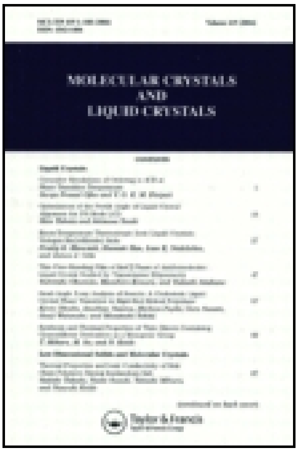

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Dynamic Viscoelastic Behavior of Smectic Liquid Crystalline Side-Chain Polymers

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Dynamic Viscoelastic Behavior of Smectic Liquid Crystalline Side-Chain Polymers

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A series of cholesterol-containing liquid crystalline side-chain polymers (pChMO-n, n = 5 and 11, the carbon number of the side alkyl chain) and a butoxybiphenyl containing liquid crystalline side-chain polymer (pBBMO-n, n = 6) have been prepared. The dynamic viscoelastic properties of these liquid crystalline polymers in the smectic A and isotropic phases were investigated with parallel-plate simple shear geometry. The slope of G′ against frequency in the smectic A phase is relatively small due to the influence of the smectic structure of the side chains. In the isotropic phase, the slope of G′ curves for these polymers is smaller than that in the flow region observed on isotropic amorphous polymers. Furthermore, the G′ curve for these three polymers in the isotropic phase has various slopes. This difference in the slope in the isotropic phase is accounted for by the difference in the molecular structure such as length of the side flexible spacer and the type of mesogenic groups.

Keywords: liquid crystalline side-chain polymer, dynamic viscoelastic properties, smectic A Phase, isotropic transition, elasticity, molecular organization

INTRODUCTION

Thermotropic liquid crystalline polymers should possess fluidity and optical anisotropy in their mesophases. For evaluating the liquid crystallinity of the liquid crystalline polymers, measurements of the rheological properties are indispensable as well as those of optical properties. The rheological measurements of many conventional polymers have provided valuable information for industrial application of the polymers. Such valuable information should be obtained also for the liquid crystalline polymers which are expected to be used as materials with high performance and function.

In this decade, many rheological measurements on thermotropic liquid crystalline main-chain polymers, in particular viscosity measurements, have been reported,[1,2] because of their importance in practical application. The striking rheological phenomena of these polymers are the following:

1) The "three-region flow curve," which is proposed as a characteristic of liquid crystals,[3] has also been observed in the nematic phases.[4]

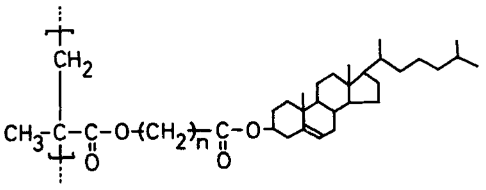
2) the viscosity of the nematic phase of these polymers is considerably smaller than that of the isotropic phase.[5,6]

For liquid crystalline side-chain polymers, however, despite high interest due to their unique molecular structure, information on their rheological properties is limited; only melt viscosities[7] and viscosity of solution of such polymers[8,9] have been reported. In our previous work, temperature dependence of Young's moduli (E′ and E″) near the glass transition point, and temperature dependence of shear storage modulus (G′) for cholesterol-containing smectic side chain polymers have been discussed.[10,11] In the present study, we carried out dynamic viscoelastic measurements of two cholesterol-containing side-chain polymers, and a butoxy biphenyl-containing side-chain polymers as a function of frequency and temperature in the isotropic and smectic A phases. In particular, great attention was given to the viscoelastic behavior at the transition point from the smectic A phase to the isotropic one. It seems that the results of such measurements enable us to understand the difference in mobility of the macromolecules due to the difference in the molecular structure, and also the transition mechanism of the smectic side-chain polymers.

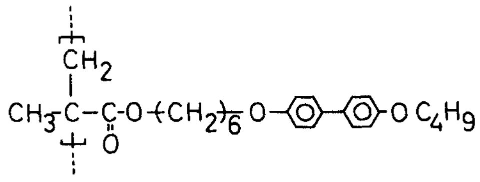
EXPERIMENTAL

Materials

The cholesterol containing polymers used here were two poly(cholesteryl ω-(methacryloyloxyl)alkanoates) (pChMO-n, *n* representing the carbon number of the alkyl spacer of the side-chain, *n* = 5, 11). The synthesis[12] and the results[13] of DSC measurement and small angle X-ray investigations have been described. The butoxy biphenyl containing polymer is poly(botoxybiphenyloxy ω-(methacryloyloxy)hexane) (pBBMO-n, *n* = 6). The results of DSC and the dielectric measurements have been reported.[14] The general structures of pChMO-n and pBBMO-n are as follows:



pChMO-n, n = 5, 11



pBBMO-6

Thermal Analyses

The thermal analyses were made on DSC (Perkin Elmer DSC-7) using Ga (99.9999%) for low temperatures, and In (99.9999%) for high temperatures as calibration substances. The scanning speed was 20°C/min. The DSC curve on the second heating run was used for all discussions.

Dynamic Viscoelastic Measurements

All of the dynamic viscoelastic measurements were made on a Dynamic Rheospectra DVE-V4 (KU-0; Rheology Co. Ltd.) with parallel-plate simple shear geometry. Usually, rheological measurement at high frequency range (10^2–10^3 Hz) is very difficult due to dominance of negative factor, for example, inertia term due to the plate and/or sample. The present apparatus (DVE-V4) has been developed to measure the dynamic viscoelasticity at high frequency (to 10^3 Hz). A sample cell is illustrated in Figure 1. A moving plate was inserted to the sample which was heated above the isotropic temperature. The strain amplitude ("x_0" in Figure 1) in this study is 0.5–10.0 μm. The temperature was controlled by PID with a heating stage. The storage (G′) and loss (G″) parts of the shear modulus were obtained in oscillatory shear over an angular frequency range of 0.628–6273.7 rad/sec and in a temperature range of −20–200°C. All measurements were carried out in an atmosphere of prepurified nitrogen to avoid thermal decomposition by the existence of oxygen.

RESULTS AND DISCUSSION

Phase Transition and Liquid Crystalline Phase

Phase transition temperatures of the polymers are listed in Table I. All of these polymers exhibit the smectic A phase, which has been confirmed by optical observation and by SAXS.[13,15] A two-layer packing structure, in which the short spacer does not allow overlapping of side-chains, was proposed for pChMO-5, and

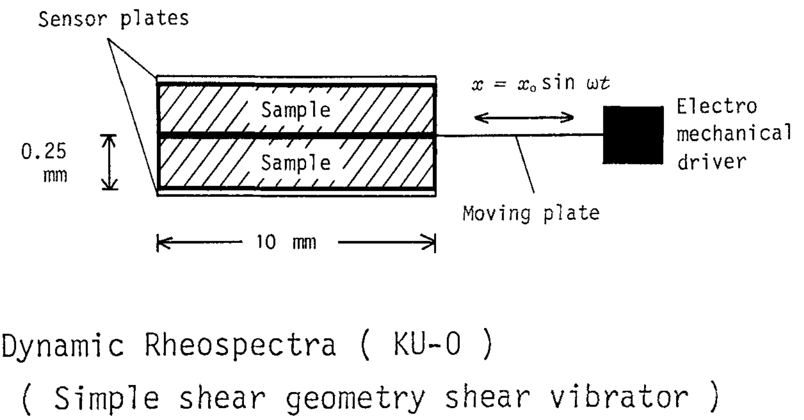


FIGURE 1 Schematic illustration of sample cell for dynamic viscoelastic measurement.

TABLE I

Thermal properties of the polymers

Polymer code	W_m	T_m (°C)	T_g (°C)	T_1 (°C)	T_{cl} (°C)	ΔS_{cl} (J / mol K)
pChMO-5	64000	63*	49	--	184	6.04
pChMO-11	58000	59*	43	105	151	3.35
pBBMO-6	67000	128	--	--	157	11.09

* Observed only on the first heating run.

pBBMO-6. Both the two-layer packing structure and an overlapping single-layer packing structure, in which the side-chains of one polymer overlap with those of neighboring polymers, were proposed for pChMO-11; in the smectic A phase of pChMO-11, the two different packing structures were simultaneously formed below T_1, and only the single-layer packing structure was formed in a temperature range from T_1 to T_{cl}. The coexistence of the two different packing structures have been discussed in detail elsewhere.[16] Thermal measurements and X-ray investigations have indicated that the single-layer packing structure predominates over the two-layer packing structure in pChMO-11. The two-layer packing structure below T_1 in pChMO-11 might be formed only near ends of a main chain, and be located in between the domains of the single-layer packing structure. X-ray investigations[16] have shown that the two-layer packing structure melts to the isotropic state at T_1.

Dynamic Viscoelastic Behavior

The moduli-frequency behavior of pChMO-5, pChMO-11, and pBBMO-6 at various temperatures above T_g are shown in Figures 2, 3 and 4, respectively.

In the smectic A phase (temperature range from T_g to T_{cl} determined by DSC), the slope of G′ against frequency is smaller than that of amorphous polymer melts,[17] and the values of G′ and G″ are close to each other. The values of G′ is higher than those of G″ at lower temperatures for pChMO-5 and pChMO-11; the storage modulus (G′) as an elastic term of pChMO-5 completely dominates the loss modulus (G″) at 120 and 140°C, and G′ of pChMO-11 is also higher than G″ at 90, 100 and 110°C. Such behavior of G′ of the two polymers well reflects the high ordered packing structure of the side-chains in the smectic phase.

Near and above T_{cl}, the rheological properties of pChMO-5 is different from those of pChMO-11, although the transition behavior of the two polymers with

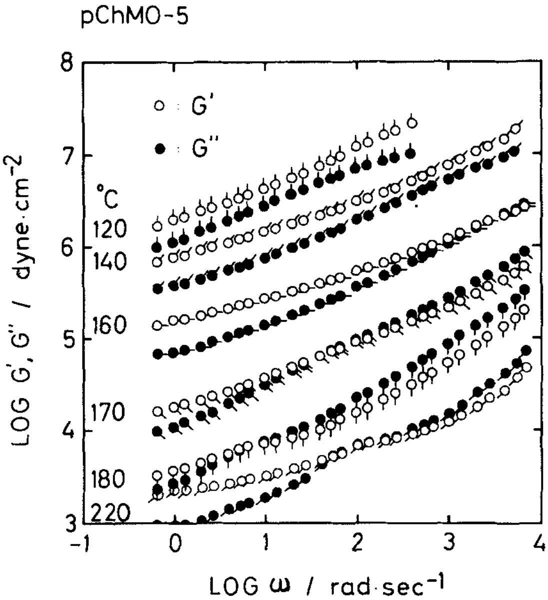


FIGURE 2 Frequency dependence of dynamic shear moduli for pChMO-5 at various temperatures.

regard to DSC measurement and microscopic observation is similar to each other. In the present article, a phase of the two polymers above T_{cl} is called "isotropic phase" from a viewpoint of thermal analysis and microscopic observation. In Figure 2, the slope of G′ at 220°C is still small even above T_{cl} (183°C). At a temperature near T_{cl} of pChMO-11 in Figure 3, however, the slope of G′ becomes larger with increasing temperature, as is distinct from the case of pChMO-5. In the smectic phase of pChMO-11, a part of the smectic structure of the side-mesogenic groups transforms to the isotropic form at T_1 (105°C) as described above. The longer flexible spacers of pChMO-11 contribute to the mobility of the side-mesogenic groups; in particular, the side-chains in the end portions of the main-chain seem to have much mobility. Therefore, these factors make the smectic-isotropic transition of pChMO-11 smoother than that of pChMO-5; i.e., the transition of pChMO-11 at T_{cl} occurs with narrower range of temperature. In the smectic phase, striking differences in the viscoelastic behavior between pChMO-5 and pChMO-11 caused by difference in the packing structure were not observed in this study. However, the macromolecules of pChMO-n seem to move easily in the single-layer packing structure, because the mesogenic groups of one macromolecule in the single-layer packing structure are surrounded with the methylene spacer of neighboring macromolecules. In contrast to the case of the single-layer packing structure, the mesogenic groups of one macromolecule in the two-layer packing structure are surrounded with rigid mesogenic groups of neighboring macromolecules. In this case, strong interaction between the mesogenic groups hinders mobility of the macromolecules.

On the other hand, although pBBMO-6 has a shorter flexible spacer and has

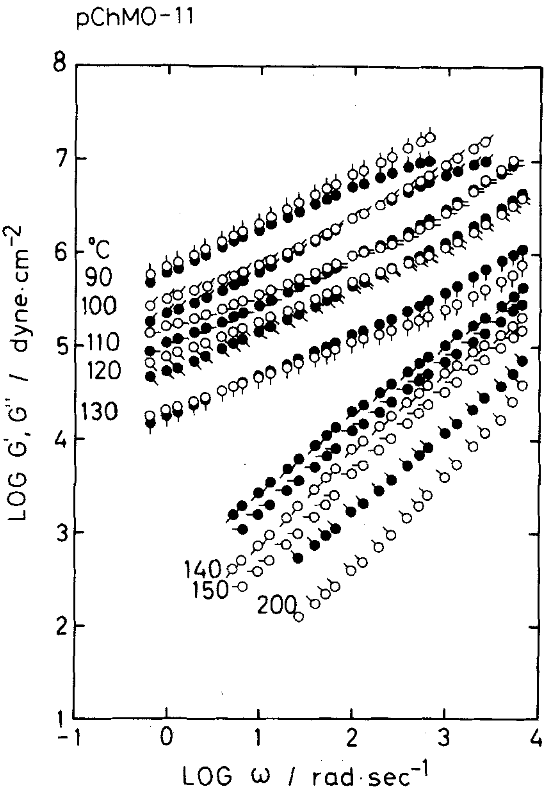


FIGURE 3 Frequency dependence of dynamic shear moduli for pChMO-11 at various temperatures.

the same packing structure as pChMO-5, the moduli-frequency behavior of pBBMO-6 (Figure 4) is similar to that of pChMO-11 rather than that of pChMO-5. The ether bond, which links the mesogenic group to the spacer, and the relatively compact mesogenic groups contribute to mobility of the side-mesogenic groups of pBBMO-6.

When G′ is plotted against temperatures at various frequencies, the difference in the transition behavior of the polymers in terms of the molecular structure becomes clearer. The temperature dependence of G′ for pChMO-5 and pBBMO-6 are shown in Figures 5 and 6, respectively. G′ of pChMO-5 at various frequencies decreases gradually with increasing temperature, and it steeply decreases with temperatures just below T_{cl}. However, G′ changes scarcely above T_{cl}. This maintenance of G′ value in the isotropic phase is accounted for by the lesser mobility of the macromolecules. In pChMO-5, the dense attachment of the rigid side-chain, which consists of two rigid ester bonds, a short flexible spacer, and a large and rigid cholesteryl group, would prevent the system from the rapid isotropicalization. X-ray investigations for pChMO-5 have suggested that the non-liquid crystalline molecular organization of the macromolecules remains even above T_{cl} determined by DSC measurement.[11,15] Small angle X-ray diffraction diagrams at various temperatures for pChMO-5 are shown in Figure 7. A sharp reflection peak (d_1) with

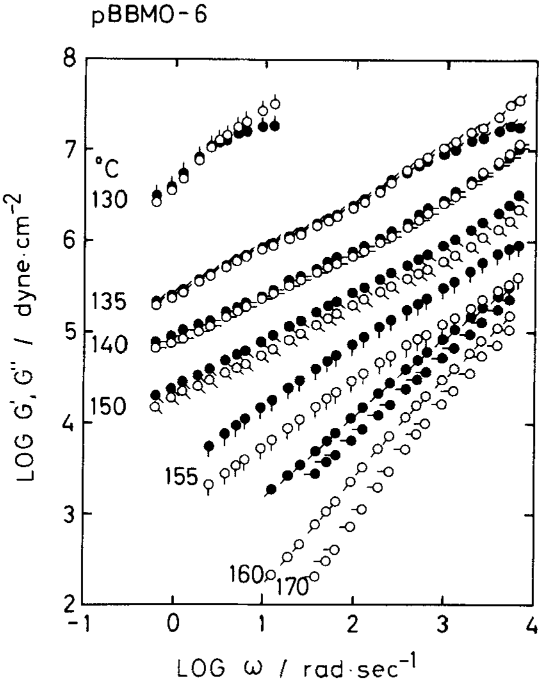


FIGURE 4 Frequency dependence of dynamic shear moduli for pBBMO-6 at various temperatures.

its second reflection (d_2) is attributable to the two-layer packing structure of the side-chains in the smectic A phase. This d_1 peak disappears at T_{cl}. However, a broad reflection peak (d_3) is observed even above T_{cl}. No other endothermic peak was observed above T_{cl} on the DSC curve, and any liquid crystalline texture was not observed above T_{cl}; i.e., the system is optically isotropic above T_{cl}. Therefore, this broad peak (d_3) is not due to another liquid crystalline structure,[15] but due to non-liquid crystalline molecular organizations, in which the side-chains are disordered, but the position of the macromolecules is similar to that in the smectic phase. Dense attachment of the large and rigid side-chains makes the smectic-isotropic transition of the polymers occur with broader range of temperature. Schematic illustrations of macromolecular shapes, and those of the liquid crystalline and non-liquid crystalline molecular organizations of macromolecules for pChMO-5 are shown in Figure 8. The side-chains are arranged into lamellate form, and one macromolecule forms a rectangular plate (Figure 8, (a)-1) in the smectic phase. When the temperature approaches T_{cl}, the large and rigid side-chains start to spread mainly on the circular plane drawn by the side-chain long axis as a radius (Figure 8, (a)-2 and (b)-2). Above T_{cl}, the side-chains are disordered and produce the loose rod-like form of the macromolecule (Figure 8, (a)-3), and macromolecules form the non-liquid crystalline molecular organization (Figure 8, (b)-3). Although the plate-like macromolecules of rectangular form in the liquid crystalline phase can slip from each other, the macromolecules forming the loose rod-like form hardly slip from each other. The loose rod-like form starts to become disordered with increasing temperature, and one macromolecule forms a tube washer-like form.

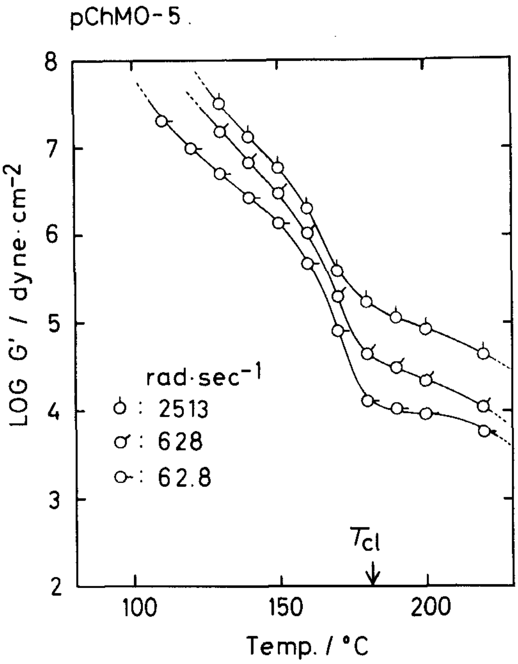


FIGURE 5 Temperature dependence of shear storage modulus (G') for pChMO-5 at various frequencies.

The maintenance of elasticity above T_{cl} seems to arise from the largeness of molecular interactions between the tube washer-like macromolecules with the large and rigid side-chains.

On the other hand, although the decrease of G' of pBBMO-6 against temperature is much smaller than that of amorphous polymers, G' of pBBMO-6 does not stay constant against temperature in contrast to that of pChMO-n. The side-chain of pBBMO-6 has compact mesogenic groups, which attach to the flexible spacer via a flexible ether bond; the side-chain of pBBMO-6 is the most flexible among the three polymers. Smallness of the side-chains and flexibility of the whole side-chain makes the smectic-isotropic transition occur with narrower range of temperature. Therefore, it is difficult to consider that the side-chains of pBBMO-6 form the rod-like form which consists of rigid and large side-chains, and is due to slow transition.

Liquid crystalline side-chain polymers forming liquid crystalline phases have the side-chains having strong interaction induced by such as permanent dipoles in the side-chain or long rigid shape of the side-chain; pChMO-5 containing cholesterol has interaction in terms of the shape, and pBBMO-6 containing biphenyl groups has interaction in terms of the permanent dipoles. For liquid crystalline side-chain polymers, a certain degree of interaction of the side-chain is held even in the isotropic phase. In contrast to the stronger interactioin between the side-chains of pChMO-5 above T_{cl} in terms of the shape of the side chains, the side-chains of pBBMO-6 seem to hold weaker interaction in terms of the permanent dipoles of the biphenyl groups above T_{cl}.

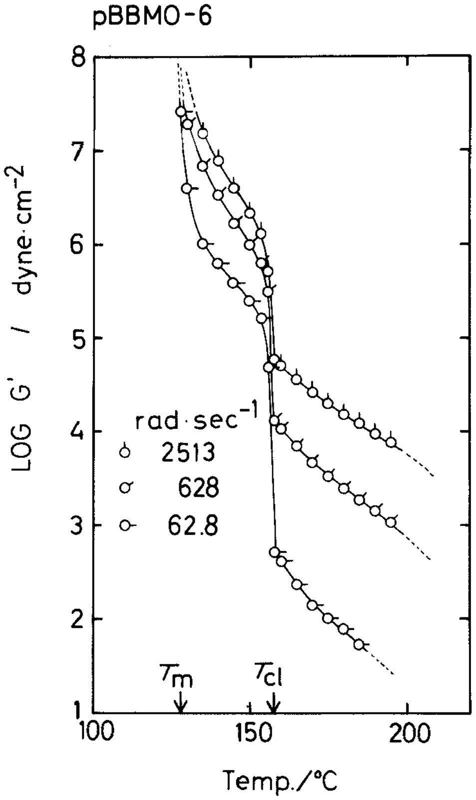


FIGURE 6 Temperature dependence of shear storage modulus (G′) for pBBMO-6 at various frequencies.

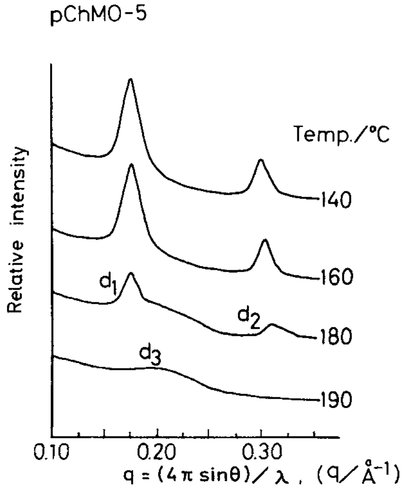


FIGURE 7 X-ray diffraction diagrams on the second heating run for pChMO-5.

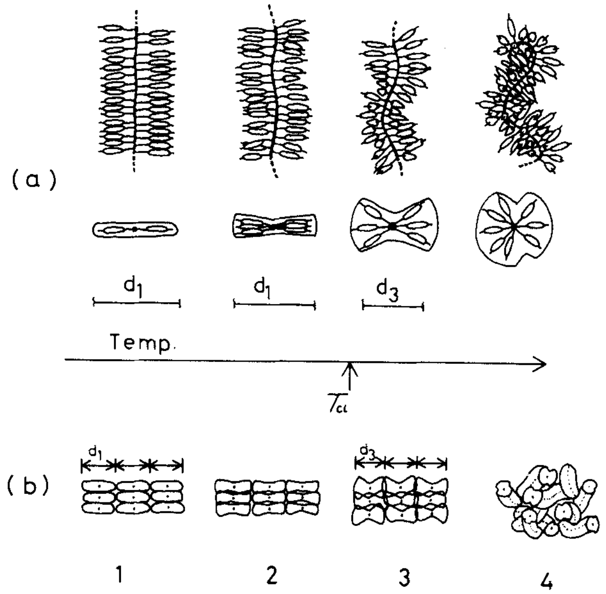


FIGURE 8 Schematic illustrations of macromolecular shapes and the macromolecular organizations for pChMO-5; (a) through and edge view of one macromolecule, (b) edge view of macromolecular organizations: (1) and (2) the smectic A phase, (3) just above T_{cl}, (4) the isotropic phase.

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