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The packing structure of side chains of liquid-crystalline side-chain polymers before and during heat treatment

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Six varieties of liquid-crystalline side-chain polymers, poly (cholesteryl ω-(methacryloyloxy)alkanoates) (*p*ChMO-*n*, $n = 1,2,3,4,5,7$, the carbon number of the alkyl chain), were studied by differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS). On and after the first cooling run from the isotropic state, these polymethacrylates gave the same smectic phase. However, on the first heating run for virgin samples, unique phenomena were observed, similar to those frequently observed on the first heating run for thermotropic liquid-crystalline polymers. The thermal properties of the first heating run for these six polymers showed different tendencies between *p*ChMO-*n* (*n*–1–3) and *p*ChMO-*n* (4–7). Although the DSC curve of *p*ChMO-*n* (n = 4, 5 and 7) exhibited the melting and clearing points on the first heating run, the DSC curve of *p*ChMO-*n* (n = 1, 2 and 3) exhibited an exothermal peak between the glass transition and the clearing point on the first heating run. This difference, probably due to the difference in the spacer length of these polymers, was investigated quantitatively by small-angle X-ray scattering by which the micro-change of the packing structure of the side chains of the polymers was traced.

1. Introduction

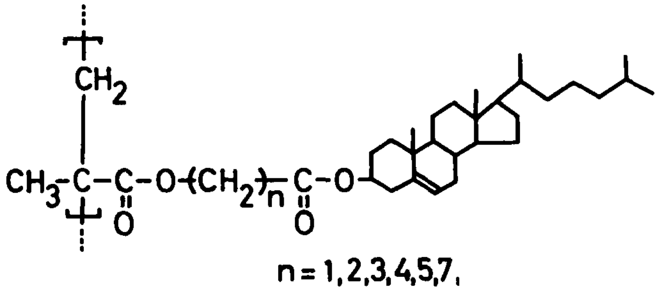
It is well known that the motion of the mesogenic groups of liquid-crystalline side-chain polymers is decoupled from that of the main chain of the polymer by introducing flexible spacers in the liquid-crystalline state [1]. In our previous work on the liquid-crystalline side-chain polymers we found that increasing the length of the flexible spacer enables the mesogenic groups to orient more easily in the liquid-crystalline state [2, 3]. Nevertheless, the arrangement of the side-mesogenic groups should still be affected by the motion of the main chain owing to the linkage of the side chains to the main chain.

There exist complicated, non-singular states before realizing a true liquid-crystalline state of thermotropic liquid-crystalline polymers. For the thermotropic liquid-crystalline polymers, therefore, phase transition points and transition enthalpies are commonly determined by data obtained on and after the second heating run to avoid the effect of thermal history. On the first heating run, although samples exhibit optical anisotropy and have some fluidity, the arrangement of the side chains does not seem to be that expected in a true liquid-crystalline state. Despite the careful preparation of experimental conditions, the phenomena observed on the first heating run for virgin samples, prepared without any particular heat treatments, are generally different from those observed on and after the second heating run. For example, the exothermal peak on the DSC curves is observed on the first heating run [3]; the clearing point obtained on the first heating run is somewhat higher than that obtained on and after the second heating run; and the endothermal peak of the melting point is observed only on the first heating run or on the heating run after annealing just above the glass transition point [4]. One cause of these phenomena may be related to the experimental procedure such as the sample settling into the DSC pan. However, there must be scientific reasons attributable to the sample state itself. These particular phenomena observed on the first heating run seem to be caused by the nature of the chemical linkage of the side-mesogenic groups to the main chain, that is to say, by the combination of the properties of backbone polymers with those of liquid-crystalline portions. It goes without saying that the flexible spacers play an important role in this combination.

In the present study, virgin samples of a series of poly (cholesteryl ω-(methacryloyloxy)alkanoates) (*p*ChMO-*n*, *n* representing the carbon number of the flexible spacer, $n = 1, 2, 3, 4, 5, 7$) were studied by differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS). In the smectic phase of these polymers the side-mesogenic groups organize into lamellae in which the main chain lies perpendicular to the long axis of the side chain. These lamellae gather systematically and form a two-layer packing structure [3] of the side chains; the side chains of one polymer do not overlap with those of the neighbouring polymers in this packing structure. The layer spacings (d) obtained by SAXS provide information on the size of the packing structure. In order to obtain more detailed information about the contribution of the spacer length to the arragnement (the packing structure) of the side-mesogenic groups of the liquid-crystalline side-chain polymers, the layer spacing (d) on the first heating run and on and after the first cooling run for the polymers with various spacer lengths was traced by SAXS. By tracing them on different runs, we can discover how the arrangement of the side chains in initial states of the virgin samples changes into an intrinsic one (equilibrium) in true liquid-crystalline states. The difference in the spacer length provided the different process of change in the arrangement. Therefore, the unique phenomena observed in thermal analysis should be explained from the structural point of view. Indeed there is some difficulty in controlling an initial state of the sample, but these investigations will be related with the chain dynamics of structural change at the non-equilibrium state in the liquid-crystalline side-chain polymers. Furthermore, the results obtained here are useful when performing other dynamic measurements, for example, rheological studies or electrooptical studies, and are essential to supply basic knowledge of the processing technology of the liquid-crystalline side-chain polymers.

2. Experimental part

The general structure of *p*ChMO-*n* is



The substances were prepared as described previously [2]. Polymers were precipitated several times from the benzene solution by dilution with methanol after radical polymerization. After drying, the polymers were obtained as white powder. Degrees of polymerization, estimated by the GPC method [3], were about 100. Samples used in this study were dried in vacuum for 1 week and left at room temperature for about 2 weeks in a desiccator. In this paper the powder samples, without any particular pre-treatment after precipitation, are called 'virgin samples'. Several measurements were carried out on these powder samples in the following manner.

The thermal analyses were made on DSC (Perkin–Elmer DSC-7) using Ga (99·9999 per cent) for low temperatures, and In (99·9999 per cent) for high temperatures as the calibration substances. The scanning speed was 20°C/min. The transition temperatures and the transition entropies were determined on the second heating run. The data obtained on the second heating run were close to those obtained on the subsequent heating run after annealing for 15 min at a temperature 80 K above T_g. 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. In the case of the first heating run of the virgin sample, in order to obtain a better contact between the sample and the pan cell, a small amount of finely pulverized sample (filtered through a 200 mesh filter) was used. Except for fitting the temperature of the sample to the starting temperature of the measurement, no thermal pre-treatment was conducted.

Polarized microscopic observation was carried out using a Nikon XTP-11 microscope equipped with a heating stage system (Mettler FP-800).

The X-ray investigations were performed with a 6 m point-focusing small-angle scattering camera [5] (at the High-Intensity X-ray Laboratory, Kyoto University) with Ni-filtered CuKα radiation. The layer spacings were measured on 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 T_{cl} with a pair of tweezers was used.

3. Results and discussion

3.1. *Ordinary behaviour of pChMO-n*

The liquid-crystalline phase of *p*ChMO-*n* was observed between the glass transition point (T_g) and the clearing point (T_{cl}) on and after the first cooling run. Observations with a polarizing 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 'fine grain', similar to the fine confocal texture of the smectic phase of low-molecular liquid crystals. On the X-ray scattering pattern of the stretched oriented samples, a series of sharp layer reflections at small scattering angles were observed in the direction perpendicular to the drawing axis, and broad crescents at wide angles were observed in the direction parallel to the drawing axis. The relative positions of the small-angle reflections and the wide-angle arcs with respect to the drawing axis show 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 *p*ChMO-*n* is a smectic A phase.

Transition temperatures and transition entropies at $T_{cl}(\Delta S_{cl})$, obtained on the second heating run of the DSC measurement, are shown in the table [3]. A melting point (T_m) was observed only on the first heating run for *p*ChMO-4, *p*ChMO-5 and *p*ChMO-7. The T_m values obtained here are close to T_g in comparison with the value

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

	T_g/°C	T_m/°C	T_{re}/°C	T_{cl}/°C	ΔS_{cl}/J K^{-1} mol^{-1}
*p*ChMO-1	125	—	*c*. 180†	219	3·75
*p*ChMO-2	85	—	*c*. 150†	231	4·24
*p*ChMO-3	57	—	*c*. 120†	208	4·33
*p*ChMO-4	50	68†	—	217	5·21
*p*ChMO-5	49	63†	—	184	6·04
*p*ChMO-7	45	60†	—	163	6·99

† Observed only on the first heating run.

of 3/2 (T_m/T_g) for conventional polymers. Close values of T_m and T_g also have been reported for other liquid-crystalline side-chain polymers [6]. These results do not seem to be strange for such polymers in which the side chains are capable of moving independently from the motion of the main chain. The melting point will be discussed in detail later. On and after the second heating run for *p*ChMO-4, *p*ChMO-5 and *p*ChMO-7 and all of the heating runs for *p*ChMO-1, *p*ChMO-2 and *p*ChMO-3, T_g and T_{cl} were observed. Increasing the length (n) of the side-alkyl chain as the flexible spacer up to 4 the T_g decreases, and then becomes almost constant with n more than 4. Similar results have been observed in other liquid-crystalline side-chain polymers [7, 8]. For the liquid-crystalline side-chain polymers with an appropriate spacer length, T_g seems to be independent of the spacer length. Increasing n up to 7 T_{cl} decreases, although showing the even–odd effect. The transition entropy at T_{cl} increases with increasing n. This fact seems to indicate that the order of the orientation of the side chains increases with increasing n in the liquid-crystalline state. Detailed discussion about T_{cl} and ΔS_{cl} has been described in a previous paper [3].

3.2. *Behaviour of pChMO-n (n = 1, 2, 3) on the first heating run*

DSC curves and interplanar distances (determined from the position of the d_1 peak; notation of d_1 is given in figures 4–6) against temperature on the first run for *p*ChMO-1, *p*ChMO-2 and *p*ChMO-3 are shown in figures 1, 2 and 3, respectively. X-ray diffraction diagrams of *p*ChMO-1, *p*ChMO-2 and *p*ChMO-3 at an appropriate temperature on the first heating run are shown in figures 4, 5 and 6, respectively. In these figures, the reflection peak corresponding to d_1 is attributable to the packing structure of the side chains (d_2 being second in order).

On the DSC curves for *p*ChMO-1, *p*ChMO-2 and *p*ChMO-3 (figures 1 (*a*), 2 (*a*) and 3 (*a*)), these three polymers did not exhibit the T_m peak but the base-line shift of T_g and the T_{cl} peak. In addition to T_g and T_{cl}, a broad exothermic peak (T_{re}) was always observed between the T_g and T_{cl} peaks on the first heating run. This exothermic peak on the first heating run indicates that the degree of arrangement of the mesogenic groups above T_{re} is higher than that below T_{re}. This assumption is supported by the fact that the shape of X-ray reflection peaks of *p*ChMO-n (n = 1, 2, 3), a shape which reflects the arrangement order of the side chains, becomes sharper with increasing temperature around T_{re} on the first heating run (figures 4, 5 and 6). On the other hand, as shown in figures 1 (*b*), 2 (*b*) and 3 (*b*), the interplanar distances (d_1) of *p*ChMO-n (n = 1, 2, 3) increase to almost double the calculated length of the side chain with increasing temperature around T_{re}. Shorter values of the interplanar distance and broadness of the reflection peak below T_{re} show that the side chains are arranged in an incomplete structure which seems to be affected by the conformation of the main

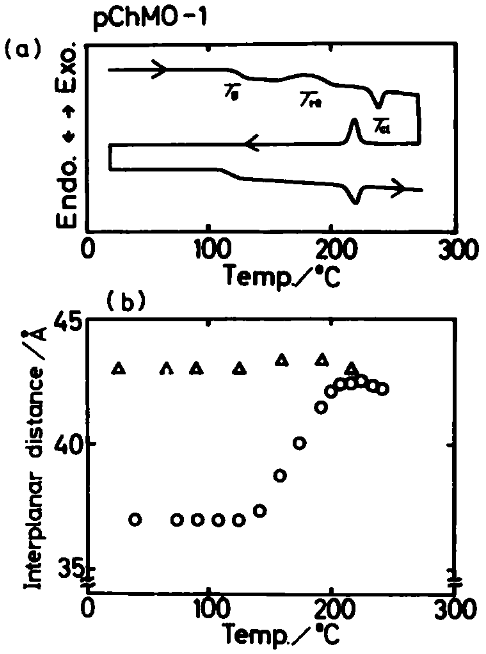


Figure 1. The DSC curve (*a*) of *p*ChMO-1 on the first run and the subsequent heating run (T_g, glass transition point; T_{re}, rearrangement point; T_{cl}, clearing point), and plots of interplanar distance (*b*) against temperature on the first run for *p*ChMO-1 (○, on the first heating run; △, on the first cooling run).

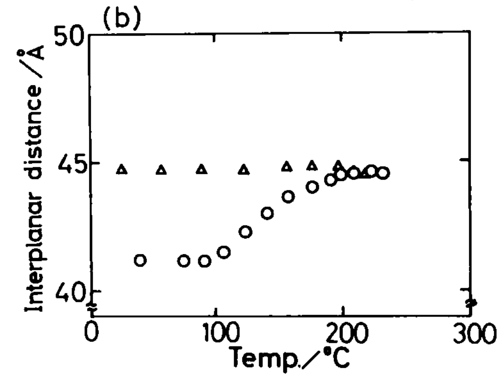


Figure 2. The DSC curve (*a*) of *p*ChMO-2 on the first run and the subsequent heating run (T_g, glass transition point; T_{re}, rearrangement point; T_{cl}, clearing point), and plots of interplanar distance (*b*) against temperature on the first run for *p*ChMO-2 (○, on the first heating run; △, on the first cooling run).

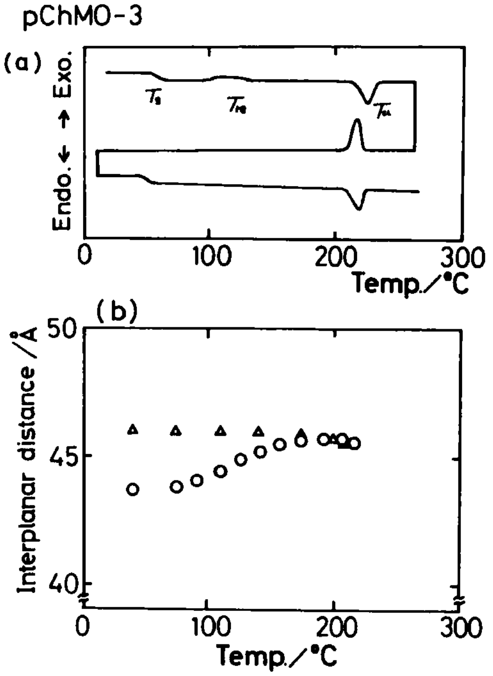


Figure 3. The DSC curve (*a*) of *p*ChMO-3 on the first run and the subsequent heating run (T_g, glass transition point; T_{re}, rearrangement point; T_{cl}, clearing point), and plots of interplanar distance (*b*) against temperature on the first run for *p*ChMO-3 (○, on the first heating run; △, on the first cooling run).

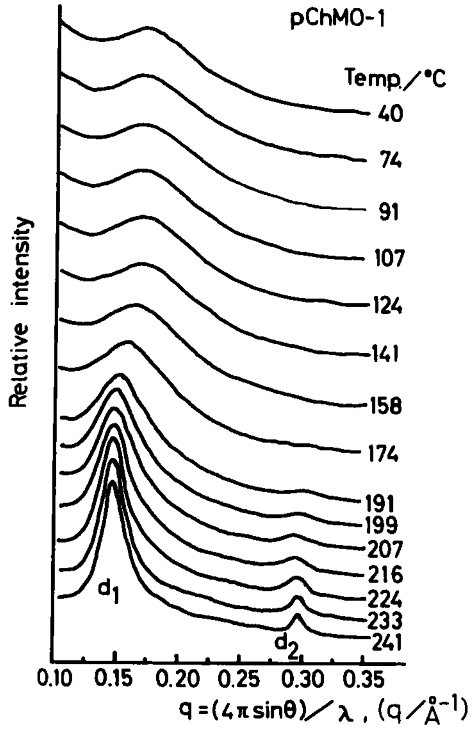


Figure 4. X-ray diffraction diagrams on the first heating rung for *p*ChMO-1.

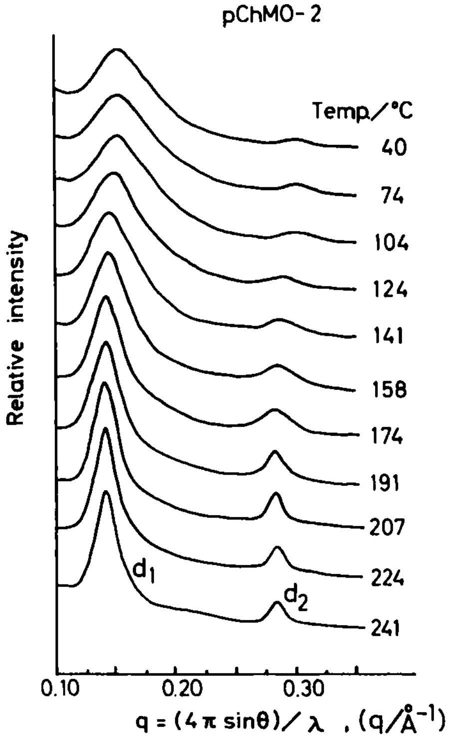


Figure 5. X-ray diffraction diagrams on the first heating run for *p*ChMO-2.

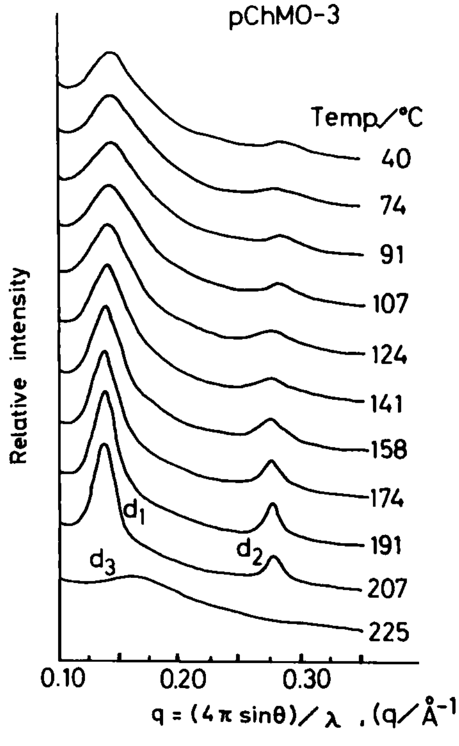


Figure 6. X-ray diffraction diagrams on the first heating run for *p*ChMO-3.

chain and is retained during solidification and drying. In contrast to such behaviour on the first heating run, the interplanar distance (d_1) on the first cooling run is almost constant against temperature and agrees approximately with double the calculated value of the side chain. This constant value of the interplanar distance is consistent with the formation of a two-layer packing structure [3] of the side chains in the smectic phase. Thus, T_{re} is due to the rearrangement of the side chains, a process in which the incomplete arrangement of the side chains in the initial stage changes into an intrinsic orderly arrangement in the liquid-crystalline state during the first heating run. The rearrangement process is shown schematically in figure 7, which is based on the data of SAXS. The incomplete structure changes gradually into a more orderly one around T_{re}. Under microscopic observation the specimen, during T_{re}, shows fluidity and optical anisotropy. However, from a structural point of view described previously, it is not a true liquid-crystalline state, but a quasi-liquid-crystalline state.

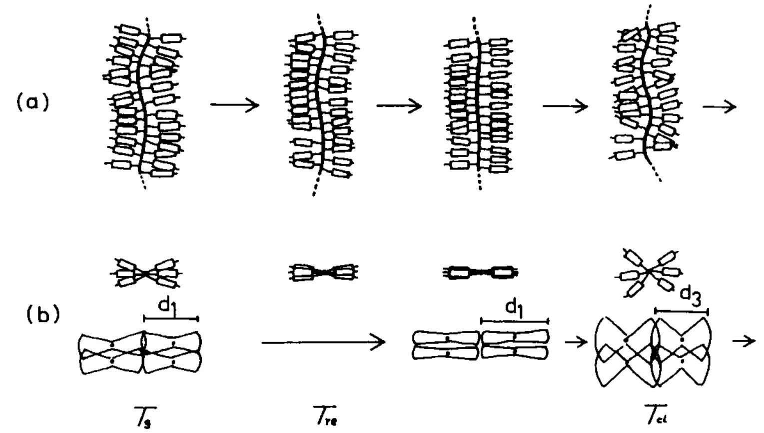


Figure 7. Schematic illustrations of the packing structure of the *p*ChMO-*n* ($n = 3$) on the first heating run; (*a*) through view, (*b*) edge view.

One reason why the rearrangement does not occur just above T_g is that the side chains have less mobility owing to the shortness of their side-flexible spacer. The increment of the interplanar distance (d_1) becomes lower with increasing n, and T_{re} also decreases with increasing n (for *p*ChMO-1: T_{re} is about 180°C; for *p*ChMO-2; about 150°C; for *p*ChMO-3: about 120°C). These facts prove that the increment of n contributes to a decoupling of the motion of the mesogenic groups from that of the main chain.

On and after the second heating run, even though samples were annealed above or below T_g for several days, a peak corresponding to T_{re} was not observed. Moreover, the interplanar distance (d_1) was almost constant on the first cooling run and on the following heating run from T_g to just below T_{cl}. For the three polymers having a shorter spacer the true arrangement of the side chains in the liquid-crystalline state was realized on and after the first cooling run.

3.3. *Behaviour of pChMO-n (n = 4, 5, 7) on the first heating run*

On the DSC curves for *p*ChMO-4, *p*ChMO-5 and *p*ChMO-7 (figure 8 (*a*), 9 (*a*) and 10 (*a*), T_m and T_{cl} are observed on the first heating run. However, on and after the second heating run, T_g was observed instead of T_m. Although T_g of these polymers

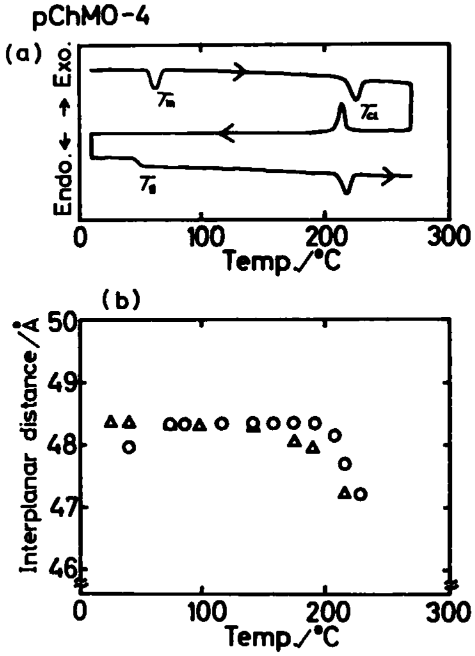


Figure 8. The DSC curve (*a*) of *p*ChMO-4 on the first run and the subsequent heating run (T_m, melting point; T_g, glass transition point; T_{cl}, clearing point), and plots of interplanar distance (*b*) against temperature on the first run for *p*ChMO-4 (○, on the first heating run; △, on the first cooling run).

exists above room temperature, T_m was observed again after annealing at room temperature for about 1 week. This fact suggests that some groups of the polymer can move at room temperature. Unfortunately, we were unable to detect the other lower glassy transition (T_β) by the DSC method. Figure 11 shows the change in the interplanar distances of *p*ChMO-1 and *p*ChMO-7 against time at room temperature (below T_g for both polymers) after cooling runs. No change in the texture of these two polymers against time (about 300 hours) was observed under an optical microscope. The interplanar distance of *p*ChMO-1 hardly changed for about 300 hours. Although the other glassy point (T_β) of *p*ChMO-1 was not detected by DSC, if present T_β seems to exist above room temperature. As mentioned previously, the side chains of *p*ChMO-1 have less mobility owing to the shortness of the spacer. Therefore, once the mesogenic groups of *p*ChMO-1 are oriented into a liquid-crystalline arrangement, the structure seems to be retained for a long time. In contrast to the case of *p*ChMO-1, however, the interplanar distance of *p*ChMO-7 considerably changed. Although T_g was observed also above room temperature, the distance increased with time toward the value obtained for the virgin sample. Thus, the micro-structural change in the packing structure of the side chains was found using the SAXS method. This result strongly suggests the existence of T_β below room temperature. Considering the T_m peak observed on the first heating run or on the heating run after annealing at room temperature, some parts contributing to crystallization seem to have segmental motions at room temperature.

The state of these polymers below T_m seems to be semi- or partial crystal, because the transition enthalpy at T_m is comparatively small (for *p*ChMO-4; *c*. 1·44 kJ mol^{-1},

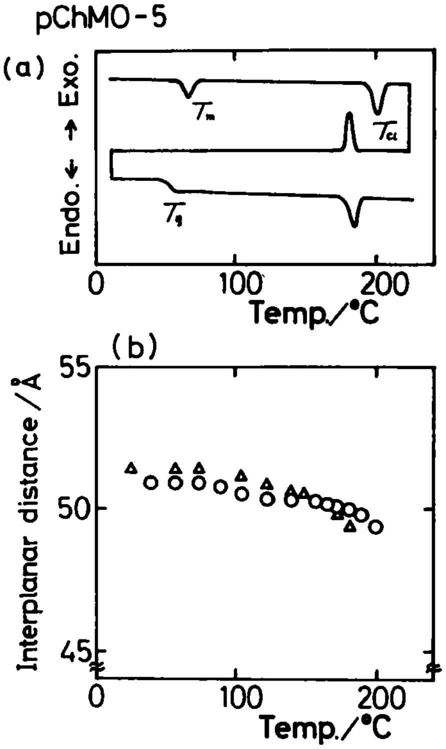


Figure 9. The DSC curve (*a*) of *p*ChMO-5 on the first run and the subsequent heating run (T_m, melting point; T_g, glass transition point; T_{cl}, clearing point), and plots of interplanar distance (*b*) against temperature on the first run for *p*ChMO-5 (○, on the first heating run; △, on the first cooling run).

for *p*ChMO-7; *c.* 2·65 kJ mol^{-1}). The order of the whole system above T_m (i.e. endothermal transition) should become lower than that below T_m. However, the shape of the X-ray reflection peak which is attributable to the arrangement of the side chains becomes sharper with increasing temperature above T_m (figures 12, 13 and 14). These facts suggest two things: firstly, considering the side-mesogenic motion which seems to start after melting of the main chain and/or side-methylene spacers, this T_m is probably related to the partial melting of the main chain and/or the side-methylene spacer. The melting of these parts allows the mesogenic groups to orient orderly; in particular, the melting of the side-methylene spacer seems to promote the decoupling of the motion of the side-mesogenic groups from that of the main chain. Therefore, the degree of the arrangement of the side-mesogenic groups above T_m becomes higher than that below T_m. Secondly, in contrast to the case of *p*ChMO-n ($n = 1, 2, 3$), the side-mesogenic groups of *p*ChMO-*n* ($n = 4, 5, 7$) seem to be able to move as soon as the melting of crystalline parts occurs (figure 14; the shape of the reflection peak becomes sharper just above T_m). Thus, increasing the length of the flexible spacer enables the mesogenic groups to move more easily. This supports the well-known assumption that the motion of the side-mesogenic groups is decoupled from that of the main chain by the flexible space [1].

The interplanar distances of *p*ChMO-4 and *p*ChMO-5 are almost constant on both heating and cooling runs and agree with double the calculated length of the side

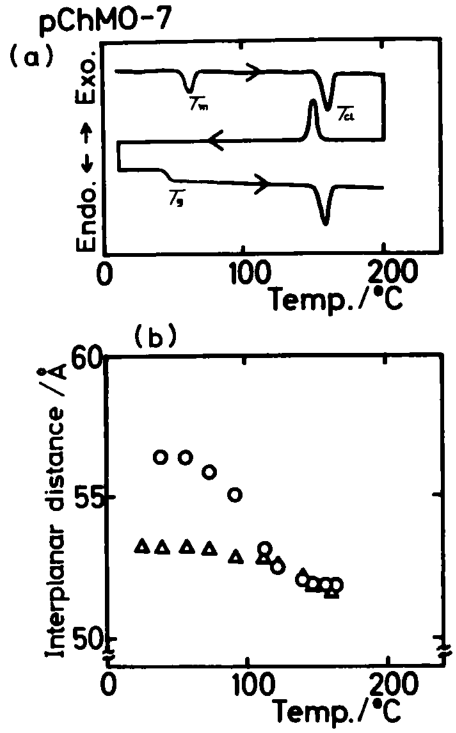


Figure 10. The DSC curve (*a*) of *p*ChMO-7 on the first run and the subsequent heating run (T_m, melting point; T_g, glass transition point; T_{cl}, clearing point), and plots of interplanar distance (*b*) against temperature on the first run for *p*ChMO-7 (○, on the first heating run; △, on the first cooling run).

chain (figure 8 (*b*) and 9 (*b*)). Having more than this length ($n = 4$) the spacer seems to play an effective role in the decoupling of the motion of the side chains from that of the main chain. On the other hand, the interplanar distance of *p*ChMO-7 decreases with increasing temperature on the first heating run and slightly decreases with temperature on and after the first cooling run (figure 10 (*b*)). Similar results were reported for other side-chain polymers exhibiting a smectic A phase [9]. Furthermore, the interplanar distances obtained on cooling are shorter than double the calculated value of the side chain, while those obtained for the virgin sample below T_m are approximately consistent with it. These results suggest that the side chains have an elongated conformation and do not overlap with one another in the initial partial crystalline state of *p*ChMO-*n* ($n = 4$–7) and also in the liquid-crystalline state of *p*ChMO-4 and *p*ChMO-5. The shortness of the interplanar distances on and after the first cooling run for *p*ChMO-7 is probably due to the partial overlapping of the side chains or the tilting of the side chain against the main chain, or because the side chain is not in its fully extended all-trans conformation in the liquid-crystalline state. The observed shortness is about 0·3 nm; this value seems to be larger than that expected owing to a conformational change. In contrast to the case of *p*ChMO-7, it has been reported that the interplanar distance increases with increasing temperature in the S_c phase of other side-chain polymers [6, 10]. Moreover, in our previous work [3], the partial overlapping structure of the two-layer packing structure was confirmed in *p*ChMO-9, 10, 11 by observing the X-ray reflection attributable to the overlapping

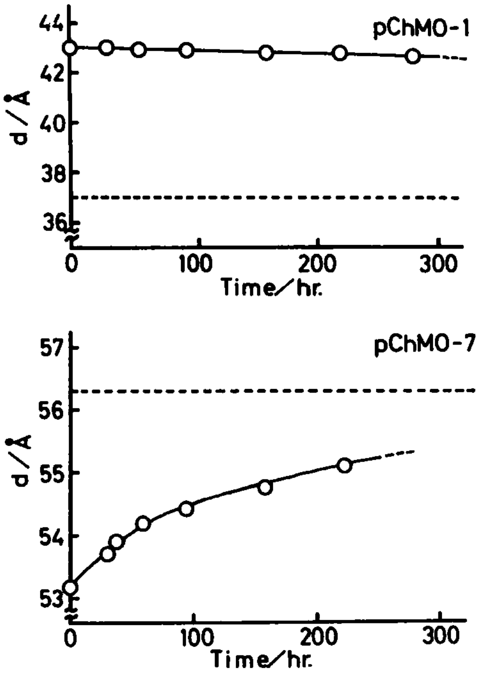


Figure 11. Plots of interplanar distance (d_1) of *p*ChMO-1 and *p*ChMO-7 against time at room temperature (- - -, interplanar distance obtained for each virgin sample).

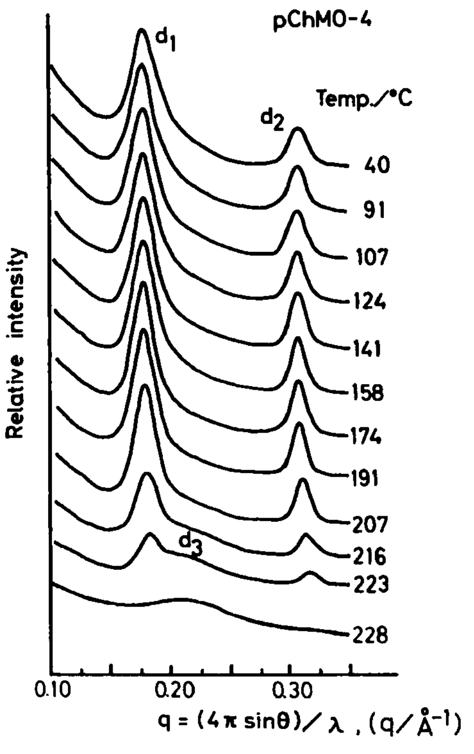


Figure 12. X-ray diffraction diagrams on the first heating run for *p*ChMO-4.

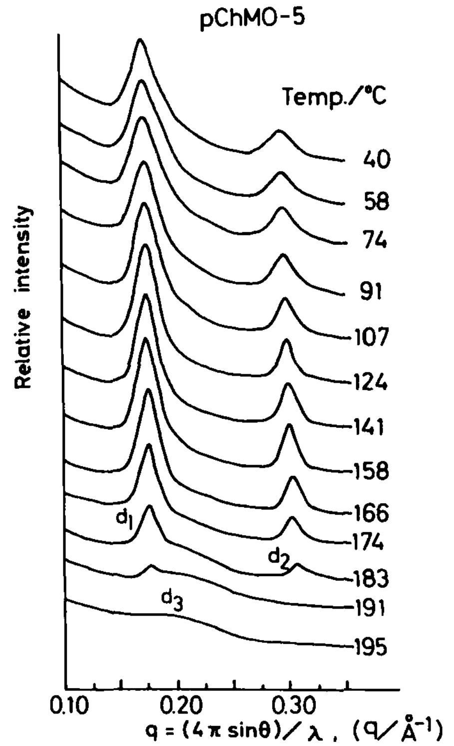


Figure 13. X-ray diffraction diagrams on the first heating run for *p*ChMO-5.

moiety of the side chains. Therefore, in *p*ChMO-7, in addition to the change in the conformation of the side chain, alkyl tails of mesogenic cholesteryl groups of neighbouring polymers seem to overlap partially in the liquid-crystalline state. The length ($n = 7$) of the spacer is probably too long to form the ideal two-layer packing structure of the side chains.

3.4. *Behaviour of pChMO-n (n = 1–7) on the second heating run*

On the second heating run of the DSC curve of *p*ChMO-*n* ($n = 1$–7), T_g and T_{cl} were observed. The behaviour of the interplanar distances of *p*ChMO-*n* against temperature on the second heating run just after the first cooling run is nearly identical with that on the first cooling run. On the diagrams of the reflection peaks of *p*ChMO-3, *p*ChMO-4 and *p*ChMO-5, d_3 peak, which was observed on the first heating run, was also observed just above T_{cl} on the second heating run. In addition to schematic illustrations of the process of T_{re}, the packing structure just above T_{cl} on the heating run is assumed in figure 7, based on the reflection peak corresponding to d_3 observed for *p*ChMO-3, 4, 5 (figures 6, 11 and 12). At this temperature, although the broad reflection peak probably suggests the existence of a different liquid-crystalline state, the change of the texture into another liquid-crystalline state was not observed under polarized light. Furthermore, no additional endothermal peak was observed on DSC up to the temperature at which the d_3 peak on the reflection diagram completely disappears. Therefore, it seems that the side chains which were arranged into lamallae below T_{cl} cannot behave isotropically just above T_{cl} due to the linkage of the side chains to the main chain.

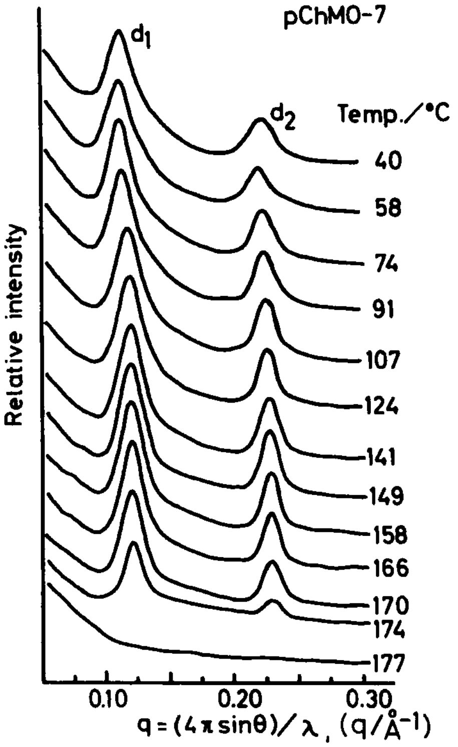


Figure 14. X-ray diffraction diagrams on the first heating run for *p*ChMO-7.

4. Conclusions

As already reported [3], from the viewpoint of thermal study, increasing the length of the spacer enables the side-mesogenic groups to orient more easily. This was also supported from a structural point of view by this study.

In the case of *p*ChMO-*n* ($n = 1, 2, 3$), the exothermic peak on the first heating run is due to the rearrangement motion of the side-mesogenic groups. In this rearrangement, the interplanar distances attributable to the packing structure of the side chains increase with increasing temperature toward double the calculated value of the side-chain; double the calculated value is consistent with the two-layer packing structure of the side chains. The increment of the interplanar distance during T_{re} decreases with an increase in the spacer length. Thus, the decoupling of the motion of the side chains from that of the main chain is advanced by the increment of the spacer length. In the case of *p*ChMO-*n* ($n = 4, 5$), such a change in the interplanar distances by the rearrangement of the side chains was not found. However, the shape of the reflection peaks of *p*ChMO-*n* ($n = 4, 5$) starts to change just above T_m. Considering the fact that no motion of the side chains of *p*ChMO-*n* ($n = 1, 2, 3$) can occur until T_{re}, the side-mesogenic groups of *p*ChMO-*n* ($n = 4, 5$) are, therefore, more mobile than those of *p*ChMO-*n* ($n = 1, 2, 3$). It was observed that the mesogenic groups of *p*ChMO-7 have mobility even after freezing the main-chain motion below T_g, although the mesogenic groups of *p*ChMO-1 have little mobility below T_g. This fact suggests the existence of T_β of *p*ChMO-7 below room temperature. Also for the other polymers having the T_m peak on the first heating run, T_β seems to exist below room temperature. Thus, for *p*ChMO-*n*, although the side-mesogenic groups are affected by the linkage of the side chain to the main chain, the spacer length (*n*) more than 4 seems to play an effective role in the decoupling of the motion of the side chains from that of the main chain.

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