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THE PHYSICAL PROPERTIES OF A SIDE-CHAIN TYPE POLYSILOXANE LIQUID-CRYSTALLINE POLYMER WITH ELECTRORHEOLOGICAL EFFECT

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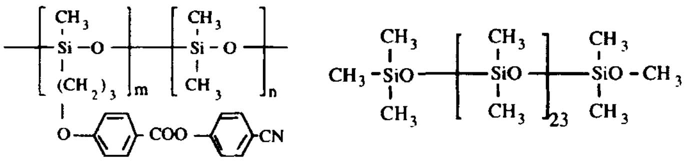
Abstract The fundamental physical properties of a side-chain type polysiloxane liquid crystalline polymer, which shows a large electrorheological (ER) effect when diluted with poly-dimethylsiloxane (PDMS), were investigated by means of x-ray diffraction and dielectric measurements. From the results of X-ray diffraction it was found that at about 40°C the polymer undergoes a first-order phase transition from the smectic phase to the isotropic phase. A dielectric absorption due to the δ-process was observed, the activation energy was determined to be 81kJ/mol. In addition, a relatively large conductivity was found in this polymer, the apparent activation energy of which is about 93 kJ/mol.

INTRODUCTION

The liquid crystalline polymers (LCPs) have been extensively investigated because of their various advantages such as high fluidity, the effect of self reinforcement, high speed solidification. As examples of practical uses, engineering plastics[1] and display devices[2] are well-known and in recent years many other applications have been proposed[3-5]. Inoue *et al.* reported that a thermotropic liquid crystalline polymer consisting of benzoic acid phenylester mesogenic groups as side chains of the siloxane polymer main chain diluted with poly-dimethylsiloxane (PDMS) showed a large electrorheological (ER) effect[6], i.e., the increase in viscosity by application of an electric field. ER-fluids have received considerable attention because of their potential applicability for active control devices such as dampers, shock absorbers, clutches and brakes. The above polymer blended ER fluid has been of considerably practical interest, since this system has many advantages as compared with other ER fluids such as the particle-dispersion[7] and the homogeneous systems[8]. So far, however, the mechanism of ER effect for this fluid has not been clarified. Furthermore, there has been very little information about fundamental physical properties of the above LCP. Before exploring the mechanism of ER effect, we need to investigate the physical properties of the pure polymer not diluted with PDMS. In this paper, in order to investigate the phase sequence and dielectric properties, we carried out X-ray diffraction and the dielectric measurement of this polymer.

EXPERIMENTAL AND RESULTS

The sample was synthesized by Asahi Chemical Industry[9]. It is a random copolymer consisting of benzoic acid phenylester mesogenic groups as side chains of the siloxane polymer main chain (see Figure 1). As mentioned above, this polymer diluted with dimethylsilicone shows a large ER effect. However in this study we used pure polymer.



(a) (b)

FIGURE 1 Chemical structures of (a) LCP and (b) PDMS.

The sample for X-ray diffraction was prepared by dropping on a glass plate ($20\times20mm^2$) at 100°C without any orientation process. After spreading the polymer on the plate, it was cooled down to the room temperature at the rate of ca. 20°C/min. The X-ray measurement was carried out by a banzai-type X-ray diffractometer for liquid interfaces (Nagoya University) and the X-ray source was the CuK_α line ($\lambda=1.54051$Å). The temperature of the cell was controlled in an oven to an accuracy of ±0.2°C. The data were collected during heating.

As shown in the inset of Figure 2, below about 35°C a sharp X-ray diffraction peak appears and the spacing corresponding to its position is about 37 Å, which is nearly equal to the length of mesogenic group, indicating that the lower temperature phase is the smectic phase. With increasing temperature, the intensity of the peak decreases and above 40°C the peak completely disappears without any diffuse scattering left. Therefore, the higher temperature phase is concluded to be isotropic. This is also confirmed by an observation through a polarizing microscope. The integral intensity of the peak decreases gradually with increasing temperature as shown in Figure 2. This result shows that the smectic and the isotropic phases coexist in a wide temperature range.

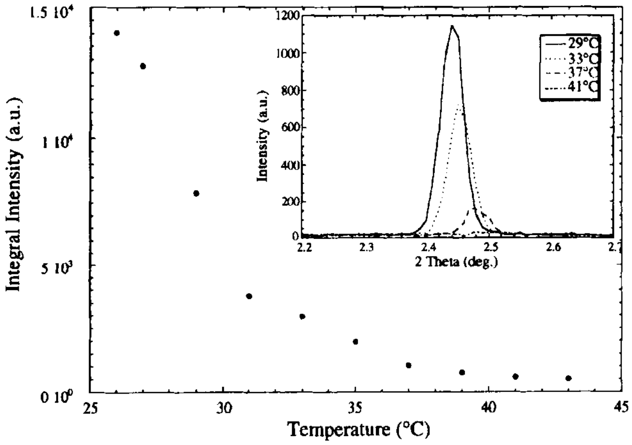
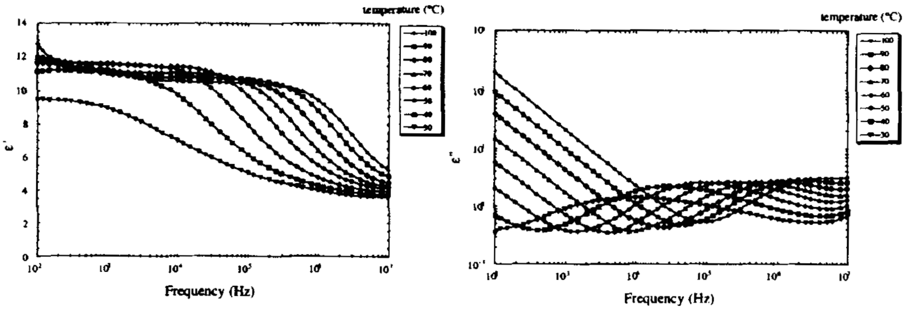


FIGURE 2 Temperature dependence of integral intensities of X-ray diffraction peak (see inserted Figure), which correspond to the smectic layer spacing.

This result has an important implication for the mechanism of this ER effect. The large ER effect is reported to appear above 50°C, where the polymer is isotropic. It should be noted that the present polymer is not immiscible with PDMS[10] and so the existence of the latter may not affect the phase transition of the former in the ER fluid. This suggests that the liquid crystalline property is not directly connected to the ER effect.

The dielectric measurements were carried out by an impedance analyzer (HP 4192A) at 30 frequencies in logarithmic sweep from 100 Hz to 100 kHz. The sample was sandwitched between ITO-coated glass plates separated by spacers of 100 μm. The data were collected during the heating process.

The temperature dependences of the real and imaginary parts of the dielectric constant are shown in Figure 3 (a) and (b), respectively, where it should be noted that the ordinate axis is linear in Figure 3 (a), but logarithmic in Figure 3 (b). An absorption peak is observed, which shifts to higher frequencies with increasing temperature. This relaxation is considered to correspond to the mesogenic motion in the direction of the applied electric field, which is called the δ–process[11]. It was shown that the temperature dependence of the relaxation frequency obeys the Arrhenius law with the activation energy being 81kJ/mol in the temperature range measured.



(a) (b)

FIGURE 3 Frequency dispersions of real and imaginary part of dielectric Constant at various temperatures (30-100°C).

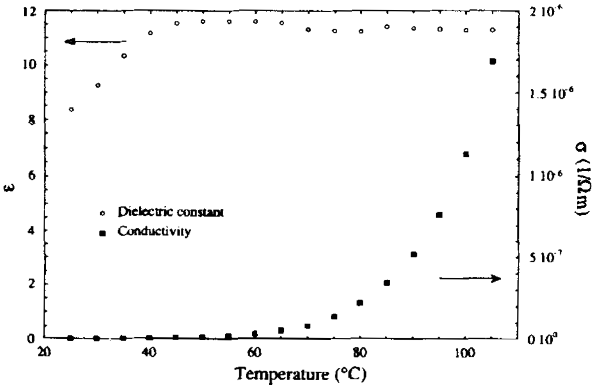


FIGURE 4 The temperature dependences of the dielectric constant (○) and the conductivity (■) calculated from the impedance data.

As shown in Figure 3 (b), the imaginary part increases linearly with the slope of -1 in logarithmic scale at low frequencies, indicating that this increase comes from the conductivity. In general, the imaginary part of the dielectric constant ε"(ω) is related to the conductivity σ(ω) as ε"(ω)=σ(ω)/ω. Figure 4 shows the temperature dependences of the real part of the dielectric constant at 500 Hz and the conductivity calculated from the above relation at 100Hz. Above the transition temperature the dielectric constant is almost constant , while below it the dielectric constant decreases with decreasing the temperature. This decrease may be due to the hindrance of the mesogenic motion in the smectic phase. On the other hand, the conductivity steeply increases with increasing the temperature in the isotropic phase. The Arrhenius plot of the conductivity is seen in Figure 5. It is clearly seen that the temperature dependence of the conductivity is linear in Arrhenius plot in the isotropic phase. The apparent activation energy for the conductivity of this polymer is about 93 kJ/mol.

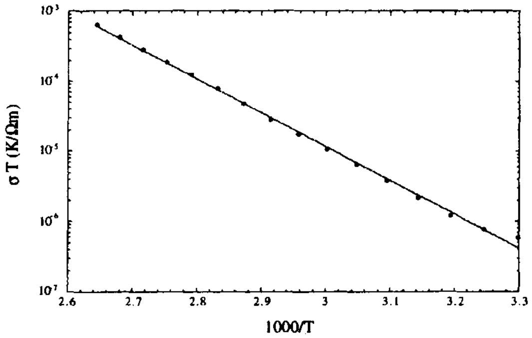


FIGURE 5 Arrhenius plot of the conductivity. The activation energy is estimated to be 93kJ/mol.

CONCLUDING REMARKS

The physical properties of a side-chain type polysiloxane liquid crystalline polymer, which attracts much attention for the potential applicability to ER fluids, were investigated by means of x-ray diffraction and dielectric measurements. A first-order phase transition from the smectic to the isotropic phase was found at around 40°C. A relaxation due to the δ-process was observed; it contributes the dielectric constant (*ca.* 12) in the low frequency region. In addition, this polymer has large conductivity (5×10^{-7} 1/Ωm at 90°C), which perhaps originates from free ions. The dielectric constant and the conductivity of this polymer thus obtained are larger than those of PDMS ($\varepsilon=2.4$, $\sigma=1 \times 10^{-14}$ 1/Ωm at 90°C) which are used as the diluent in the ER fluid. These results may become an important clue to understand the mechanism of the ER effect. As reported by Inoue *et al.*, in the ER fluid the polymer forms droplets in PDMS. In the presence of an electric field, therefore, the droplets will be elongated when the polymer and PDMS are different in dielectricity and/or conductivity by the electrostriction, as has been investigated in the other polymer mixtures by Torza *et al.*[12]. Thus, we conjecture that the ER effect is related to the deformation of droplets under a field. Studies on the structural change under a field are now in progress.

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