

Dynamic Viscoelastic Properties of Liquid Crystalline Polymers

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Dynamic viscoelastic and dielectric properties of thermotropic liquid crystalline polymers of various structures have been found to be greatly affected by the geometrical shapes of molecules. The reason may be that the molecular motion of liquid crystalline polymers is mainly rotation about the molecular axis and ease of the motion changes depending on the shapes of molecules. By changing the volume of substituent attached to the main chain, it would be possible to control the activity of this molecular motion.

1. Introduction

Thermotropic liquid crystalline polymers (abbreviated as LCPs, hereafter) with aromatic backbone have excellent mechanical properties primary because of their rigidity¹⁾. Despite their rigidity, the local motion by the relaxation in the main chain is relatively active even at room temperature. The properties suggest that the LCPs may be useful for vibrational-damping materials with high rigidity. In designing such materials, it is important to clarify the relationship between the relaxation mechanism of the LCPs and their chemical structure. Hence, the present paper reports the results on the dynamic viscoelastic and dielectric measurements of LCPs with various chemical structure.

2. Experimental

The structure and composition of LCP samples examined here are summarised in Fig. 1. They are categorized into four classes according to their geometrical shape of the molecules as follows. (A): rod-like LCPs, (B): LCPs with bend structure in the backbone (bend), (C): LCPs with deviation with respect to molecular axis (crank), (D): LCPs with substitution.

The samples provided for dynamic viscoelastic measurements are pressed into lath-like shape of $45 \times 4 \times 0.5$ mm. The dynamic viscoelastic measurements were performed by a viscoelastic analyzer RSA II (Rheometrics) and a Rheo-vibrone (Orientec). The measurements were carried out in two deformation modes: the bending mode measurements were made for all samples at the frequency of 10 Hz, and tensile mode measurements were also done for the A-type LCPs at 110 Hz. The measurements were carried out on the temperature sweep mode and the frequency sweep mode. The latter results were used to calculate the activation energy of the transition of the materials. The rigidity of the materials is evaluated by the complex modulus, while the vibration-damping property is discussed on the basis of the magnitude of $\tan \delta$: the larger value of $\tan \delta$ indicates more effective vibration damping.

The dielectric properties were examined for the materials A-2 and C-1. The test sample was injected into a plate ($80 \times 80 \times 2$ mm) and electrodes of thin aluminium were attached on both sides. The dielectric measurements of the sample A-1 and C-1 were performed over the frequency range of 30~30 kHz and the temperature range of $-70 \sim 110^\circ\text{C}$, us-

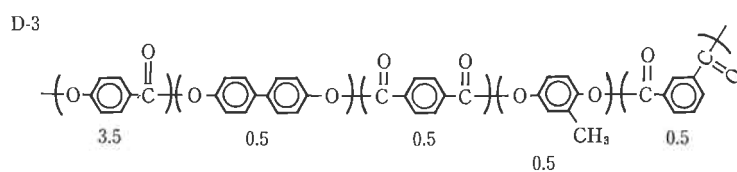
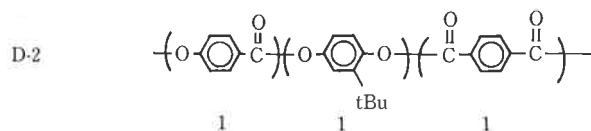
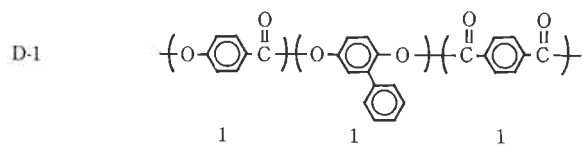
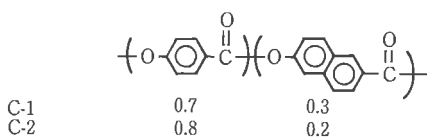
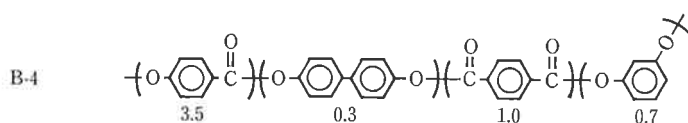
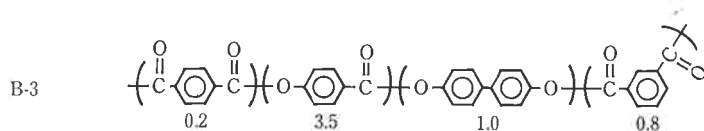
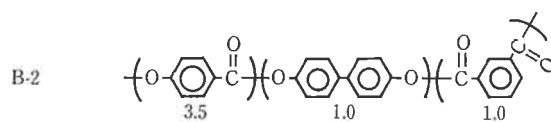
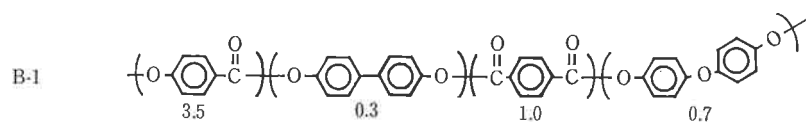
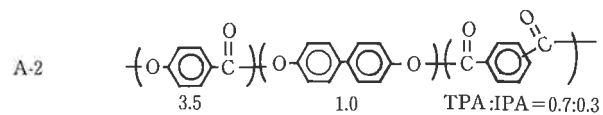
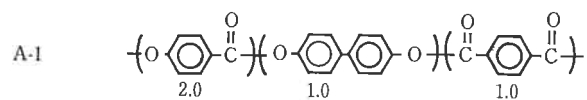


Fig. 1 Thermotropic LCPs examined

ing a dielectric constant measurement apparatus (transformer bridge method) in a constant temperature bath (ANDO ELEC. CO.).

3. Results and Discussion

[1] Rod-like LCPs

Fig. 2 shows the temperature dependence of $\tan \delta$ (tensile) for A-1 and A-2 of rod-like molecules. The behaviour of the $\tan \delta$ for these two LCPs is quite similar. One distinct peak at -20°C and two minor peaks at 50 and 100°C . were observed. The peak at the lowest temperature is most intense and the other two peaks are relatively weak. The storage modulus E' of these LCPs decreases monotonously with temperatures.

Fig. 3 shows the temperature dependence of the dielectric constant (ϵ'') of A-2, in which we find that the feature and the location of the lower temperature peak at 110 Hz are similar to those of $\tan \delta$ curve at 110 Hz for A-2 in Fig. 2. This observation suggests that both mechanical and dielectric relaxations should arise from the same molecular relaxation process.

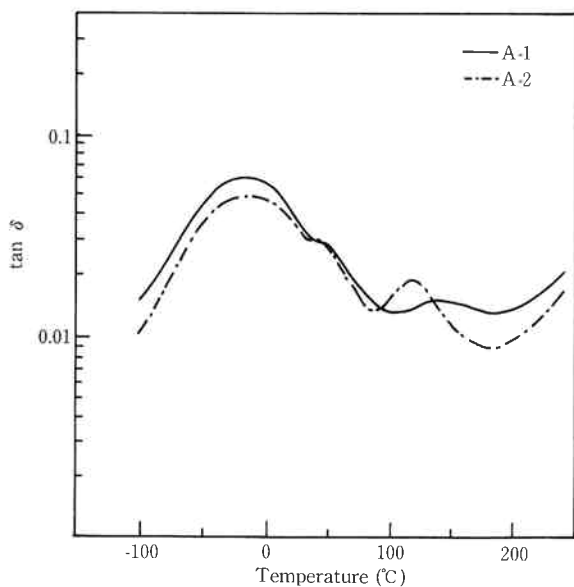


Fig. 2 Temperature dependence of $\tan \delta$ for rod-like LCPs

In these LCPs the aromatic rings are directly connected by the ester linkages. The dielectric properties of these LCPs as pointed out above arise from the electric dipole moments located on the ester groups. Namely, the motion of ester groups contributes to this relaxation process. As illustrated in Fig. 4, for the motion of the ester groups correlates with the counter aromatic ring, this aromatic-ester unit can rotate only about the O-C (phenyl) bond^{2),3)}. Our viscoelastic and dielectric results consistent with this relaxation mechanism. The temperature in lower peak corresponds to the onset of this rotational motion. The motion of the aromatic-ester unit in the rod-like LCPs would be local rotation. This rotational motion could be less restricted even at low temperature. The activation energy of this relaxation behaviour for A-2 is 13 kcal/mol.

[2] LCPs with Bend Character in the Backbone

Fig. 5 shows the temperature dependence of $\tan \delta$ (bending) for 4 species of LCPs with bend structure

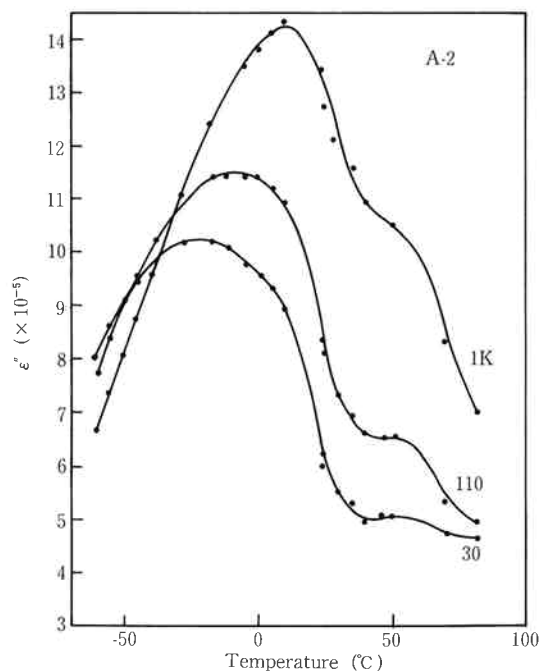


Fig. 3 Temperature dependence of ϵ'' for A-2

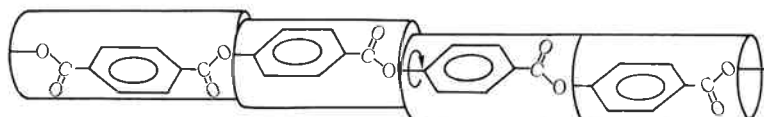


Fig. 4 Local mode motion of rod-like LCPs

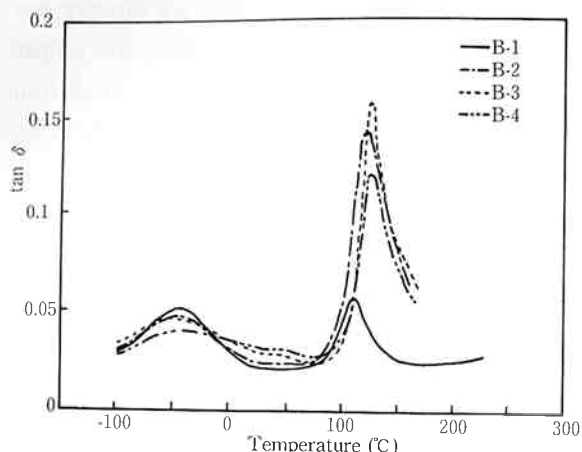


Fig. 5 Temperature dependence of $\tan \delta$ for LCPs with bend structure

in their backbones (type B). These four polymers exhibit a similar $\tan \delta$ curve. The characteristic feature of the $\tan \delta$ curve is that the appearance of new intense peak at higher temperature in addition to the relaxation peak at lower temperature. The higher temperature relaxation peak corresponds to the glass transition. The E' curve exhibits a step fall in this temperature region. For B-1, the activation energy calculated from the results of frequency-sweep measurements over 0.1, 1 and 10 Hz was 115 kcal/mol for the peak at higher temperature and 17 kcal/mol for the peak at lower temperature. The lower temperature transition with a small activation energy should again be attributed to the local rotational and vibrational motion of the aromatic-ester units. It is clear that the new relaxation peak at higher temperature is caused by the introduction of bending units into the originally rod-like LCPs. If these ben-

ding units undergo rotational and vibrational motions through the aromatic-ester linkage, such motions would not remain local but would become cooperative. Schematic illustration of such cooperative motion is given in Fig. 6. This large-scale cooperative motion is first activated in rising temperature up to about 100°C and is observed as glass transition with large $\tan \delta$ peak. This new peak is slightly shown for A-2 in Fig. 2 and is clearer with increasing the component of the bending unit for type B. B-1 only has bending unit made up of ether linkage and the other's bending unit is isophthalic acid. The effect of bending unit made up of ether linkage for $\tan \delta$ is smaller than isophthalic acid.

[3] Crank type LCPs

Fig. 7 shows the temperature dependence of $\tan \delta$ (bending) for the 2 species of LCPs with a deviation axis from the local molecular direction (crank shape). The tendency is similar for the two crank polymers, by virtue of their geometric feature. The characteristic of $\tan \delta$ curve for the crank type LCPs is appearance of additional intense peak around room temperature between two relaxation peaks observed in Fig. 5. The activation energy calculated from the results frequency-sweep measurements over 0.1, 1 and 10 Hz was 22 kcal/mol for the peak at middle temperature and 154 kcal/mol for the peak at the highest temperature. The former with a small activation energy should be local motion and the latter agree with the value observed for type B.

The aromatic fraction of the crank part in a molecule increases with C-2 and C-1. The value of

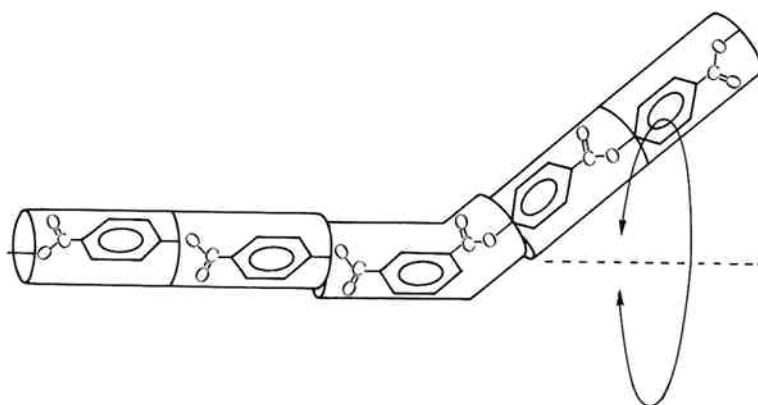


Fig. 6 Cooperational motion of LCPs with bend structure

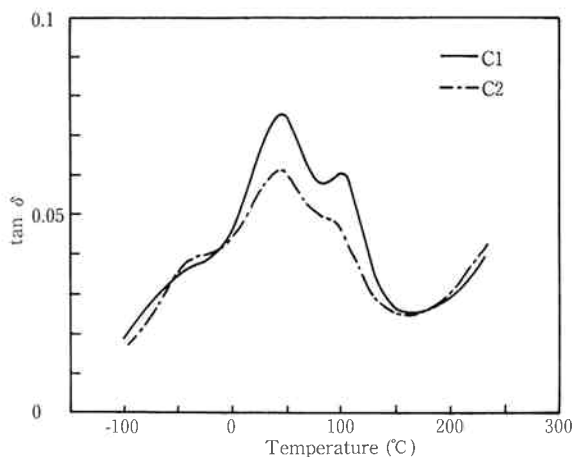


Fig. 7 Temperature dependence of $\tan \delta$ for crank shape LCPs

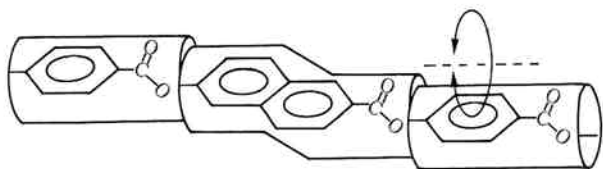


Fig. 8 Local mode motion of crank shape LCPs

$\tan \delta$ for C-1 around 50°C is larger than C-2. It is clear therefore that this relaxation process is attributed to the aromatic-ester unit of the crank part. If the aromatic-ester unit of the crank part undergoes rotational motion as shown in Fig. 8, the motion probably more restricted than that in type A and less tight than that for the bending part in type B.

Fig. 9 shows the results for C-1 in the dielectric relaxation measurement at different frequencies (110, 3 k and 30 kHz). The location and shape of the peak in ϵ'' curve at 110 Hz is similar to those observed in mechanical measurements, which suggests that both mechanical and dielectric relaxation process can be identical as was the case with for A-2.

[4] LCPs with Substitutions

Fig. 10 shows the temperature dependence of $\tan \delta$ (bending) for 3 species of LCPs containing hydroquinone with different substituted groups (phenyl, quaternary butyl and methyl groups). Both the LCP with a phenyl group and the LCP with a quaternary butyl group are composed of two rod-like units and one substituted unit in the same fraction ratio. There are 2 major peaks in the $\tan \delta$ curves for these

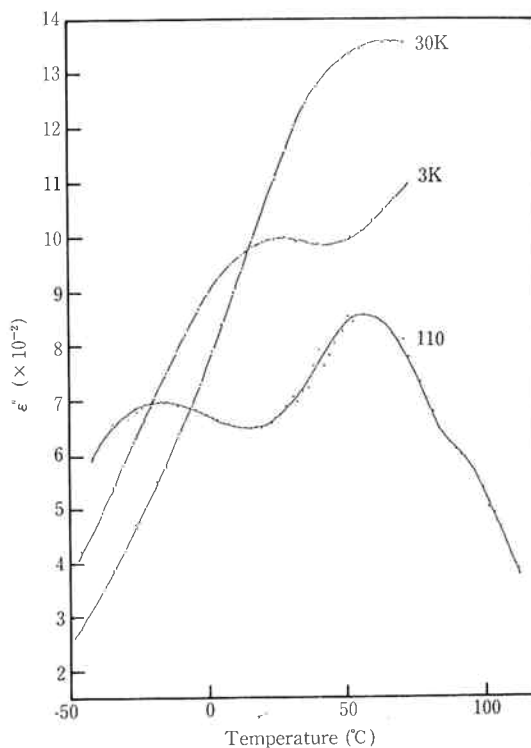


Fig. 9 Temperature dependence of ϵ'' for C-1

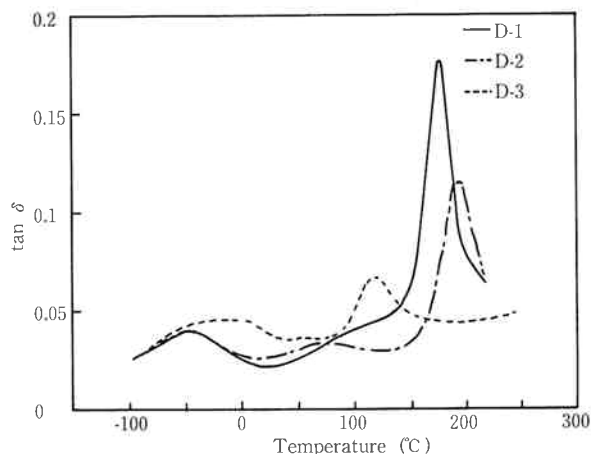


Fig. 10 Temperature dependence of $\tan \delta$ for LCPs with substitution

three LCPs. As is the mentioned before, the one is the peak attributed to the motion of the rod-like aromatic-ester unit, and the other is the peak attributed to the large-scale cooperative motion. The origin of the peak around room temperature is not clear, but it may be the relaxation of the substituted groups.

The glass transition temperature for the D-1 is lower than that for the D-2. That is probably attributed to the larger volumetric size of the

substituted group in D-1 (phenyl) than that in D-2 (quaternary butyl). The peaks at lower temperature, however, are not affected by the size of the substituted groups.

4. Conclusion

The modes of the thermal motion in all aromatic series of thermotropic LCPs is rotational and vibrational motion around the local axes such as aromatic-ester unit. In these relaxation mode, mechanical and dielectric relaxation behavior clearly depend on the geometrical shape of the molecule. A systematic investigation of basic physical properties such as this study would be enable to design the material with required function. For example, in designing the vibration-damping materials, it will be

possible to optimize the desirable performance of the materials in designing the molecular structure.

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