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Coexistence of two different side chain packing structures in a smectic phase of liquid-crystalline side chain polymers

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Ten varieties of liquid-crystalline side chain polymers, poly(cholesteryl- ω -(methacryloyloxy)alkanoates) (pChMO- n , $n=1, 2, 3, 4, 5, 7, 9, 10, 11$ and 15 ; the carbon number of the alkyl chain), were studied by differential scanning calorimetry and small angle X-ray scattering. On and after the first cooling run from the isotropic state, these polymethacrylates gave the same smectic phase. X-ray investigations showed that pChMO- n with short spacers ($n=1-7$) has a two layer (bilayer) S_A packing structure, and pChMO- n with a longer spacer ($n=15$) has a single layer (monolayer) S_A packing structure. However, these two types of packing structure appear simultaneously in pChMO- n ($n=9-11$) below their phase transition temperature. To clarify the manner of the coexistence of the two different structures the smectic layer spacing and X-ray diffraction patterns were examined by small angle X-ray scattering at various temperatures.

1. Introduction

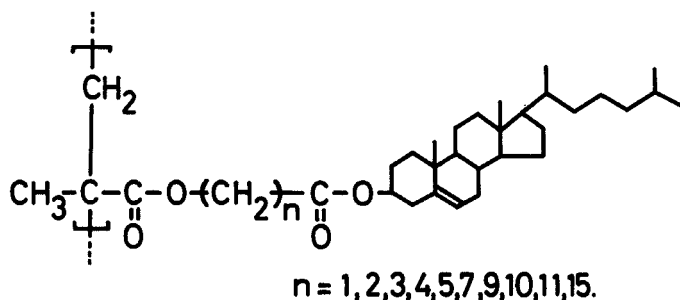
It is now widely accepted that flexible spacers of liquid-crystalline side chain polymers play an important role in the formation of liquid-crystalline phases by mesogenic groups. Many reports [1] have shown that nematic, cholesteric, and smectic phases can be observed in liquid-crystalline side chain polymers depending on the nature of the flexible spacer. In our previous work [2] on liquid-crystalline side chain polymers, we found that increasing the length of the flexible spacer enables the mesogenic groups to orient themselves more easily in the same liquid-crystalline state. In the smectic phase formed by liquid-crystalline side chain polymers, two different packing structures of the side chains due to a difference in the spacer length have been reported; polymers having shorter spacers have a two layer (bilayer) packing structure [2–7], whereas polymers having longer spacers have a single layer (monolayer) packing structure [2–4, 6–9]. The latter have been accounted for by an overlapping structure in which side mesogenic groups of one polymer are surrounded by long methylene spacers of neighbouring polymers. The single layer packing structure is stabilized by an increment in the length of the flexible spacer [2] or by the interaction of the strong constant dipoles in the mesogenic groups such as cyanobiphenyl groups [8]. The two kinds of packing structure for the smectic A phase have been designated S_{A_2} for the two layer packing structure, and S_{A_1} for the single layer packing structure [4]. In both phases, for liquid-crystalline side chain polymers, the side chains are organized into lamellae, and one macromolecule forms a flat, slender plate of rectangular form; the main chain lies parallel to the long axis of the rectangular form, and the side chains are perpendicular to the main chain. However, dynamic properties of the polymers having the S_{A_1} structure seem to differ from that of the polymers having the structure S_{A_2} , for example differences in dynamic viscoelastic properties between the S_{A_1} side chain polymer and the S_{A_2} side chain polymer have been reported [10].

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Some investigators have suggested a possibility of the coexistence of the two different packing structures in the same smectic phase [2, 7, 8]. It seems that such coexistence does not occur in low molecular mass liquid crystals. It has already been pointed out that the two different packing structures simultaneously exist in the smectic A phase of three side chain cholesterol containing polymers, poly(cholesteryl- ω -(methacryloyloxy)alkanoates) (pChMO- n , $n=9, 10$ and 11) [2]. In the present study, in order to clarify the manner of the coexistence of the two different packing structures of pChMO- n , smectic layer spacings were traced by small angle X-ray scattering (SAXS) during heating and cooling runs. This study enables us to understand the molecular organization of the liquid-crystalline side chain polymers and the dynamic properties of such polymers.

2. Experimental

The general structure of pChMO- n is



The substances were prepared as described elsewhere [11]. Polymethacrylates were prepared by radical polymerization in benzene at 60°C with azo-bis-isobutyronitrile (AIBN) as initiator. The polymers were precipitated several times from benzene solution by dilution with methanol after radical polymerization. After drying, the polymers were obtained as a white powder. Degrees of polymerization were estimated by gel permeation chromatography (GPC) and were about 100 ($M_w/M_n = 2.3-3.0$) [2]. Samples used in this study were dried in vacuum for 1 week and left at room temperature for about 2 weeks in a desiccator. Several measurements were carried out on these powder samples in the following manner.

The thermal analyses were made by differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7) using gallium (99.9999 per cent) for low temperatures, and indium (99.9999 per cent) for high temperatures as the calibration substances. The scanning speed was $20^\circ\text{C min}^{-1}$. The transition temperatures and entropies were determined on the second heating run. The glass transition point was estimated from the midpoint of the sloping portion of the line during the base line shift. The melting and clearing points were determined at the maximum peak positions.

Polarized optical microscopic observations were carried out using a Nikon XTP-11 microscope equipped with a Mettler FP 800 heating stage.

The X-ray investigations were performed with a 6 m point focusing small angle scattering camera [12] (at the High-Intensity X-ray Laboratory of Kyoto University) with Ni-filtered $\text{Cu-K}\alpha$ radiation. The smectic layer spacings were measured on the second heating run for powder samples in a vacuum chamber equipped with a heating stage. The temperature was controlled by PID with an error of about 0.1°C . To confirm the type of mesophase, the oriented sample which had been drawn just below the clearing point with a pair of tweezers was used.

3. Results and discussion

3.1. Ordinary transitional behaviour of pChMO-*n*

The transition temperatures for pChMO-*n* are listed in the table. The liquid-crystalline phase of pChMO-*n* was observed between the glass transition point (T_g) and the clearing point (T_{cl}) on and after the first cooling run. The glass transition point decreases with increasing *n* up to *n*=4 and then becomes almost constant with *n*>4; thus the glass transition point is independent of spacer length at *n*>4. The clearing point decreases with increasing *n* up to *n*=7, although showing the odd-even effect. On the other hand, the clearing point of polymers having longer spacers (*n*>7) is almost constant. Detailed discussions for T_g and T_{cl} have been described elsewhere [2].

For pChMO-*n* (*n*=1–3) on the first heating run, in addition to the glass transition and clearing points, a broad exothermal peak (T_{re}) was observed. A melting point (T_m) was observed only on the 1st heating run for pChMO-*n* (*n*>4). Discussion about the exothermal peak and the melting point have been described in detail elsewhere [3].

For pChMO-*n* (*n*=9–11), a phase transition point (T_1 ; broad, endothermal peak) was observed between the glass transition and clearing points. Below T_1 , two independent reflections at small scattering angle were observed. T_1 will be discussed in detail later.

The transition entropy at T_{cl} increased with increasing *n* from *n*=1–7, but it drops precipitously and then increases again with increasing *n* from *n*=9–15. This result suggests that the order of the orientation of the mesogenic groups increases with *n* up to *n*=7 and that the order in the liquid-crystalline phase between T_1 and T_{cl} increases with *n* from *n*=9–15 [2].

Observations with a polarized optical microscope for these samples showed that the birefringence was retained over the entire temperature range of the liquid-crystalline phase. The texture of these polymers was of a fine grain appearance, similar to the fine confocal texture of the smectic phase of low-molecular mass liquid crystals (see figure 1(a)). Only for pChMO-15, was the bâtonnet texture observed with annealing just below the clearing point (see figure 1(b)). Furthermore, the X-ray scattering pattern of the stretched oriented samples shows a series of sharp layer reflections at small scattering angle in the direction perpendicular to the drawing axis,

Transition temperatures and the transition entropies at T_{cl} for pChMO-*n* (*n*=1, 2, 3, 4, 5 and 7) on the second heating run.

	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$	$T_{re}/^\circ\text{C}$	$T_1/^\circ\text{C}$	$\Delta S_1/\text{JK}^{-1}\text{mol}^{-1}$	$T_{cl}/^\circ\text{C}$	$\Delta S_{cl}/\text{JK}^{-1}\text{mol}^{-1}$
pChMO-1	125	—	<i>c.</i> 180†	—	—	219	3.75
pChMO-2	85	—	<i>c.</i> 150†	—	—	231	4.24
pChMO-3	57	—	<i>c.</i> 120†	—	—	208	4.33
pChMO-4	50	68†	—	—	—	217	5.21
pChMO-5	49	63†	—	—	—	184	6.04
pChMO-7	45	60†	—	—	—	163	6.99
pChMO-9	47	61†	—	144	4.76	151	0.80
pChMO-10	48	62†	—	113	0.40	154	2.69
pChMO-11	43	59†	—	105	0.36	151	3.35
pChMO-15	41	55†	—	<i>c.</i> 95‡	<i>c.</i> 0.10‡	156	7.26

† Observed only on the first heating run.

‡ Peak on DSC curve is too weak and broad to calculate exactly.

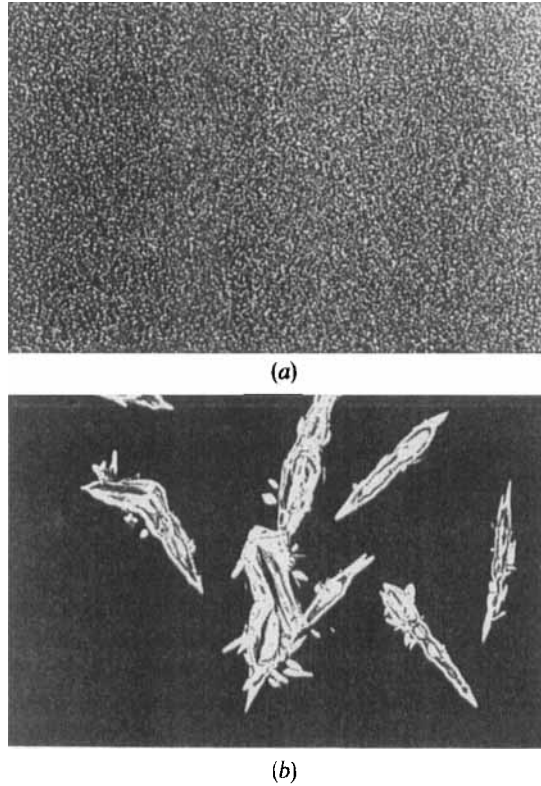


Figure 1. (a) Fine grain confocal texture of pChMO-7 at 100°C, magnification $\times 100$. (b) Bâtonnets texture of pChMO-15 after annealing for 10 min. at 157°C, magnification $\times 400$.

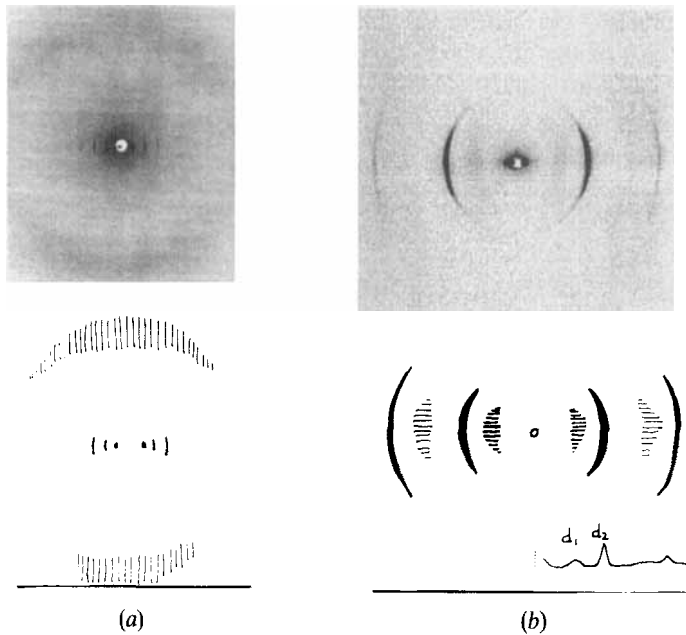


Figure 2. X-ray diffraction pattern of a uniaxial oriented sample of pChMO-11; (a) using a flat plate camera with a specimen to film distance of 110 mm; (b) using a 6 m point focusing small angle scattering camera. d_1 and d_2 reflections are attributable to the two layer

and broad crescents at wide angle in the direction parallel to the drawing axis (see figure 2(a)). The relative positions of the small angle reflections and the wide angle arcs with respect to the drawing axis shows that the side chains are perpendicular to the drawing axis; the main chain is parallel to the drawing axis. These results indicate that the liquid-crystalline phase of pChMO- n is a smectic A phase.

3.2. X-ray investigations of pChMO- n ($n=1, 2, 3, 4, 5$ and 7) at various temperatures

The smectic layer spacings (estimated from the first order reflection peak) plotted against temperature on the second heating run for pChMO- n ($n=1-5$ and 7) are shown in figure 3. The values of the layer spacings near T_g for these polymers agree well with double the calculated length of the side chain in its most extended confirmation [3]. This fact indicates that pChMO- n ($n=1-5$ and 7) has a two layer packing structure; the smectic phase of these polymers is the S_{A_2} phase. The clearing point of pChMO- n ($n=1-5$ and 7) is the transition from S_{A_2} phase to the isotropic one. An increase in the transition entropy at T_{c1} with n suggests that the order of the S_{A_2} structure of pChMO- n rises with increasing n up to 7 [2]; increasing the length of the flexible spacer (n) up to $n=7$ enables the mesogenic groups to orient more easily in the S_{A_2} phase.

The layer spacings on and after the first cooling run for pChMO- n ($n=1-5$ and 7) in the S_{A_2} phase scarcely change with temperature. The spacings, however, decrease when the temperature approaches T_{c1} . This decrease of the layer spacing seems to be due to the decrease of the order parameter, and have also been reported for other liquid-crystalline side chain polymers [4]. The side chains, which are arranged into lamellate plates at lower temperature, are spread on the circular plane, drawn by the side chain

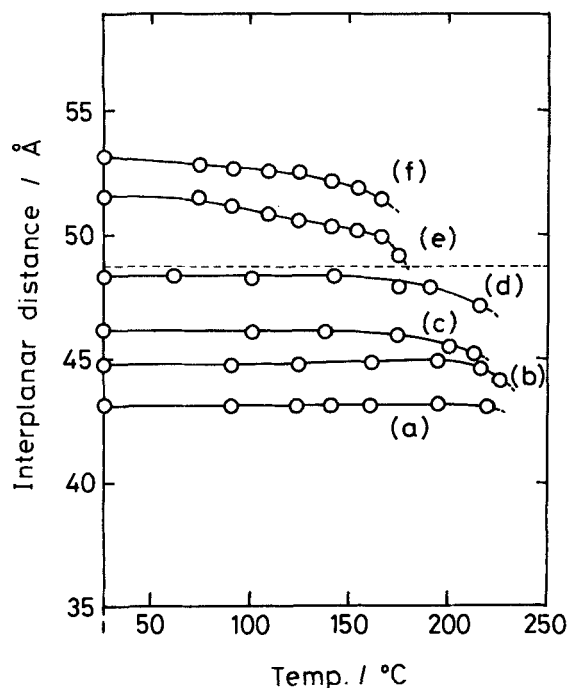


Figure 3. Plots of smectic layer spacing against temperature on the second heating run for pChMO-1 (a), pChMO-2 (b), pChMO-3 (c), pChMO-4 (d), pChMO-5 (e) and pChMO-7 (f); ---, double the calculated value of the side chain of pChMO-4 (c. 48.8 Å).

axis, as a radius; the shape of one macromolecule changes from a rectangular plate in the S_{A_2} phase to a defective cylinder in the isotropic phase just above T_{ci} [3].

3.3. X-ray investigations of pChMO- n ($n=9-11$ and 15) at various temperatures

3.3.1. X-ray diffraction patterns of pChMO- n ($n=9-11$ and 15)

An X-ray diffraction pattern obtained from a stretched sample of pChMO-11 below T_g and its schematic representation are shown in figure 2, and an X-ray diffraction diagram for pChMO-11 at various temperatures is shown in figure 4. The X-ray diffraction pattern shows a pair of diffuse crescents at wide angle showing the absence of ordering within the smectic layer planes. Two pairs of the layer reflections (d_1 and d_2) are observed independently at small angle. The interplanar distances estimated from broad (d_1) and sharp (d_2) reflections at small angle are 52.6 Å for d_1 and 35.1 Å for d_2 . Although the d_1 reflection disappeared at T_1 on heating and reappeared at T_1 on cooling, the d_2 reflection was observed from below T_g to T_{ci} on both heating and cooling. As has been described elsewhere [2], these values of the two interplanar distances suggest the coexistence of two different packing structures; the smectic layer spacing estimated from d_1 is consistent with the S_{A_2} structure and that estimated from d_2 is compatible with the S_{A_1} structure. X-ray diffraction diagrams for pChMO-9, pChMO-10, and pChMO-15 at various temperatures are shown in figures 5, 6 and 7, respectively. The possibility of two different reflections from one structure can be

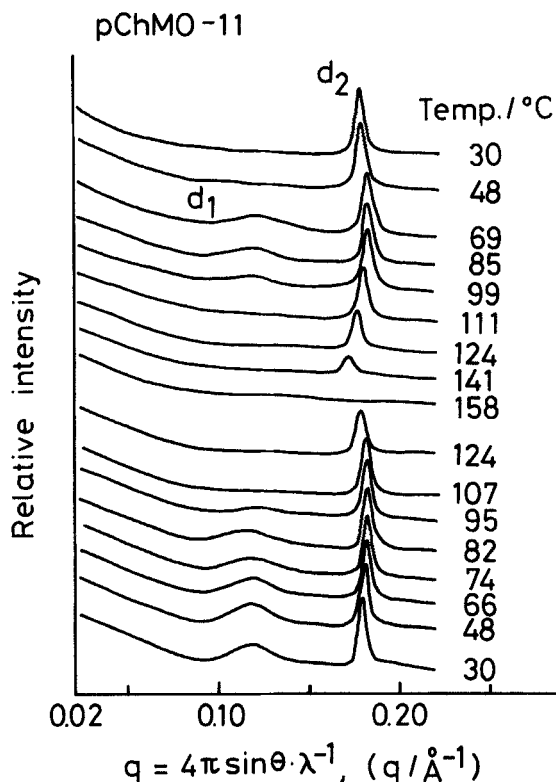


Figure 4. X-ray diffraction diagrams on the first run for pChMO-11.

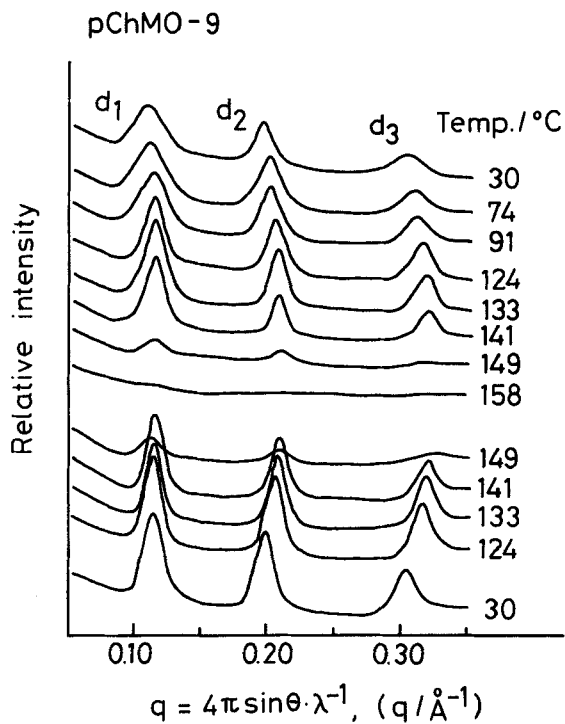


Figure 5. X-ray diffraction diagrams on the first run for pChMO-9.

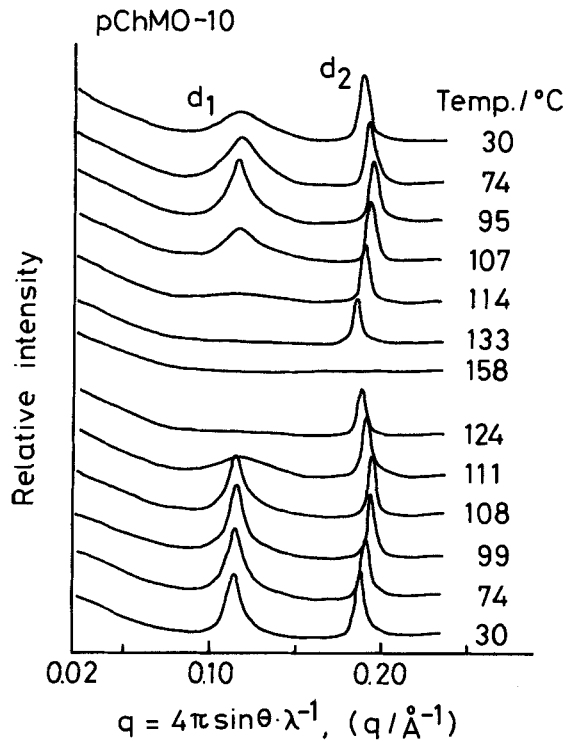


Figure 6. X-ray diffraction diagrams on the first run for pChMO-10.

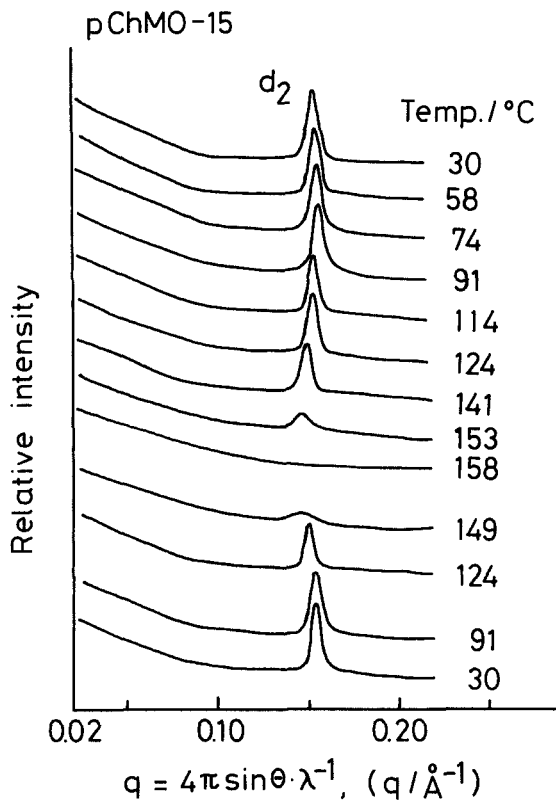


Figure 7. X-ray diffraction diagrams on the first run for pChMO-15.

eliminated due to the following observations: (1) although the d_1 reflection disappears at T_1 on the heating run, the d_2 reflection is maintained up to T_{ci} ; (2) pChMO- n ($n = 1-7$) exhibit only the d_1 reflection with its high order ones due to the S_{A_2} structure [3], and pChMO-15 exhibits only the d_2 reflection with its high order ones due to the S_{A_1} structure (see figure 7); (3) the d_1 reflection becomes broader and weaker with n in contrast to growth of the d_2 reflection with n . Therefore, pChMO-9 seems to be the boundary of these structural differences. This is supported by the results of the transition entropies plotted against n . The X-ray diffraction pattern of pChMO-9 and pChMO-10 is similar to that of pChMO-11. As is shown in figures 4, 5 and 6, however, the d_1 reflection becomes broader and weaker with increasing n from $n = 9-11$, and it disappears on the diffraction pattern for pChMO-15 (see figure 7). The increase in the length of the spacer is considered to be unfavourable to the S_{A_2} packing structure. Therefore, only the sharp d_1 reflection was observed in the diffraction diagram for pChMO-15.

3.3.2. The two layer packing structure of pChMO- n ($n = 9-11$)

The smectic layer spacings estimated from d_1 and d_2 for pChMO-9, pChMO-10 and pChMO-11 and from only d_2 for pChMO-15 are plotted against temperature on the first run shown by figures 8, 9, 10 and 11, respectively. The temperature dependence of the layer spacing on the first heating run is affected by the structure below T_m . On and

after the second run, following the first run, however, the temperature dependence of the layer spacing is similar to that on the first cooling run. On the first heating run, the layer spacing (d_1) of pChMO-9, pChMO-10 and pChMO-11 below T_g are 54.4 Å, 54.8 Å and 52.6 Å (see figures 8–10), respectively. In all cases, the layer spacing (d_1) of pChMO- n ($n=9-11$) is slightly short compared with double the calculated value of the side chain. This shortness of the layer spacing (d_1) has been discussed in detail elsewhere [2] and indicates partial overlapping of the tails of the cholesteryl groups of neighbouring polymers; the side chains form the partial overlapped two layer packing structure.

The layer spacing (d_1) for pChMO-9 and pChMO-10 on and after the first cooling run is almost constant on increasing the temperature (*c.* 54 Å for pChMO-9 and *c.* 55 Å for pChMO-10; see figures 8–9) in the S_{A_2} phase, and that of pChMO-11 increases from 52.6 Å to 54.8 Å with increasing temperature (see figure 10). The increase in the layer spacing (d_1) of pChMO-11 on increasing the temperature reflects the increased mobility of the side chains; it seems that the large free volume of the side chains due to the longer flexible spacer does not allow the partial overlapping of the tails of the mesogenic groups in the two layer packing structure. Recalling the observations that the shape of the d_1 reflection of pChMO- n ($n=9-11$) becomes broader and weaker with increasing spacer length (n) (see figures 4–6) and that the transition entropy plotted against n has a sharp negative inflection at $n=9$ at which the d_2 reflection due to the single layer packing structure appears, too long a flexible spacer disturbs the side chains on forming the two layer packing structure, i.e. the S_{A_2} phase predominates over the S_{A_1} phase in pChMO-9 and the S_{A_1} phase becomes predominant in pChMO-10 and pChMO-11.

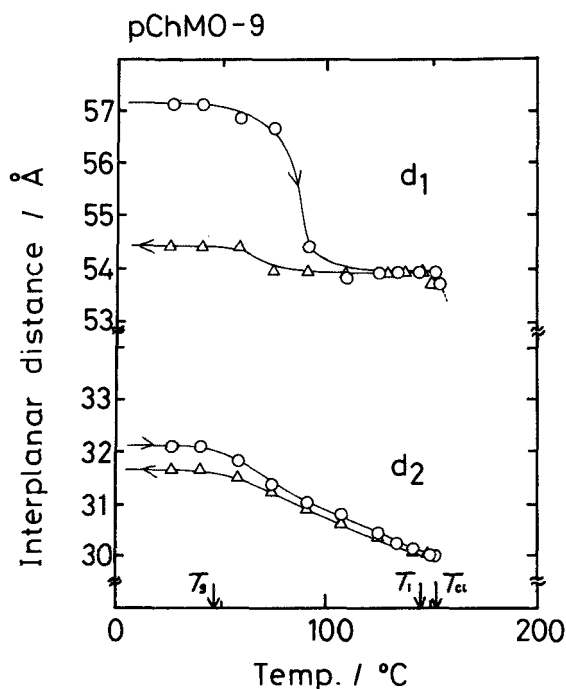


Figure 8. Plots of smectic layer spacings d_1 and d_2 against temperature on the first run for pChMO-9; the calculated value of the side chain is *c.* 30.5 Å.

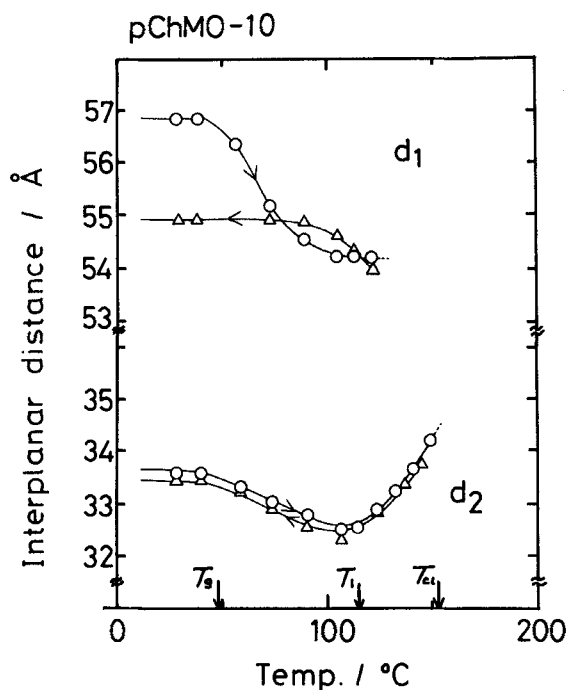


Figure 9. Plots of smectic layer spacings d_1 and d_2 against temperature on the first run for pChMO-10; the calculated value of the side chain is *c.* 31.8 Å.

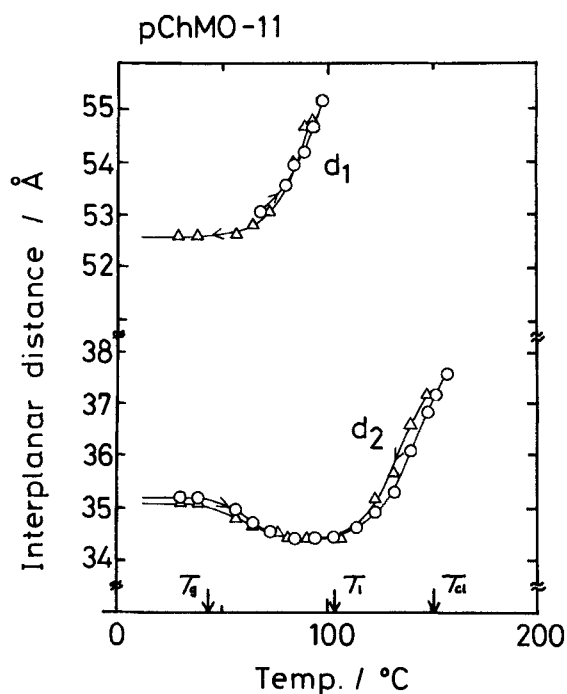


Figure 10. Plots of smectic layer spacings d_1 and d_2 against temperature on the first run for pChMO-11; the calculated value of the side chain is *c.* 33.0 Å.

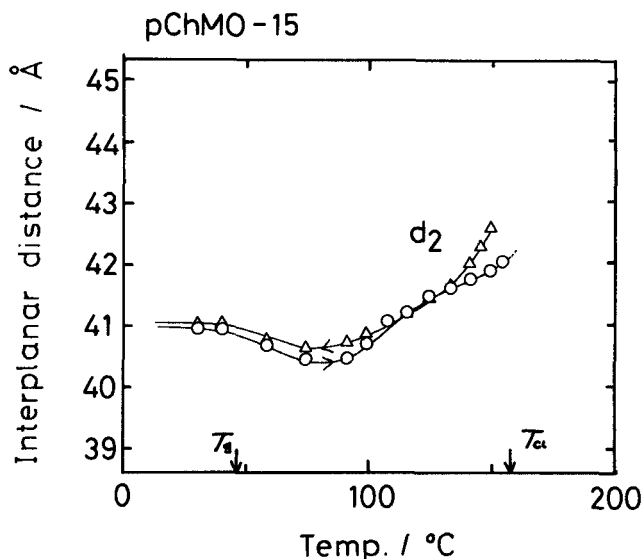


Figure 11. Plots of smectic layer spacing d_2 against temperature on the first run for pChMO-15; the calculated value of the side chain is c. 38.0 Å.

3.3.3. The single layer packing structure of pChMO- n ($n=9-11$ and 15)

The values of the layer spacing (d_2) below T_g are 31.8 Å for pChMO-9, 33.4 Å for pChMO-10, 35.1 Å for pChMO-11 and 41.1 Å for pChMO-15 (see figures 8–11). These values are compatible with the formation of the single layer packing structure (S_{A_1}). In the S_{A_1} phase, if the cholesteryl groups of one polymer are completely surrounded by the spacer methylene chains of the neighbouring polymer (the tail of the mesogenic groups is close to the position where the side chains and the main chain join), the layer spacing (d_2) should agree well with the calculated length of the side chain, and the increase in the layer spacing (d_2) against n should be 1.3 Å per methylene unit. On the other hand, if the cholesteryl groups of one polymer are close to those of adjacent polymers along the direction of the long axis of the side chain, the layer spacing (d_2) should be longer than the calculated length of the side chain, and the increase in the layer spacing (d_2) against n should be 2.6 Å per methylene unit. However, the measured layer spacing (d_2) is fairly long compared with the calculated length of the side chain, and the increase in the layer spacing (d_1) is approximately 1.6 Å per methylene unit. These facts seem to indicate that the cholesteryl groups of one polymer of pChMO- n ($n=9-11$ and 15) are situated near the middle of the methylene spacer of adjacent polymers in the S_{A_1} structure below T_g .

The layer spacing (d_2) attributable to the S_{A_1} structure of pChMO-9 decreases with increasing temperature (see figure 8). The layer spacing (d_2) of pChMO-10 and pChMO-11 decreases with increasing temperature below T_1 at which point the d_1 reflection produced by the S_{A_2} structure disappears, and increases with increasing temperature from T_1 to T_{c1} . Considering the closeness of the values of T_1 and T_{c1} of pChMO-9, it is clear that the layer spacing (d_2) of pChMO- n ($n=9-11$) decreases with increasing temperature in the temperature range in which the S_{A_2} structure coexists with the S_{A_1} structure. This decrease in the layer spacing (d_2) for pChMO-9, pChMO-10 and pChMO-11 is about 1.8 Å, 1.2 Å and 0.7 Å from T_g to T_b , respectively.

Considering the predominance of the S_{A_1} phase over the S_{A_2} phase in pChMO-10 and pChMO-11, the small decrease in the layer spacing (d_2) seems to be due to the stabilization of the S_{A_1} structure. The increase in the layer spacing (d_2) above T_1 for pChMO-10 and pChMO-11 seems to occur due to the disordering of the single layer packing structure; the thermal motion of the side chains loosens the S_{A_1} structure. The plots of the layer spacing (d_2) against temperature for pChMO-15 are similar to those for pChMO-11. However, the decrease in the layer spacing (d_2) for pChMO-15 is smaller than that of pChMO-11, and the manner of the change in the spacing (d_2) is smoother than that for pChMO-11 owing to the absence of another competitive structure (S_{A_2}).

3.3.4. Coexistence of the two different packing structures

Comparing the transition entropy at T_1 with that at T_{c1} for pChMO-9, pChMO-10 and pChMO-11 (see the table), and comparing the shape of the d_1 reflection of the polymers with that of the d_2 reflection (see figures 4–6), it is clear that the two layer packing structure (S_{A_2}) predominates over the single layer (S_{A_1}) one in pChMO-9, and that the single layer packing structure becomes predominant in pChMO-10 and pChMO-11. Furthermore, it appears that increasing the spacer length facilitates the orientation of the side chains in the single layer packing structure of pChMO- n ($n=9-11$ and 15). On the other hand, the S_{A_2} and S_{A_1} structures exist simultaneously below T_1 for pChMO- n ($n=9-11$). It seems that such coexistence of two different structures in single liquid-crystalline phase does not occur in low molar mass liquid crystals. Why are two different structures formed simultaneously by the same polymers having a definite length of the spacer? Some reasons have been considered, for example a wide molecular weight distribution or the existence of impurities could be possible answers. However, these reasons are not enough to explain the systematic appearance and disappearance of the two different reflections. In particular, the molecular weight distribution and the residues of impurities, which are difficult to be reproduced, can be eliminated as possible answers, because of the report of two independent, sharp X-ray reflection peaks at small angle for pChMO-10 synthesized by Freidzon *et al.* [7]. They have not emphasized the coexistence of the two different structures in the report, but two different sharp reflection peaks, at 3.2 nm and 5.5 nm, were observed simultaneously at 25°C [7].

In the side chain polymers, the side mesogenic groups are attached to the main chain homogeneously. However, the mobility of the side chain attached near to the ends of the main chain should be different from that of the side chain attached near to the middle of the main chain. This difference seems to be one reason of the coexistence of the two different structures in the same smectic phase. In this case, the domain of the two layer packing structure is formed among some domains of the two layer packing structure is formed among some domains of the single layer packing structure. The two different structures seem to be divided by a disclination point which is situated at the end of the main chain (see figure 12).

For the transition at T_1 , two kinds of transition are considered; a transition from the two layer packing structure (S_{A_2}) to the single layer packing structure (S_{A_1}) or a transition linearly to the isotropic phase. In the former case, the molecular shape, which is a flat rectangular plate, does not change at the transition; only the position of the flat plate of the macromolecule seems to slide parallel to the long axis of the side chain. In this case, the d_1 reflection peak suddenly disappears at T_1 , such that the intensity of the d_2 reflection peak should increase above T_1 . On the other hand, in the latter case, the

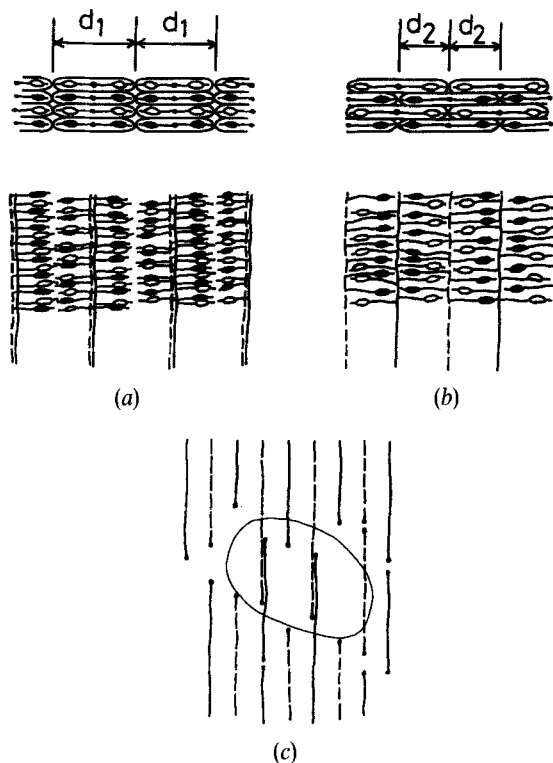


Figure 12. Schematic illustrations of the packing structure of pChMO- n ; (a) edge and cross-sectional view of the two layer packing structure ($n=1-5$ and 7); (b) edge and cross-sectional view of the single layer packing structure ($n=15$); (c) cross-sectional view of the coexistence structure ($n=9-11$); the two layer packing structure domain (enclosed by the circle) is formed among the domains of the single layer packing structure.

molecular shape should change from the flat plate to the isotropic form. For pChMO- n ($n=1-7$), the transition from the S_{A_2} phase to the isotropic one occurs gradually; the position of the side chains forming the S_{A_2} structure at first disorders, and then the random coil of the main chain ensues [3, 10]. In this case, the d_1 reflection peak becomes broader and weaker with temperature, and its intensity decreases near the transition point.

The layer spacing (d_1) of pChMO-9 and pChMO-10 decreases with increasing temperature just below T_i . This decrease is similar to that of pChMO- n ($n=1-5$ and 7) just below T_{c1} at which the transition from the two layer packing structure (S_{A_2}) to the isotropic phase occurs. On the other hand, the layer spacing (d_1) of pChMO-11 increases steeply just below T_i . The increase in the layer spacing (d_1) of pChMO-11 just below T_i seems to be attributable to a small change in the two layer packing structure, i.e. from the partial overlapping form to the non-overlapping one. The small change seems to be caused by an increase in the free volume of the side chains. The two layer packing structure (S_{A_2}) disappears at T_i in the course of this small change. The shape of the d_1 reflection peak is very broad just before the disappearance of the S_{A_2} structure. The order of the S_{A_2} structure just below T_i seems to be very low; the side chains forming the S_{A_2} structure just below T_i seem to possess a low order parameter value.

Furthermore, the intensity of the d_2 reflection due to the single layer packing structure scarcely changes after the disappearance of the d_1 reflection at T_1 . If T_1 was the transition from S_{A_2} to S_{A_1} , the intensity of the d_2 reflection should increase at T_1 . Thus, experimental results for pChMO- n ($n=9-11$) suggest that the transition at T_1 is the transition from the S_{A_2} phase to the isotropic one. Therefore, an interface between one domain of the S_{A_1} phase and the other domains seems to be a thin amorphous layer above T_1 for pChMO- n ($n=9-11$).

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