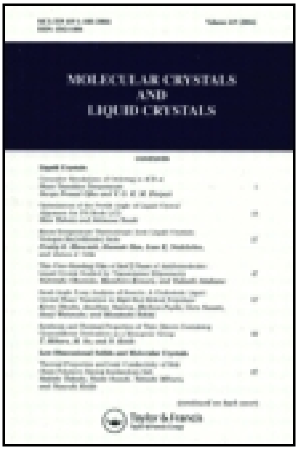

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Study on Phase Transition in Liquid Crystalline Side-Chain Polymers

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STUDY ON PHASE TRANSITION IN LIQUID CRYSTALLINE SIDE-CHAIN POLYMERS

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ABSTRACT Five series of copolymers of cholesteryl 11-methacryloyloxyalkanoate (ChMO-10) with non-mesogenic monomers (t-butyl methacrylate and n-alkyl methacrylates (carbon number n; n=1,4,12,18)) were studied by DSC method. In each copolymer, the clearing point (*T*cl) decreases gradually with decreasing the molar fraction of ChMO-10. The slope of the *T*cl curve becomes steeper with increasing the length of the non-mesogenic n-alkyl chain, but few difference is observed between the compounds with 12 and 18 carbon atoms of the non-mesogenic group. In the case of the copolymer with t-butyl methacrylate, the slope of the *T*cl curve is steeper than that of the copolymer with n-butyl methacrylate. Consequently, the *T*cl was affected by the effects of both the chain length and the bulkiness of non-mesogenic group.

INTRODUCTION

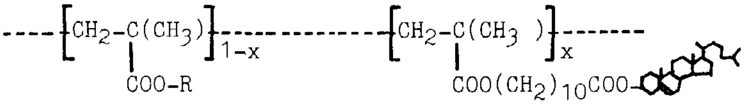
Some liquid crystalline side-chain homopolymers and copolymers were investigated by many other workers[1,2]. Shibaev et al. synthesized the copolymers of cholesteryl 12-methacryloylaminoalkanoate (ChAA-11) with n-alkyl methacrylates or with n-alkyl acrylates[3]. And, it was reported that clearing point (*T*cl) tended to decrease with decreasing the molar fraction of ChAA-11, and that the slope of *T*cl curve tended to be steeper with increasing the length of non-mesogenic n-alkyl chain.

In our previous work, homopolymers (pChMO-n) of cholesteryl ω-methacryloyloxyalkanoates (ChMO-n, carbon number n; n=1,2,3,4,5, 7,9,10,11 and 15) were studied. In these compounds, the *T*cl decreases with increasing n up to 7, accompanying the even-odd effect, but it shows almost constant in compounds having more than 7 carbon atoms4). In this work, the copolymers of ChMO-10 with non-mesogenic monomers (n-alkyl methacrylate, n=1,4,12 and 18, and t-butyl methacrylate) were studied by DSC method to get more detailed information about the effects of both the length and the molar fraction of non-mesogenic group on phase transition.

EXPERIMENTAL

Monomer (ChMO-10) was synthesized in our laboratory from cholesterol, 11-bromoundecanoic acid and methacrylic acid. Its preparation was described in our previous paper4).

The copolymer synthesized is shown in following scheme. Here, as non-mesogenic monomers, the commercial materials were used after the vacuum distillation.



$$\text{----}\left[CH_2-\underset{\displaystyle COO-R}{C}(CH_3)\right]_{1-x}\text{--------------}\left[CH_2-\underset{\displaystyle COO(CH_2)_{10}COO-}{C}(CH_3)\right]_{x}\text{-------}$$

where, R is alkyl group. The copolymers were abbreviated here as follows,

$R=C_nH_{2n+1}$

n=1, pChMO-10-MMA ; n=4, pChMO-10-BMA

n=12, pChMO-10-DDMA ; n=18, pChMO-10-ODMA

R=$(CH_3)_3C$, pChMO-10-t-BMA

The copolymers of ChMO-10 with the non-mesogenic monomers were prepared by free radical polymerizations. Polymerizations were carried out at 60°C in benzene in a sealed tube for 24 hr with azo-bis-isobutyronitrile as the initiator. In order to isolate and purify the polymer, the reaction mixture was poured into methanol. Purity of the copolymers was confirmed by disappearance of monomer's signal in ^{1}H-NMR spectra. The molar fraction of ChMO-10 in these copolymers was determined by comparing the integral value of spectra of ^{1}H-NMR signal of cholesteryl group with that of non-mesogenic n-alkyl chain. The ^{1}H-NMR spectrum of pChMO-10-t-BMA(molar fraction of ChMO-10 is 39.6%) as a typical spectrum of copolymer is shown in Fig. 1.

Thermal measurements were carried out by differential scanning calorimeter (Perkin Elmer DSC-1B). Polarized microscopy observations were made by using a Nikon XTP-11 microscope equipped with a heating stage system (Mettler FP-800).

RESULTS AND DISCUSSION

In Fig. 2, the glass transition points (Tg) and the Tcl of copolymers (pChMO-10-MMA, pChMO-10-BMA, pChMO-10-DDMA and pChMO-10-ODMA) were plotted against the molar fraction of ChMO-10.

The Tg of pChMO-10-DDMA and pChMO-10-ODMA could not be observed in the temperature range in these measurements, because the Tg are lower than about 20°C. On the other hand, the Tg of pChMO-10-MMA increases with decreasing the molar fraction of ChMO-10, while it decreases in the pChMO-10-BMA. Our results fit with the well known Gordon-Tayler's equation, which is shown as follows, for copolymer consisted of two components$^{5)}$.

$$Tg = w_1 Tg_1 + w_2 Tg_2$$

where, Tg is glass transition point of copolymer, Tg^1 and

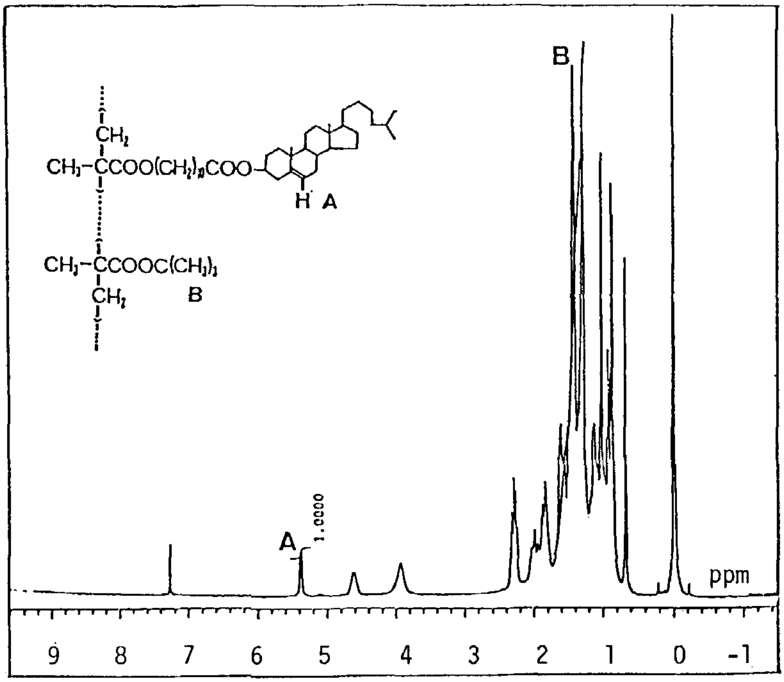


Fig. 1. The ^{1}H-NMR spectrum of pChMO-10-t-BMA(molar fraction of ChMO-10 is 39.6%).

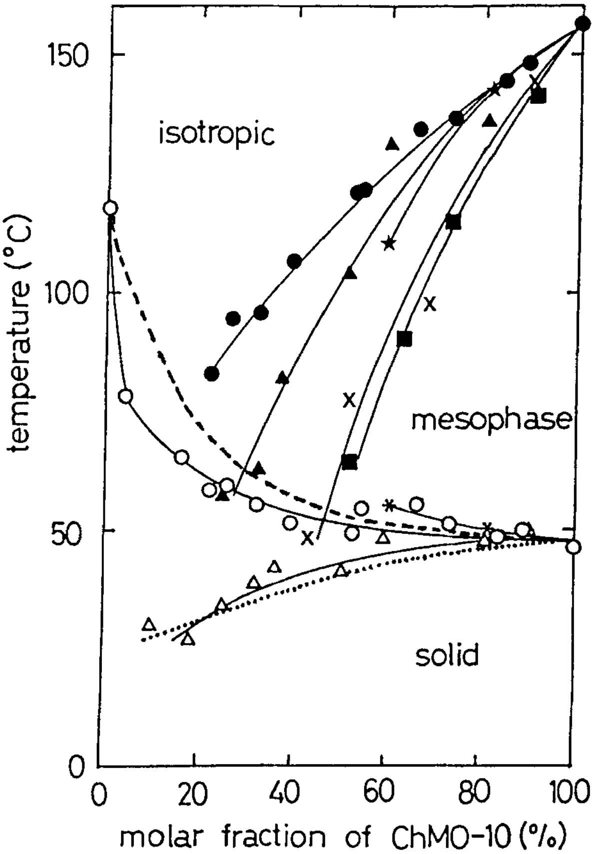


Fig. 2. Plot of transition temperatures against the molar fractions of ChMO-10 for the series of copolymers on heating. *T*cl; pChMO-10-MMA (●), pChMO-10-BMA (▲), pChMO-10-DDMA (X), pChMO-10-ODMA (■), pChMO-10-t-BMA (★), *T*g; pChMO-10-MMA (○), pChMO-10-BMA (△), pChMO-10-t-BMA (✱).
Theoretical curve for pChMO-10-MMA, – – – – – .
Theoretical curve for pChMO-10-BMA, …………… .

Tg_2 are the glass transition points of homopolymer of each component monomer in the copolymer, respectively. And w_1 and w_2 are weight fractions of each component in the copolymer, respectively. Change of flexibility could be suggested by the Tg measurements, and a decreasing of Tg means an increasing of the flexibility. A behavior of Tg shown in Fig. 2 indicates that the chains of pChMO-10-BMA are more flexible than those of pChMO-10-MMA.

The Tcl of these copolymers decreases with decreasing the molar fraction of ChMO-10. Similar results have reported for different systems3). The Tcl curve of pChMO-10-BMA against the molar fraction of ChMO-10 in this work is very similar to the result reported previously by Shibaev et al1). It is confirmed by the microscopic observations that the optical anisotropy of their liquid crystalline phase decreases with decreasing the molar fraction of ChMO-10. These decreasing will be explained by an effect of dilution. Here, the dilution means that the molar fraction of ChMO-10 as a mesogenic monomer unit decreases in the copolymer. This effect is more remarkable in the copolymers having long non-mesogenic n-alkyl chain. Then, with decreasing the molar fraction of ChMO-10, the liquid crystalline phases of pChMO-10-ODMA disappear at about 50% molar fraction of ChMO-10.

The slopes of the Tcl curves of these copolymers were steeper than those of copolymers of ChAA-11 with non-mesogenic monomers3). This difference may be explained considering that ester bonds of ChMO-10 are more flexible than amide bonds of ChAA-11.

The slope of the Tcl curve becomes steeper with increasing the carbon numbers of non-mesogenic n-alkyl chain of comonomer unit in the copolymer up to 12, and few difference is shown between pChMO-10-DDMA and pChMO-10-ODMA. This arises from also the dilution effect. Here, the dilution means that, a weight fraction of mesogenic group decreases with increasing of the length of the non-mesogenic n-alkyl chain in the copolymer having the same molar fraction of ChMO-10. The ratio of carbon number of octadecyl group to that of dodecyl one is 3/2, while the ratio of butyl group to methyl one is 4/1. Therefore, the dilution effect becomes weaker in the copolymers having longer non-mesogenic n-alkyl chain more than 12 carbon atoms.

In these copolymers, an existence of the non-mesogenic n-alkyl chain may disturb an arrangement of the mesogenic groups, because the mesogenic group and the non-mesogenic one overlap each other. That is to say, thermal motion of the non-mesogenic group disturb the arrangement of the mesogenic groups. It will be easily expected that the disturbance becomes larger with increasing the length of the non-mesogenic n-alkyl chain. On the other hand, from the result of the measurement of Tg, as mentioned above, the Tg of the copolymers decreases with increasing the length of the non-mesogenic n-alkyl chain(Fig. 2), and the flexibility of a main chain seems to increase with decreasing the Tg. The motion of the main chain also seems to disturb the alignment of side chains. Then, the increasing of flexibility of the main chain affects the formation of the liquid crystalline state.

Consequently, the slope of the Tcl curves becomes steeper with increasing the length of the non-mesogenic n-alkyl chain owing to the above effects. However, when the length of the non-mesogenic n-alkyl chain is longer than that of the flexible spacer, the large difference of the slope is not observed. One of the reasons is as follows. The motion of the short non-mesogenic n-alkyl groups affects the flexible spacer of ChMO-10 directly, to the contrary, the motion of the longer non-mesogenic n-alkyl ones does not affect the rod-like mesogenic groups much.

In Fig. 2, Tcl and Tg of pChMO-10-t-BMA are also plotted against the molar fraction of ChMO-10. Although the dilution effect in pChMO-10-t-BMA seems to be the same as that in pChMO-10-BMA, the slope of the Tcl curve of pChMO-10-t-BMA is steeper than that of pChMO-10-BMA. Furthermore, the copolymer containing about 50% molar fraction of ChMO-10 showed no liquid crystalline phase. On the other hand, while the Tg of pChMO-10-BMA decreases with decreasing the molar fraction of ChMO-10, the Tg of pChMO-10-t-BMA increases. Therefore, in this copolymer, the bulkiness of t-butyl groups considerably affected to the arrangement of mesogenic groups, though t-butyl groups decrease the flexibility of the polymer chains. Thus, it is considered that the effect of the bulkiness of non-mesogenic alkyl side chain is more predominant than the dilution effect and the flexibility of chains.

CONCLUSION

Phase transitions of the copolymers consisted of side chain mesogenic group and side chain non-mesogenic one were studied. The clearing points of these copolymers are much influenced by both the length and the bulkiness of the non-mesogenic group. In the copolymers having comparatively short n-alkyl non-mesogenic group, the clearing points are much affected by the small difference of chain length of the non-mesogenic group. On the other hand, in the copolymers having long n-alkyl non-mesogenic group, clearing points are less affected by the difference of the length of non-mesogenic group. Further, in the copolymer having bulky non-mesogenic group like t-butyl one, the Tcl curve against the molar fraction of ChMO-10 drops steeply, because the bulky group separates the distance between the mesogenic side chains and disturbs the arrangement of mesogenic one.

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