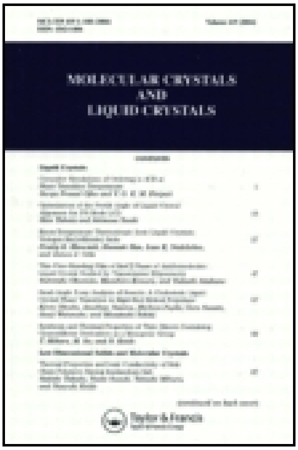

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In order to explore the motion of low molecular compound (LMW) of which chemical structure is similar to the mesogenic groups of liquid crystalline main-chain (LCP) in LCP/LMW composite system was studied by means of dielectric measurements and director order parameter (Sd) determinations by dielectric relaxation spectroscopy. The unaligned PLC exhibits a dielectric absorption of the α-relaxation process occurs in the glassy state. On the other hand, the unaligned material including 40 mol% of LMW in composite system exhibits a new dielectric absorption, which is based on the δ-relaxation process as judged by the activation energy. The director order parameter (Sd) varied from 0.16 to −0.30. It found that the dielectric behavior of the PLC/LMW composite system is very similar to that of liquid crystalline side-chain polymers.

Keywords: liquid crystal/composite system/dielectric properties

INTRODUCTION

Since thermotropic liquid crystalline polymers having groups in the side-chain were synthesized in the late 1970's by Ringsdorf, Finkelmann and Wendorff, and by Shibaev and Plate and their co-workers,[1–3] they have been the subject of intense research activity and their possible uses as optical information storage media[2,4,5] and as non-linear optical materials.[6,7] These novel materials combine the electro- and magneto-active properties of low molar mass mesogens with good physical properties of macromolecules.

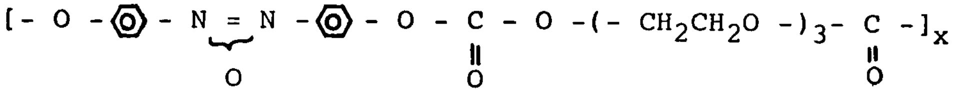
Generally liquid crystalline polymers in a mesomorphic state are more viscous than liquid crystalline low molecular compounds. Therefore, the response time of liquid crystalline polymers to an external stimulation such as electric and magnetic fields is much greater than that of liquid crystalline low molecular compounds. In order to improve the response time, the method available for the introduction liquid crystalline low molecular compound of which chemical structure is similar to mesogenic side chain of liquid crystalline polymers is introduced to the liquid crystalline polymers and the behavior of their composite system have been reported.[8] Recently in the study of photochemical induced isothermal phase transition in liquid crystalline polymers, the order parameter of liquid crystalline side-chain polymer having mesogenic phenyl benzoate doped with a photochromic compound at low temperature are higher than any of the co-polymer although it dropped abruptly at the reduced temperature, $T_{red} = 1$.[9]

We are interested in the molecular dynamics of LCP/LMW composite system. As described elsewhere in detail,[10,11] in the case of electro-field-induced alignment, the response of the material is dependent on the dielectric anisotropy, $\varepsilon'(\omega)$, of the liquid crystal. This frequency-dependent quantity may be positive or negative as a result of dielectric relaxation of the principal permittivities $\varepsilon_{\|}'(\omega)$ and $\varepsilon_{\perp}'(\omega)$. Thus homeotropic or planar alignment may be achieved for liquid crystalline polymers by choice of the frequency of the directing electric field.[12,13]

In this paper, we describe the molecular motion in liquid crystalline polymer and low molecular compound composite system and the alignment behavior of their system.

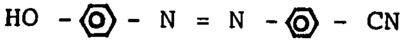
EXPERIMENTAL

The liquid crystalline main-chain polymer of polycarbonate type (PC96) and low molecular compound (HCB) used for our investigation have the following structure: L. C. Polymer (PC96),



$$[-O-\bigcirc-\underset{O}{N=N}-\bigcirc-O-\underset{\overset{\|}{O}}{C}-O-(-CH_2CH_2O-)_3-\underset{\overset{\|}{O}}{C}-]_x$$

Low molecular compound (HCB),



The clearing temperature is 145°C and the glass transition temperature (Tg) was 13°C, respectively. Molecular weight was 9600. The dielectric measurements were made in the range 25 to 10^5 Hz using a GenRad 1689 Digibridge, a Hewlett-Packard 87B computer. The polymer sample was contained in a three-terminal dielectric cell and was in the form of a disc about 1.0 cm diameter and 100 μm in thickness. The dielectric loss data are presented here as $G/\omega = \varepsilon''Ca$ where G is the equivalent parallel conductance of sample, ω = 2¶*f*/Hz, ε'' is the dielectric loss factor and Ca is the interelectrode capacitance. The sample for the dielectric measurement was prepared by cooling to room temperature at a rate of approximately 0.03K min^{-1} from the isotropic phase.

The sample was aligned in the dielectric cell by following procedure. The cell was heated to isotropic phase and was maintained at this temperature 10 min before a.c. electric voltage (100 and 300 V rms) at frequency (1–10 kHz) was applied. The cell with voltage maintained was cooled slowly to room temperature at rate of about 0.03K min^{-1}. The source of V was removed, the cell was short-circuited to remove any extraneous polarization and was connected to the digibridge for the dielectric measurements to be made at any desired temperature.

RESULTS AND DISCUSSION

Figure 1 shows plots of G/ω against $\log_{10} f$ for unaligned sample (PC96) obtained at given temperature in the range of 28.1 to 70.3°C. One broad absorption feature is observed, and loss peaks becoming observable in this frequency range about 15°C above the grass transition curves are asymmetric and of a form commonly seen for the α-relaxation in amorphous glass-forming polymer materials and the width at the half-height of the loss curves for unaligned (PC96) is >2.3 units of $\log_{10}$, which is to be compared with 1.14 for single relaxation process. This observation, taken with the large apparent activation energy (282 kJ/mol), suggest that the major peak part of the relaxation above Tg is associated with the microbrownian motion of the dipolar groups along the chain (α-process) where the motions are cooperative and the strong temperature dependence for the frequency of maximum loss *fm*. The mechanism for the α-process in the liquid crystalline polymer should differ from that is amorphous polymeric and non-polymer glass-forming materials.[14]

Figure 2 shows plots of G/ω against $\log_{10} f$ for unaligned (PC96) and unaligned (PC96)/HCB with 30 to 60 mol% of HCB at 46.2°C. It is clearly seen that the new loss curves of unaligned samples of the concentration 40 and 50 mol% of HCB (HCB40 and HCB50) appear in the low frequency region. The width at the half-height of the loss curves is about 2.5 units of $\log_{10}$. The Arrhenius plot for HCB 40 and 50 are seen in Figure 3. It is clearly seen that the temperature dependence of the relaxation frequency is nonlinear in the Arrhenius-plot. However, the apparent activation energies for HCB40 and 50 at low temperature are 150 and 156

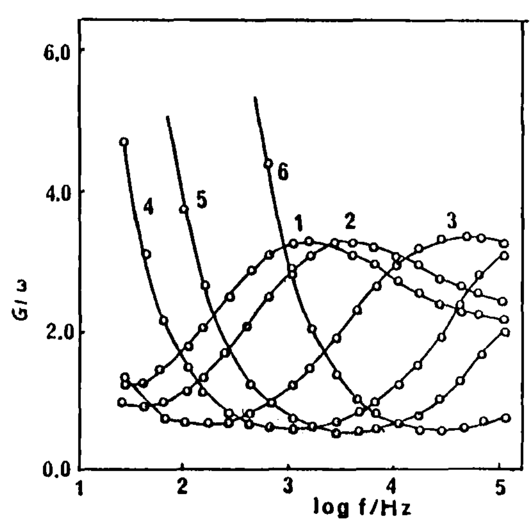


FIGURE 1 Frequency (f) dependence of the dielectric loss factor (G/ω) at different temperature for unaligned polymer (PC96). Curves 1–6 correspond to 28.1, 30.3, 36.6, 46.4, 54.0 and 70.3°C.

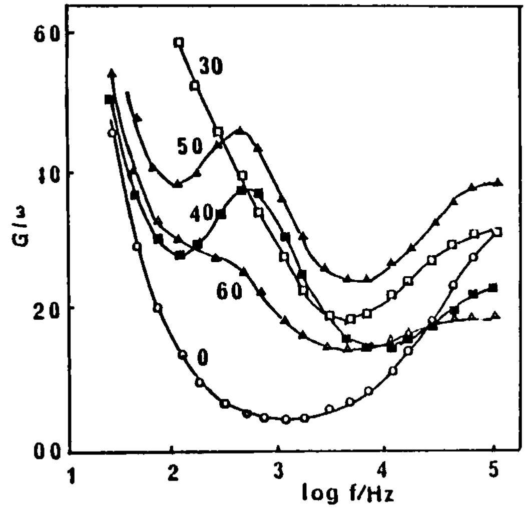


FIGURE 2 Frequency (f) dependence of the dielectric loss factor (G/ω) for unaligned PC96/HCB composite system at 46.0°C. Curves 0–60 correspond to the concentration of low molecular compound (HCB).

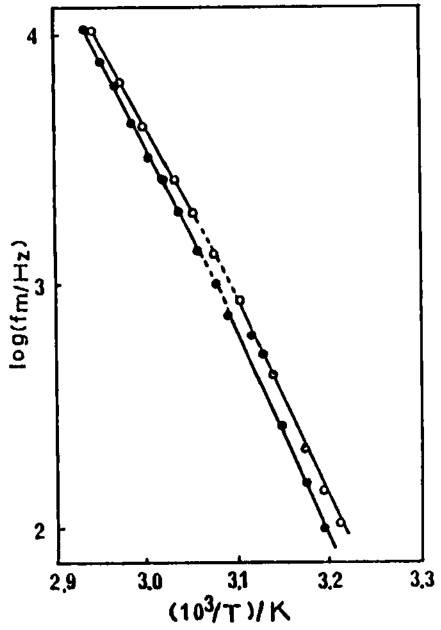


FIGURE 3 Arrhenius plots of the dielectric relaxation frequencies (*fm*) for unaligned HCB 40 (○) and HCB 50 (●); *fm* = frequency of maximum loss factor.

kJ/mol, respectively, and those values at high temperature are 126 and 136 kJ/mol, respectively. Those values for HCB40 are the same as those of HCB50 and/or agree well with published data.[15] Consequently, we assigned this relaxation to rotations of the mesogenic group around the backbone chain, i.e., δ-process. As shown in Figure 3, the Arrhenius plots lie on two straight lines intersecting at definite temperature. These definite temperatures for HCB40 and 50 were about 52°C. This fact suggests that the phase transition exists in liquid crystal state for both samples.

We tried an alignment of HCB40 in the present of 100V rms/1–10 kHz and 300V rms/1–10 kHz. Figure 4 shows for the unaligned and partial aligned HCB40 at 46.2°C. It is clearly seen that the loss curves of the aligned sample of 100V rms/1 kHz applied are more symmetric and of increased amplitude compared with the loss curve of the unaligned phase. The curves appears to be due to the δ-process. However, the loss curves of the aligned sample 100V rms/10 Khz, 300V rms/1–10 kHz applied are more broad and of decreased amplitude compared with that of the unaligned phase. It is possible to evaluate the director order parameter (Sd) of those samples. In a full homeotropically aligned mesophase the director and aligning electric field direction are parallel, i.e., $n \parallel E$, and Sd is unity. For a planarly aligned mesophase, the director and the aligned electric direction are perpendicular, i.e., $n \perp E$ and Sd is -0.5. For unaligned samples Sd is zero. The dynamic process is expressed by the Fuoss-Kirkwood empirical relaxation function so that this relation is written as,

$$G/\omega = \alpha_\delta \mathrm{sech}[\beta_\delta \ln(f/fm_{,\delta})] + \alpha_\alpha \mathrm{sech}[\beta_\alpha \ln(f/fm_{,\alpha})] \qquad (1)$$

where α_i is $(G/\omega)_{\max}$ for process i, which $i = \alpha$ and δ, β is the distribution parameter and fm, i is the relaxation frequency. It is possible to estimate the dielectric in-

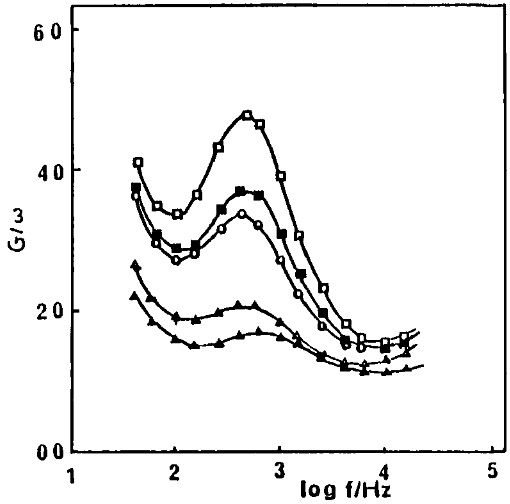


FIGURE 4 Frequency (f) dependence of the dielectric loss factor (G/ω) for unaligned and partial aligned HCB 40 at 46.2°C. (■); unalignment, (□); 100V rms/1kHz, (○); 100V rms/10kHz, (▲); 300V rms/1kHz, (▲); 300V rms/10kHz.

crement ($\Delta\varepsilon''$) for the entire relaxation using the Fuoss-Kirkwood's parameter β_i and α_i. This dielectric increment $(\Delta\varepsilon')_i$ for process i is proportional to $A_i = \alpha_i/\beta_i$, where i is α or δ-process. The relation between Sd and the ratio of $(A_{PA,\delta})/(A_{U,\delta})$ is given by[11]

$$(A_{PA,\delta})/(A_{U,\delta}) = 1 + 2Sd \qquad (2)$$

The loss data for unaligned, partially aligned samples were analyzed using Equation 1 by the computer simulation using six adjustable parameters. The director order parameter (Sd) obtained from Equation 2 are 0.16 to −0.30 for the partially aligned samples with 100V rms/1 kHz to 300V rms/1-kHz, respectively. The value of Sd is also given by the ratio maximum loss factor for partially aligned and unaligned sample[16];

$$Sd = \left(\frac{1}{2}\right)[\varepsilon''_m)_{PA,\delta}/(\varepsilon''_m)_{U,\delta} - 1] \qquad (3)$$

They agreed very closely with those obtained by Equation 2. From these results, a schematic plan of the alignment of (PC96)/HCB composite system is illustrated in Figure 5. The low molecular compound in the composite system aligned at random in the space between the liquid crystalline main-chain and the alignment of HCB may be changed in the present of a.c. field applied. It is concluded that molecular dynamics of the (PC90)/HCB composite system shows the same behavior

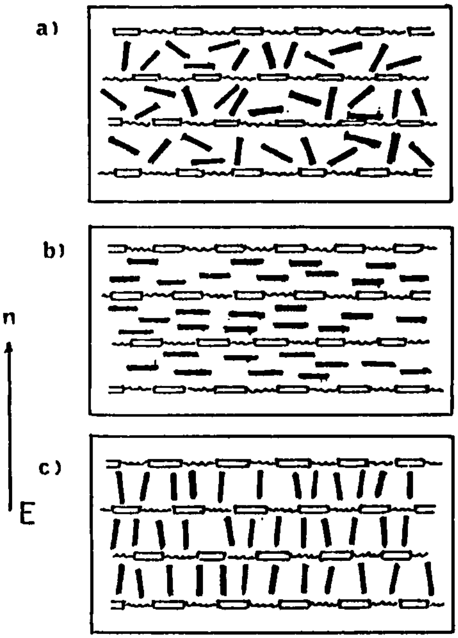


FIGURE 5 Scheme of alignment. a); unalignment, Sd = 0, b); full planarly, Sd = −0.5, c); full homeotropic, Sd = 1.

as if they were the mesogenic groups in the side-chain of liquid crystalline side-chain polymers.

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