X-ray diffraction study of 'side-on fixed' homopolysiloxanes from nematic to smectic C phases

M. F. Achard[a]; S. Lecommandoux[a]; F. Hardouin[a]

[a] Centre de Recherche Paul Pascal, Université Bordeaux I, Pessac, France

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by M. F. ACHARD, S. LECOMMANDOUX and F. HARDOUIN*

Centre de Recherche Paul Pascal, Université Bordeaux I, 33600 Pessac, France

The X-ray patterns for the nematic phase in a series of side-on fixed polysiloxanes show different kinds of diffuse elements which imply complex short range ordering. A systematic structural study of the evolution of the patterns versus two molecular parameters, namely the spacer length and the length of the terminal aliphatic tails, suggests the possible occurrence of a smectic C phase for certain values of these parameters. Taking into account these tendencies, new synthesis led to a nematic–smectic C polymorphism observed for the first time in side-on fixed polysiloxanes.

1. Introduction

In side-on fixed polymers, the mesogenic groups are attached laterally to the polymer main chain through a flexible spacer. Unlike their terminal analogues, these lateral polymers have been found so far to be mainly nematic and changes in the polymer backbone type, in the spacer length or in the terminal aliphatic tails have not modified this tendency [1–7]. Only strong modifications of the mesogenic core architecture have led to a smectic A phase [8, 9]. Further, on the basis of conoscopic observations on oriented samples, the existence of a biaxial nematic phase has been claimed for polymethacrylates with long spacers [10].

Another striking feature concerns small angle neutron scattering experiments (SANS) [11–14] which gave evidence for a jacketed structure on the scale of the chain dimension in the nematic phase of side-on polymers. The backbone is strongly stretched in the average direction imposed by its mesogenic groups which form a jacket around it. Moreover, the influence of the spacer length on this nematic jacketed structure has been recently examined by SANS: the anisotropy of the backbone conformation is clearly reduced when the spacer length increases, implying a smaller jacketed effect [13], and vanishes for long spacers [14]. Moreover recent SANS experiments show that an increase in the length of the tails reduces the jacketed effect to a lesser extent [14]. Simultaneously, X-ray diffraction analysis [7, 15] on single domains reveals a rich local order in the nematic phase which suggests inter- and intra-chain correlations between the mesogenic groups.

We report here on a systematic structural study of a series of 'side-on fixed' homopolysiloxanes:
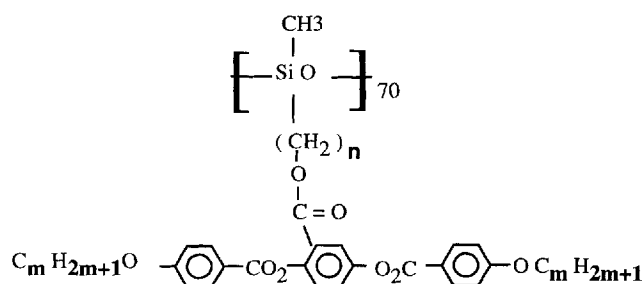
and we describe the influence of two molecular parameters on the structural behaviour of these polymers, namely the length n of the spacer ($n = 4, 6, 10, 11$) and the lengths of the aliphatic tails m ($m = 1$ to 12).

The mesomorphic properties were first characterized by the usual methods (DSC and optical microscopy) and as shown in table 1, all of these homopolymers are nematic.

Orientation of the samples was achieved by cooling from the isotropic state to room temperature in a 4·2 T magnetic field. X-ray scattering experiments were performed using CuK_α radiation from an 18 kW rotating anode X-ray generator. A flat pyrolitic graphite (0 0 2) monochromator delivered a 0·5 × 0·5 mm² beam on to the sample. The scattered radiation was collected on a two-dimensional imaging plate system. The instrumental resolution in reciprocal space was $\Delta q = 2·5$ mm² Å⁻¹ FWHM in both vertical and horizontal directions. The sample-to-detector distance was 186 mm. The X-ray patterns of the magnetically oriented polymers were recorded at room temperature in their nematic or glassy states. Because of the alignment procedure, the samples

* Author for correspondence.

Table 1. Phase behaviour of the $P_{n,m,m}$ polysiloxane series.

n	m	g		N		I
4†	1	●	53	●	154	●
4†	2	●	36	●	158	●
4†	3	●	48	●	130	●
4†	4	●	36	●	120	●
4†	6	●	18	●	99	●
4†	8	●	24	●	93	●
4†	12	●	27	●	87	●
6	4	●	28	●	113	●
10†	3	●	10	●	93	●
10	4	●	17	●	98	●
11	4	●	16	●	94	●

† From reference [15].

n: Spacer length; m: aliphatic tail length; g: glassy state; N: nematic; I: isotropic liquid.

have a uniaxial symmetry around the magnetic field direction (i.e. the meridian).

2. Results

2.1. *General*

The observed diffraction patterns show several common features: first, the lack of any Bragg reflection and the anisotropy of the patterns attest that all the samples are in orientated nematic or glassy nematic states and second, the presence of the usual wide angle diffuse rings located on the equator confirms that the mesogenic cores are oriented along the magnetic field direction. Besides these common features, a part of the diffracted X-rays is localized on diffuse lines and diffuse spots. Such scattered intensity is related to local fluctuations away from the mean anisotropic liquid-like order, and reveals different kinds of short range order.

Referring to the pattern for $P_{4,4,4}$ previously described [7], several diffuse elements can be seen, in addition to the usual wide angle diffuse ring (a) of figure 1: (i) on the
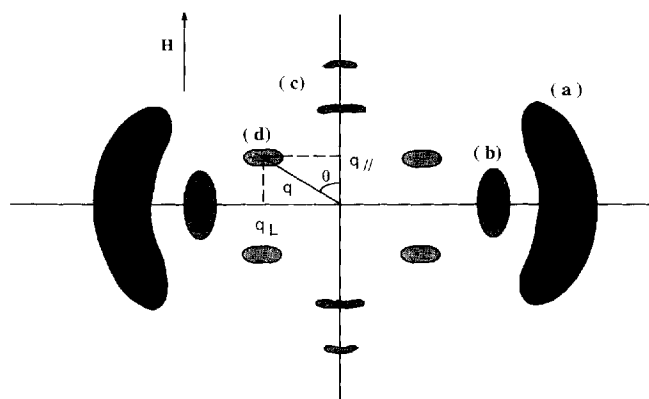
equator, there are diffuse spots (b) at a wavevector $q_\perp = 2\pi/7\,\text{Å}^{-1}$ (q is the moment transfer vector, $q = 2\pi/d$). Such diffuse spots are more readily observed if the polymer repeat unit has a silicon atom. This diffuse scattering can be interpreted as the liquid-like arrangement of siloxane moieties. Its location on the equator suggests that the siloxane backbones, at least on a local scale, lie parallel to the director. (ii) Along the meridian, and perpendicular to it, there is a set of equidistant diffuse lines (c) with a well-defined periodicity along the director. They correspond to the intersection with the Ewald sphere of a set of parallel and equally spaced reciprocal planes. They are due to uncorrelated periodic columns of mesogenic groups. Their period in direct space is 28 Å. Their width and their lateral extension are, respectively, proportional to the inverse of the length (140 Å) and to the diameter of each column ($< 10\,\text{Å}$). (iii) Four diffuse spots (d) are located at small angles off the meridian. Their maxima correspond to a wavevector $q = 0.41\,\text{Å}^{-1}$ and to a tilt angle $\theta = 55°$. The projections of q along the director and along the meridian are respectively $q_\| = 0.235\,\text{Å}^{-1}$ and $q_\perp = 0.335\,\text{Å}^{-1}$.

We now aim towards an understanding of the evolution of these different diffuse elements when the aliphatic tail length m or the spacer length n is systematically varied.

2.2. *Effect of* m *and* n *on the diffuse peaks* (a)

All the polymers $P_{n,m,m}$ exhibit the wide angle diffuse peaks (a) on the equator. They are associated with the disordered lateral arrangement of the mesogenic groups oriented along the direction of the external field. They correspond to a distance of about 4.45 Å. This average lateral distance is not altered by elongation of the aliphatic tails with a constant spacer. On the contrary, this distance increases significantly from $n = 10$ (4.45 Å) to $n = 11$ (4.75 Å), suggesting a modification of the liquid-like association of the mesogenic groups for a very long spacer.

2.3. *Effect of* m *and* n *on the diffuse peaks* (b)

The diffuse spots (b) are only observed for polymers with short spacers ($n = 4$ and 6) and with short aliphatic tails ($m = 1$, 2, 3, 4). Their absence for long spacers ($n = 10$ and 11) and long tails ($m = 8$, 10, 12) suggests that the interference from siloxane backbones is suppressed, not only by the increased steric hindrance due to the lengthening of the lateral flexible parts of the mesogenic groups, but also by the strong decoupling of the backbone and mesogenic side groups [16]. Indeed this decoupling leads to lower anisotropic orientational interactions between siloxane backbones, and this can explain the weakness of the jacketed structure observed by SANS on a larger scale on increasing the spacer or the tails' lengths

Figure 1. Schematic representation of the X-ray pattern of the oriented nematic phase for side-on fixed polysiloxanes.

Table 2. Influence of m and n on parameters connected with the diffuse lines (c).

n	m	$d = 2\pi/q_{\parallel}/\text{Å}$	$L_{ext}/\text{Å}$	$\xi_{\parallel}/\text{Å}$
4	1	21·6	24	220
4	2	24·8	27	170
4	3	26	29·5	160
4	4	28	33	140
6	4	27	33	100
4	6	invisible	—	—
4	8	invisible	—	—
4	12	invisible	—	—
10	4	invisible	—	—
11	4	invisible	—	—

[13, 14]. Thus, the analysis of these diffuse spots underlines the predominant role of the flexible parts on the chain anisotropy.

2.4. *Effect of* m *and* n *on the diffuse lines* (c)

This third kind of diffuse element consists in a set of equidistant diffuse streaks (c). One can recall that many X-ray diffraction patterns of side-end fixed LCP exhibit such streaks perpendicular to the director with a periodicity usually equal to the side chain length [17]. In the present case, for side-on fixed LCP, the observed periodicity $d = 2\pi/q_{\parallel}$ is also close to the mesogen size L_{ext} in its extended conformation (SASM model) (see table 2). As usually observed this type of diffuse line appears only at the level $l \geqslant 2$ of the reciprocal plane. These lines mean that the mesogenic groups tend to align themselves in rows or strings over a short range. The correlation length $\xi_{\parallel}$ of this local order may be estimated from the width of the diffuse streaks along the director and one can note in table 2 that $\xi_{\parallel}$ is somewhat larger for the shortest terminal chains.

As mentioned in table 2, the diffuse lines (c) are only observed for short aliphatic tails $(m = 1$ to $4)$ and for short spacers $(n = 4, 6)$, and the associated order is connected to the flexibility of the system: increase of the aliphatic tail length or of the spacer length leads to disappearance of the diffuse lines and, as a result, of the periodic strings of mesogenic groups. Note that the side groups which tend to align themselves in strings over a short range do not necessarily originate from the same polymer molecule, even if their correlation length $\xi_{\parallel}$ is the same order of magnitude as $R_{\parallel}$ the quadratic size of the chain in the direction of the external field [11]. Actually, these strings are favoured by the jacketed structure, but they do not give direct evidence of polymer chain extension, since they are frequently observed for the oblate smectic phase of side-end fixed polymers [17], as well as for the nematic or smectic phases of low molar mass mesogens [18].

2.5. *Effect of* m *and* n *of the diffuse spots* (d)

The four diffuse spots (d), located at small angles off the meridian, have been previously interpreted as strong S_C fluctuations [7, 15]. Nevertheless no S_C phase has been observed up to now in homologues of series of side-on fixed polymers, and such behaviour is quite unusual when large cybotactic groups exist in the nematic phase. In addition, the diffuse spots (d) are elongated in the direction parallel to the equator and, in this sense, differ from S_C off-axis spots which are located on an inner ring on the pattern.

For the polymers under study, the characteristics of the spots (d), namely the wavevector q and tilt angle θ, are summarized in tables 3, 4 and 5. In addition, the distances $a_{\parallel}$ and $a_{\perp}$ corresponding in real space to $q_{\parallel}$ and $q_{\perp}$ and the length of the mesogenic group in its extended conformation L_{ext} are also reported. Tables 3 and 4 correspond to the evolution of these parameters as a function of the aliphatic tail length at constant spacer, and table 5 as a function of the spacer length at constant tail length. These

Table 3. Evolution of the parameters connected with the diffuse spots (d), at constant short spacer $n = 4$, versus the aliphatic tail length m.

n	m	q	θ	$a_{\parallel}/\text{Å}$	$a_{\perp}/\text{Å}$	$L_{ext}/\text{Å}$
4	1†	—	—	—	—	—
4	2	0·45	54·5	24	17	27
4	3	0·43	56	26	18	29·5
4	4	0·41	55	26·5	18·5	33
4	6	0·33	54	32·5	23·5	38
4	8	0·28	53	37	28	44
4	12	0·18	41	46	53	55

† No diffuse spot (d).

Table 4. Evolution of the parameters connected with the diffuse spots (d), at constant long spacer $n = 10$, versus the aliphatic tail length m.

n	m	q	θ	$a_{\parallel}/\text{Å}$	$a_{\perp}/\text{Å}$	$L_{ext}/\text{Å}$
10	3	0·49	55	22	15·5	29·5
10	4	0·42	55	26	18	33

Table 5. Evolution of the parameters connected with the diffuse spots (d), at constant aliphatic tail length $m = 4$, versus the spacer length n.

n	m	q	θ	$a_{\parallel}/\text{Å}$	$a_{\perp}/\text{Å}$	$L_{ext}/\text{Å}$
4	4	0·41	55	26·5	18·5	33
6	4	0·41	54	26	19	33
10	4	0·42	55	26	18	33
11	4	0·39	52	26	20·5	33

data deserve several comments: (*i*) as is apparent from the X-ray patterns of figures 2, 3 and 4, the off-axis diffuse spots (*d*) are essentially connected with the aliphatic tails *m*: they do not exist for $m = 1$ ($P_{4,1,1}$), appear weakly for $m = 2$ ($P_{4,2,2}$), and then their intensity grows regularly with increasing *m* from $m = 3$ ($P_{4,3,3}$) to $m = 12$ ($P_{4,12,12}$). Moreover their position is clearly influenced by this molecular parameter *m*, since they shift to lower *q* with lengthening aliphatic tails (see table 3).

For a long spacer, the diffuse spots (*d*) always appear connected with local correlations of the terminal aliphatic tails (see table 4).

On the other hand, their existence and position remain nearly unchanged when the spacer length is varied
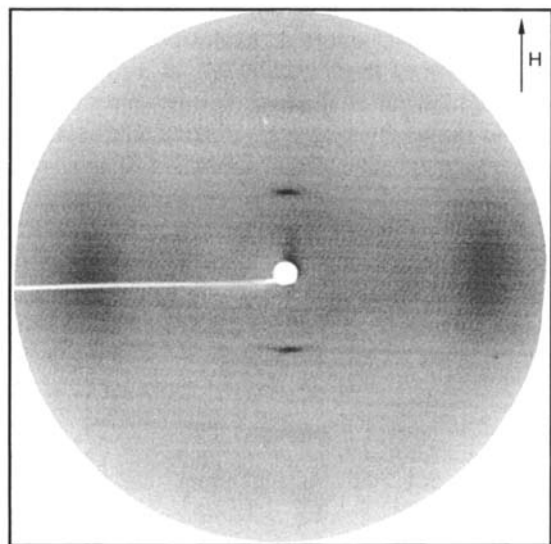

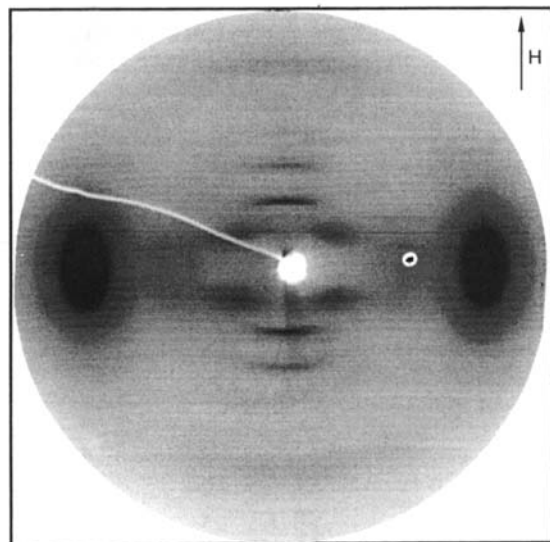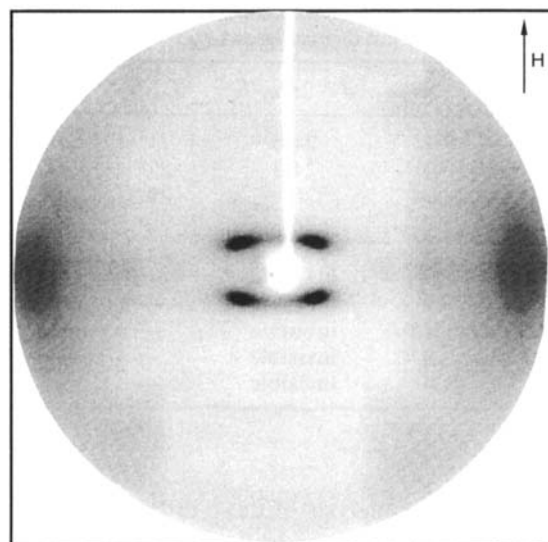Figure 4. X-ray pattern for $P_{4,8,8}$.

(with constant tail $m = 4$) (see table 5), at least from $n = 4$ to 11.

Thus we can claim that the diffuse spots (*d*) relate to local correlations of the aliphatic tails, which are tilted with respect to the magnetic field, the mesogenic cores remaining, on average, oriented along this direction. Such correlations are not spacer length dependent (see table 5). A hypothetical way to explain the origin of these diffuse spots is to imagine the existence of 'tilted blocks' constituted of mesogenic units in which the aliphatic tails are correlated and tilted with respect to the mesogenic cores (see figure 5). The corresponding correlation lengths of neighbouring 'tilted blocks' remain limited ($40\,\text{Å} < \xi_{\parallel} < 125\,\text{Å}$ and $30\,\text{Å} < \xi_{\perp} < 60\,\text{Å}$, but increasing with *m*).

Concerning the period of one elementary block, the projection along the director, $a_{\parallel}$, regularly increases with *m* and remains smaller than the mesogen length L_{extended} (see tables 3 and 4), which is in agreement with the idea of tilted tails. In our schematic description the experimental tilt angle Θ nearly corresponds to the average angle of the terminal aliphatic tails and a simple geometrical argument leads to the relationship $a_{\parallel\text{calc.}} = l_0 + 2l_1 \cos\Theta$, where l_0 is the length of the aromatic rigid core and l_1 the length of one aliphatic tail measured by an SASM model in its most extended conformation. Table 6 shows a rather good agreement between the experimental and calculated values of $a_{\parallel}$.

In addition, the $a_{\perp}$ values correspond to the lateral period of the blocks which does not exceed a few associated mesogenic units (see tables 3, 4 and 5), and correlatively $a_{\perp}$ also increases with the length of the aliphatic external parts.

One should note that there is no discrepancy between

Figure 2. X-ray pattern for $P_{4,1,1}$.

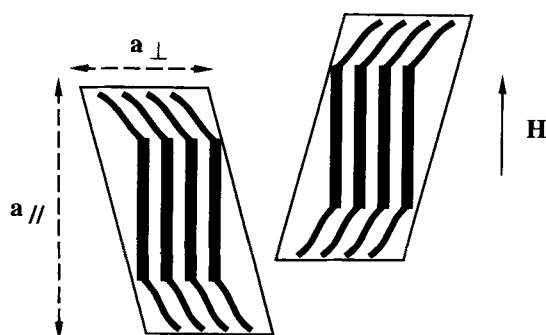Figure 3. X-ray pattern for $P_{4,3,3}$.

Figure 5. Schematic representation of 'tilted blocks' constituted of mesogenic groups in which the aliphatic tails are correlated and tilted with respect to the mesogenic cores.

Table 6. Comparison of the length $a_{||}$ corresponding in real space to the projection of the wavevector q along the director for the (d) spots and the calculated value $a_{||calc.}$ from the schematic representation of tilted tails.

n	m	$a_{||calc}/\text{Å}$	$a_{||}/\text{Å}$
4	2	24	24
4	3	26	26
4	4	27·5	26·5
4	6	30·5	32·4
4	8	33·5	37
4	12	46·5	46

this schematic representation of 'tilted blocks' and the position of the diffuse spots (a) centred on the equator, since these spots indicate that the mesogenic groups are on average aligned along the magnetic field direction, while the tilt of the flexible extremities with respect to the cores appears correlated only over a very short range. Thus the diffuse spots (d) are the signature of a specific arrangement of associated mesogenic units directly connected with local correlations between the terminal chains of the mesogens. Up to now, such an unusual local order is only observed with non-cylindrically shaped molecules possessing a lateral aliphatic chain branched to the rigid core.

2.6. Additional diffuse elements for long spacers

Additional X-ray information on the patterns of the polymers with long spacer $n = 10$ and 11 corroborate this interpretation (see figure 6). Indeed on these patterns (for example, for $P_{10,4,4}$ on figure 7) four additional diffuse spots (e) are seen at small angle. They are off the meridian axis, clearly located on an inner ring and characterized by a wavevector q' and a tilt angle Θ'. As suggested and subsequently proved (see §2.), they are identified in this case with so-called smectic C cybotactic groups, manifesting themselves in mass density fluctuations which correspond to translational and orientational correlations of the

mesogenic groups forming layers tilted with regard to the field. These additional diffuse spots (e) coexist with the diffuse spots (d) previously described, but they are located at lower wavevector and lower tilt angle than the spots (d). One can first remark that, unlike the (d) spots, the position of the (e) spots is not influenced by the length of the aliphatic tails $(m$ parameter). On the other hand, an increase of the spacer length leads to a clear shift to lower
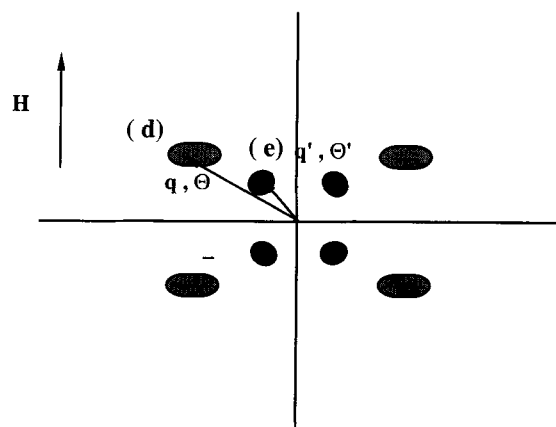

Figure 6. Schematic representation of the X-ray pattern of the oriented nematic phase for side-on fixed polysiloxanes with long spacers.
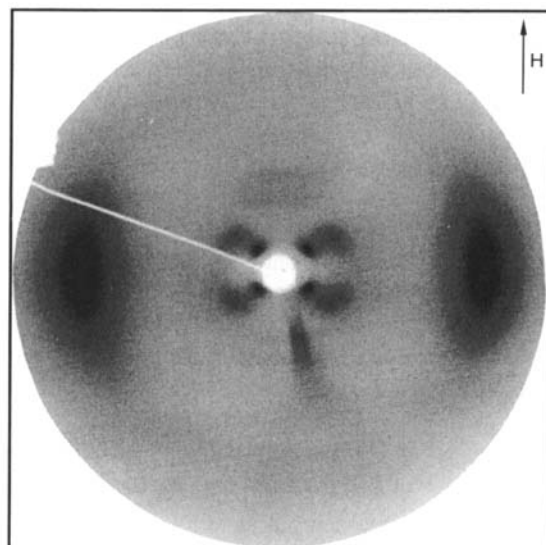

Figure 7. X-ray pattern for $P_{10,4,4}$.

Table 7. Additional diffuse spots (e) observed for long spacers.

n	m	q'	θ'	$d'_{||}/\text{Å}$	$d'_{\perp}/\text{Å}$	$a_{||}/\text{Å}$
10	3	0·23	52	44	34·5	26
10	4	0·24	51·5	42	33·5	26·5
11	4	0·206	44	44·5	43	26

wavevector and lower tilt angle (see table 7). The projection of the q' vector on the direction of the magnetic field leads to the distance $d'_\|$. This parameter is larger than the length $a_\|$ determined from the spots (d) and involves associated mesogenic groups with partial overlapping cores in this S_C pre-ordering. As shown in table 7, $d'_\|$ does not change with the spacer length, whereas Θ (and $d'_\perp$) strongly varies with n.

Moreover, the intensity of these additional diffuse spots (e) clearly grows from $P_{10,3,3}$ to $P_{10,4,4}$ and this observation suggests the possible occurrence of a smectic C phase in such side-on fixed polysiloxanes for longer aliphatic tails and, of course, with a long spacer ($n = 10$ or 11).

2.7. *The onset of smectic C phases*

The preceding structural results therefore encouraged us to synthesize new homopolymers with $n = 10$ and longer tails ($m = 6$–12): $P_{10,6,6}$, $P_{10,8,8}$, $P_{10,10,10}$, and $P_{10,12,12}$. In this way, we have obtained a very satisfying result, since a nematic–smectic C sequence is definitely found (by means of the classical methods of characterization) for the first time in side-on fixed polysiloxanes (see table 8).

One should note that the N–S_C temperature increases with the length of the aliphatic parts; this thermal behaviour is usually observed for classical LMW mesogens without a lateral chain.

The oriented X-ray patterns confirm the existence of a S_C phase at room temperature for these new homopolymers: the spots (e) are now condensed into four Bragg peaks located off the meridian axis on an inner ring (see figure 8). The second order reflection is detected too. Moreover, the diffuse spots (d) associated with local correlations between tilted aliphatic tails coexist with the Bragg spots (e) in the S_C patterns for $P_{10,6,6}$, $P_{10,8,8}$ and $P_{10,10,10}$. The structural parameters of the spots (e) (see table 9) noticeably differ from those observed for the spots (d). This remark confirms the different origins of these two kinds of element. Nevertheless, referring to the $P_{10,10,10}$ and $P_{10,12,12}$ behaviours which indicate that the diffuse spots (d) tend to collapse into the second reflection order of the Bragg spots (e), the question of a

Table 8 Phase behaviour of the $P_{10,m,m}$ polysiloxanes versus the aliphatic tail length m.

n	m		g		S_C		N		I
10	6	●	15	●	34	●	96	●	
10	8	●	13	●	54	●	93	●	
10	10	●	10	●	62	●	88	●	
10	12	●	8	●	63	●	81	●	

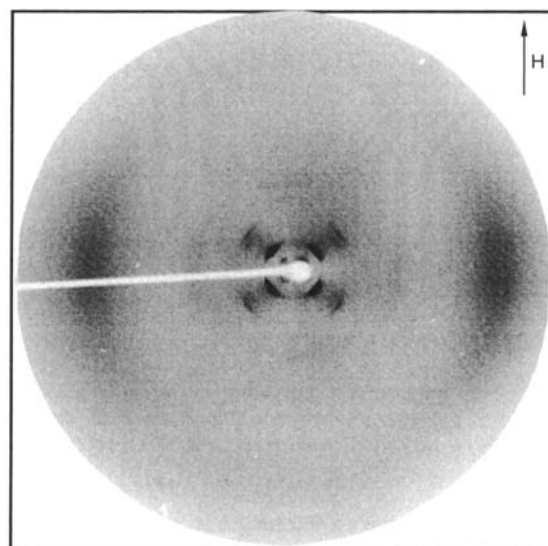G: glassy state; S_C: smectic C; N: nematic; I: isotropic liquid.

Figure 8. X-ray pattern for $P_{10,10,10}$.

Table 9. Structural parameters of the smectic C phases obtained for long spacer and long aliphatic tails.

n	m	q'	θ'	$d'_\|/\text{Å}$	$a_\|/\text{Å}$
10	6	0·24	53	43·5	29
10	8	0·22	51·5	45·8	32
10	10	0·21	50·5	47	—
10	12	0·20	39	40·5	—

possible lock-in between two kinds of positional correlation is raised.

3. Conclusions

A systematic and accurate structural study of the local order in the nematic phases of a series of side-on fixed homopolysiloxanes was carried out. The following main points have been clearly demonstrated: (i) on oriented patterns, the four symmetrical diffuse spots, labelled (d) in this study, originate from local correlations of the aliphatic parts of the mesogenic units instead of from S_C cybotactic groups as previously interpreted for laterally attached polymers [7, 15], as well as for low molar mass liquid crystals with a lateral aliphatic chain [19, 20]. In this sense, these spots appear characteristic of a laterally branched architecture. (ii) The occurrence of additional diffuse spots, labelled (e), which unambiguously correspond to cybotactic S_C groups, corroborate this hypothesis. (iii) As expected by the evolution of the intensity of the spots (e), some modifications of the molecular parameters, essentially the lengthening of the aliphatic tails, in addition to the presence of a long spacer, lead to the occurrence of a smectic C phase, revealed for the first time in side-on fixed polymers. (iv) Despite the fact that similar molecular

conditions have already been satisfied for side-on fixed polyacrylates [5], no smectic mesomorphism has been observed in this latter case. The only difference between these polyacrylates and the polysiloxanes under study lies in the fixation of the spacer onto the mesogenic core through a carboxylate group for the polysiloxanes. Probably the presence of this COO group in terms of conformation and polarity promotes a smectogenic arrangement. A similar difference is found with the parent laterally branched mesogens [21]. (v) Finally, one should remark that only the anisotropic (*b*) spots could give some structural information connected to the anisotropy of the backbone conformation; locally the jacketed effect weakens with the lengthening of the spacer, but also with lengthening of the aliphatic tails, as already proved by SANS on the scale of the polymer chain [13, 14].

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