogenmethylsiloxane chains with different $DP_n$ ($DP_n = 67$ and $DP_n = 29$) and octamethylcyclotetrasiloxane. Note on table 1, that there is no large difference in the average degree of polymerization of these different poly(hydrogenmethyldimethylsiloxane) backbones ($50 < \overline{DP_n} < 90$) used to synthesize the 'diluted' polymers and the commercially available polyhydrogenmethylsiloxane homopolymer (from Petrach, $DP_n = 67$). In addition, the random distribution of the hydrogenmethyl- and dimethyl-siloxane units has been systematically monitored by $^{29}$Si NMR as previously reported [25, 28 (*d*), 29]. The proportion of Si–H groups has been determined by $^{29}$Si NMR and $^{1}$H NMR (within 2%). The mesomorphic properties were characterized by the usual methods: optical microscopy, differential scanning calorimetry and X-ray diffraction on oriented samples.

Table 1. The various polymer chains used. $X$ is the proportion of Si–H groups; $DP_n$ is the degree of polymerization.

| $X$ | $\overline{DP_n}$ (±5) |
|---|---|
| 1 | 67 |
| 0·90 | 55 |
| 0·70 | 50 |
| 0·55 | 55 |
| 0·49 | 85 |
| 0·42 | 90 |
| 0·35 | 85 |
| 0·09 | 70 |

### 2.1. *Homopolymers*

We will first focus interest on the effects of the variations in molecular structure of the mesogen (spacer length $n$ and aliphatic tail length $m$) on the mesomorphic and thermodynamic properties of the homopolymers. The transition temperatures and entropy changes are listed in table 2 for precursor mesogens and homopolymers.

#### 2.1.1. *Influence of the spacer length n*

Figure 1 illustrates the effect on the transition temperatures of the spacer length $n$ for the same alkyl tail ($\mathrm{P}_{n,4,4}$ series). Both glass transition and clearing temperatures decrease with increasing $n$ and no smectic mesomorphism exists.

We recall that in this $\mathrm{P}_{n,4,4}$ series, the 'jacketed effect' is large for the short spacer ($n = 4$), somewhat weaker for $n = 6$ [23] and considerably reduced for $n = 11$ [26]. Thus, increasing $n$ leads to lower conformational restriction on the polymer. From a thermodynamic point

Table 2. Transition temperatures and entropy changes for the vinylic precursors and the corresponding side-on fixed homopolysiloxanes ($DP_n = 70$). ( ) indicates monotropic transition, Cr: crystalline phase, SmC: smectic C phase, N: nematic, I: isotropic liquid, g: glassy state. $\Delta S$ in J mol$^{-1}$ K$^{-1}$ for vinyl derivative and in J µm$^{-1}$ K$^{-1}$ for polymers.

| | | Vinyl derivatives | | | | | | | | | Homopolymers | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n$ | $m$ | Cr | | SmC | | N | | I | $\Delta S_{\mathrm{IN}}$ | $\Delta S_{\mathrm{NSmC}}$ | g | | SmC | | N | | I | $\Delta S_{\mathrm{IN}}$ | $\Delta S_{\mathrm{NSmC}}$ |
| 4 | 1 | • | 135 | — | | • | (108) | • | 2 | — | • | 53 | — | | • | 154 | • | 2·1 | — |
| 4 | 2 | • | 136 | — | | • | (130) | • | 3·5 | — | • | 36 | — | | • | 158 | • | 3·5 | — |
| 4 | 3 | • | 105 | — | | • | (100) | • | 3·4 | — | • | 48 | — | | • | 130 | • | 3·1 | — |
| 4 | 4 | • | 100 | — | | • | 113 | • | 4·2 | — | • | 36 | — | | • | 130 | • | 3·2 | — |
| 4 | 6 | • | 107 | — | | • | (101) | • | 4·1 | — | • | 18 | — | | • | 99 | • | 2·9 | — |
| 4 | 8 | • | 96 | — | | • | (95) | • | 4·2 | — | • | 24 | — | | • | 93 | • | 3·4 | — |
| 4 | 12 | • | 71 | — | | • | 86 | • | 5·9 | — | • | 27 | — | | • | 87 | • | 4·9 | — |
| 6 | 4 | • | 82 | — | | • | 102 | • | 3·6 | — | • | 28 | — | | • | 113 | • | 2·5 | — |
| 10 | 3 | • | 77 | — | | • | (76) | • | 2 | — | • | 7 | — | | • | 93 | • | 2·6 | — |
| 10 | 4 | • | 59 | — | | • | 87 | • | 3 | — | • | 17 | — | | • | 99 | • | 2·3 | — |
| 10 | 6 | • | 47 | — | | • | 85 | • | 3 | — | • | 15 | • | 34 | • | 96 | • | 3·1 | 1·2 |
| 10 | 8 | • | 44 | • | (31) | • | 87 | • | 5·2 | 7·7 | • | 13 | • | 54 | • | 93 | • | 3·3 | 2 |
| 10 | 10 | • | 38 | • | 44 | • | 85 | • | 4·8 | 8·4 | • | 10 | • | 62 | • | 88 | • | 3·1 | 2·6 |
| 10 | 12 | • | 32 | • | 54 | • | 84 | • | 5·1 | 9·8 | • | 8 | • | 63 | • | 81 | • | 2·9 | 3 |
| 11 | 4 | • | 76 | — | | • | 87 | • | 3·1 | — | • | 16 | — | | • | 97 | • | 2·1 | — |
| 11 | 8 | • | 46 | • | (36) | • | 84 | • | 3·7 | 8·0 | • | 11 | • | 50 | • | 88 | • | 2·5 | 1 |

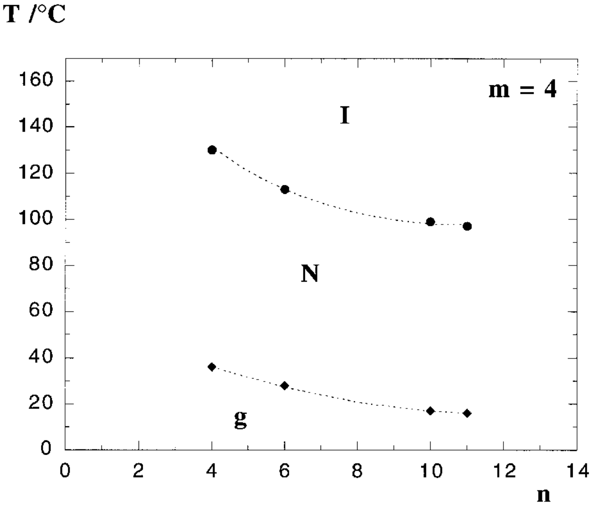


Figure 1. Transition temperatures $T$ as a function of the spacer length $n$ in the homopolymer series $P_{n,4,4}$ (I: isotropic phase, N: nematic phase, g: glassy state).

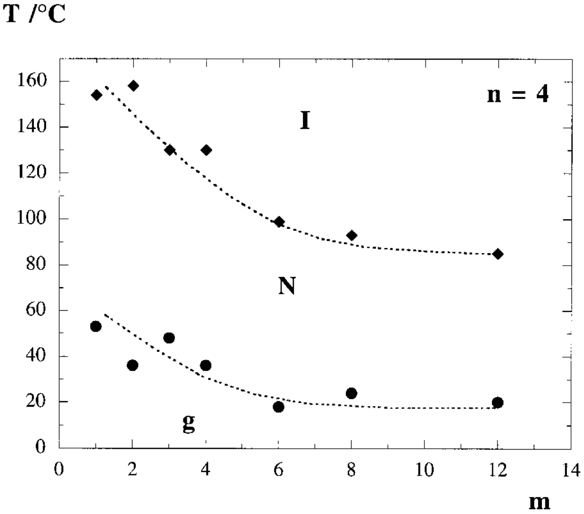


Figure 2. Transition temperatures $T$ as a function of the aliphatic tail length $m$ in the homopolymer series $P_{4,m,m}$ (I: isotropic phase, N: nematic phase, g: glassy state).

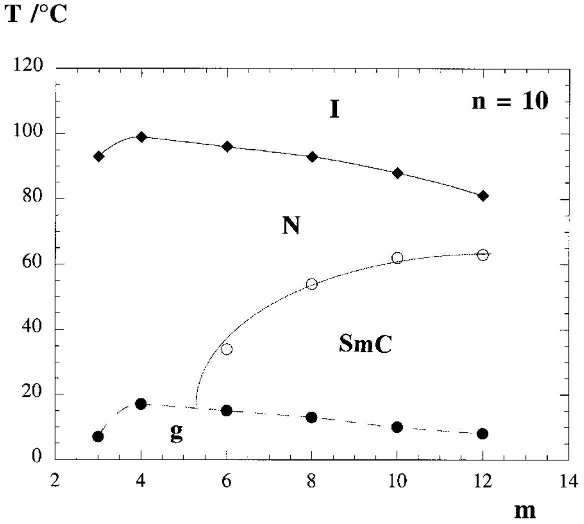


Figure 3. Transition temperatures $T$ as a function of the aliphatic tail length $m$ in the homopolymer series $P_{10,m,m}$ (I: isotropic phase, N: nematic phase, SmC: smectic C phase, g: glassy state).

of view, the decrease in the entropy changes $\Delta S_{IN}$ as the length of the spacer increases (table 2) could be a signature of the diminution of the 'jacketed effect'. However a comparable evolution is observed for the vinylic precursors (table 2). Thus the existence of a short lateral alkylene chain definitely favours the mesogen–mesogen packing and as a consequence induces for the polymers a strong coupling of mesogen–polymer which influences the global conformation of the backbone.

In addition, from the vinyl derivative to the corresponding homopolymer, the higher values of $\Delta T$ ($\Delta T = T_{\mathrm{INpolymer}} - T_{\mathrm{INvinyl\ precursor}}$) for short spacers (table 2) show that the nematic phase is promoted more: this is an indirect confirmation of the contribution of the polymer backbone to the orientational order.

### 2.1.2. *Influence of the aliphatic terminal chains m*

The effect of the aliphatic end groups $m$ on the mesomorphic and thermodynamic properties of the homopolymers appear more complex, and two behaviours are observed depending on the spacer length. The evolution of the transition temperatures versus $m$ are reported in figures 2 and 3 for short ($n = 4$) and long ($n = 10$) spacers, respectively.

2.1.2.1. *Short spacer.* In spite of the even–odd effect observed for the ($P_{4,m,m}$ series, figure 2), the clearing temperatures decrease drastically with increasing $m$ for the first members of the series ($m < 6$) and this effect is damped for longer chains ($m \geqslant 6$). Note in table 2 that the lengthening of the aliphatic tails, which corresponds to an increase of the flexibility, also depresses the I–N transition temperature for the vinylic precursors. Nevertheless, for short tails ($m < 6$) $T_{IN}$ are clearly higher in the case of polymers: this suggests a larger contribution of the polymer backbone to the nematic order in agreement with SANS studies [26].

In addition, the non-monotonous evolution of the entropy change $\Delta S_{IN}$ versus $m$ in the $P_{4,m,m}$ series (table 2) can be seen as the result of competition between contradictory tendencies. Indeed, the lengthening of the aliphatic parts leads to strong reinforcement of the local order of the mesogens as observed by X-ray, which is directly connected to the correlations of the aliphatic tails [27], as for the precursors [30, 31]. On the contrary, the lengthening of the terminal chains disfavours the jacketed effect, as proved by the diminution of the polymer chain anisotropy detected by SANS [26]. This competition between the increase of the nematic order due to the correlations of the aliphatic extremities and the decrease of the nematic order due to the lower backbone contribution is clearly detected by the evolution of $\Delta S_{IN}$. From $m=2$ to 6, the influence of the aliphatic tail correlations is counterbalanced by a diminution of the backbone anisotropy and $\Delta S_{IN}$ slightly decreases. A subsequent increase of $m$ leads to a strong enlargement of $\Delta S_{IN}$ which could be connected with the reinforcement of the local order of the mesogens.

Finally, note in figure 2 the diminution of the glass transition temperature with increasing $m$ which reflects the internal plastification usually observed on increasing the proportion of the paraffinic parts.

2.1.2.2. *Long spacer.* This allows the motions of the mesogenic side groups to partially decouple from those of the polymer backbone. In this sense, it is not surprising to find no significant discrepancy between the evolutions of $T_{IN}$ or $\Delta S_{IN}$ for the polymers and vinylic precursors on varying $m$ (e.g. $\mathbf{P}_{10,m,m}$ series, table 2). $T_{IN}$ slightly decreases with increasing $m$ and on average $\Delta S_{IN}$ increases. Note that the sudden gaps in $\Delta S_{IN}$ observed between $m=6$ and $m=8$ for the vinylic derivatives and between $m=4$ and $m=6$ for the polymers originate from the occurrence of large smectic C cybotactic groups detected by X-ray analysis in the nematic phase [27]. Indeed the essential point revealed by increasing the aliphatic tails for a long spacer ($n=10$ and $n=11$) is the onset of smectic C phases. This result derived from a systematic structural study by X-ray analysis [27] of the evolution of the local order in the nematic phases of these homopolymers, an evolution which predicted the occurrence of smectic C phases for long spacers and aliphatic tails. Consequently, a nematic–smectic C polymorphism was observed in the side-on fixed polysiloxanes for five homopolymers ($\mathbf{P}_{10,6,6}$, $\mathbf{P}_{10,8,8}$, $\mathbf{P}_{10,10,10}$, $\mathbf{P}_{10,12,12}$ and $\mathbf{P}_{11,8,8}$).

As shown in figure 3 ($\mathbf{P}_{10,m,m}$ series), increasing the paraffinic terminal chains stabilizes the smectic C phase to the detriment of the nematic phase, as usually observed for classical rod-like low molar mass mesogens. Correlatively, the N–SmC entropy change increases with $m$ indicating an improvement of the smectic C ordering (table 2). On the other hand, the lengthening of the spacer from $n=10$ to $n=11$ disfavours the layering order as shown by the N–SmC transition temperature and N–SmC entropy change.

Finally, we should remember that almost all side-on fixed polymers hitherto synthesized exhibit only the nematic phase and the existence of a smectic polymorphism remains an exception [27, 32–35]. Thus, despite similar molecular conditions (the same long spacer and the same terminal chains as the polysiloxanes under study), no smectic mesomorphism has been observed in the corresponding side-on fixed polyacrylates [4]. The first side-on attached LCP exhibiting a smectic A phase was reported in napththalene–cyclohexyl side-on fixed polymers [32, 33]. Besides the polysiloxanes under study [27], some new results have announced a smectic C phase in polynorbornenes with laterally attached mesogens terminated with perfluorinated segments [34]. More recently there have been reported side-on polyacrylates with a different position of attachment of the spacer on the mesogenic core, these showing a smectic A phase for long spacers and long alkoxy chains or a polar group [35].

## 2.2. *Copolymers*

Keeping in mind that in LCP there is a conflict between the drive towards maximization of the entropy of the flexible polymer backbone and minimization of the energy of a liquid crystalline system, a good synthetic route to modify this competition is to change the proportion of the mesogenic groups with respect to the backbone. This can be achieved in polysiloxanes by diluting the mesogenic content with dimethylsiloxy units. Some stimulating studies have been carried out on side-end fixed copolysiloxanes [28] and only a few examples of 'diluted polymers' have been briefly reported in the case of side-on fixation [21–23].

Note that a systematic study of the influence of the proportion of mesogenic groups is difficult without preparing well controlled poly(hydrogenmethylsiloxane-co-dimethylsiloxane) chains with comparable degrees of polymerization and the desired proportion of hydrogenmethylsiloxane. Indeed, commercially available copolymer backbones exhibit large differences in the average degree of polymerization $\overline{DP_n}$ and the choice of the proportion of mesogenic side groups is strictly limited. Thus, the synthesis of the well defined copolymer chains described above is completly justified.

We will now study the influence of the proportion $X$ of mesogenic groups on the liquid crystalline thermodynamic and structural properties of the corresponding copolymers.

### 2.2.1. *Influence of the proportion of mesogenic side-groups on the mesomorphic and thermodynamic properties*

2.2.1.1. *On the nematic phase.* For the side-on fixed copolymers under study, the polymorphism, the transition temperatures, and the enthalpy and entropy changes are summarized in table 3. Considering these data, several general effects are noticed.

Table 3. Transition temperatures and entropy changes for the side-on fixed copolysiloxanes (SmC: smectic C phase, N: nematic, I: isotropic liquid, g: glassy state). $\Delta S$ in J $\mu$m$^{-1}$ K$^{-1}$ for polymers. Data for the homopolymers are also recalled (bold script).

| Copolymers | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *n* | *m* | *X* | g | | SmC | | N | | I | $\Delta S_{IN}$ | $\Delta S_{NSmC}$ |
| 4 | 4 | **1** | • | **36** | | | • | **130** | • | **3·2** | |
| 4 | 4 | 0·9 | • | 37 | | | • | 130 | • | 1·9 | |
| 4 | 4 | 0·7 | • | 25 | | | • | 120 | • | 2·0 | |
| 4 | 4 | 0·55 | • | 21 | | | • | 100 | • | 1·8 | |
| 4 | 4 | 0·49 | • | 20 | | | • | 95 | • | 1·3 | |
| 4 | 4 | 0·42 | • | 19 | | | • | 88·5 | • | 1·0 | |
| 4 | 4 | 0·35 | • | 16 | | | • | 82 | • | 0·6 | |
| 4 | 4 | 0·27 | • | 7 | | | • | 71 | • | 0·4 | |
| 4 | 4 | 0·09 | • | 4 | | | | | • | | |
| 6 | 4 | **1** | • | **28** | | | • | **113** | • | **2·5** | |
| 6 | 4 | 0·55 | • | 25 | | | • | 82 | • | 0·9 | |
| **10** | 4 | **1** | • | **17** | | | • | **99** | • | **2·3** | |
| 10 | 4 | 0·55 | • | 20 | | | • | 89 | • | 0·8 | |
| 10 | 4 | 0·35 | • | 22 | | | • | 71 | • | 0·4 | |
| **10** | 6 | **1** | • | **15** | • | **34** | • | **96** | • | **1·5** | **0·5** |
| 10 | 6 | 0·70 | • | 16 | • | 46 | • | 83 | • | 1·5 | 1·6 |
| 10 | 6 | 0·55 | • | 14 | • | 51 | • | 77 | • | 0·85 | 1·9 |
| 10 | 6 | 0·49 | • | 13 | • | 55 | • | 79 | • | 1·0 | 3·3 |
| 10 | 6 | 0·09 | • | −10 | • | 49$^{a}$ | | — | • | 0·5$^{a}$ | — |
| 10 | 6 | 0·35 | • | 12 | • | 55 | • | 71 | • | 0·5 | 3·0 |
| **10** | 8 | **1** | • | **13** | • | **54** | • | **93** | • | **3·3** | **2** |
| 10 | 8 | 0·9 | • | 14 | • | 54 | • | 90 | • | 2·9 | 1·7 |
| 10 | 8 | 0·7 | • | 11 | • | 64 | • | 87 | • | 1·6 | 3·7 |
| 10 | 8 | 0·55 | • | 12 | • | 64 | • | 80 | • | 1·1 | 4·7 |
| 10 | 8 | 0·49 | • | 13 | • | 70 | • | 84 | • | 1·2 | 4·7 |
| 10 | 8 | 0·35 | • | 11 | • | 68 | • | 77 | • | 0·6 | 3·8 |
| 10 | 8 | 0·09 | • | −13 | • | 58$^{a}$ | | — | • | 0·6$^{a}$ | — |
| **10** | **10** | **1** | • | **10** | • | **62** | • | **88** | • | **3·1** | **2·6** |
| 10 | 10 | 0·49 | • | 5 | • | 63 | • | 83 | • | 1·8 | 3·6 |
| 10 | 10 | 0·35 | • | 5 | • | 68 | • | 73 | • | 0·5 | 2·5 |
| **11** | 4 | **1** | • | **16** | | | • | **97** | • | **2·1** | |
| 11 | 4 | 0·55 | • | 20 | • | 38 | • | 92 | • | 1·6 | 0·8 |
| 11 | 4 | 0·35 | • | 24 | • | 55 | • | 81 | • | 0·7 | 1·8 |
| **11** | 8 | **1** | • | **11** | • | **50** | • | **88** | • | **2·5** | **1** |
| 11 | 8 | 0·70 | • | 11 | • | 67 | • | 87 | • | 1·8 | 3·1 |
| 11 | 8 | 0·55 | • | 9 | • | 69 | • | 86·5 | • | 1·4 | 3·4 |
| 11 | 8 | 0·42 | • | 8 | • | 73 | • | 82 | • | 0·9 | 4·1 |
| 11 | 8 | 0·35 | • | 4 | • | 74 | • | 81·5 | • | 0·7 | 3·9 |
| 11 | 8 | 0·30 | • | 6 | • | 70 | • | 80 | • | 0·75 | 3·3 |
| 11 | 8 | 0·09 | • | −10 | • | 60$^{a}$ | • | — | • | 0·5$^{a}$ | — |

[a] Values for the I–SmC transition.

First, in nematic copolymer series (e.g. $P_{4,4,4}X$), the glass transition temperature $T_g$ decreases on diluting the mesogenic contents with dimethylsiloxy units (figure 4). This reduction in $T_g$ indicates that the backbone is more flexible in the copolymers than in the homopolymers. A similar effect was found for side-end fixed polysiloxanes [28(*c*)]. However, the $T_g$ values remain considerably higher than that of a poly(dimethylsiloxane) backbone ($T_g \approx -120$°C) due to the dominant ordering effect of the mesogenic moieties. Secondly, as observed in LC side-end fixed polymers, either polysiloxanes [28] or polyvinyl ethers [29], the clearing temperatures decrease gradually on decreasing the proportion of mesogenic side groups (table 3). Figure 4 shows an example of a nematic copolymer series ($P_{4,4,4}X$) where both $T_{IN}$ and $T_g$ decrease with $X$; the copolymer with $X = 0{\cdot}09$ does not show any mesophase down to the glassy state.

We note in table 3 that whatever the $P_{n,m,m}X$ series, the $\Delta S_{IN}$ values systematically decrease from homopolymer to copolymer. This implies that the nematic order is clearly disfavoured by an increase in the backbone flexibility. Thus, despite a more flexible backbone,

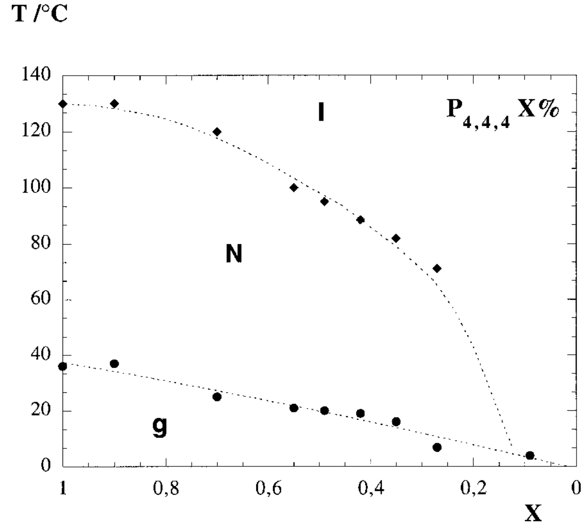


Figure 4. Transition temperatures $T$ as a function of the mesogenic ratio $X$ in the 'diluted' copolymer series $P_{4,4,4}X$ (I: isotropic phase, N: nematic phase, g: glassy state).

the orientational interactions between side groups are weaker ($\Delta H_{\mathrm{IN}}\downarrow$ as $X\downarrow$) and as a consequence the nematic order is destabilized.

2.2.1.2. *On the nematic-smectic C polymorphism.* The most striking point is that the 'dilution' does not influence the nematic and the smectic C phases in the same way. The example of the $P_{10,8,8}X$ series is reported in figure 5: contrary to the nematic state, the smectic C phase is stabilized on decreasing the proportion of mesogenic units. A similar behaviour is found for the $P_{10,6,6}X$, $P_{10,10,10}X$, and $P_{11,8,8}X$ series. Moreover, in the case of the $P_{11,4,4}X$ series, a smectic C phase which does not exist in the homopolymer is induced and stabilized by lowering $X$ (table 3). In addition, note in figure 5 and table 3 that for a very low content of mesogenic groups (9%) for the $P_{10,8,8}X$ series, the smectic arrangement is kept. This difference in behaviour between the nematic phase and the smectic C phase with dilution is certainly due to a difference in the mesogen–mesogen interactions in the phase.

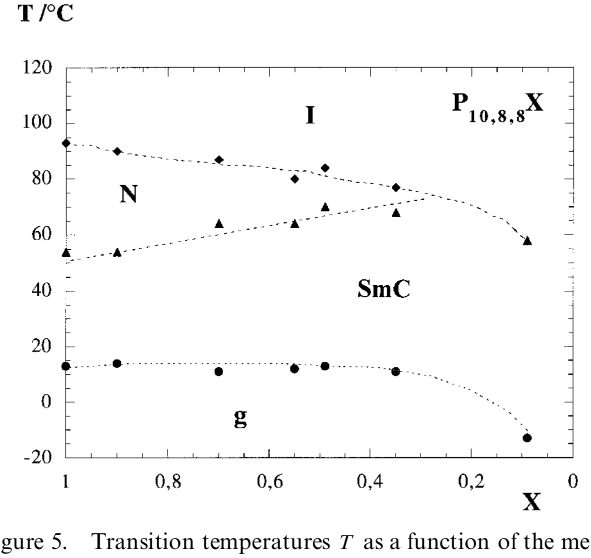


Figure 5. Transition temperatures $T$ as a function of the mesogenic ratio $X$ in the 'diluted' copolymer series $P_{10,8,8}X$ (I: isotropic phase, N: nematic phase, SmC: smectic C phase, g: glassy state).

Thus, surprisingly we notice on figure 6 ($P_{10,8,8}$ series) that the nematic–smectic C transition enthalpy $\Delta H_{\mathrm{NSmC}}$ does not exhibit a monotonous evolution with the dilution: on passing from the homopolymer to the copolymers $\Delta H_{\mathrm{NSmC}}$ first increases, implying that the lateral mesogenic interactions are greatly favoured by the increase of backbone flexibility in the case of this smectic C arrangement. For lower contents of mesogenic side groups, a diminution of the $\Delta H_{\mathrm{NSmC}}$ value is observed. By comparison, note that the isotropic–nematic transition enthalpy $\Delta H_{\mathrm{IN}}$ regularly decreases on lowering $X$.

Similar evolutions of $\Delta H_{\mathrm{NSmC}}$ (or $\Delta S_{\mathrm{NSmC}}$) are observed for all the copolymer series. Nevertheless, the optimum proportion of mesogenic pendents corresponding to the maximum of $\Delta H_{\mathrm{NSmC}}$ or $\Delta S_{\mathrm{NSmC}}$ ($x_{\max}$) varies with the aliphatic tail length $m$ and with the spacer length $n$ (figure 7). Indeed, at constant spacer, an increase of $m$ leads to higher values of $X_{\max}$, while at constant tail length, an increase of $n$ leads to lower values of $X_{\max}$.

### 2.2.2. *Influence of the proportion of mesogenic side groups on the structural properties of the smectic C phases*

It is more difficult to describe the structural arrangement in the case of a tilted smectic C phase. Indeed, a

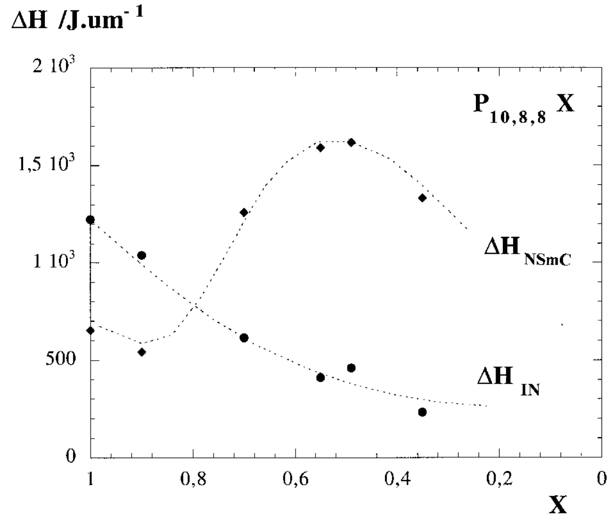


Figure 6. N–SmC transition enthalpies $\Delta H$ (Joules per momomer unit) as a function of the mesogenic ratio $X$ in the 'diluted' copolymer series $P_{10,8,8}X$.

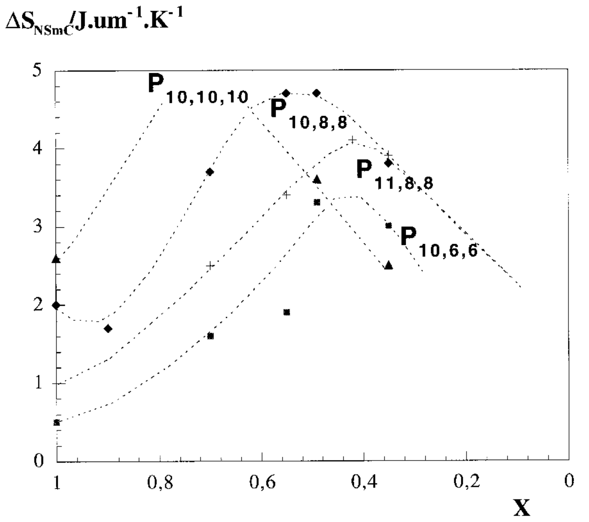


Figure 7. N–SmC transition entropies $\Delta S$ (Joules per momomer unit per Kelvin) as a function of the mesogenic ratio $X$ in the 'diluted' copolymer series $P_{10,10,10}X$, $P_{10,8,8}X$, $P_{10,6,6}X$, $P_{11,8,8}X$.

comparison of the layer spacing $d$ is not sufficient since an additional parameter has to be taken into account, namely the tilt angle $\theta$. X-ray patterns of oriented polymers in the smectic C phase are usually characterized at small angles by four off-axis Bragg spots (i.e. mesogenic groups oriented along the external field and layers tilted with respect to this direction) corresponding to a wave vector $q = 2\pi/d$ and a tilt angle $\theta$. The projection of the wave vector along the director gives the length $d_{//} = 2\pi/q \cos\theta$ of the 'object' responsible for the layering arrangement (backbone plus mesogenic parts). These values are summarized in table 4.

The side-on fixed $P_{n,m,m}X$ series globally exhibit the same tendency in the smectic C phase: from the homopolymer to the copolymers, a decrease of $q$ is observed (table 4). This also corresponds to a limited increment of the layer spacing (+2–7 Å) from $X = 1$ to $X = 0{\cdot}35$, followed by a very important increment for subsequent dilution (+20–25 Å) from $X = 0{\cdot}35$ to $X = 0{\cdot}09$. We can emphasize that this behaviour for $X = 0{\cdot}09$ is not yet understood. Figure 8 shows the identical evolution of $d$ for two series with different spacers and the same mesogen ($P_{10,8,8}X$ and $P_{11,8,8}X$) which indicates that the influence of the spacer on the layer spacing is negligible.

Moreover, the regular evolution of $d$ is accompanied by a non-monotonous variation of the tilt angle (figure 9): from the homopolymer to the copolymers, $\theta$ first decreases to a limited proportion of mesogenic side groups and then increases for a subsequent reduction of $X$. As a consequence $d_{//}$ varies with $X$ revealing strong modifications of the 'object' forming the layers as the proportion of mesogenic groups is reduced (table 4).

Table 4. Structural data for the smectic C phases of homopolymers (bold script) and copolymers. $q$: wave vector, $\theta$: tilt angle, $d$: layer spacing, $d//$: projection along the magnetic field direction, ⟨⟩ indicates data corresponding to SmC cybotactic groups in a nematic phase.

| $n$ | $m$ | $X$ | $q$/Å$^{-1}$ | $\theta$/° | $d$/Å | $d\|\|$/Å |
|---|---|---|---|---|---|---|
| **10** | **6** | **1** | **0·24** | **53** | **26·1** | **43·5** |
| 10 | 6 | 0·70 | 0·22 | 50·5 | 28·5 | 44·9 |
| 10 | 6 | 0·55 | 0·21 | 44 | 29·9 | 41·6 |
| 10 | 6 | 0·49 | 0·21 | 45 | 29·9 | 42·3 |
| 10 | 6 | 0·35 | 0·20 | 53 | 31·4 | 52·2 |
| 10 | 6 | 0·30 | 0·19 | 52 | 33·0 | 53·7 |
| 10 | 6 | 0·09 | 0·12 | 44 | 52·0 | 72·8 |
| **10** | **8** | **1** | **0·22** | **51·5** | **28·5** | **45·8** |
| 10 | 8 | 0·90 | 0·21 | 51·5 | 29·2 | 46·9 |
| 10 | 8 | 0·70 | 0·21 | 51 | 29·2 | 46·4 |
| 10 | 8 | 0·55 | 0·21 | 30 | 29·9 | 34·5 |
| 10 | 8 | 0·49 | 0·21 | 52 | 29·9 | 48·6 |
| 10 | 8 | 0·35 | 0·20 | 53 | 31·4 | 52·2 |
| 10 | 8 | 0·09 | 0·12 | 55 | 52·4 | 91·3 |
| **10** | **10** | **1** | **0·21** | **50·5** | **29·9** | **47·0** |
| 10 | 10 | 0·49 | 0·20 | 49 | 31·0 | 47·2 |
| 10 | 10 | 0·35 | 0·17 | 53·5 | 35·9 | 60·4 |
| **10** | **12** | **1** | **0·20** | **39** | **31·4** | **40·4** |
| **11** | **4** | **1** | **⟨0·26⟩** | **41·5** | **⟨24·1⟩** | **⟨32·3⟩** |
| 11 | 4 | 0·55 | 0·24 | 49·5 | 26·2 | 40·3 |
| 11 | 4 | 0·35 | 0·23 | 46 | 27·3 | 39·3 |
| **11** | **8** | **1** | **0·21** | **50** | **29·2** | **45·4** |
| 11 | 8 | 0·70 | 0·21 | 47 | 29·9 | 44·0 |
| 11 | 8 | 0·55 | 0·21 | 46 | 29·9 | 43·0 |
| 11 | 8 | 0·35 | 0·20 | 41 | 31·4 | 41·6 |
| 11 | 8 | 0·09 | 0·11 | 46 | 57·0 | 82·0 |

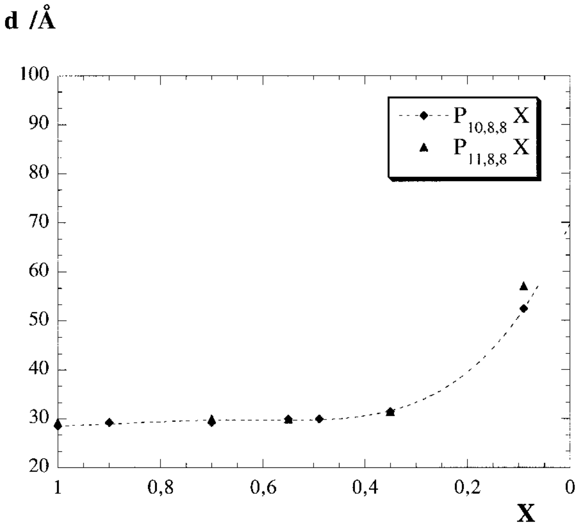


Figure 8. Layer spacing $d$ as a function of the mesogenic ratio $X$ in the 'diluted' copolymer series $P_{10,8,8}X$ and $P_{11,8,8}X$.

Finally, it is interesting to note that the minimum for the tilt angle and for the length of the 'object' responsible for the layering arrangement approximatively corresponds

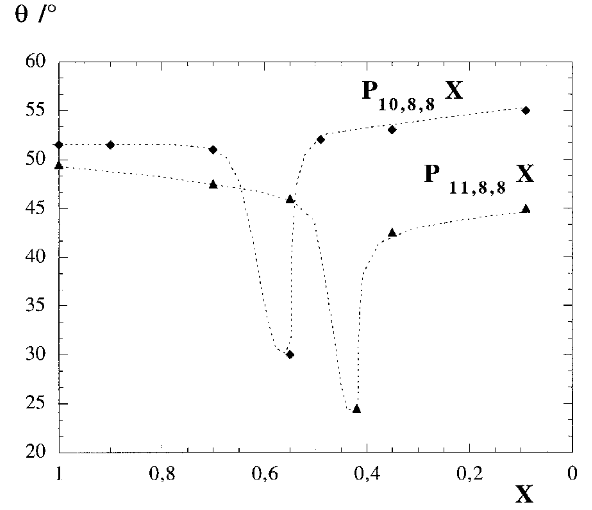


Figure 9. Tilt angle $\theta$ as a function of the mesogenic ratio $X$ in the 'diluted' copolymer series $P_{10,8,8}X$ and $P_{11,8,8}X$.

to the proportion $X_{max}$ corresponding to the maximum of $\Delta H_{NSmC}$ and $\Delta S_{NSmC}$ (figure 7). With dilution of a SmC homopolymer, a thermodynamic stability of the SmC phase is reached, corresponding to a layer organization formed from 'objects' with a minimum length $d_{//}$ tilted at a minimum angle $\theta$. Nevertheless, to explain this evolution, a modification of the arrangement of the mesogenic groups cannot be ruled out in the case of side-on fixed polymers and probably the contribution of the polymer chain is not the same for all proportions of the mesogenic entities. In this sense, small angle neutron scattering (SANS) experiments have been recently made on the polymer $P_{10,6,6}$ 55%. The main result of this study is the reversible change of backbone conformation from the nematic to the smectic C phase, with a confinement of the backbone between the smectic layers [36]. Additional systems of diluted copolymers are currently under study.

At this stage a question is raised: are these thermodynamic features of the nematic and smectic C phases specific for side-on fixation or not?

### 2.2.3. *Comparison with side-end fixed LCP*

To compare the effect of the dilution of the mesogenic content on the properties of side-on and side-end fixed LCP, two side-end fixed copolymer series have been synthesized with the same polymer chains.

The first system (namely $P_{6,4}X$) exhibits the same nematic–smectic C polymorphism as the side-on LCP under study. The transition temperatures and the structural parameters are listed in table 5. We note in figure 10 that the isotropic–nematic and nematic–smectic C temperatures are depressed on decreasing the mesogenic contents: thus in the opposite way to side-on

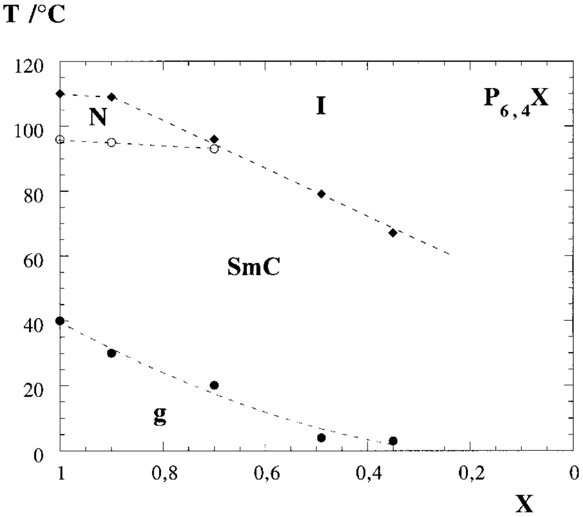
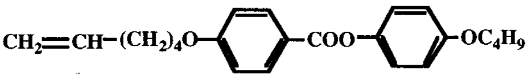


Figure 10. Transition temperatures $T$ as a function of the mesogenic ratio $X$ in the 'diluted' side-end copolymer series $P_{6,4}X$ (I: isotropic phase, N: nematic phase, SmC: smectic C phase, g: glassy state).

Table 5. Transition temperatures and structure parameters for the 'diluted' copolymer series $P_{6,4}X$ made from the mesogenic precursor shown:



$CH_2{=}CH{-}(CH_2)_4O{-}C_6H_4{-}COO{-}C_6H_4{-}OC_4H_9$

(I: isotropic phase, N: nematic phase, SmC: smectic C phase, g: glassy state, $q$: wavevector, $\theta$: tilt angle, $d = 2\pi/q$, $d// = 2\pi/q \cos\theta$).

| | Transition temperatures °C | | | | | | | Structure | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $X$ | g | • | SmC | • | N | • | I | $q$/Å$^{-1}$ | $\theta$/° | $d$/Å | $d_{//}$/Å |
| 1 | | 40 | • | 96 | • | 110 | | 0·26 | 29·5 | 24·2 | 21 |
| 0·9 | | 30 | • | 95 | • | 109 | | 0·26 | 18 | 24·2 | 23 |
| 0·7 | | 20 | • | 93 | • | 96 | | 0·255 | 12 | 24·6 | 24 |
| 0·49 | | 4 | • | — | • | 79 | | 0·235 | <5 | 26·7 | ~27 |
| 0·35 | | 3 | • | — | • | 67 | | 0·20 | <5 | 31·4 | ~32 |

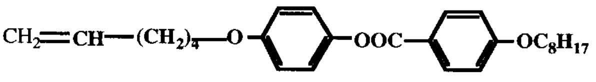
copolymers, both nematic and smectic C phases are destabilized by the increase of the backbone flexibility for side-end fixation (the nematic phase even disappears for $X < 0{\cdot}7$). A similar effect has been already reported in the case of copolyvinyl ethers [35]. These differences are extended to the structure: if the tilt angle is strongly affected by the dilution, it decreases monotonously with the mesogen ratio (table 5). In addition, the layer spacing $d$ increases with a decrease of $X$: $+7$ Å from the homopolymer to the copolymer $P_{6,4}$ 55%, which is comparable to the behaviour of side-on fixed LCP.

In order to complete the comparison, a second system (namely $P_{6,8}X$%) which exhibits a SmA–SmB polymorphism has been studied. The transition temperatures and the structural parameters are listed in table 6. We note in figure 11 that both smectic phases (SmA and SmB) are destabilized with decreasing $X$. In the smectic A phase, we also observed a stronger increase in the layer distance $d$ with decreasing $X$: $+13$ Å from the homopolymer to the copolymer $P_{6,8}$ 30%. This behaviour has been accounted for by Diele *et al.* [37] as the result of a swelling of a sublayer containing the polysiloxane backbone in a microphase separation model. SANS experiments have shown that the polymer backbone keeps a significant oblate shape in the SmA phase on reducing the proportion of mesogenic groups [38]. This anisotropy can be interpreted as a chain more or less confined and micro-segregated between the mesogenic layers as demonstrated by Noirez *et al.* [39].

## 3. Conclusions

The systematic study of side-on fixed LCP deals with the influence of the different molecular parameters, namely spacer length, aliphatic tail length and proportion of mesogenic side groups on the thermodynamical and structural properties.

Table 6. Transition temperature and structure parameters for the 'diluted' copolymer series $P_{6,8}X$ made from mesogenic precursor shown:



(I: isotropic phase, SmA: smectic A, SmB: smectic B phase, g: glassy state, $q$: wavevector, $\theta$: tilt angle, $d = 2\pi/q$, $d/l = 2\pi/q \cos\theta$).

| | Transition temperatures/°C | | | | | | | Structure | |
|---|---|---|---|---|---|---|---|---|---|
| $X$ | g | • | SmB | • | SmA | • | I | $q$/Å$^{-1}$ | $d$/Å |
| 1 | | 42 | • | 75 | • | 154 | | 0·19 | 33 |
| 0·55 | | 17 | • | 55 | • | 136 | | 0·16 | 40 |
| 0·30 | | 2 | • | 42 | • | 108 | | 0·14 | 46 |

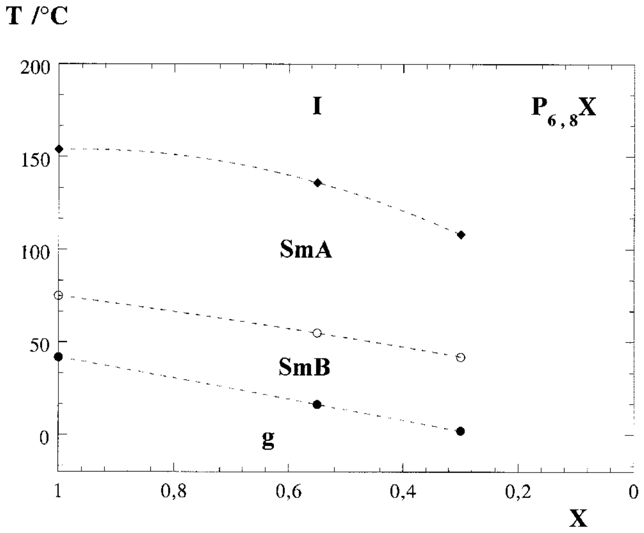


Figure 11. Transition temperatures $T$ as a function of the mesogenic ratio $X$ in the 'diluted' side-end copolymer series $P_{6,8}X$ (I: isotropic phase, SmA: smectic A phase, SmB: smectic B phase, g: glassy state).

Considering first the homopolymers, we have shown that the nematic phase is promoted for short spacers and short aliphatic tails. When the degree of freedom of the system increases for larger spacers, a nematic–smectic C polymorphism occurs; in that case, the lengthening of the paraffinic terminal chains favours the layering order to the detriment of the nematic order.

The second important point of the paper concerns the influence of dilution. In fact, dilution is a special way of changing the data relating to the competition between the backbone entropy and the mesogenic order. First, the nematic phase is systematically destabilized by the dilution effect for side-on LCP, corresponding to a decrease in the mesogen–mesogen interactions. On the contrary, the interactions in the smectic C phase of side-on LCP are favoured by weak dilution. In fact, the flexibility of the polymer backbone increases which allows larger lateral interactions between the mesogens. Nevertheless, after an optimal ratio (corresponding to $X_{\max}$), the diminution of the number of mesogenic groups becomes the relevant factor and the interactions in the smectic C phase decrease. The evolution is different in the case of smectic side-end LCP (SmA, SmB, SmC): the dilution systematically disfavours the smectic order.

These observations underline the question of the participation of the backbone polymer in the smectic organization. While it is now well established that in side-end fixed SmA polymers, a diminution of the mesogenic content is accompanied by a segregation of the chains between the layers, the behaviour of side-on fixed LCP seems to be more complicated. Complementary SANS experiments are currently in progress [40] in order to study the chain conformation in the smectic C phase for diluted side-on LCP before and after the optimal proportion $X_{\max}$.

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