trans and gauche conformers. For the polymers with $y = 4$, 5, and 9, the conformations of bond 3 have been shown to be gauche.

We speculate that in the mesomorphic state, the extended segments containing the aromatic and x-alkylene residues can rotate and delineate cones of rotation. In the crystalline state their rotational motion is inhibited. The repeat distance in the draw direction is essentially the same in both states. This is necessary in order to support the highest number of H-bonds. The ability to rotate is probably due to the presence of gauche conformers in the y-alkylene segments, explaining why no mesomorphicity was observed in the fully trans $y = 2$ polymers.

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Registry No. Poly(ester amide) $y = 3$, $x = 1$, 114677-86-0; poly(ester amide) $y = 3$, $x = 3$, 114677-88-2; poly(ester amide) $y = 3$, $x = 4$, 114677-89-3; poly(ester amide) $y = 3$, $x = 7$, 114677-92-8; poly(ester amide) $y = 3$, $x = 8$, 114677-93-9; poly(ester amide) $y = 3$, $x = 11$, 114677-95-1; poly(ester amide) $y = 3$, $x = 14$, 114677-97-3; poly(ester amide) $y = 5$, $x = 11$, 114678-16-9; poly(ester amide) $y = 5$, $x = 14$, 114678-18-1; poly(ester amide) $y = 9$, $x = 3$, 114678-20-5; poly(ester amide) $y = 9$, $x = 4$, 114678-21-6; poly(ester amide) $y = 9$, $x = 7$, 114678-22-7; poly(ester amide) $y = 9$, $x = 8$, 114678-23-8; poly(ester amide) $y = 9$, $x = 11$, 114678-24-9; poly(ester amide) $y = 9$, $x = 12$, 114691-78-0; poly(ester amide) $y = 9$, $x = 14$, 114678-25-0; poly(ester amide) $y = 2$, $x = 14$, 114677-84-8; poly(ester amide) $y = 3$, $x = 14$, 114677-97-3; poly(ester amide) $y = 4$, $x = 14$, 114678-08-9; poly(ester amide) $y = 5$, $x = 14$, 114678-18-1; poly(ester amide) $y = 2$, $x = 7$, 114677-82-6; poly(ester amide) $y = 4$, $x = 7$, 114678-04-5; poly(ester amide) $y = 2$, $x = 4$, 114677-81-5; poly(ester amide) $y = 3$, $x = 6$, 114677-91-7; poly(ester amide) $y = 4$, $x = 4$, 114678-01-2; poly(ester amide) $y = 5$, $x = 4$, 114678-10-3.

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Dependence of the Packing Structure of Mesogenic Groups on the Flexible Spacer Length of Liquid Crystalline Side-Chain Polymers

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ABSTRACT: Poly(cholesteryl ω-(methacryloyloxy)alkanoates) (pChMO-n, n = 1–5, 7, 9–11, 15, the carbon number of the alkyl chain), which are liquid crystalline side-chain polymers, were studied by differential scanning calorimetry and by small-angle X-ray scattering. The clearing point decreases with increasing n up to 7 and shows the even–odd effect, but it becomes almost constant with $n > 7$. The plot of transition entropy at the clearing point against n has a sharp negative inflection at $n = 9$. X-ray investigations show that the packing of mesogenic groups in pChMO-n with short spacers (n = 1–7) differs from that in pChMO-n with longer ones (n = 9–15). These two types of packing coexist in pChMO-n (n = 9–11) below their phase transition temperatures.

Introduction

Liquid crystalline side-chain polymers combine the properties of low molecular weight liquid crystals with those of polymers.[1–3] Investigations during this decade have shown that a flexible spacer linking the mesogenic group to the polymer main chain plays an important role in the realization of the liquid crystalline state.[4]

Finkelmann and Rehage have summarized the data on a number of liquid crystalline side-chain polymers and showed that the clearing point (T_{cl}) of these polymers generally decreases with increasing length of the flexible spacer.[5] Recently, however, Simon and Coles have reported on a side-chain polysiloxane in which T_{cl} increases

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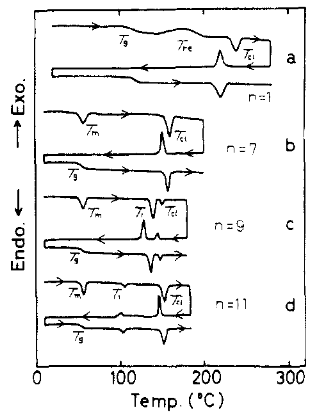


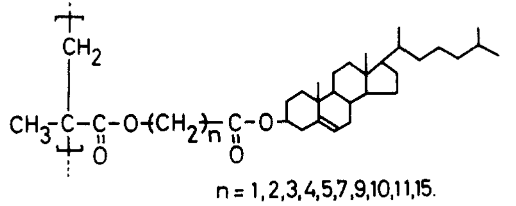
Figure 1. DSC curves of pChMO-1 (a), pChMO-7 (b), pChMO-9 (c), and pChMO-11 (d) on first run and following heating run.

with increasing length of the flexible spacer.[6] Furthermore, many reports have shown that nematic, cholesteric, and smectic phases can be observed in those polymers that have a sufficiently long flexible spacer.[7,8] However, the identification of the liquid crystalline phase in such polymers is based on criteria used for low molecular weight liquid crystals. Some investigators have reported the coexistence of two packing structures of the mesogenic groups in a single liquid crystalline phase,[9,10] which does not occur in low molecular weight liquid crystals.

In this work, a series of poly(cholesteryl ω-(methacryloyloxy)alkanoates) (pChMO-*n*, *n* representing the carbon number of the flexible alkyl side chain, *n* = 1–5, 7, 9–11, 15) have been synthesized. These polymers were studied by differential scanning calorimetry (DSC) and by small-angle X-ray scattering (SAXS) to determine their thermal properties and the packing structures of the mesogenic groups.

Experimental Section

The general structure of pChMO-*n* is



The polymers were prepared as described previously.[11] Degrees of polymerization were estimated to be ~100 by GPC. It has been reported that the phase behavior of liquid crystalline side-chain polymers is not influenced by degree of polymerization when the latter is >20.[12] The transition temperatures and transition entropies were determined by DSC (Perkin-Elmer DSC-1B) using Ga (99.9999%) for low temperatures, and In (99.9999%) for high temperatures as the calibration substances. The scanning speeds of the heating runs were 10 and 20 °C/min. Polarized microscopic observation was made by using a Nikon XTP-11 microscope equipped with a heating stage system (Mettler FP-800). The X-ray investigations were carried out on oriented and unoriented samples with a 6-m point-focusing small-angle scattering camera[13] with Ni-filtered Cu Kα radiation in a vacuum chamber equipped with a heating stage. The temperature was controlled by PID with an error of about 0.1 °C. Oriented samples were prepared by mechanical drawing with tweezers just below T_{cl}.[14]

Results and Discussion

The liquid crystalline phases of pChMO-*n* were observed between the glass transition point (T_g) and the clearing point (T_{cl}). On DSC measurements, virgin samples of pChMO-*n* (*n* = 1–3) showed broad exothermic peaks between T_g and T_{cl} on heating (Figure 1a), which may be attributable to rearrangement of the mesogenic groups. A phase transition point (T_l, endothermal) in the liquid crystalline state was observed in pChMO-*n* ($n \geq 9$) (Figure 1c). Observations with a polarizing microscope showed that the birefringence was retained over the entire temperature range of the liquid crystalline phase. The optical clearing points agree approximately with those obtained by DSC measurement. The texture of all the samples was similar to the confocal texture reported for the smectic phase of other liquid crystalline side-chain polymers.[15] A change in the texture of pChMO-*n* (*n* = 9–15) was not observed at T_l. However, the optical anisotropy of pChMO-9 decreased at T_l. For pChMO-15, the bôtannets texture was observed only when annealing near T_{cl}. The compounds with short spacers (*n* = 1–3) tended to pyrolyze on repeated heatings because of their high T_{cl}.

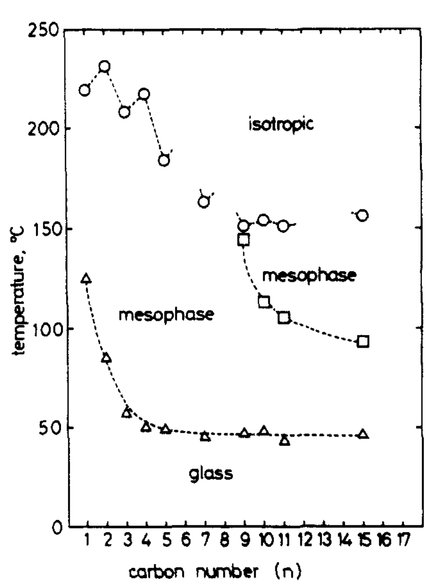


Figure 2. Plot of transition temperatures against *n* for the series of pChMO-*n* (second heating): (○) clearing point (T_{cl}); (□) liquid crystal–liquid crystal phase transition point (T_l); (△) glass transition point (T_g).

In Figure 2, the transition temperatures of pChMO-*n*, determined by DSC on a second heating, are plotted against *n*. The T_g decreases with increasing *n* up to 4 and then becomes constant with $n > 4$; thus T_g is independent of spacer length at $n > 4$. Similar results have been observed in other side-chain polymers.[6,16]

The T_{cl} decreases with increasing *n* up to 7, although showing the even–odd effect that has been observed in low molecular weight liquid crystals[17] and in liquid crystalline main-chain polymers.[18] The high values of T_{cl} in pCHMO-*n* (*n* = 1–4) may be attributable to high-density packing of the mesogenic groups, as has been observed in similar polymers with a relatively short spacer.[5,15] The decrease of T_{cl} with increasing *n* in pChMO-*n* ($n > 9$) is probably due to internal plasticization. The even–odd effect observed here is attributable to the conformation of the side chain: the angle of the long axis of the mesogenic cholesteryl group with the main chain is different in polymers having even or odd carbon numbers in the alkyl spacer group.[6,19] On the other hand, T_{cl} is almost constant in pChMO-*n* ($n > 7$) despite of the effect of internal plasticization by the increasingly long spacer. The diminution of the even–odd effect seems to be caused by a decrease in the difference of the cholesteryl angle with the main chain. The T_l in pChMO-*n* ($n \geq 9$) decreases with increasing *n*.

In Figure 3, the transition entropies at T_{cl} and T_l, determined on a second heating, are plotted against *n*. The

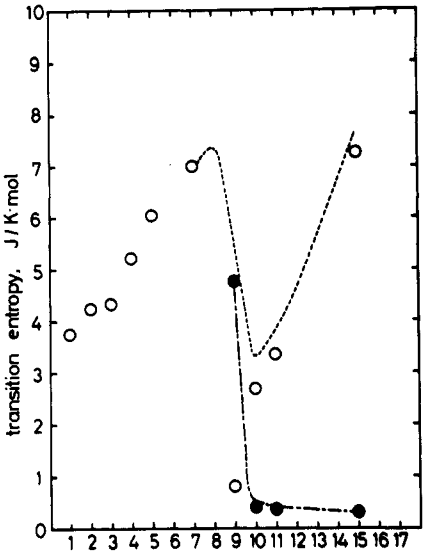


Figure 3. Plot of transition entropies against n: (○) at T_{cl}; (●) at T_1; (---) the total sum.

Table I
Interplanar Distances for the Series pChMO-*n* at 40 °C

sample	interplanar distances, Å						
	d_1	d_2	d_3	d_4	d_5	d_6	d_7
pChMO-1	43.0		21.5		14.4		
pChMO-2	44.7		22.3		14.9		
pChMO-3	46.0		23.0		15.3		
pChMO-4	48.3		24.2		16.1		
pChMO-5	51.7		25.9		17.2		
pChMO-7	53.3		26.6		17.8		
pChMO-9	54.4	31.7		20.7			
pChMO-10	54.9	33.4		21.5			
pChMO-11	52.8	35.1		22.3		17.6	
pChMO-15		41.1				20.6	13.6

transition entropy at T_{cl} increases with increasing n from 1 up to 7, but at $n = 7$ it drops precipitously and then increases again with increasing n from 9 to 15. On the other hand, the transition entropy at T_1 decreases sharply with increasing n from 9 to 10 and then decreases slightly with increasing n from 10 to 15. These results seems to indicate that the order of the orientation of the mesogenic groups increases with n up to 7 and that the order in the liquid crystalline phase between T_1 and T_{cl} increases with n from 9 to 15; according to Blumstein et al.,[18] the transition entropy is proportional to the orientational order parameter. Furthermore, the sum of the transition entropies drops precipitously at $n = 9$. The order of the entire system seems to become lower at $n =$ 9–11. The sharp change in the transition entropy at T_{cl} is probably due to a difference in arrangement of the mesogenic groups.

Figure 4 shows X-ray diffraction diagrams of pChMO-n obtained at 40 °C after cooling from T_{cl}, and Table I shows the interplanar distances of the corresponding reflections. In drawn samples, these reflection peaks are observed in the direction perpendicular to the fiber axis, suggesting that the side chains of pChMO-n orient perpendicularly to the main chain, which is parallel to the fiber axis. Similar results have been observed in other liquid crystalline side-chain polymers.[10,20,21] The sharpness of the diffraction peaks and the texture observed with the polarizing microscope suggest that the liquid crystalline phase of pChMO-n is smectic.

For pChMO-n having short spacers (n = 1–7), the reflections corresponding to d_1, d_3, and d_5 were observed up to T_{cl}, and the distance d_1 changed very little on the first cooling and on subsequent heating. The intensity of the reflections decreases with increasing scattering angle, and the reflections have the same angle intervals in each sample. These facts indicate that d_3 and d_5 are respectively the second- and third-order reflections of d_1. The intensities of d_3 and d_5 increase with n up to 7. It is considered that the order of the orientation of the mesogenic groups becomes higher with increasing n, which supports the results on transition entropy. Thus increasing the length of the flexible spacer contributes to a decoupling of the motion of the mesogenic group with the main chain, and increasing the spacer length enables the mesogenic groups to orient more easily.

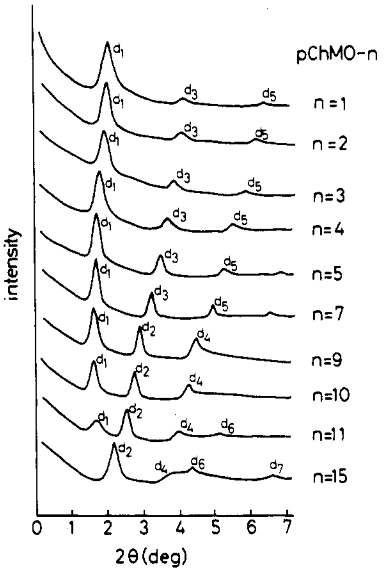


Figure 4. X-ray diffraction diagrams for the series of pChMO-n at 40 °C.

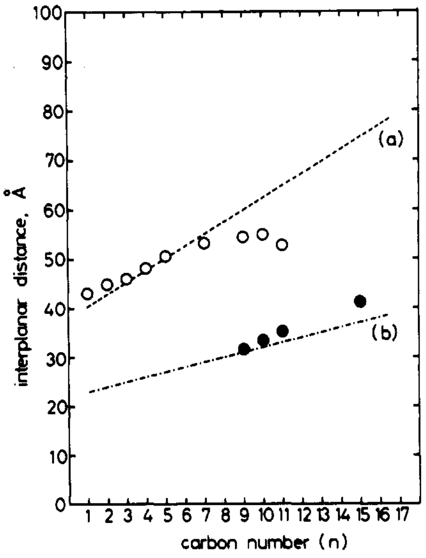


Figure 5. Plot of interplanar distances against n for the series of pChMO-n: (○) d_1; (●) d_2; (---) (a) double the calculated value of the side chain; (–-–) (b) the calculated one.

For pChMO-n with longer spacers (n = 9–11), the reflections corresponding to d_1, d_2, and d_4 were observed. The d_1 reflection, which became broader and weaker with increasing n, disappeared at T_1 on heating and reappeared at T_1 on cooling. In contrast, the d_2 reflection was observed from below T_g and T_{cl} on both heating and cooling.

For pChMO-15, the reflections corresponding to d_2, d_4, d_6, and d_7 were observed. These reflections were retained

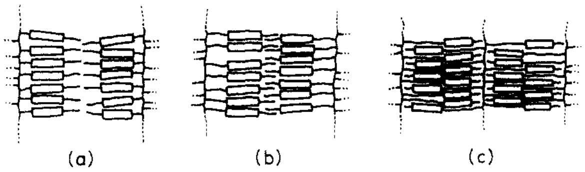


Figure 6. Schematic illustrations of the packing structures of the side chain: (a) two-layer packing structure (pChMO-*n*, *n* = 1–7); (b) partial overlapped two-layer packing structure (pChMO-*n*, *n* = 9–11); (c) single-layer packing structure (pChMO-*n*, *n* = 9–15).

to T_{cl}, except for d_4, which disappeared at T_1. The d_6 and d_7 reflections seem to be the second- and third-order reflections of d_2, respectively.

In Figure 5, the interplanar distances d_1 and d_2 obtained below T_g are plotted against *n*, where the dotted line (a) and the dashed line (b) indicate respectively double the calculated value of the length of the side chain and the calculated value. The values of d_1 for pChMO-*n* (*n* = 1–7) agree well with double the calculated values. For pChMO-*n* (*n* = 9–11), d_1 becomes smaller than double the calculated value with increasing *n*. On the other hand, the values of d_2 for pChMO-*n* (*n* = 9–15) agree approximately with the calculated values.

Schematic representations of the packing structure of side chains, which are based on d_1, d_2, and d_4 and on the suggestion of Shibaev et al.,[10] are shown in Figure 6. The side chains, including the cholesteryl groups, seem to organize into lamellae, and their three-dimensional structure looks like the lamellate structure proposed by Zugenmaier for other side-chain polymers.[14] In pChMO-*n* (*n* = 1–7), the interplanar distance d_1 indicates that the relatively short spacer does not allow overlapping of the side chains containing cholesteryl groups. Therefore, pChMO-*n* (*n* = 1–7) seems to have a two-layer packing structure of the side mesogenic groups (Figure 6a). This structure was retained to T_{cl}. On the other hand, in pChMO-15 the mesogenic groups are in an overlapping single-layer packing structure, in which the cholesteryl groups of one polymer are surrounded by the spacer methylene chains of neighboring polymers (Figure 6c). Considering the value of the transition entropy at T_{cl} and the reflection peak d_2 with its second- and third-order reflections, this structure of pChMO-15 seems to have high order. This structure was also retained to T_{cl}. In pChMO-*n* (*n* = 9–11), the reflections corresponding to d_1 and d_2, which indicate the two-layer and single-layer packing structures, respectively, coexist below T_1 on both heating and cooling. The interplanar distance d_1 is shorter than double the calculated value for the side chain, probably because of partial overlapping of the side chains or tilting of the side chain against the main chain. In these polymers, tails of cholesteryl groups of neighboring polymers seem to overlap partially (Figure 6b) owing to high mobility of the side chains; the reflection corresponding to d_4 is attributable to this overlapping. On the other hand, the reflection corresponding to d_1 disappeared at T_1, and only d_2 with its second-order reflection was observed above T_1. Thus in pChMO-*n* (*n* = 9–11), two different packing structures coexist below T_1, and only the single-layer structure exists in the temperature range between T_1 and T_{cl}. Therefore, the transition of T_1 can be attributed at a transition from the two-layer packing structure (Figure 6b) to a single-layer packing or to the isotropic state. The latter explanation seems more likely because (1) there was no change in the intensity of the d_2 reflection of pChMO-*n* (*n* = 9–11) around T_1 on both heating and cooling and (2) the optical anisotropy of pChMO-9 under the polarizing microscope decreased above T_1. Furthermore, on comparison of the transition entropies at T_1 and T_{cl} of pChMO-*n* (*n* = 9–11) with those of pChMO-*n* (*n* ≥ 10), it appears that the two-layer packing structure scarcely exists or it has a low order of orientation. Further investigations are needed on the transition at T_1 and on the coexistence of the two different structures. However, it is clear that the two-layer packing structure predominates over the single-layer one in pChMO-9 and that the single-layer structure becomes predominant in pChMO-10,11. Furthermore, for the single-layer packing structure in pChMO-*n* (*n* = 9–15), it appears that increasing the spacer length facilitates the orientation of the side chains.

Conclusion

The packing structure of the side-chain mesogenic groups of pChMO-*n* with short spacers is different from that of pChMO-*n* with longer spacers. The boundary of the structural difference is around pChMO-9. The coexistence of two different packing structures of the mesogenic groups was observed in pChMO-*n* (*n* = 9–11). If the coexistence of two different packing structures is observed for other side-chain polymers, new criteria will be needed for identifying the liquid crystalline phase of side-chain polymers.

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Registry No. pCHMO-1, 111801-88-8; pCHMO-2, 111825-75-3; pCHMO-3, 108491-29-8; pCHMO-4, 111801-89-9; pCHMO-5, 77222-09-4; pCHMO-7, 111801-91-3; pCHMO-9, 111801-93-5; pCHMO-10, 53880-96-9; pCHMO-11, 111801-95-7; pCHMO-15, 111801-97-9.

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