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Side chain polysiloxanes with fluorinated mesogenic groups

The role of the fluorine content on the properties of the smectic A state

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A series of liquid crystalline polymers has been synthesized in which fluorinated or semi-fluorinated mesogenic moieties are used as side groups linked to a polysiloxane backbone. Clear-cut differences in the structure of the smectic A phase are evidenced between fluorinated polymers and their classical non-fluorinated homologues. In a comparative analysis, we discuss the relevance of the steric hindrance of perfluorinated sequences and of the microsegregation of the backbone in response to these modifications as related to the fluorine content in the side group and to the proportion of mesogenic groups.

1. Introduction

The fluorine atom has been used for a long time as a substituent in place of hydrogen on the aromatic cores of rod-like mesogens. Varying the position and number of substitutions allows one to modify the range of mesomorphism, as well as other physical properties (dipole moment, viscosity) [1–4]. In more recently synthesized materials, fluorine has replaced hydrogen in the flexible extremities of mesogens [5–8]. Such a partial or total fluorination of one of the end chains of a classical rod-like molecule leads to asymmetric compounds, mostly smectogens. In spite of the different character of each end with respect to many parameters (stiffness, volume, molecular interactions, polarization), no special feature could be observed in the smectic A structures of such materials in connection with their molecular dissymmetry: in particular the layer spacings have been shown to be commensurate with the molecular length [9]. This indicates a random up and down distribution of the fluorinated and non-fluorinated ends in the layers. In other words there is neither pairing nor microphase separation in these systems.

In this paper, we focus on the influence of such fluorinated or semi-fluorinated mesogenic moieties used as side groups in comb-like polymers. Even in the absence of fluorine, these side chain polymers present a constitutive dissymetry which is clearly evidenced by the need to define a spacer and a tail in the mesogenic side group. These polymers exhibit preferentially S_A phases for which the layer thickness is or is not commensurate with the length of the side group, depending, for example, on the respective sizes of the spacer and the tail [10]. Detailed structural studies have been

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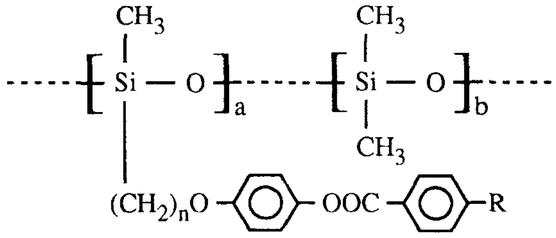
conducted in this domain [11]. Another structural question which is frequently addressed is the location of the backbone in the smectic structure of these polymers. Most often considered is a micro-segregated structure in which the backbone is confined between sublayers of mesogenic groups [12, 13]. This question can also be nicely tackled using the so-called 'diluted' polymers, in which the number of mesogenic groups is less than the number of segments of the backbone [14].

Systematic structural analysis of various families of compounds varying these molecular parameters is thus important to the understanding of the organization of these liquid crystalline polymers in the smectic state. In order to achieve a consistent comparative study, we have synthesized a series of homologous fluorinated and non-fluorinated polysiloxanes including a set of diluted materials. Structural modifications are observed in connection with molecular changes in the side groups and finally these are discussed with respect to the model of microsegregation.

2. Materials

The general formula corresponding to the series of polysiloxanes which have been synthesized is the following:



in which a, b, n and R are the molecular parameters which we have varied.

The ratio $(a/a+b)\times 100 = x$ per cent defines the proportion of mesogenic groups. In our compounds, two types have been used. Either x per cent = 100 per cent ($\overline{DP}_n \approx 37$), i.e. the resulting material is an 'undiluted' homopolymer, or x per cent = 30 per cent ($\overline{DP}_n \approx 29$), i.e. the resulting material is a 'diluted' copolymer. Two spacer lengths, $n = 4$ or 6, have been chosen in order to modify the coupling with the backbone. The groups R contain fluorine in most cases:

$R = C_6F_{13}$ ($n = 6$ only): the corresponding polymers are labelled **P6, F$_6$** x per cent.

$R = OCF_3$: the corresponding polymers are labelled **P*n*, OCF$_3$** x per cent.

$R = O(CH_2)p(CF_2)qF$: the corresponding polymers are labelled **P*n*, H$_p$F$_q$** x per cent.

However, since $p + q = 8$ in the third case, the compounds with an isometric classical aliphatic tail, $R = O(CH_2)_8H$, have also been prepared for the sake of comparison. The corresponding polymers are labelled **P*n*,8** x per cent.

The synthesis of each polymer involves three main steps:

(i) The synthesis of the *p*-substituted benzoic acid containing the R group. The methods are described in [9] for the *p*-perfluoroalkylbenzoic acid and for *p*-(semi-fluoroalkyloxy) benzoic acids and in [10] for the *p*-octyloxybenzoic acid. The *p*-trifluoromethoxybenzoic acid is commercially available (Fluorochem Limited).

(ii) This acid is linked to the appropriate *p*-alkenyloxyphenol via a classical esterification to produce a vinyl mesogenic group.

(iii) The final polymer is obtained by attaching this vinylic precursor to the commercial polysiloxane backbone following a classical hydrosilylation reaction [10] in the presence of [H_2PtCl_6, $6H_2O$] catalyst.

The extent of substitution was determined by ^1H NMR (Brüker WH 270 MHz in $CDCl_3$ as solvent); for all samples it exceeded 95 per cent).

3. Experimental results (characterization of the mesophases)

The polymorphism was first analysed by optical microscopic observations (Olympus BH-2) using a Mettler FP 82 HT hot stage. The textures were established after annealing just below the clarification temperature and observed between crossed polarizer and analyser. The transition temperatures were assessed by DSC measurements (Perkin–Elmer DSC 7). The enthalpies of the transitions were also determined from these measurements. The characterization was completed by X-ray diffraction on powder samples using a Guinier camera (Hüber) and monochromatic $CoK_{\alpha 1}$ radiation. With these three methods we have characterized S_A, S_C and S_B mesophases in the different polymers.

All S_A and S_C phases exhibit fan shaped textures. The uniaxial character of the S_A phase was evidenced by the occurrence of homeotropic domains. These become birefringent at the S_A–S_C transition, if any, and a reversible change from a uniform fan to a broken fan texture can also be noticed. The S_B phase had no typical texture and could not be readily differentiated microscopically.

As generally observed, the X-ray patterns of the S_A or S_C phases exhibit at small angles one or several 001 Bragg reflections from which the layer spacing d is deduced. At wide angles a diffuse scattering is observed which denotes a liquid-like short range within the layers. A S_B phase is characterized by one sharp reflection at wide angles resulting from the condensation of the diffuse scattering observed in the S_A or S_C phases; the corresponding wavevector characteristic of the organization of the mesogens within the smectic layers ranges between $(2\pi/4{\cdot}5)\,Å^{-1}$ and $(2\pi/4{\cdot}3)\,Å^{-1}$. Figures 1 (*a*) and (*b*) are two selected examples of the variation of the layer spacing d with temperature for polymers **P6,H$_5$F$_3$** 100 per cent (S_C–S_A) and **P6,H$_5$F$_3$** 30 per cent (S_B–S_C–S_A) which show a classical behaviour. The layer spacing of the smectic A phase decreases with increasing temperature. In the smectic C phase, the layer spacing increases rapidly near the S_C–S_A transition, as expected from the second order character of this phase change, with a continuous variation of the tilt angle value down to zero at the transition (the associated heat is very weak $\Delta H \leqslant 1\,J\,g^{-1}$). The layer thickness throughout the smectic B phase is nearly constant and larger than in the S_A or S_C phase. The discontinuity observed at the S_B–S_A or S_B–S_C transition is consistent with first order character (the associated heat is $\Delta H \approx 3\,J\,g^{-1}$). Finally, the X-ray patterns recorded at room temperature show additional features in a few cases. These relate to the number of harmonics and/or a supplementary scattering at wide angles:

(i) For **P6,OCF$_3$** 100 per cent, the second order of reflection observed in the S_A phase disappears, while the 3rd and 4th orders intensify. Two Bragg reflections, which are also noticed with **P4,OCF$_3$** 100 per cent and all **P*n*,OCF$_3$** 30 per cent compounds, are observed at $(2\pi/4{\cdot}5)\,Å^{-1}$ and $(2\pi/4{\cdot}1)\,Å^{-1}$. This could indicate that the mesogenic groups with fluorinated short tails tend to organize on a bidimensional array within the layers.

(ii) For **P6,F$_6$** 100 per cent fifth-order appears in addition to the first and third orders of the S_C phase. All the even orders are absent.

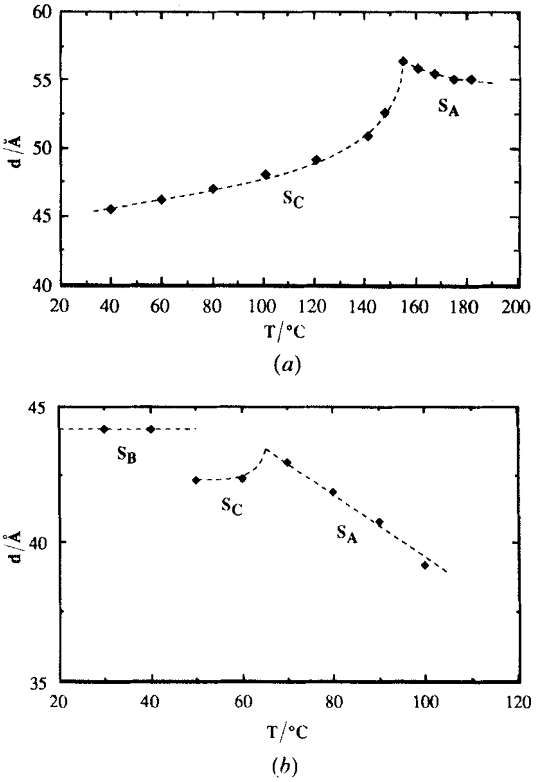


Figure 1. Variation of the thickness of the smectic layers versus temperature. (*a*) For **P6,H$_5$F$_3$** 100 per cent, (*b*) for **P6,H$_5$F$_3$** 30 per cent.

These modifications, as well as the heat peaks observed at low temperature on the DSC recordings, are attributed to 3D states. However, a clear connection between the results of both techniques regarding these ordered phases is difficult to see owing to different thermal treatments of the samples.

Table 1 summarizes the results of these observations for the polymers. The values of d (the layer spacing in the smectic A phase) and of the d/L ratios (where L represents the length of the side group measured using all-*trans*-stereomodels, including the Si–mesogen bond) complete this table. Note that all the polymers exhibit a smectic A phase when mesomorphic. This was highly desirable for the consistency of the structural study presented later.

Table 2 provides similar information regarding the polymorphism of the vinylic derivatives. The structural parameters have been omitted: suffice to say that the value of d/L (where L is the length of the mesogen) is equal to 0·90 in all the smectic A phases. Note that the latent heat at the smectic A–isotropic transition is roughly constant for these compounds, $\Delta H_{S_A-I} \approx 10\,\mathrm{J\,g^{-1}}$.

4. Discussion

In this part, we first highlight the features which differentiate the fluorinated and non-fluorinated polymers: we conduct a comparative analysis of the undiluted polymers, and then we examine the consequences of dilution in both systems. Finally

Table 1. Transition temperatures (°C) enthalpies (Jg^{-1}) at the clearing point and layer spacings *d*(Å) in the smectic A phase for all samples. S_B, smectic B; S_C, smectic C; S_A, smectic A; I, isotropic.

Polysiloxane	T_g or T_m	S_B		S_C		S_A		I	ΔH_{S_A-I}	*d*	*d*/*L*‡
P6,8 100%	48	●	77			●	154	●	8·5	33·2	0·96
P4,8 100%†	—	●	50			●	129	●	6·5	30·4	0·95
P6,H$_5$F$_3$ 100%	21			●	155	●	185	●	4·2	56·4	1·61
P6,H$_4$F$_4$ 100%	34			●	166	●	221	●	5·9	56·4	1·61
P4,H$_5$F$_3$ 100%	47			●	149	●	195	●	4·5	52·9	1·63
P4,H$_4$F$_4$ 100%	37			●	162	●	233	●	2·8	52·2	1·61
P6,F$_6$ 100%	115			●	150	●	203	●	3·2	47·4	1·50
P6,OCF$_3$ 100%	104					●	168	●	7·6	26·5	1·02
P4,OCF$_3$ 100%	80					●	139	●	6·4	22·5	0·96
P6,8 30%	0	●	44			●	105	●	10·3	46·0	1·33
P4,8 30%	−10	●	21			●	87	●	9·9	42·5	1·33
P6,H$_5$F$_3$ 30%	46	●	51	●	65	●	105	●	5·5	43·0	1·23
P6,H$_4$F$_4$ 30%	19	●	55			●	102	●	5·1	43·0	1·23
P4,H$_5$F$_3$ 30%	—	●	23	●	48	●	77	●	3·5	36·9	1·13
P4,H$_4$F$_4$ 30%	−2					●	66	●	2·0	46·2	1·42
P6,F$_6$ 30%	93			non mesomorphic					—	—	—
P6,OCF$_3$ 30%	72					●	78	●	1·0	35·0	1·35
P4,OCF$_3$ 30%	47					●	52	●	0·6	32·2	1·37

† From [23]. ‡ See text. —, undetermined.

Table 2. Transition temperatures (°C) and enthalpies at the clearing point (Jg^{-1}) for vinyl derivatives. C, crystal; S_B, smectic B; S_C, smectic C; S_A, smectic A; N, nematic; I, isotropic.

Compound	C		S_B		S_C		S_A		N		I	ΔH_{S_A-I}
V6,8	●	51·3			●	56·8	●	61·0	●	78·6	●	3·0†
V4,8	●	59·6					●	(57·3)	●	74·3	●	2·9†
V6,H$_5$F$_3$	●	59·4					●	106·6			●	9·7
V6,H$_4$F$_4$	●	81·6			●	(75·9)	●	109·7			●	9·7
V4,H$_5$F$_3$	●	66·5					●	108·4			●	10·4
V4,H$_4$F$_4$	●	88·12					●	116·6			●	10·1
V6,F$_6$	●	96·0									●	—
V6,OCF$_3$	●	49·3					●	58·8			●	10·4
V4,OCF$_3$	●	53·0	●	55·8							●	—

‡( ): monotropic transition, —, undetermined. † $\Delta H_{S_A-N}+\Delta H_{N-I}$.

we formulate a hypothesis in order to encompass these new results within a synthetic description of the layer structure of side chain liquid crystalline polysiloxanes.

To analyse the consequences of fluorination in homopolymers (*x* per cent = 100 per cent), we consider first the clearing temperatures (table 1).

(i) They are much higher for the fluorinated homopolymers than for the homologous vinylic mesogenic intermediates given in table 2. From this point of view, the fluorinated polymers do not behave differently from classical comb-like polymers—the hydrogenated **P*n*,8** polymers for instance.

(ii) They increase clearly with the fluorine content (filled symbols in figure 2). These variations are qualitatively and quantitatively similar to those observed for low molecular weight compounds (figure 3) and are explained by the stiffness of the fluorinated tail.

(iii) They increase with the spacer length for **P*n*OCF$_3$** 100 per cent, which is usually the case for comb-like polysiloxanes—**P*n*,8** 100 per cent for instance. However, the opposite is observed for **P*n*,H$_p$F$_q$** 100 per cent (figure 2).

More significant differences between fluorinated and non-fluorinated polymers arise from a comparison of the enthalpies at the clearing point and a comparison of the layer spacings. In this regard, the characteristic behaviour for non-fluorinated systems can be illustrated by previously published results for the series **P5,*m*** 100 per cent polymers [10] summarized in table 3. Typically, the structure of the smectic A phase of a **P*n*,*m*** 100 per cent polymer changes from $S_{A_d}(d/L>1)$ to $S_{A_1}(d/L\leqslant 1)$ with increasing *m*. This change takes place for $m \approx n$ and is connected to a crossover in the value of the enthalpy at the S_A–I transition (figure 4). As expected, the behaviour of **P4,8** 100 per cent and **P6,8** 100 per cent, for which $m>n$, is consistent with this description; that is, the smectic structure is $S_{A_1}(d/L<1)$ and ΔH_{S_A-I} is large (by analogy with the enthalpies for the **P5,*m*** polymers). In contrast, the values of d/L, clearly larger than 1, and the weaker ΔH_{S_A-I} values classify the smectic A phases of **P4,H$_p$F$_q$** 100 per cent or **P6,H$_p$F$_q$**

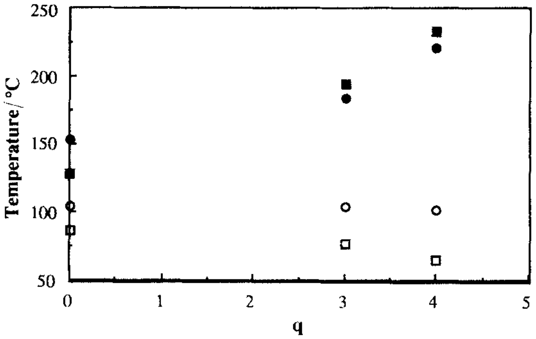


Figure 2. Clearing temperatures as a function of the number, *q*, of perfluorinated carbons in the tail. (●), **6,H$_p$F$_q$** 100 per cent; (■), **4,H$_p$F$_q$** 100 per cent; (○), **6,H$_p$F$_q$** 30 per cent; (□), **4,H$_p$F$_q$** 30 per cent.

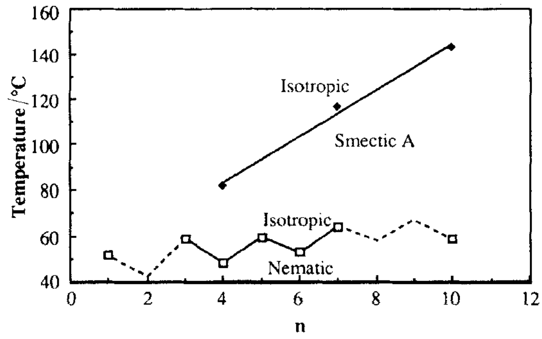


Figure 3. Comparison of clearing temperatures between fluorinated and hydrogenated compounds in the series R–Φ–COO–Φ–OC$_6$H$_{13}$. (□), $R=C_nH_{2n+1}$; (◆), $R=C_nF_{2n+1}$.

100 per cent as partially bimolecular S_{A_d}, despite the fact that $p+q=8>n$. Such a partially bimolecular structure has never been observed before with polysiloxanes substituted with mesogenic side groups in which the tail is longer than the spacer. Furthermore, this structure is not the natural arrangement of fluorinated molecular mesogenic groups for which the smectic A layers are monomolecular ($d/L \approx 0{\cdot}9$), whatever the nature of the fluorinated extremity—CF_3, OCF_3, $(CF_2)_{q-1}CF_3$, $(CH_2)_p(CF_2)_{q-1}CF_3$ [9]. One should remember, for example, that this is also the case for the homologous fluorinated vinyl precursors of our polymers which all show S_{A_1} phases and large clearing enthalpies.

To discuss the behaviour of the **P*n*,OCF$_3$** 100 per cent polymers, we stress a typical structural property of the smectic A phases of polymers characterized by $m \ll n$ (i.e. **P*n*,1** ≡ **P*n*,OCH$_3$** and **P*n*,CN** series [10], see also **P5,1** in table 3): these are generally partially bimolecular (S_{A_d}). The behaviour of the **P*n*,OCF$_3$** 100 per cent polymers appears therefore completely unusual because of their S_{A_1} structure ($d/L \approx 1$) and high values of ΔH_{S_A-I} compared to those of **P*n*,1** or **P*n*,CN**. To conclude this analysis, the consequence of fluorination in the homopolymers can be roughly summarized as a reversal of the structural behaviour of the smectic A phase as a function of tail length, and the usual monomolecular structure for $m(p+q) \gg n$ becomes partially bimolecular, and vice versa for $m=q=1<n$.

Let us now consider the consequences of both dilution and fluorination. As for the clearing temperatures, the fluorinated polymers do not depart from the rule that dilution destabilizes the smectic A phase in side chain polymers [15, 16] (table 1). A specific feature lies in the downward orientation of the curve representing the clearing temperature as a function of the fluorine content when $x=30$ per cent (open symbols in

Table 3. Thermal and structural data for polymers of the **P5,*m*** 100 per cent series [10].

Polymer	$\Delta H_{S_A-I}/J\,g^{-1}$	d/L	Structure
P5,1 100%	3·0	1·35	S_{A_d}
P5,2 100%	3·4	1·20	S_{A_d}
P5,3 100%	3·8	1·06	S_{A_d}
P5,4 100%	5·2	1·00	S_{A_1}
P5,6 100%	8·1	(0·93)†	S_{A_1}
P5,8 100%	11·9	0·91	S_{A_1}

† ( ) Interpolated value.

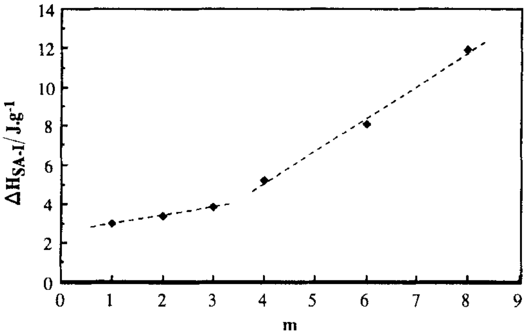


Figure 4. Enthalpies at the smectic A–isotropic transition as a function of tail length, *m*, in the **P5,*m*** 100 per cent series (from table 3).

figure 2). The opposite is observed in molecular mesogens for which an increased fluorine content of the flexible aliphatic chain always stabilizes the smectic A state [9] (see also figure 3). The most dramatic consequences for the polymers is that mesomorphic the properties of **P6,F6** 100 per cent have been eliminated in **P6,F$_6$** 30 per cent. This is the reason why this type of side group with a perfluorinated tail has been forsaken in our work in favour of partially fluorinated mesogenic groups. Another effect of the dilution in fluorinated polysiloxanes is observed in the values of the enthalpies at clearing (table 1): to an increase in ΔH_{S_A-I} with x for non-fluorinated polymers there corresponds a decrease for the fluorinated systems (another example of this behaviour can be found in the literature [15]).

It has been reported so far that dilution modifies the smectic A layers of comb-like polysiloxanes in such a way the the layer thickness increases with decreasing the proportion of mesogenic groups [14, 15]. This behaviour has been accounted for by Diele *et al.*, as the result of a simple swelling of a sublayer containing the polysiloxane backbone in a micro-segregated model [14]. According to this assumption, the uppermost swelling of the backbone sublayer which can be expected is $\Delta d_{\max} \approx 10$ Å for x varying from 100 per cent to 30 per cent. This limiting value corresponds to full extension of the non-mesogenic dimethylsiloxane sequences in a direction parallel to the director.

In table 4 we have reported for our systems the difference between the layer spacings of the diluted polymers and those of the homologous homopolymers ($\Delta d = d_{30\,\text{per cent}} - d_{100\,\text{per cent}}$) in order to make a comparison with $\Delta d_{\max}$. The agreement with our reference compounds, the **P*n*,8** polymers, causes no problem. The values of Δd larger than 10 Å, as generally observed when $m > n$, can be explained by the unfolding of the flexible extremities of the mesogenic groups which are less constrained at $x = 30$ per cent than in a close packed S_{A_1} structure at $x = 100$ per cent. The slight increase in the enthalpies of clarification in the diluted **P*n*,8** polymers is noteworthy: a weak coupling with the orientational order parameter could be connected to the stretching of the non-mesogenic segments of the backbone resulting from maximum swelling of the sublayer. This is suggested by the high values of the enthalpies at the isotropic–nematic transition for some dimers and for linear semi-flexible liquid crystalline polymers which are clearly related to a strong conformational order of their flexible spacers [17, 18]. Applying this hypothesis of microsegregation leads one to consider that the monomolecular structure of the mesogenic sublayer in **P*n*,OCF$_3$** 100 per cent polymers is also retained in the diluted systems: Δd is just less than the maximum value. One can also observe in this case that ΔH_{S_A-I} decreases markedly at $x = 30$ per cent. In contrast, the unexpected decrease in the layer spacing ($\Delta d < 0$) observed with the **P*n*,H$_p$F$_q$**

Table 4. Differences between the smectic A layer spacings of diluted polymers ($x = 30$ per cent) and homologous homopolymers ($x = 100$ per cent).

	$\Delta d = (d_{30\,\text{per cent}} - d_{100\,\text{per cent}})/\text{Å}$	
	$n = 6$	$n = 4$
P*n*,H$_5$F$_3$	−13·4	−16·0
P*n*,H$_4^5$F$_4$	−13·4	−6·0
P*n*,OCF$_3$	+8·5	+9·7
P*n*,8	+12·8	+12·1

polymers implies a modification of the smectic structure from $x = 100$ per cent to $x = 30$ per cent in order to preserve the concept of micro-segregation: the partially bimolecular structure of the mesogens in **P*n*,H$_p$F$_q$** 100 per cent has to shift towards a S_{A_1} arrangement in **P*n*,H$_p$F$_q$** 30 per cent. To support this hypothesis one has to remember that the stable structure of fluorinated molecular systems and of the vinyl compounds is S_{A_1}. For example, a monomolecular structure of the mesogenic sublayer can reasonably be imagined for the **P6,H$_p$F$_q$** 30 per cent polymers: it would correspond to a thickness of the backbone sublayer equal to 8 Å which is less than the maximum swelling, but quantitatively satisfactory. The same assumption applied to the **P4,H$_p$F$_q$** 30 per cent polymers with less flexible spacers leads one to consider either a much smaller extension of the backbone sublayer in the direction perpendicular to the smectic layers (for instance the gain would be approximately 4·5 Å, compared to $\Delta d_{max} \approx 10$ Å, for **P4,H$_5$F$_3$** 30 per cent if the mesogenic sublayer were monomolecular) or to suppose an incomplete evolution to a S_{A_1} organization of the mesogenic groups (which would apply especially to **P4,H$_4$F$_4$** 30 per cent). One can note that the enthalpies at the clearing point, which were considered as weak in the $x = 100$ per cent systems, are little modified by the dilution in the **P*n*,H$_p$F$_q$** polymers.

Finally we think that these peculiar properties of fluorinated polymers which we have pointed out can still be interpreted using a micro-segregated structure model, valid for all kinds of polysiloxanes, involving a control by steric repulsions and/or amphipatic interactions of the interpenetration of the side groups in the mesogenic sublayer. In this regard, the **P*n*,8** 100 per cent polymers can be regarded as model compounds. In the smectic A phase the confinement of the backbone is evidenced by a second order of reflection [11]; the interpenetration is obviously total in the mesogenic sublayer and accords with a favourable overlapping of the aromatic cores (the layer spacing is slightly less than the length of the side group, $m \geqslant n$). Then, the exchange of 3 or 4 methylenic groups for a perfluorinated sequence in the tail of the **P*n*,8** polymers is definitely responsible not only for a strong increase in the steric hindrance, together with a decrease in the flexibility, but also for a worsening of the interactions between fluorocarbon tails and hydrocarbon spacers. As a result, one can expect the interpenetration to be more difficult: the observed partially bilayer structure is therefore no surprise, considering either that there is insufficient space to pack the spacers and the tails in a smectic A_1 structure or that the unfavourable interactions repel them apart. To support this interpretation, one can also refer to the polymorphism in table 1 which shows that a smectic C phase is systematically observed in the **P*n*,H$_p$F$_q$** 100 per cent polymers. One knows that the molecular tilt increases the available molecular area per mesogen in the layers and can be the sign of a possible relief of steric hindrance. A similar analysis holds for the **P6,F$_6$** 100 per cent polymer.

As for the **P*n*,OCF$_3$** per cent polymers, the smectic C phase is no longer observed. In addition, their S_{A_1} structures indicate an easier interpenetration and show micro-segregation through a second order of reflection, like the **P*n*,8** 100 per cent polymers. These observations agree with the fact that an OCF$_3$ group is less bulky than the H$_p$F$_q$ sequence. However, one must note that the overlapping of the aromatic cores is surely not at its best in this case. Even though an OCF$_3$ group is not much larger than an OCH$_3$ group, the difference can suffice to favour the interpenetration, at the expense of an optimal overlapping of the aromatic cores (the difference in the values of the dipoles of the two groups might also be relevant to this behaviour). Therefore, the structure, either S_{A_1} or S_{A_d} in the **P*n*,OCX$_3$** 100 per cent polymers (X = F or H), would result from a subtle balance between steric constraints and amphiphilic interactions.

Finally, one can expect an easier interpenetration from dilution in all cases. When S_{A_1} at $x = 100$ per cent, the structure has no reason to be modified at $x = 30$ per cent, and this expectation seems satisfactorily confirmed with the **P*n*,8** and **P*n*,OCF$_3$** polymers. On the other hand, a partially bimolecular pairing accounting for steric hindrance at $x = 100$ per cent is likely to prefer a S_{A_1} arrangement of the mesogenic sublayer at $x = 30$ per cent: one can argue in this way for the **P*n*,H$_p$F$_q$** polymers. The differences in the swellings of the backbone sublayer which appear if one applies the hypothesis of well-segregated sublayers at $x = 30$ per cent can be assigned to better close packing of neighbouring side groups in the mesogenic sublayer, related to better core–core interaction in the **P*n*,8** 30 per cent polymers than in **P*n*,OCF$_3$** 30 per cent or **P*n*,H$_p$F$_q$** 30 per cent polymers, the latter requiring obviously a larger lateral extension. From this point of view, the dimethylsiloxane sublayer at $x = 30$ per cent would simply play the role of an isotropic intermediate lamellum, the layer thickness of which adapts to the required area per mesogenic unit in the upper and lower anisotropic sublayers. This conclusion agrees with recent observations made on liquid crystalline 'linear' twins with dimethylsiloxane spacers [19]: lengthening the spacer has the same consequences on the layer thickness in the smectic A phase of these dimers as a decrease in x in the polysiloxanes.

5. Conclusions

This study of a series of polysiloxanes with fluorinated mesogenic groups has mainly given evidence for clear-cut differences in the structure of the smectic A phase compared to that of the classical non-fluorinated homologues. Peculiarly, it is found that the classical change from a partially bimolecular structure to one that is monomolecular, which occurs when the length of the tail exceeds the length of the spacer, appears oddly to be reversed by fluorination. However, instead of being confusing, these differences allow us to propose a common S_A arrangement for comb-like polysiloxanes. This schematic organization requires us to assume the confinement of the siloxane backbone in all cases. In its sublayer, the backbone accommodates itself in such a way as to optimize the interpenetration of the mesogenic groups linked to chains from contiguous layers (especially when the proportion of mesogenic groups is reduced). This interpenetration appears essential in order to stabilize the layers through a kind of weak physical cross-linking (involving aromatic core–aromatic core or dipole–dipole interactions): the fact that no purely bilayer structure, S_{A_2}, has been obtained so far with side chain polysiloxanes supports this idea.

Finally, one can also remark that no microphase separation based on the incompatibility of the aliphatic parts and the fluorinated segments—which could have been anticipated by analogy with diblock molecules made of hydrocarbon moieties—has been observed either in diluted systems or in undiluted systems [20, 21]. In a forthcoming paper we will address further these problems of compatibility in a large study involving the polymers described in this work and molecular mesogens in the smectic A state [22].

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