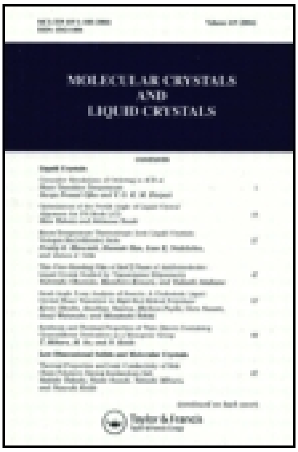

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Viscoelastic Properties of Low Temperature Thermotropic Liquid Crystalline Polymers

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VISCOELASTIC PROPERTIES OF LOW TEMPERATURE THERMOTROPIC LIQUID CRYSTALLINE POLYMERS

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Abstract Main-chain type thermotropic liquid crystalline polymers HPC-P having lower liquid crystalline temperature were obtained by esterification of hydoxypropyl cellulose. Two different samples were obtained, the one is HPC-P(1) having DS=2.4 and another one is HPC-P(2) having DS=2.8. Logarithmic curves of dynamic modulus(G') and loss modulus(G") against frequency obtained at different temperatures within liquid crystalline temperature range can be superposed to obtain a single composite curve for both samples. The composite curves for G' show lower frequency side plateau(Ca. 300 dyne/cm^2). The log G' against temperature curves for both samples decrease with increasing temperature upto transition temperature and then increase upto T_C and then decrease again with increasing temperature above T_C showing maxima at around T_C.

INTRODUCTION

Rheology of Polymeric Liquid Crystals of rod-like molecules has been summarized briefly sometimes and the behaviors are inductively summarized by some authors[1,2]. Rheological behaviors of thermotropic main-chain type liquid crystalline polymers have been studied by many investigators[3,4]. The knowledge, however, for rheological properties for thermotropic liquid crystalline polymer at their liquid crystalline temperature has not yet been summarized inductively. Moreover, different results have often been reported on a same material[4,5]. One of the reasons is the difficulty to control the sample history at the initial state of a specimen, because they can never attain the isotropic melt state without any chemical structural change. A main-chain type thermotropic liquid crystalline polymer HPC-P having lower liquid crystalline temperature was obtained by esterification of hydroxypropyl cellulose. The dynamic viscoelastic properties of this materials at the liquid crystalline state and also at the isotropic state have been studied.

EXPERIMENTAL

Samples

20g. of HPC-SL(Mw=104000), manufactured by Nihon Soda Co., were dried in vacuum, and after drying for 24 hours in zeolite were dissolved in 500 ml. of acetone. 20 ml. of pyridine (OH × 1.5 equivalent) were added, and the sample was cooled. 66 ml. of propionyl chloride was then added by trickling over a period of 1-2 hours. The sample was then refluxed for 1 hour at 60°C-70°C, and poured into a large volume of distilled water, producing a white oily precipitate. This was re-precipitated and refined several times in distilled water and acetone, washed thoroughly in distilled water, and dried in vacuum. Two separate samples were prepared, one (referred to below as HPC-P(1)) which was prepared by shorter reaction time (one and half hours) and the other (HPC-P(2)) which was prepared by longer reaction time (two hours). The former (HPC-P(1)) was showing a somewhat greenish iridescent cholesteric color at room temperature, while the latter (HPC-P(2)) was transparent and colorless at room temperature and showed a violet cholosteric color at approximately 70°C. The difference of reaction time causes the difference of DS values of the samples as shown later.

When cellulose derivatives form liquid crystals, they normally display a cholesteric phase, and we can assume from the above that HPC-P also becomes a cholesteric liquid crystal.

Characterizations

Measurement of Degree of Substitution

Substitution was measured using reverse titration. Approximately 100 mg of the prepared HPC-P was precisely weighed, and dissolved in 10ml of 1/10N HPC and three drops of 1/10N Phenolphthalein were added, and titration carried out with 1/10N NaOH.

The results showed DS=2.4 for HPC-P(1), and DS=2.8 for HPC-P(2).

Microscopic Examination under Polarized Light

Under direct polarized light, the field of vision began to darken at 140-160°C for HPC-P(1), and at 180°C had become completely isotropic. HPC-P(2) displayed a typical two-phase region at 150-170°C, had undergone a phase reversal at 170°C and was completely isotropic at 180°C.

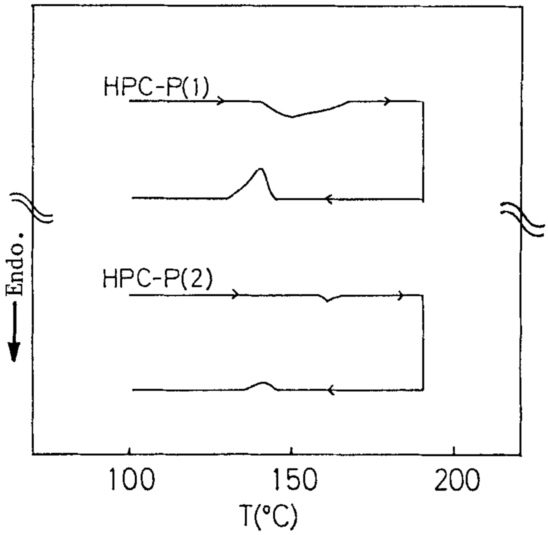

FIGURE 1 DSC curves for for Samples.
Ascending: 0.5°C/ min.
Descending: -0.5°C/ min.

Measurement of DSC

Peaks, thought to be due to phase transition between the liquid crystalline and isotropic states, were observed at 162°C (rising temperature) for HPC-P(2) (Figure 1). The heat of transition obtained by DSC for HPC-P(1) was $\Delta H = 0.186$ cal/g. and for HPC-P(2), $\Delta H = 0.237$ cal/g..

Equipment

The equipment used for the measurement of dynamic viscoelasticity, was the KU-O type, already reported elsewhere[6]. Commercially available equipment for the measurement of dynamic viscoelasticity (the DVE Rheospectra manufactured by the Rheology Corp, KYOTO.) was modified to allow the use of liquid crystal samples; the measurement area was made into parallel flat plates, to apply a simple shear deformation to the sample. The use of this equipment facilitates temperature control, and permits the measurement of minute changes up to very high frequencies(1kHz). During measurement, linearity was continually checked by the use of a Lissajous'figure.

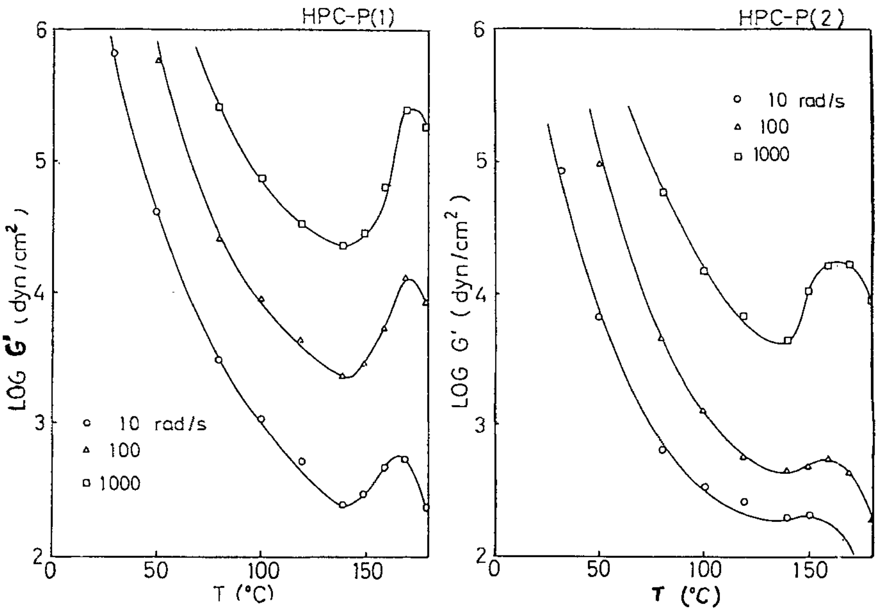

FIGURE 2 Temperature dependence of dynamic modulus G'.

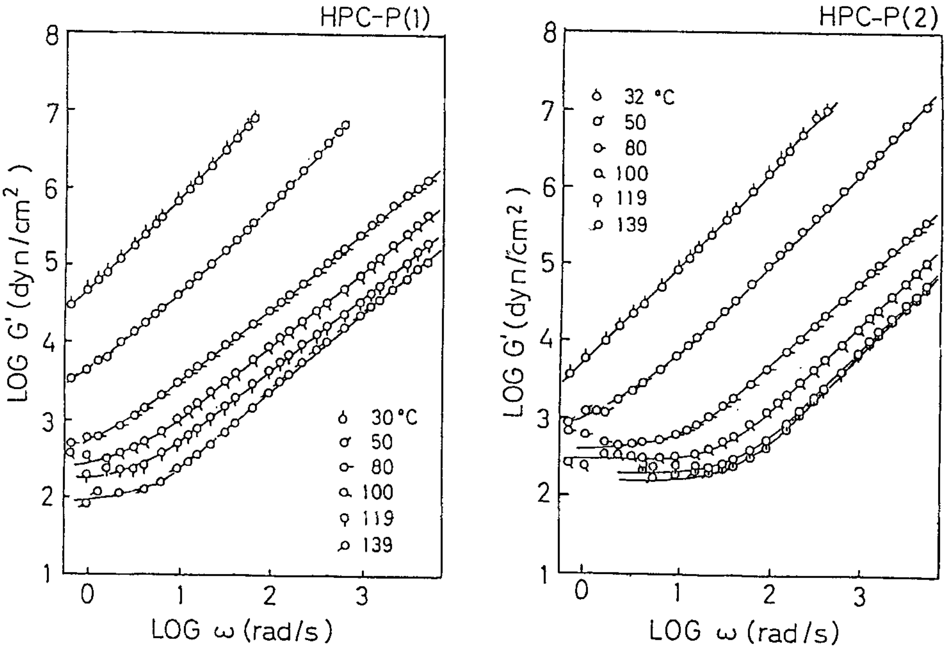

FIGURE 3 Frequency dependence of G'.

RESULTS AND DISCUSSION

Temperature Dependence of G'

Figure 2 shows the graphs showing the temperature dependence of G' at frequencies of 10 rad/sec, 100 rad/sec, and 1000 rad/sec. G' appears to have a tendency to show minima and maxima against temperature, with this tendency being more pronounced at higher frequencies. Further, microscopic examination under polarized light suggests that the temperature range in which G' increases with temperature is the two-phase range, where the isotropic and liquid-crystal phases coexist, and that the temperature range on the high-temperature side where G' decreases with rising temperature is the range where the isotropic phase only exists.

There have been few reports of this tendency in G'. Moreover, when similar experiments have been carried out on low molecular weight thermotropic liquid crystals, whereas η' showed a maximum at the phase transition from the liquid crystal to the isotropic phase, G' showed no such maximum. This suggests that the tendency of G' to show a maximum at the liquid crystal - isotroic phase transition is a characteristic peculiar to liquid crystals of high molecular weight. This is cosidered that this is because at the transition to the isotropic phase, the tension in the entangled molecular chains increases as a result of active micro-Brownian motion in the molecular chains. This would fit in with the fact that the tendency for G' to show a maximum is more marked at high frequencies, where the effect of entanglement is greater.

Frequency Dependence of G'

Since, compared with G', the changes in G" were unremarkable in all temperature ranges, the following report refers mainly to the results concerning G'.

1) Liquid Crystal Phase Temperature Range

At low temperatures near to room temperature, G' rises almost in proportion to frequency, leveling out at the high-frequency side. Conversely, at the low-frequency end a plateau appears for values of G'= 100-1000 dyne/cm^2(Figure 3). This type of low-frequency plateau can also be observed in particle dispersed systems, but whereas in these systems the Lissajous'figure loses its linearity in response to even the slightest strain,

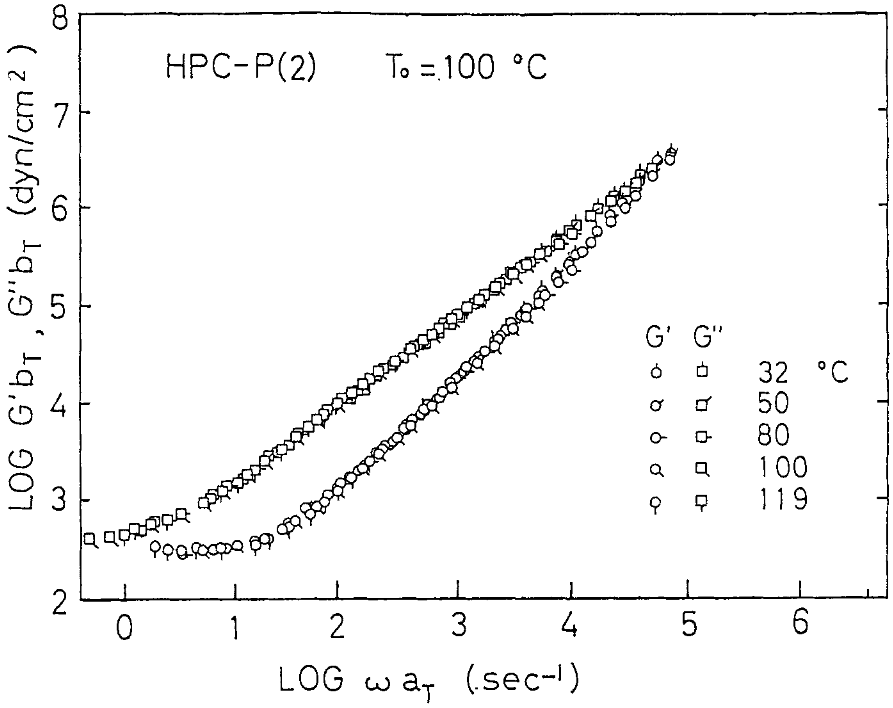

FIGURE 4 Composite curve obtained by time-temperature superposition for HPC-P(2). Reference temperature:100°C.

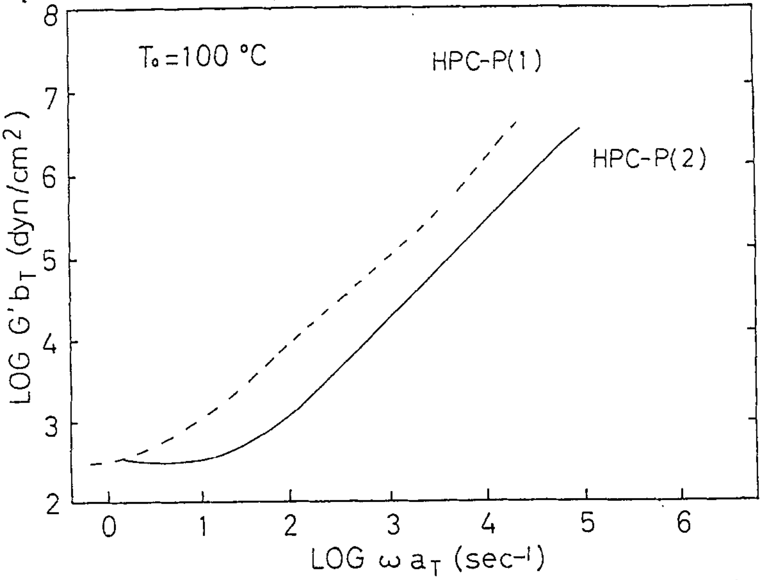

FIGURE 5 Comparison of the composite curves for HPC-P(1) and HPC-P(2).

in this system linearity was preserved even with a strain of 20 %. From this, we consider that the plateau on low-frequency side is due to long-period relaxation of the supper structure of the liquid crystal, but this is a topic requiring further investigation.

When determining the frequency dependence of G' (or G") over a wide frequency range, the principle of time-temperature superposition is most useful. It would be extremely interesting, from both an academic and a practical viewpoint, if this principle could also be applied to liquid crystal systems, but there are few reports of this sorts[8].

Figure 4 shows the superposed G'-ω (G"-ω) curves(allowing shifts in the direction of the vertical axis, b_T) for HPC-P(2) with 100 °C as standard temperature, for temperatures from 30-100 °C, for which we can assume the sample was in the liquid crystal phase alone. All the curves fitted neatly onto a single composite curve. Shifts in the direction of the vertical axis are normally ignored in the case of amorphous polymers[9]. For crystalline polymers the necessity of vertical shift is considered to a result of the degree of crystallization, or of the degree of orientation of the crystalls[10-12], but it is as yet unclear what causes them in liquid crystal systems.

Hitherto there have been few reports on viscoelastic behaviors of liquid crystals over a wide frequency range such as shown in Figure 4. This Figure is particularly interesting in that it covers virtually the whole frequency range of the flow region, G' shows a plateau on the low-frequency side due to long-period relaxation of the supper structure or textures. In Fig.4, a_T represents the shift factor in the direction of the horizontal axis. For a_T, it was found, by using the standard method[9], that the WLF formula applied reasonably well.

Figure 5 shows the composite curves for HPC-P(1) and HPC-P(2), carrying out superposition with 100 °C as standard temperature. The shape of the curve is the same, and it is clear that the whole graph for HPC-P(1), with its higher degree of substitution, is shifted towards the high-frequency side. This indicates that the relaxation tome has been shortened as a result of the increase in molecular motion due to the increasing of the free volume which results from the flexible side chains. It has been considered that flexible side chains can play a role as a solvent in macromolecular thermotropic liquid crystals, and the present results provide rheological evidence for this. The difference between the shift factors for HPC-P(1) and

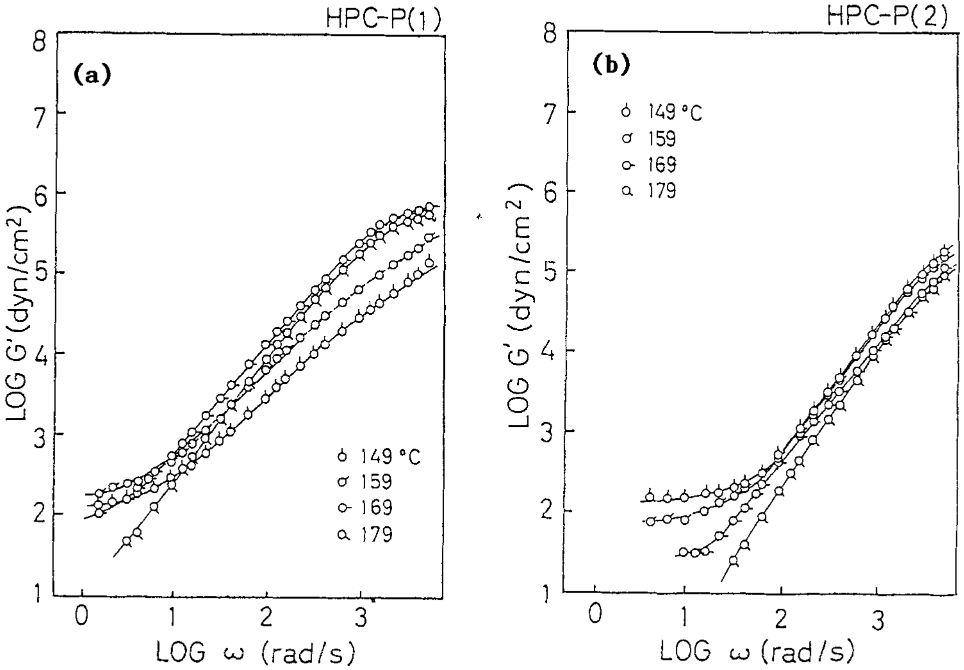

FIGURE 6 Frequency dependence of G'. (Two-phase temperature and isotropic temperature ranges).

HPC-(2) was within the margin of error.

2) Isotropic Temperature Range

In the isotropic temperature range, G' for both HPC-P(1) and HPC-P(2) was proportional to the frequency to the power of approximately 1.6(Fig. 6). The result for HPC-P(1) shows a plateau on the high-frequency side, thought torepresent a rubber-like region(Fig. 6a). In fact, G'is greater than G" in this region, suggesting that entanglement is occurring.

3) Two-Phase Range

As the slope of G' gradually increases, it approaches the slope of the isotropic region (Fig.6). Further, as can be seen particularly clearly in the case of HPC-P(2), the plateau at the low-frequency side gradually disappears with rising temperature. This fact also shows that the plateau on the low-frequency side is related to the superstructure of polymeric liquid crystal.

Further, in order to investigate the viscoelastic behavior in its two-phase region, we postulated the additivity of G'(or G") at liquid crystalline

$$G'_{bi} = \phi_{LC}\, b_T G'_{LC}(\omega a_T) + [1 - \phi_{LC}]\, G'_{iso}(\omega a'_T)$$

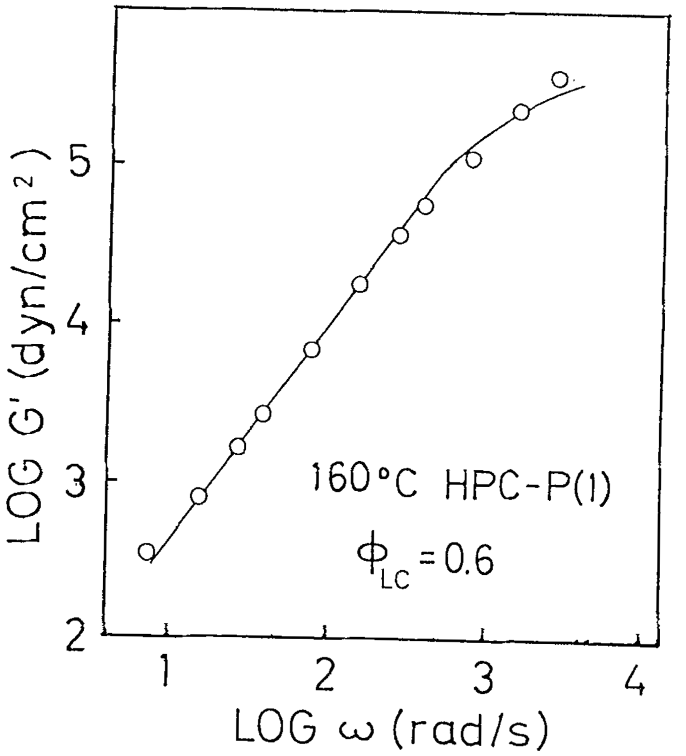

FIGURE 7 G' in two-phase region.
Open circles : Experimental results for HPC-P(1) at 100 ^{o}C.
Solid line: Caluculated curve by the Equation.

temperatures and G'(or G") at isotropic temperatures, depending on the volume fractions. This means we corrected the values of G' (or G") in each phase by multiplying these by the volume fractions obtained a value for G'(or G") for the two-phase region (See equation below).

$$G'_{bi} = \phi_{LC}\, b_T G'_{LC}(\omega a_T) + [1 - \phi_{LC}]\, G'_{iso}(\omega a'_T)$$

For the isotropic region we ignored the shift in the direction of vertical axis, on the basis of facts observed in time-temperature superposition in amorphous polymers[9]. Fig.7 shows the experimental results at 160°C and the calculated curve for G' for HPC-P(1) when Φ_{LC} was taken as 0.6 in the above equation. It is clear that there is a close approximation between the calculated curve and experimental value.

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