

## Phase transition and the packing structure of the side mesogenic groups of liquid crystalline side-chain copolymers

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### Summary

Copolymers consisting of cholesteryl 11-methacryloyloxyundecanoate (ChMO-10) and *t*-butyl methacrylate (*t*-BMA) were studied by DSC method and by small angle X-ray scattering method (SAXS). Although homopolymer (pChMO-10) has two different packing structures which are a single-layer packing structure and a two-layer packing one, copolymers (co-pChMO-10-*t*-BMA) have only the single layer packing one in their mesophase. Furthermore, transition entropy at a clearing point of co-pChMO-10-*t*-BMA (80/20) is larger than that of pChMO-10. Adequate distance of the mesogenic groups in the direction of a short axis of the mesogenic groups, produced by introduction of non-mesogenic units, seems to stabilize the single-layer packing structure.

### Introduction

Liquid crystalline side-chain polymers exhibit several kinds of liquid crystalline phases by adequate length of the spacer(1). Also, adequate lateral distance of side mesogenic groups, produced by introduction of the non-mesogenic units as comonomer to the liquid crystalline side-chain polymers, probably enables the polymer to exhibit several mesophases. However, liquid crystallinity of the polymers decreases with increasing molar fraction of the non-mesogenic co-monomer in general(2-4).

Liquid crystalline side-chain polymers seem to have much possibility of industrial applications. Recently, many workers take interest in not only liquid crystallinity of the polymers but high function of them. Mesogenic and/or non-mesogenic high functional groups have been introduced as guest particles or as co-monomers to the polymer matrices(5). Much introduction of such functional groups, however, seems to have an adverse effect on the orientation of the side mesogenic groups. In particular, bulky non-mesogenic units as comonomer seem to strongly disturb the orientation of the mesogenic groups.

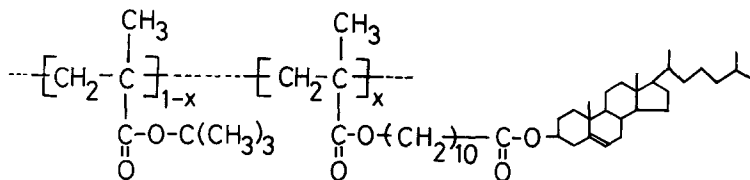
In the present work, the copolymers consisting of cholesteryl 11-methacryloyloxyundecanoate (ChMO-10) as mesogenic monomer and *t*-butyl methacrylate (*t*-BMA) as non-mesogenic groups were prepared. The copolymer, co-pChMO-10-*t*-BMA, was studied by DSC method and by small angle X-ray scattering method (SAXS) to clarify the effect of

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bulky non-mesogenic comonomer on the orientation of the mesogenic groups.

### Experimental

The general structure of co-pChMO-10-t-BMA is



co-pChMO-10-t-BMA

where  $x$  is molar fraction(%) of ChMO-10 as mesogenic unit; i.e. the polymer of  $x=100$  is a homopolymer, pChMO-10. The mesogenic monomer (ChMO-10) was prepared as described elsewhere (5). For the non-mesogenic monomer, the commercial material was used after the vacuum distillation. Copolymers were polymerized by free radical polymerization and precipitated several times from the benzene solution by dilution. The molar fraction of ChMO-10 in the copolymers was determined by  $^1\text{H-NMR}$  method(4). Degrees of polymerization, estimated by GPC method, were listed in Table 1.

The thermal analysis were made on DSC(Perkin-Elmer DSC-1B). The scanning speed was  $20^\circ\text{C}/\text{min}$ . The X-ray investigations were performed with a  $6\pi$  point-focusing small-angle scattering camera (at the High-Intensity X-ray Laboratory, Kyoto University) with Ni-filtered  $\text{CuK}\alpha$  radiation. The layer spacings were measured on powder samples in a vacuum chamber equipped with a heating stage.

### Results and Discussion

Phase transition temperatures and transition entropies obtained by DSC method were listed in Table 1. Homopolymer (pChMO-10) and copolymers(80/20) and (60/40) exhibit smectic A phase(7). The clearing point decreases with decreasing the molar fraction of ChMO-10. The transition point ( $T_1$ ) observed for pChMO-10 was not observed for the copolymers. For co-pChMO-10-t-BMA (40/60) and (20/80), the liquid crystalline phase was not observed. The melting point of the copolymer increases with increasing the fraction of non-mesogenic units, and the transition entropy at the melting point increases also with increasing the fraction of t-BMA. These results support the assumption that the crystalline phase of the pChMO-n is partial crystal of the alkyl spacer and/or the main chain(7). On the other hand, comparing the transition entropy at the clearing point( $\Delta S_{C1}$ ) with regard to the molar fraction of ChMO-10,  $\Delta S_{C1}$  of the copolymer(80/20) is the largest among the polymers.

X-ray diffraction diagrams of pChMO-10, copolymer(80/20), and copolymer (60/40) were shown in Figure 1, 2, and 3, respectively. As is shown in Fig. 1, a  $d_1$  reflection peak

Table. 1  
Phase transition temperatures and the transition entropies  
of pChMO-10 and pChMO-10-*t*-BMA.

	Fr*	M <sub>w</sub>	T <sub>m</sub>	T <sub>g</sub>	T <sub>1</sub>	T <sub>c1</sub>	ΔS <sub>m</sub>	ΔS <sub>c1</sub>
	(%)	(x10 <sup>4</sup> )	(°C)	(°C)	(°C)	(°C)	(x10 <sup>-3</sup> J/g K)	
pChMO-10	100	5.9	62**	48	113	157	13.8	4.28
copolymers <sup>†</sup>								
(80/20)	81.7	11.3	74	--	--	141	22.1	6.88
(60/40)	59.6	7.6	77	--	--	112	22.4	6.14
(40/60)	39.6	5.8	80***	--	--	--	--	--
(20/80)	20.3	5.3	100***	--	--	--	--	--

<sup>†</sup> co-pChMO-10-*t*-BMA, \* Molar fraction of ChMO-10 estimated by <sup>1</sup>H-NMR; \*\* Observed only on the 1st heating run; \*\*\* a peak on DSC curve is too broad to calculate exactly.

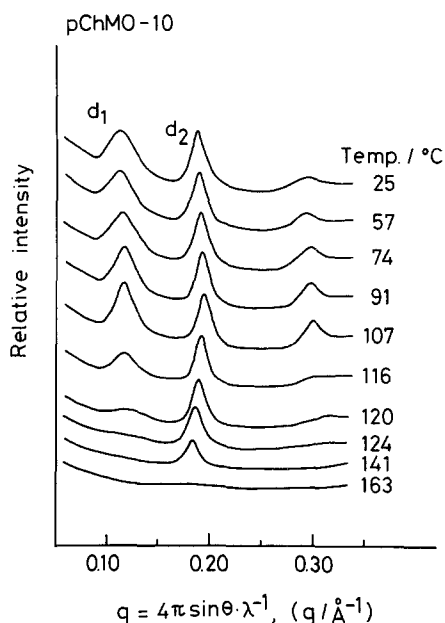


Fig. 1. X-ray diffraction diagrams on the 2nd heating run for pChMO-10.

attributable to a two-layer packing structure and a d<sub>2</sub> reflection peak attributable to a single-layer packing structure are observed in pChMO-10(8). Although the d<sub>1</sub> reflection disappears at T<sub>1</sub>, the d<sub>2</sub> reflection was retained up to T<sub>c1</sub>. On the other hand, as shown in Fig. 2 and Fig. 3, d<sub>1</sub> reflection peak is not observed for the copolymers (80/20) and (60/40), but only d<sub>2</sub> reflection peak with its second order one

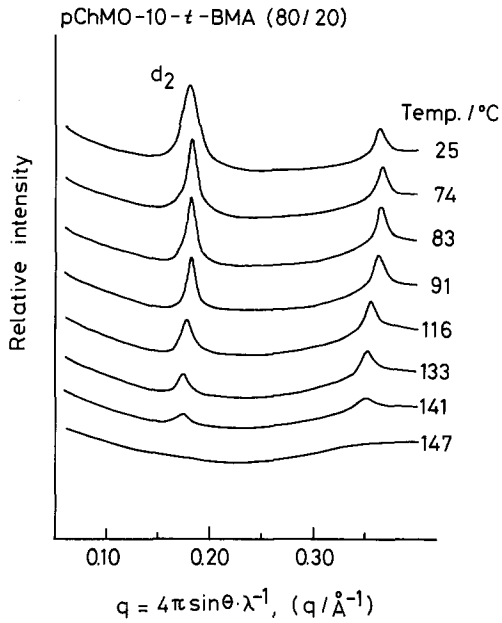


Fig. 2. X-ray diffraction diagrams on the 2nd heating run for copolymer(80/20).

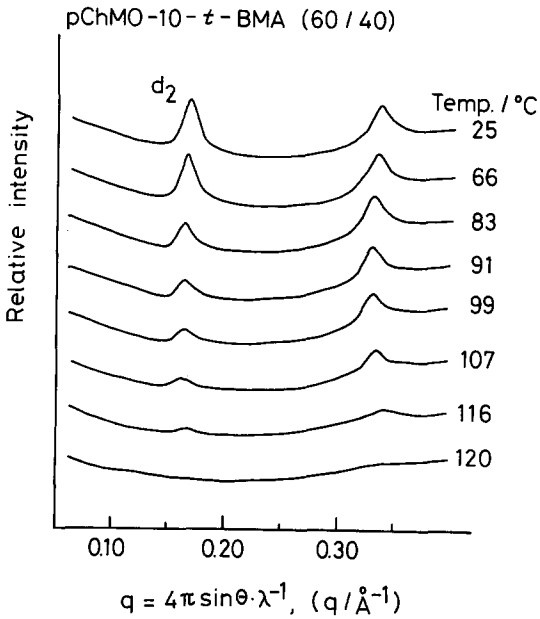


Fig. 3. X-ray diffraction diagrams on the 2nd heating run for copolymer(60/40).

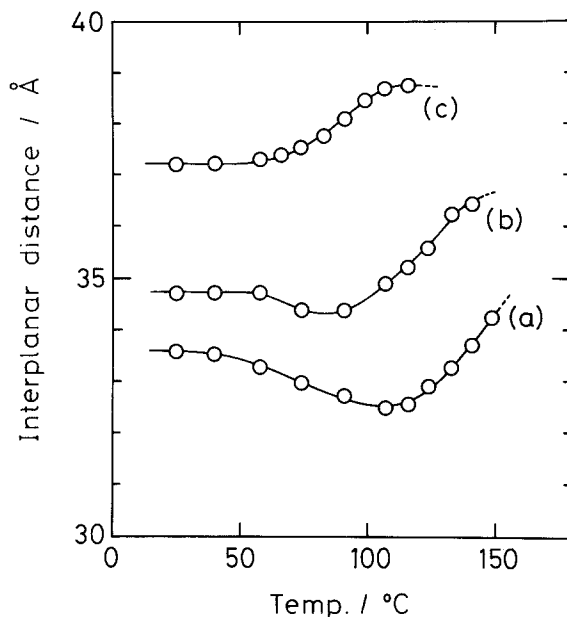


Fig. 4. Plots of layer spacing( $d_2$ ) against temperature on the 2nd heating run for; (a) pChMO-10, (b) copolymer (80/20), (c) copolymer (60/40).

is recognized. These results indicate that the copolymers do not have the two-layer packing structure in their smectic phase. Furthermore, the shape of the  $d_2$  reflection of copolymer (80/20) is slightly sharper than that of pChMO-10. This fact suggests that introduction of the bulky groups seems to have an adverse effect on the formation of the two-layer packing structure. Distance of the mesogenic groups in the direction of the short axis of the mesogenic groups, produced by the introduction of adequate amount of such non-mesogenic groups, seems to favor the formation of the single-layer packing one.

Temperature dependence of layer spacing( $d_2$ ) for pChMO-10, copolymer (80/20), and copolymer (60/40) is shown in Figure 4. Increasing of the layer spacing( $d_2$ ) near  $T_{CI}$  for each polymers is due to disorder of the packing structure. In the whole temperature range, the layer-spacing( $d_2$ ) increases with decreasing the molar fraction of ChMO-10. In two-layer packing structure of pChMO-10, the cholesteryl groups of one polymer are surrounded by alkyl spacers of adjacent polymers(Fig. 5-a). In the single-layer packing structure of the copolymers, however, thermal motion of bulky *t*-butyl groups disturbs the tight packing of the side mesogenic groups(Fig. 5-b).

Recalling the comparison of the transition entropy at  $T_{CI}$  for these three liquid crystalline polymers, the order parameter of the copolymer (80/20) appears to be the largest among three polymers. However, considering the state just above isotropic transition point, it is difficult to compare the ordering of the side-chain orientation of the polymers.

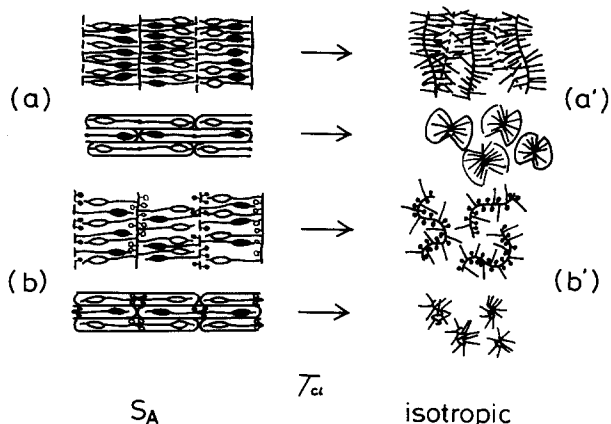


Fig. 5. Schematic illustrations of the single-layer packing structures for the homopolymer (pChMO-10) (a) and copolymers (b), and of the state just above  $T_{c1}$  for the homopolymer (a') and the copolymers (b').

In the case of homopolymer, dense attachment of the large mesogenic groups to the main chain disturbs the complete isotropic motion of the macromolecule just above  $T_{c1}$ . Non-liquid crystalline organization above  $T_{c1}$  of the liquid crystalline side-chain homopolymers having shorter spacers (pChMO-5) has been reported through rheological measurements elsewhere (9). In contrast to homopolymer, isotropicalization of the copolymer in which the large mesogenic groups sparsely attach to the main chain should occur smoothly (Fig. 5-b'). Therefore, difference of the transition entropy at  $T_{c1}$  between pChMO-10 and copolymers seems to arise from rather the difference of the state in the isotropic phase than that in the liquid crystalline phase.

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