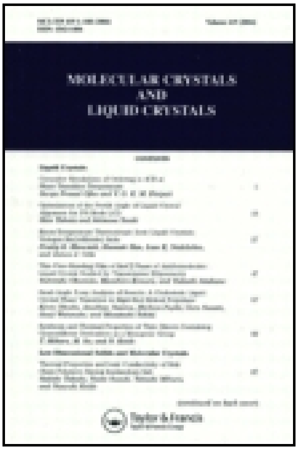


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Dynamic Viscoelastic Behavior of the Liquid Crystalline Side-Chain Polymers

T. Yamaguchi [a] & T. Asadaa [a]
[a] Department of Polymer Chemistry, Kyoto University, Kyoto, 606, JAPAN

To cite this article: T. Yamaguchi & T. Asadaa (1991): Dynamic Viscoelastic Behavior of the Liquid Crystalline Side-Chain Polymers, Molecular Crystals and Liquid Crystals, 198:1, 299-304

To link to this article: http://dx.doi.org/10.1080/00268949108033406

Mol. Cryst. Liq. Cryst., 1991, Vol. 198, pp. 299–304
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Dynamic Viscoelastic Behavior of the Liquid Crystalline Side-Chain Polymers

T. YAMAGUCHI and T. ASADA*

Department of Polymer Chemistry, Kyoto University, Kyoto 606, JAPAN

(Received July 25, 1990)

Dynamic viscoelastic properties of three liquid crystalline polymers with different spacer length (n) were investigated with parallel-plate simple shear geometry and under uniaxial extension geometry. Temperature dependence curves of G′ for the polymers were obtained at various frequencies. It was found that the slope of G′ above T_{cl} was smaller than that below T_{cl}. In particular, G′ of the polymer with the shorter spacer length (n = 5) varied very slowly with the temperature above T_{cl}. The values (10^3–10^5 dyne/cm^2 varied with the frequency) of this quasi-plateau modulus indicate that the plateau region is not due to the entanglements between the main-chain. The existence of loose entanglements between the large, rigid side chains is suggested.

INTRODUCTION

Thermotropic liquid crystalline polymers possess fluidity and optical anisotropy in their liquid crystalline phases. Therefore, measurements of rheological properties as well as those of optical properties are essential for evaluating liquid crystallinity of the polymers.

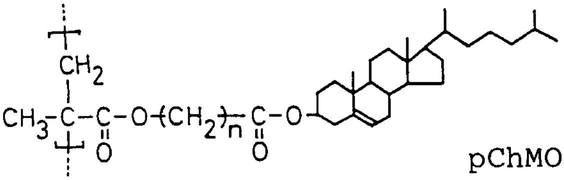
Many rheological studies on thermotropic liquid crystalline main-chain polymers, in particular melt viscosity measurements, have been reported,[1,2] stimulated by importance in practical application. For liquid crystalline side-chain polymers, however, information on their rheological properties is very limited in spite of great academic as well as practical interest due to their unique molecular structure: only a theoretical approach to nematic side-chain polymers[3] and an experimental study on only melt viscosities have been reported.[4]

In the present study, we carried out dynamic viscoelastic measurements for three liquid crystalline side-chain polymers, poly(cholesteryl ω-(methacryloyloxy)-alkanoates). These samples have been studied by DSC and SAXS in our previous studies.[5,6] The aim of the present work is to obtain information on the dynamic viscoelastic properties of the liquid crystalline side-chain polymers as functions of frequency and temperature in the liquid crystalline as well as isotropic states. Use of the information obtained here makes it possible to compare the molecular motion of the polymers with that of liquid crystalline main-chain polymers and that of conventional amorphous polymers. In particular, the viscoelastic behavior at the transition point from the smectic phase to the isotropic one was investigated in detail.

From the results of such investigations, we can understand the transition mechanism of the smectic side-chain polymers.

EXPERIMENTAL

The polymers used were three poly(cholesteryl ω-(methacryloyloxy)alkanoates) designated as pChMO-n, n representing the carbon number of the alkyl spacer of the side-chain, n = 5,7,11. The synthesis[7] and the results of DSC measurement and small angle X-ray scattering[5,6] have been described elsewhere. The degree of polymerization estimated by a GPC method was about 100. The general structure of pChMO-n is the following,



pChMO-n (n=5, 7, 11)

All of the dynamic viscoelastic measurements were made using a Dynamic Rheospectra DVE-4(KU-0; Rheology co. LTD.) with the parallel-plate simple shear geometry. The temperature was controlled by PID with a heating stage. The storage(G′) and loss(G″) shear moduli were obtained in oscillatory shear over a frequency range of 0.628–6273.7 rad/sec (0.1-999Hz) and in a temperature range of 50–200°C. The storage (E′) and loss (E″) tensile moduli were obtained using a thin film of the polymers in sinusoidal strain of 100 Hz in a temperature range of 0–100°C. All measurements are carried out in an atmosphere of prepurified nitrogen.

RESULTS AND DISCUSSION

Phase transition temperatures of the polymers are listed in Table I. All of these polymers exhibit the smectic A phase, which have been observed by polarized optical microscopy and by SAXS.[5,6] A two layer packing (S_{A2}) structure, in which overlapping of side-chains is not allowed due to the shortness of the spacer, was proposed for the smectic A phase of pChMO-5 and pChMO-7. On the other hand, two types of the packing structure were proposed for pChMO-11, i.e. the two layer packing structure and an overlapping single layer packing (S_{A1}) structure in which the side-chains of one polymer overlap with those of neighboring polymers. The two different packing structures of pChMO-11 coexist below T_1, and only the S_{A1} structure is observed from T_1 to T_{cl}.

Temperature dispersion curves of E′ and E″ at 100 Hz for pChMo-n (n = 5, 7, 11) are shown in Figure 1. E′ decreases sharply at T_g. The rate of the decrease becomes greater with increasing the spacer length (n). Corresponding to the behavior, peak of E″ becomes narrow, showing that the transition becomes sharper with increasing n. The main chain which is anchored by the large mesogenic groups

TABLE I.

Phase transition temperatures and the transition entropies on the 2nd heating run of pChMO-n (n=5, 7, 11)

	T_g/°C	T_l/°C	T_{cl}/°C	ΔS_{cl}/JK^{-1}mol^{-1}
pChMO-5	49 (a)	---	184	6.04
pChMO-7	45 (a)	---	163	6.99
pChMO-11	43 (c)	105 (b)	150	3.35

a) A two-layer packing (S_{A2}) structure of the side chains in S_A phase; b) a single layer packing (S_{A1}) structure of the side chains in S_A phase; c) coexistence of two types (S_{A1} + S_{A2}) of the packing structure.

seems to move easily with increasing n. Considering that the polymers are liquid crystalline glass below T_g, these results become experimental evidence for the assumption that longer spacer decouples the motion of the side mesogenic groups from that of the main chain. The decoupling seems to be proceeded by increment of the spacer length. Furthermore, the value of E′ below T_g becomes slightly smaller with increasing n. This result seems to be caused by the internal plasticization due to increment of flexible segments in the side chains. This supports that the decrease of T_{cl} with increasing n arises from the internal plasticization by increasing the long spacer.

Temperature dependence curves of G′ for pChMO-5 and pChMO-11 at various frequencies above T_g are shown in Figure 2. In the liquid crystalline phase (S_A phase) of pChMO-5 and pChMO-11, no plateau region was observed. In the liquid crystalline phase of the side chain polymers, domains slip each other on their surface. Furthermore, in the smectic A phase of the side-chain polymers used here, the side-chains are organized into lamellae, and their packing structure looks like the lamellae structure proposed by Zugenmaier for other side-chain polymers.[8] It seems that flat lamellate macromolecules (which will be referred to Figure 3) enable to slip each other in the direction of the long axis of the side-chain as well as the long axis of the main-chain. On the other hand, G′ curve changes its slope near T_{cl}. The slope of G′ above T_{cl} becomes smaller than that below T_{cl}. In particular, G′ of pChMO-5 almost stays constant above T_{cl}, and elasticity is maintained even in the isotropic state. Ordinary amorphous linear polymers having high molecular weight have the plateau modulus of about 10^6-10^7 dyne/cm^2. In this plateau region, long-range conformational motions of linear molecules are disturbed by entanglements. The values of G′ of the quasi-plateau region above T_{cl} of pChMO-n, however, are about 10^3-10^5 dyne/cm^2; these values are smaller than that of ordinary linear polymers. The low degrees of polymerization of pChMO-n and the molecular structure of them seem to prevent the main chains from forming entanglements between them. The existence of loose entanglements between the large and rigid side chains is suggested from consideration of the following two factors; (i) the packing structure of the side chains in the smectic A phase and (ii) the structural

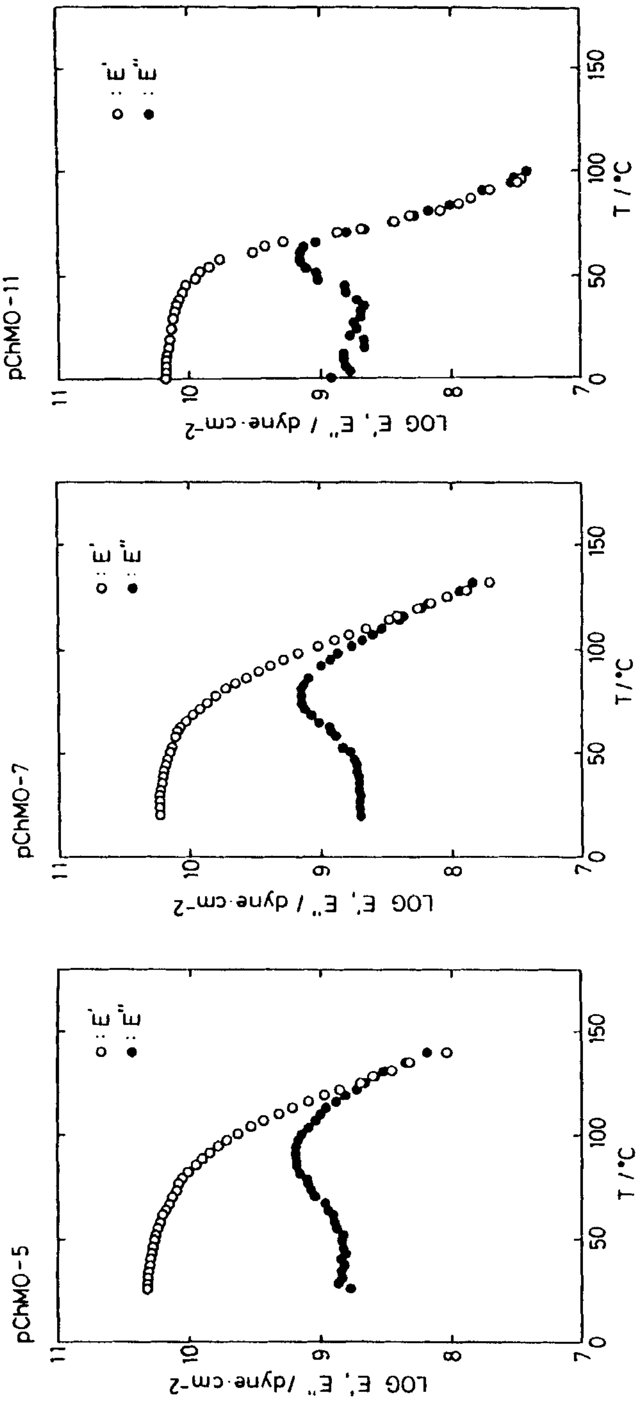


FIGURE 1 Temperature dispersion of E′ and E″ for pChMO-5, pChMO-7, and pChMO-11 at 100 Hz.

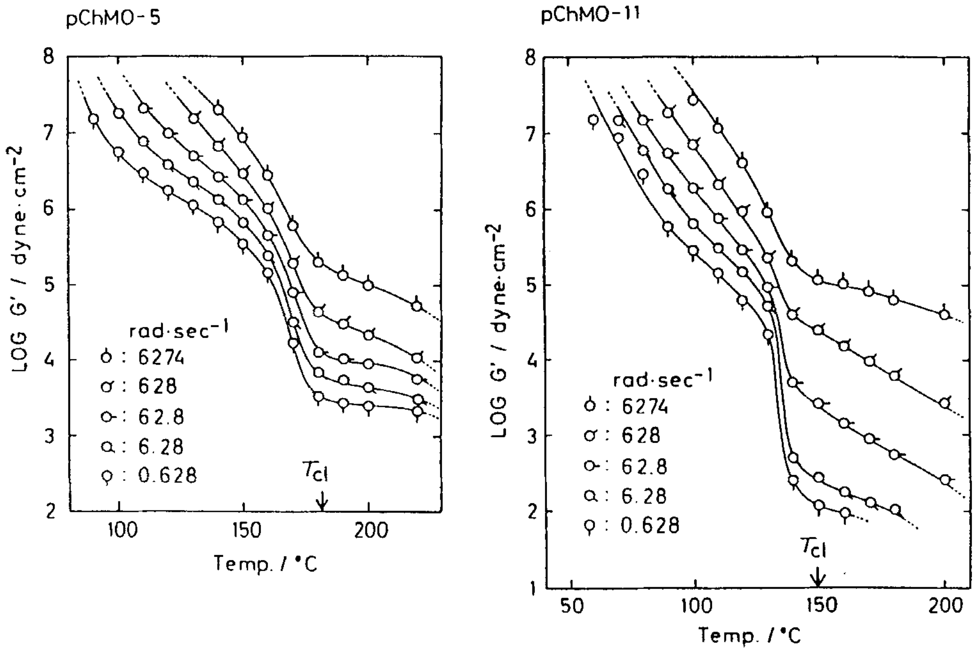


FIGURE 2 Temperature dependence of G′ for pChMO-5 and pChMO-11 at various frequencies.

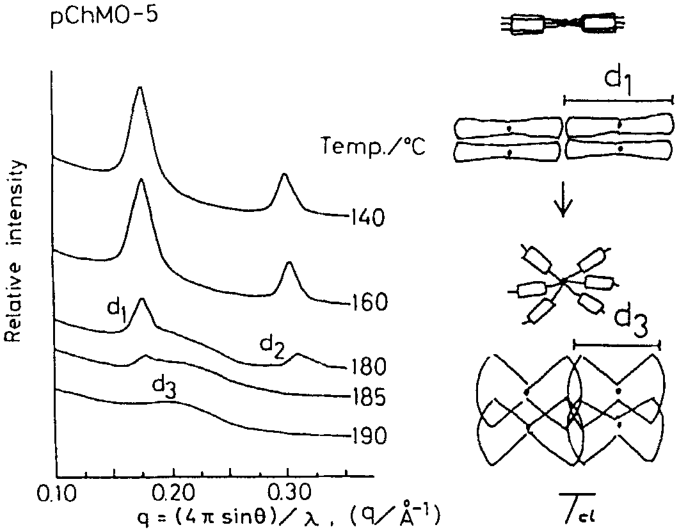


FIGURE 3 Small angle X-ray diffraction diagram for pChMO-5 and schematic illustration of the polymer.

transition process from the flat lamellate structure of macromolecules in the smectic A phase to the random structure in the isotropic phase.

Figure 3 shows small angle X-ray diffraction diagrams of pChMO-5 at various temperatures. The diffraction peak (d_1) is attributable to the two layer packing structure in the smectic A phase, and is maintained up to T_{cl}. However, another broad diffraction peak (d_3) appears at T_{cl}. This broad peak is not attributable to other liquid crystalline structure.[6] This diffraction peak (d_3) is caused by smectic-isotropic transitional process in which the large side chains arranged into lamellae below T_{cl} cannot behave isotropically just above T_{cl} due to the linkage of the side chains to the main chain. This transition model (plate-like to isotropical conformation via loose rod-like) seems to support the assumption of the loose entanglements between the side chains.

CONCLUSION

The dynamic viscoelastic properties of the liquid crystalline side-chain polymers were investigated. The glass transition becomes sharper with increasing the spacer length (n). This result seems to become experimental evidence of the assumption that increment of the spacer length proceeds the decoupling the motion of the side mesogenic groups from that of the main chain. Temperature dependence diagram of G′ shows that no plateau region exists in the mesophase. However, a quasi-plateau region (10^3-10^5 dyne/cm^2 varied with the frequency) just above T_{cl} was observed. The existence of quasi-plateau seems to be due to loose entanglements between the large and rigid side chains. The X-ray diffraction investigation suggests that the side chains in an arrangement into lamellae below T_{cl} can not move isotropically just above T_{cl}.

References

1. W. R. Krigbaum, *Polymer Liquid Crystals*, Ed. A. Ciferri, (Academic Press, New York, London), p. 275 (1982); R. B. Meyer, ibid., p. 133 (1982).
2. K. F. Wissbrun, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 1835 (1982).
3. P. Fabre, C. Casagrande, M. Veyssie, and H. Finkelmann, *Phys. Rev. Lett.*, **53**(10), 993 (1984).
4. R. Zentel and J. Wu, *Makomol. Chem.*, **187**, 1727 (1986).
5. T. Yamaguchi, T. Asada, H. Hayashi, and N. Nakamura, *Macromolecules*, **22**(3), 1141 (1989).
6. T. Yamaguchi and T. Asada, *Liq. Cryst.*, **8**(3), 345 (1990).
7. T. Yamaguchi, T. Hayashi, and N. Nakamura, *Mol. Cryst. Liq. Cryst. Lett.*, **5**(1), 23 (1987).
8. P. Zugenmaier, *Macromol. Chem., Macromol. Symp.*, **2**, 33 (1986).