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Dynamic viscoelastic behavior of cholesteric liquid crystalline side-chain copolymers

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Summary

The rheological behavior of the cholesteric side-chain copolysiloxane whose two kinds of mesogenic groups consist of cholesteryl units and biphenyl benzoate units was investigated for three different compositions: 31:69, 35:65, 37:63 (in mol%). On the frequency dependence diagram of G' for the copolymers at various temperatures, G' decreases with decreasing frequency. The slope of G' in a higher frequency region at lower temperatures (110° - 130°C) is similar to that in the flow region of amorphous polymer melts. However, the slope of G' in a lower frequency region at higher temperatures (140° - 160°C) is relatively small, and the G' curves in this region can not be superposed on to a single master curve. This deviation seems to be due to change in stability of the domain structure of the cholesteric phase. Furthermore, on the temperature dependence curve of G', G' showed a maximum near T_{cl}. This maximum of G' curve seems to be caused by molecular organization of a blue phase.

Introduction

For thermotropic liquid crystalline polymers, measurements of rheological properties are essential as well as those of optical properties. In particular, the rheological measurements of the liquid crystalline polymers should provide valuable information for industrial applications. For liquid crystalline side-chain polymers, however, despite a big interest due to their unique molecular structure, information on their rheological properties has been limited; only melt viscosities have been reported(1). In our previous work(2,3), the temperature dependence of G' for two smectic side-chain polymers has been investigated, and it has been pointed out that elasticity is maintained even in the isotropic state owing to the remain of non-liquid crystalline organization above T_{cl}. In the present study, we carried out dynamic viscoelastic measurements for three cholesteric side-chain copolymers as a function of frequency and temperature in the isotropic and cholesteric phases. In particular, great attention was paid to the viscoelastic behavior at the transition point from the isotropic phase to the cholesteric one. It seems that the results of such measurements enable us to understand the transition mechanism of the cholesteric side-chain polymers and the difference between the molecular

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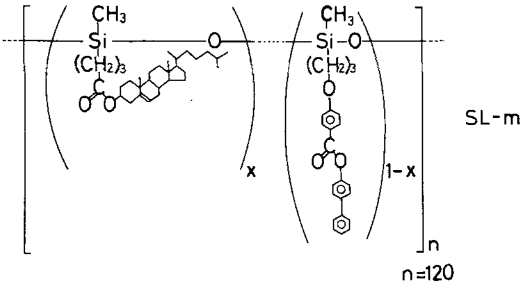
*To whom offprint requests should be sent motion of the cholesteric side-chain polymers and that of the smectic side-chain polymers.

Experimental

The general structure of the copolymers is following,



The copolymers used here were supplied by Wacker Chemie Co. Ltd. (U.S.A.). Polymer code is represented in Table 1 in this article. The transition temperature and the transition entropy were determined through DSC (Parkin Elmer DSC-7) measurements. The molar fraction of the cholesterol unit is estimated by ^{1}H-NMR method(4). All of the dynamic viscoelastic measurements were made using a Dynamic Rheospectra DVE-V4 (Rheology Co. Ltd) with the parallel-plate simple shear geometry(2). The temperature was controlled by PID with a heating stage. The storage(G') and loss(G") moduli were obtained in oscillatory shear over a frequency range of 0.628-6273.7 rad/sec(0.1-999 Hz) and in a temperature range of 30-250°C. All measurements were carried out in an atmosphere of nitrogen.

Results and Discussion

The phase transition temperatures and transition entropies of SL-m were listed in Table 1. All copolymer exhibit the cholesteric phase in the temperature range from a glass transition point (T_g) to a clearing point (T_{cl}). T_g and T_{cl} of SL-2 are the highest among the three copolymers, and ΔS_{cl} is also the largest. However, unfortunately, it can not be discussed here for lack of a detailed phase diagram against a molar fraction of a cholesteric unit. Observations with a polarized microscope, a focal conic texture was observed in liquid crystalline phase. Furthermore, a blue-phase like texture was recognized just below T_{cl} for SL-3 on the cooling run. On the other hand, wave length due to selective reflection (λ_{max}) decreases with increasing the molar fraction (x) of the cholesterol unit; i. e. increment of the side cholesteric groups makes the cholesteric pitch of SL-m short.

Frequency dependence curves of G' and G" at various temperatures for SL-3 are illustrated in Figure 1. The principle of time-temperature superposition is the most useful to know the frequency dependence of G' and G" over a wide frequency range. Modulus-frequency master curves for SL-1, SL-2, and SL-3 are shown in Figure 2, Figure 3, and Figure 4, respectively.

Table 1
Transition temperatures and transition entropies of SL-m.

polymer code	Fr.*	Pn**	T_g	T_{c1}	ΔS_{c1}***	λ_{max}+
SL-m	(%)		(°C)	(°C)	(x10^{-3} J/g K)	(nm)
SL-1	31	120	44	198	2.90	677
SL-2	35	120	50	212	3.55	540
SL-3	37	186	48	186	3.00	469

* Molar fraction of cholesteryl unit estimated by ^{1}H-NMR method. ** Degree of polymerization. *** Transition entropy at the clearing point(T_{c1}). + Wave length due to selective reflection just below T_g.

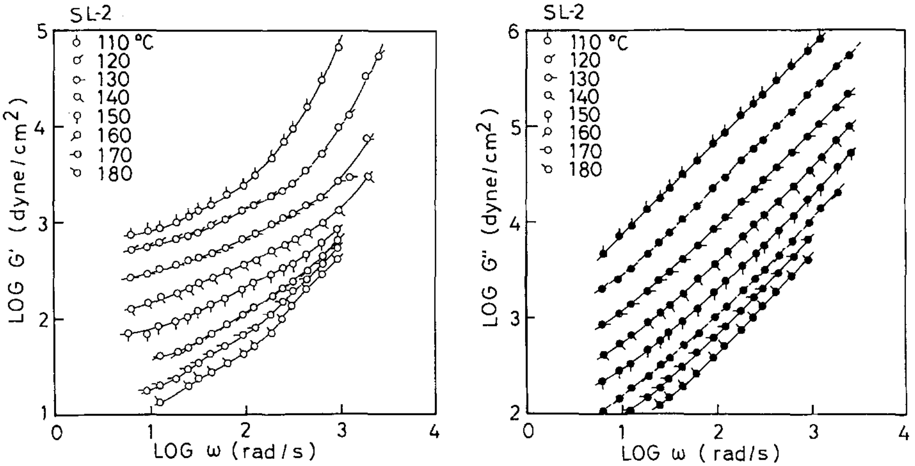


Figure 1. Frequency dependence of G' and G" for SL-2 at various temperatures.

The master curves at the reference temperature are constructed by superposition with only horizontal shifts along the frequency axis(a_T). As shown in Fig. 2, the slope of G' is about 2 in a higher frequency range at lower temperatures (110° - 130°C), and is similar to that of amorphous polymer melts and that of a nematic phase of thermotropic main chain polymer(5). Furthermore, the slope of G" of SL-m is about 1 in the whole frequency range, and is similar to that of amorphous polymer melts. These observations seem to be reflected by the liquid like properties of cholesteric (chiral nematic) phase of the system. On the other hand, in contrast to the behavior of G' in a higher frequency range at lower temperatures (110° - 130°C), the G' curves in a lower frequency range at higher temperatures (140° - 160°C) have smaller slope, and can not be superposed on to a single master curve; i. e. G' which is well superposed on to a single master curve in a higher frequency region deviates below a certain frequency on the master curve(Fig. 2-4). Furthermore, the slope of the G' curve in the deviation region on the master curve becomes slightly higher with increasing temperature; in another words, elasticity at lower frequency region is maintained higher at lower temperature. Viscoelastic properties of the liquid crystalline polymeric systems were influenced by the change in the domain structure(6). The domain structure of liquid crystalline systems is generally more stable at lower temperature. Therefore, the deviation of the G' master curves for SL-m seems to be caused by change in stability of the domain structure in the cholesteric phase.

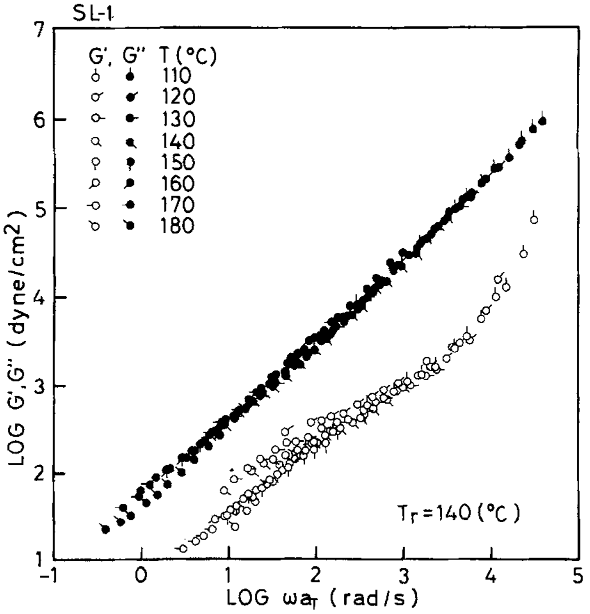


Figure 2. Moduli-frequency master curves for SL-1.

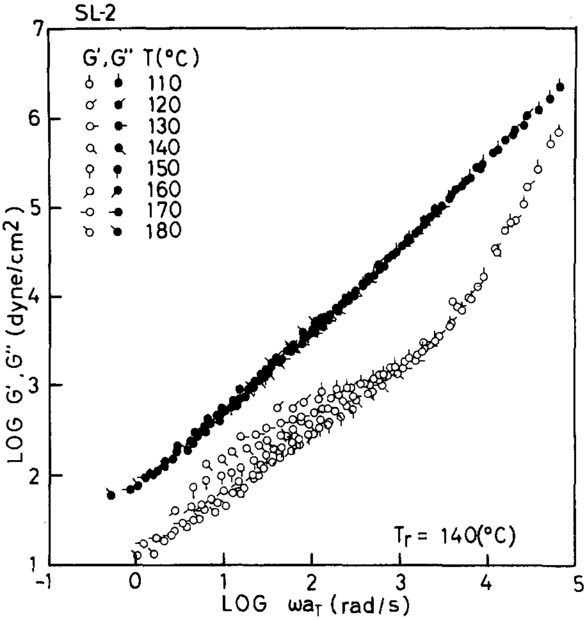


Figure 3. Moduli-frequency master curves for SL-2.

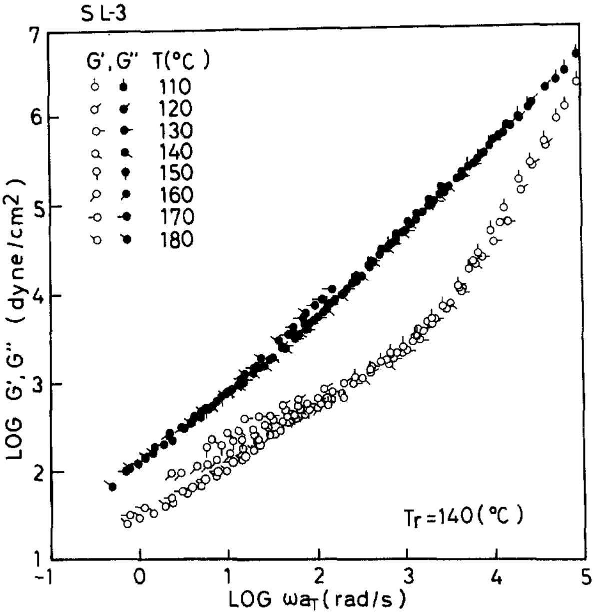


Figure 4. Moduli-frequency master curves for SL-3.

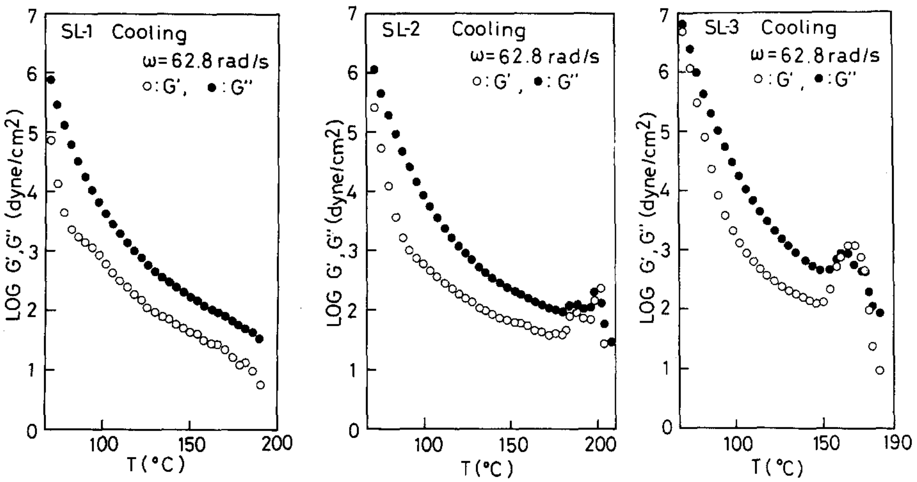


Figure 5. Temperature dependence of G' and G" for SL-m at 62.8 rad/sec on the 2nd cooling run.

The temperature dependences of G' and G" on the 2nd cooling run for SL-m at 62.8 rad/sec are shown in Figure 5. The temperature dependence curves of G' of SL-m above T_{cl} show the flow region. The G' curve of SL-2 and SL-3 has a maximum just below T_{cl}. A peak on the G' curve becomes larger with increasing the molar fraction of the cholesteric unit(x). For liquid crystalline main-chain polymers, the maximum on the G' curves near T_{cl} has been observed(7). This maximum on the G' curve for the liquid crystalline main-chain polymers seems to be accounted for by the occurrence of entanglements of the long main chains; that is to say, 1) G' decreases with increasing temperature below T_{cl} and becomes smaller than that in rubbery plateau region observed in amorphous polymer melts, because the main chains which are elongated and arranged in the liquid crystalline state do not have the entanglements, 2) G' starts to increase at T_{cl} owing to the occurrence of the entanglements of the main chains which become to have random conformation at the isotropic transition point, 3) G' decreases with increasing temperature owing to flow of the molecules, 4) G' curve against temperature for the thermotropic liquid crystalline main-chain polymers has the maximum, consequently. However, such entanglements of main chain are improbable for SL-m in which the main chains are too short to have entanglements. For low molecular mass cholesteric liquid crystals, the maximum on G' curves in blue phase just below T_{cl} has also been reported(8). The peak on the G' curve for SL-3, on which the blue phase was observed under polarized microscope, is the largest among three SL-m. Therefore, the maximum on the G' curves for SL-m seems to be due to the molecular organization in the blue phase.

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