Thermal Optical Analysis of Cholesteryl Methacrylate and Butyl Methacrylate Copolymers

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ABSTRACT: As a side chain type of liquid crystalline polymer, the copolymers of cholesteryl methacrylate and butyl methacrylate were synthesized. When the mesomorphic behavior of the copolymers was examined with a polarized microscope, the observed transition temperatures were so much varied that the mesomorphic behavior had to be studied by thermal optical analysis (TOA). TOA curves with a single peak were obtained by a sandwich-type film prepared by interposing the casting solution between two cover glasses and drying sufficiently. The mesomorphic temperature region increased with increasing mole fraction of cholesteryl methacrylate (ChMA) in the copolymers. The appearing and clearing temperatures of birefringence shifted to the higher temperature side with increasing mole fraction. The effect of pretreatment of the cover glasses with trimethyl chlorosilane was examined. The relation between the maximum intensity of the TOA curve and the film thickness was studied for both films prepared with the treated and untreated glasses. The intensity remarkably increased with increasing film thickness for the treated glasses, but no such correlation was found for the untreated glasses. A sandwich cell was prepared by the same casting method of a TOA sample with tin coated glasses. The cell was heated up to the mesomorphic temperature under a dc field of 40 V. Although no electro-optical effect was observed in the first heating step, the apparent flow instability, similar to William's domain, appeared in the cooling step from the isotropic state. Small angle X-ray diffraction patterns were obtained for the samples of both cast and annealed films. A sharp peak at $2\theta = 2.5°$ corresponding to 35.5 Å of periodicity was observed only for annealed film.

KEY WORDS   Copolymers of Cholesteryl Methacrylate and Butyl Methacrylate / Mesophase / Thermal Optical Analysis / Electro-Optical Effects / Small Angle X-Ray Diffraction /

In recent years, it has been reported that polymers with cholesteryl moieties attached to main chains through long flexible spacers exhibit enantiotropic liquid crystalline behavior.[1-5] However, the mesomorphic order in polymers with side groups containing the cholesterol moiety attached directly to the main chain has received little attention.[6-11]

In this study, attention has been directly focussed on the phase transitions of cholesteryl methacrylate (ChMA) and butyl methacrylate (BMA) copolymers without a flexible spacer.

Blumstein *et al.*[12-15] prepared the copolymers of ChMA–BMA and found a sharp peak corresponding to 35.5 Å of periodicity in the small angle X-ray scattering (SAXS) of the solid copolymers. However, they made no examination as to the mesomorphic temperature region of the polymer at the molten state. One of the authors[16] has also reported the effects of copolymer composition on the mesomorphic behavior for the ChMA–methyl methacrylate (MMA) copolymer and found, using a polarized microscope, that the polymers had a thermotropic nature. In these observations, however, isotropic transition

temperatures were found to vary considerably and hardly obtained the constant values for the same sample. Consequently, an attempt was made to measure the transitional behavior of copolymers by thermal optical analysis (TOA) to obtain reproducible results.

In this paper, TOA measurements were mainly carried out so as to investigate whether the mesomorphic range is influenced by the effects of intermolecular plasticity in ChMA–BMA copolymer compared with ChMA–MMA copolymers.[16,21]

Moreover, the data of the electro-optical effect and SAXS were also obtained for the copolymers.

EXPERIMENTAL

The materials and TOA measurements employed in this paper were reported in detail in a previous paper.[16]

Solution Polymerization

Following the method of Blumstein et al.,[15] copolymerization of ChMA–BMA was carried out in a benzene solution (the concentration of monomer; 0.1 mol l^{-1}) at 60°C with azobis-isobutyronitrile (AIBN) as the initiator (0.01 mol l^{-1}). The copolymers were precipitated in methanol. The remaining monomer was completely removed by ether extraction. The products were sufficiently dried at room temperature under vacuum. Copolymer composition was determined from the ^{1}H NMR spectra (JEOL, FT-100).

Molecular Weight of Copolymers

The number-average molecular weight (M_n) of the copolymers was determined by gel permeation chromatography with a Waters Associate GPC-200, under the following conditions: solvent, tetrahydrofuran (THF); polymer concentration, 0.02 w/v%; temperature, 40°C; column, polystyrene gel; standard materials, polystyrenes.

Electro-optical Effect of Copolymer

An experiment was carried out to confirm whether the copolymer behaves as a thermotropic liquid crystal during first cooling and the following steps. The slides coated by tin oxide were employed for a sandwich cell, and poly(tetrafluoroethylene) film (0.05 mm) was used as a spacer to fix the cell thickness. No orientation treatment was given for the surface.

The cell was heated in the heating device and the sample was viewed along the electric field direction. Visual observations were recorded by using a camera. All the photo micrographs were taken at a magnification of 50X.

RESULTS AND DISCUSSION

Table I shows the assignments of the peaks appearing in ^{1}H NMR spectra of ChMA, along with the peaks of cholesterol and the copolymers.

Identification and Properties of Copolymers

Copolymer obtained by solution polymerization at 60°C had M_n of 27,000 or 54,200, depending on the polymerization conditions, as shown in Table II. All the copolymers were soluble in benzene, chloroform and THF, but not in methanol, ether or acetone.

The composition of the copolymer was determined by the ratio of peak area appearing in the ^{1}H NMR at 0.70 ppm assigned to 18-CH$_3$ in the cholesterol group to that at 4.20 ppm assigned to the methylene group adjacent to the oxygen atom present in the BMA unit. The results obtained are listed in the column for copolymer composition in Table II.

### Phase Transition and TOA Curve

The TOA curves of the copolymers were obtained by cross-polarized microscopy for the sandwich film. All the cast films initially showed no birefringence at room temperature.

When the temperature was raised more than 80°C above T_g, birefringence appeared, getting

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Table I. ¹H NMR assignments of cholesterol,
ChMA, and poly(ChMA–BMA)

	Cholesterol[a]	ChMA[a]	Poly(ChMA–BMA)[b]
	ppm	ppm	ppm
18-CH$_3$	0.67	0.65	0.71
26,27-CH$_3$	0.87	0.86	0.89
21-CH$_3$	0.90	0.92	0.93
19-CH$_3$	1.00	0.96	1.03
III-CH$_3$	—	1.94	—
3-CH	3.49	4.70	—
6-CH	5.36	5.31	—
H$_a$	—	5.45	—
H$_b$	—	6.11	—
–O–CH$_2$–	—	—	4.20
–OH	2.07	—	—

[a] Measured at room temperature and [b] at 100°C, using
o-dichlorobenzene as a solvent.
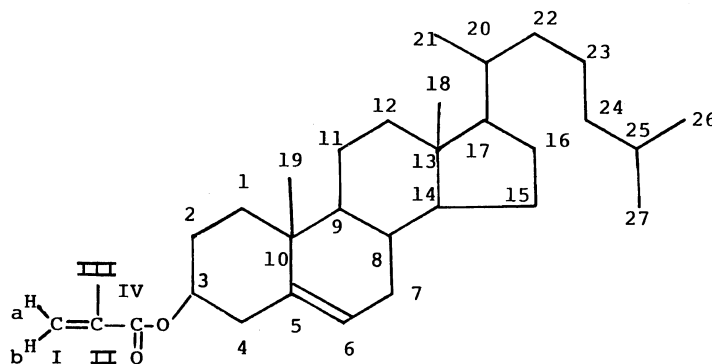
Table II. Solution copolymerization
of ChMA with BMA

Monomer feeds (mol fraction)		Composition (mol fraction)		Yields	M_n
ChMA	BMA	ChMA	BMA	%	
0.90	0.10	0.94	0.06	85:2	54,200
0.80	0.20	0.83	0.17	84.6	31,700
0.70	0.30	0.68	0.32	76.2	27,000
0.60	0.40	0.59	0.41	67.0	—
0.50	0.50	0.48	0.52	52.0	—

more distinct for the copolymers rich in
ChMA fraction.

The light intensity transmitted through the
sandwich film of copolymer containing
83 mol% of ChMA (ChMA : 83) increased

with temperature, and reached a maximum at
around 200°C, and then became weaker and
finally disappeared completely at about 260°C.
The copolymer was not fluid until 200°C, but
flowed readily above this temperature.

The birefringence at high temperature was
not clear for those with less than 60 mol%
ChMA. The higher the content of ChMA, the
more was mesomorphic behavior observed.
The TOA curve is shown in Figure 1 for
(ChMA : 0.94).

Figure 2 shows a phase diagram of the
copolymers obtained from the TOA curves. In
our experiments, the differential scanning calo-
rimetry (DSC) was used to obtain the glass
transition temperature (T_g), but no reproduc-
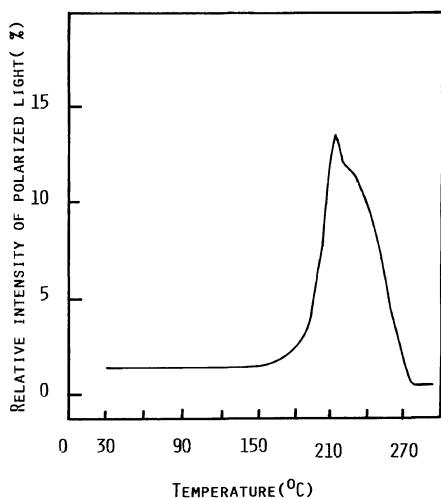ible data were obtained. Therefore, T_g data of

Figure 1. TOA curves for ChMA–BMA (0.94:0.06) copolymer film (sandwich type).
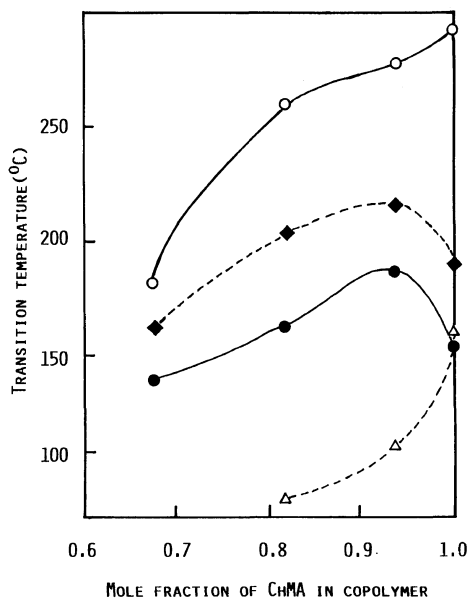

MOLE FRACTION OF ChMA IN COPOLYMER

Figure 2. Phase diagram of ChMA–BMA copolymer obtained during first heating for sandwich-type film: △, T_g reported by Blumstein et al.[11]; ●, first appearance of birefringence; ■, maximum intensity of birefringence; ○, transition temperature from a mesophase to an isotropic liquid (clearing temperature).

Blumstein et al. are referred to in Figure 2, and agree with our unpublished T_g data obtained by gas chromatography. It became clear that the copolymers except homopolymer begin to show birefringence at temperatures 80°C higher than T_g. On the other hand, the birefringence of ChMA–MMA copolymers appeared almost at T_g. The transition temperature of ChMA–BMA copolymers to anisotropic phase might be due to the intermolecular plasticization effect of flexible alkyl chain in BMA components. In ChMA–MMA copolymer, the interaction between mesogens may be depressed by the rigidity of the main chain. If the molecular motion of the copolymer increases with temperatures above T_g, the mesogens may begin to interact with each other, and the birefringence may begin to appear. In ChMA–BMA copolymer, the interaction between the mesogens would not be appreciable due to the butyl group of the comonomer in the low temperature region, but their mutual interaction is effective in the temperature above T_g by thermal motion of the mesogen.

The copolymers were not fluid in the temperature range below the dotted line in Figure 2, but flowed readily above the dotted line.

The Intensity of Birefringence and Copolymer Composition

The relation between the intensity of birefringence and thickness of cast film was examined.

Since the molecular arrangement in the cast film may possibly be effected by the presence of silanol on the glass surface, two kinds of glass plates were used for these experiments. One was treated with vapor of trichloroethylene to remove fatty contaminations (untreated glass), and the other was treated similarly and then with trimethylchlorosilane to remove the silanol (treated glass). Figure 3 shows the relation between the intensity of birefringence at room temperature and the thickness of the cast film in the first heating step of the TOA. These figures also show that the intensity increases apparently with increasing thickness of the films for both glasses.
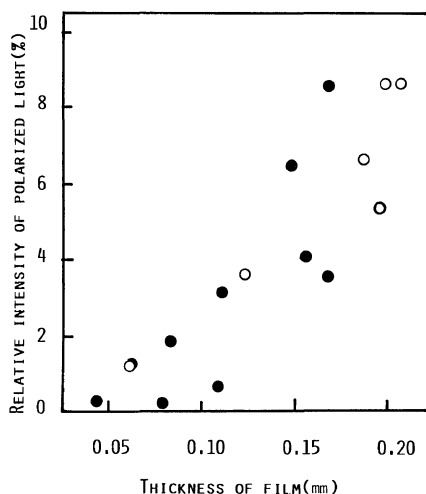
Figure 3. Relation between intensity of birefringence and film thickness of ChMA–BMA (0.82 : 0.18) copolymer at room temperature for sandwich-type film: ○, untreated glass; ●, treated glass with trimethylchlorosilane.

Figure 5. Hystereses in TOA curve for ChMA–BMA (0.94 : 0.06) copolymer during different scanning runs for sandwich-type film: ——, first heating; ------, first cooling; — - —, second heating.

with increasing ChMA content, as expected.

Hysteresis in TOA Curves

The hysteresis of TOA curves at different scanning steps were observed, and the results are illustrated in Figure 5.

When the copolymer of ChMA : 68 was cooled below the isotropic state, the birefringence appeared again at about 50°C below the isotropic temperature, and its intensity increased with lowering temperature, and then remained constant until room temperature. The TOA curve obtained in the second heating steps coincided with that of the first cooling steps as shown in Figure 5. This figure shows that the isotropic temperature during the second heating steps are evidently depressed to lower temperatures than that of the first heating step, and the TOA peak observed during the first heating step did not appear any more. It is considered that the molecular arrangement in the original cast film differs considerably from that of the annealed film.
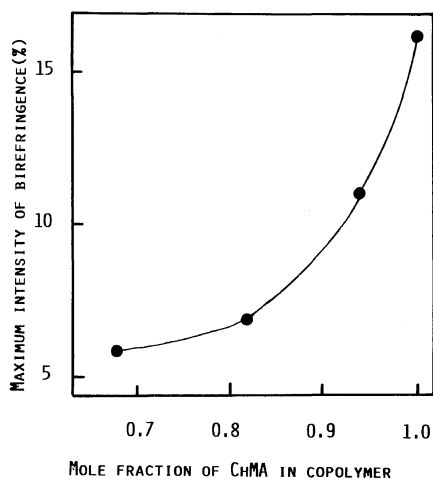
Figure 4. Relation between maximum intensity of birefringence and fraction of ChMA in copolymers during first heating: (sandwich-type film).

It is also certain that this tendency is not caused by silanol, because the samples using both glasses behaved similarly as shown in Figure 3.

Figure 4 shows the relation between the maximum intensity and the fraction of ChMA. It is evident that the light intensity increases
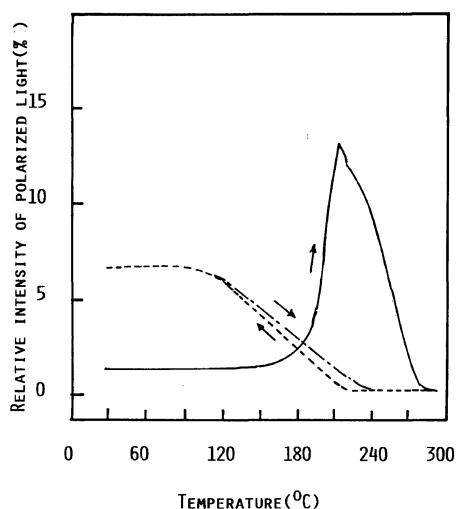
M_n of Annealed Copolymer

Since it is well known that methacrylic

polymers generally have low ceiling temperatures, the unzippering reaction of the monomer may be caused in these copolymers at the higher temperatures. The TOA peak observed during the first heating step might be caused by a complex mixture of polymer plasticized with the degradation products. Therefore, in order to confirm this possibility, GPC, IR and ^{1}H NMR spectra were measured for the annealed copolymers which were treated at 260°C for 30 min in N_2 atmosphere. IR and ^{1}H NMR spectra of the annealed sample did not change from those of the original samples. M_n of the annealed copolymer was determined again from GPC data. The results showed that both M_n of annealed and original samples agreed with each other. It is clear that unzippering of the monomer does not take place in this temperature region.

When an annealed copolymer was cast again, the film showed the same TOA peak observed during the first heating step. It is thus confirmed that the birefringence observed during the first heating step has not been caused by the degradation products but molecular rearrangement in the cast film.

X-Ray Diffraction

Blumstein *et al.*[11,14] prepared similar copolymers, and examined the solid copolymers by the SAXS. Sharp peaks were found at $2\theta = 2.5°$, corresponding to 35.5 Å of the periodicity.

In this study, the films cast and those annealed at temperatures in the mesomorphic state were examined by the SAXS to confirm the frozen mesomorphic order. The peak at $2\theta = 2.5°$ was only obtained for annealed sample containing high concentration of ChMA.

It was demonstrated that the copolymer had a smectic layer structure with the periodicity of 35.5 Å by annealing, and it may be considered that the smectic structure found by Blumstein *et al.*[17] corresponds to the frozen structure in the annealed film.

Effects of Casting Solvent on Phase Transition

The copolymers were cast into the sandwich films using benzene, chloroform and carbon tetrachloride as casting solvents. The copolymers were easily dissolved in benzene and chloroform but not in carbon tetrachloride at room temperature although it does at 55°C with difficulty.

The extent of copolymer–solvent interaction was comparable to the weight fraction activity coefficient at infinite dilution of the solvent, as determined by gas-liquid chromatography. It was concluded from specific retention volume in infinite dilution that the extent of interaction increased with the following order: carbon tetrachloride, chloroform, and benzene. The TOA curve of the film cast from chloroform agreed with that from benzene solution. The film cast from a poor solvent as carbon tetrachloride showed a wide mesomorphic temperature range as evident from a comparison of Figure 2 with Figure 6.

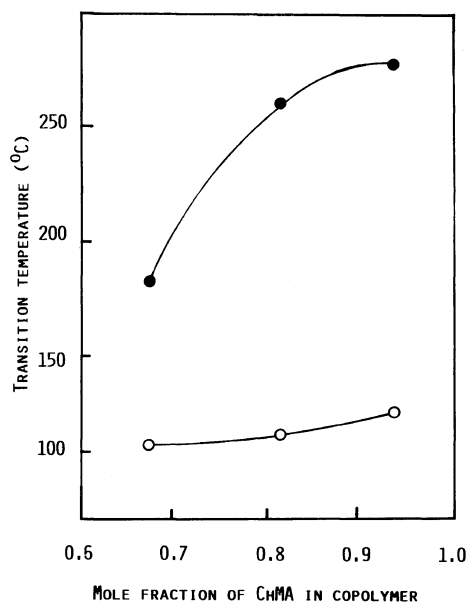Shibaev *et al.*[19] studied intermolecular motion in a dilute solution of a thermotropic

Figure 6. Phase diagram of ChMA–BMA copolymer using cast film from solution in CCl_4: ○, appearance of birefringence; ●, clearing temperature.

liquid crystalline polymer, such as cholesterol ester of poly(*N*-acryloylaminocarbonic acid) using the polarized fluorescence method. They concluded that intermolecular motion of polymer is weakened as polymer solvent interaction becomes weaker, and that the film cast from a good solvent shows no anisotropic structure, and that the film cast from a poor solvent shows anisotropic structure according to X-ray diffraction method.

On the bases of our results of the TOA, the film cast from even a poor solvent also showed no anisotropic behavior at room temperature. However the mesomorphic range obtained from poor solvent is very wide, indicating that the mesophase may possibly be more stable thermodynamically, and the polymer is more easily arranged in a liquid crystalline order.

Electro-optical Effects of Copolymer

The sandwich cell was prepared for these experiments by casting over tin oxide coated glasses in a similar manner as the TOA sample. The cell was heated to mesomorphic temperature in the heating device under a dc field of 40V. Although the birefringence due to the mesomorphic state appeared, no electro-optical effect was observed. When the temperature was lowered from the isotropic state, or when an annealed sample was heated again to the temperature of the mesomorphic state, only short rodlike segments became visible in 2 min, and continued to develop for 30 min. Then the pattern shown in Figure 7 was observed at voltages higher than 40V. It resembles quite well William's domains of the nematic copolymers reported by Krigbaum et al.[20]

The formation time for this pattern to appear was shortened with voltage. Then the pattern collapsed and dynamic scattering was observed at voltages higher than 50V. From these experiments, it is not clear whether the mesomorphic state of the polymer corresponds to a nematic phase, because a typical nematic texture was not observed with the TOA, although the William's domain like pattern was

Figure 7. Photomicrograph (original magnification 50X) of Williams domains formed after 30 min in a copolymer of ChMA–BMA (0.83 : 0.17) at 155°C (40 V dc).

observed. This flow instability shows apparently the existence of mesomorphic state in the temperature range below isotropization.

In the past few years, many papers have been published on the liquid crystalline structures in polymeric systems without a detailed description of the methods of sample preparation. This study demonstrates that the mesomorphic behavior of the copolymers were remarkably affected by the conditions of sample preparations such as thermal history of the copolymers and thickness of the cast film, but not by the surface state of glass used.

Finkelmann et al.[3,5] have pointed out that the presence of a flexible spacer between the main chain and pendant mesogenic group is necessary for an enantiotropic thermal transition for side chain type of polymers, considering that the flexible spacer may decouple the molecular motion of the main chain from the pendant group, and hence the mesogenic side group is favored by a liquid crystalline order.

In this study, TOA curves obtained during the first heating step were quite different from other steps. Consequently, the copolymers are apparently not typical enantiotropic liquid crystalline polymers. Our results support the idea of Finkelmann et al. mentioned above for the direct coupling liquid crystalline polymer. However, the monotropic property disappears

by annealing.

If the coagulative interaction between mesogens is superior to the thermal motion of the main chain, the copolymers may exhibit the mesomorphic phase observed at the following steps even in the first heating steps. Accordingly, it may be reasonable to consider that the copolymer is an enantiotropic liquid crystalline polymer in a broad sense.

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