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As is well known, liquid crystalline polymers often show an electro-rheological (ER) effect. The polymers show a remarkable viscosity increment and a relatively long response time when an electric field is applied. However, for low molecular weight liquid crystals, the ER effect is small although the response time is fast. These facts suggest that the ER effect depends on the molecular weight of the constituent materials.

Diglycerol derivatives are designed and synthesized as oligomeric liquid crystals. These materials show considerably large ER effect and short response time. Consequently, it is considered that these derivatives are expected to be useful ER fluids for many industrial purposes.

Keywords: diglycerin derivative; diglycerol derivative; ER fluid; electro-rheological effect; oligomeric liquid crystal

INTRODUCTION

After the discovery of the electro-optical effect of liquid crystals in 1960's, many researches on its possible applications have been developed, with particular attention to liquid crystal displays. However,

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other properties of liquid crystals can be exploited in order to extend their application of liquid crystals to other fields. One of these properties is the change in viscosity upon application of an electric field.

The viscosity of a material in the presence of an electric field increases with increasing field. This phenomenon is reversible; therefore, the viscosity decreases with decreasing electric field application. This phenomenon is called electro-rheological (ER) effect, and the materials showing this effect are classified as ER fluids. The ER fluids are commercially useful materials, used for example for mechanical transmission parts.

It is known that some types of liquid crystals show ER effect [1–7]. A liquid crystal polymer shows a remarkable viscosity increment and a relatively long response time when the electric field is applied because of its high inherent viscosity [8,9]. The ER effect is also observed in low molecular weight liquid crystals. However, in these cases the ER effect is small although the response time is fast. These facts suggest that the ER effect depends, among other things, on the molecular weight of the material.

Oligomeric materials containing mesogenic groups were designed in order to obtain oligomeric liquid crystals which could represent novel ER fluids. In fact, since the molecular weight of the oligomeric materials is intermediate between those of liquid crystal polymers and low molecular weight liquid crystals, these materials are expected to show a remarkable ER effect combined with a relatively short response time. Therefore, diglycerol derivatives are designed and synthesized as novel oligomeric liquid crystals possibly representing novel ER fluids.

EXPERIMENTAL

Materials

Diglycerol obtained from Sakamoto Yakuhin Kogyo Co., Ltd. was used as starting material for the synthesis of the oligomeric materials. Four substituents containing the mesogenic group were introduced into diglycerol by esterification of the four hydroxyl groups. The mesogenic groups play an important role in the arrangement of the molecules in the direction of the applied electric field. The mesogenic group chosen, an alkoxy-4′-cyanobiphenyl, contains a relatively large fragment with positive dielectric anisotropy in addition to a flexible methylene chain. The oligomeric materials obtained are 2,2′,3,3′-tetra[ω-(4-(4′-cyanobiphenyl)oxy) alkanoyloxy] dipropylether (abbreviated hereafter as TCAD-n, n is a number of carbon atoms in the methylene chain) with

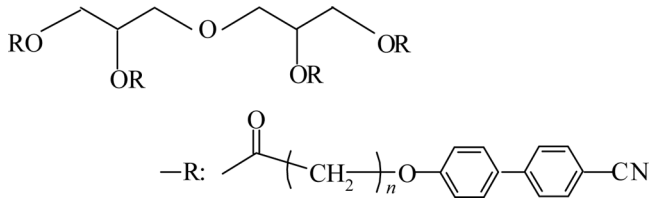

FIGURE 1 The general structure of TCAD-*n*.

$n = 4$, 5. The chemical structure of TCAD-*n* and the synthetic route followed are shown in Figures 1 and 2, respectively. After purification, the compounds were identified by ^{1}H-NMR (JEOL ALPHA-400 FT NMR) spectra.

^{1}H-NMR ($CDCl_3$)δ:7.68 (d, 8H, $J = 9.8$ Hz), 7.62 (d, 8H, $J = 8.3$ Hz), 7.51 (d, 8H, $J = 4.4$ Hz), 6.97 (d, 8H, $J = 21.0$ Hz), 5.20–5.19 (m, 2H), 4.36–4.11 (m, 4H), 3.99–3.97 (m, 8H), 3.73–3.51 (m, 4H), 2.36 (m, 8H), 1.82–1.79 (m, 8H), 1.69 (m, 8H), 1.52 (m, 8H) for TCAD-5.

^{1}H-NMR ($CDCl_3$)δ: 7.67 (d, 8H, $J = 8.5$ Hz), 7.61 (d, 8H, $J = 8.5$ Hz), 7.51 (d, 8H, $J = 3.9$ Hz), 6.96 (d, 8H, $J = 13.7$ Hz), 5.23–5.21 (m, 2H), 4.37–4.11 (m, 4H), 3.99 (m, 8H), 3.69–3.62 (m, 4H), 2.43–2.42 (m, 8H), 1.83–1.82 (m, 16H) for TCAD-4.

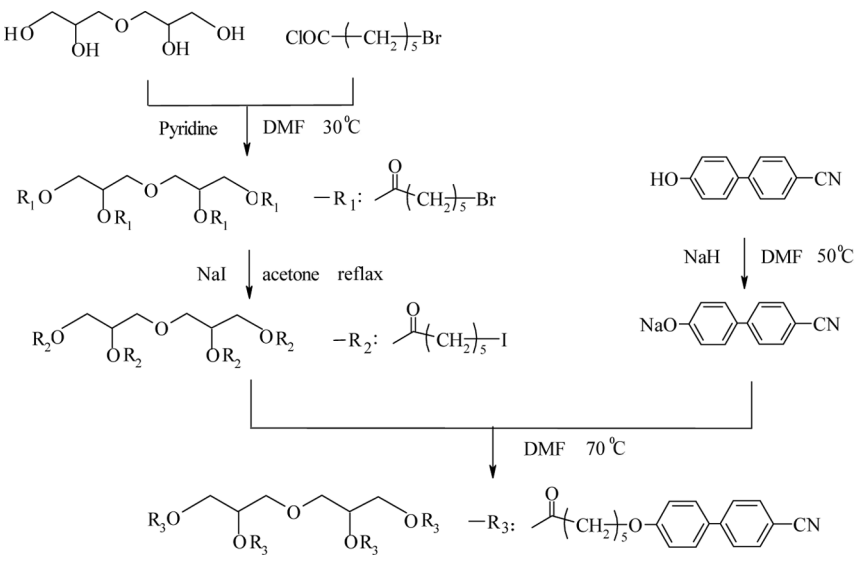

FIGURE 2 Synthetic route for TCAD-5.

Characterization

Phase transition phenomena were observed using DSC (PerkinElmer Pyris 1) and polarizing optical microscope (Nikon ECLIPSE E600) equipped with a hot stage (Mettler FP-82) and a central control processor (Mettler FP-90). Scanning rate was 2.0°C min^{-1}, and the temperature range of the measurements was $-20 \sim 120$°C. The phase transition temperature was defined at an on-set point of the DSC curves.

The measurements of dynamic viscoelasticity and ER effect were carried out by a rotational rheometer (UBM Rheosol-G2000) equipped with an electric field controller (Matsusada Precision Device high-voltage supply). All measurements were performed using a parallel plate cell, with 15.0 mm diameter and 0.3 mm gap. Shear rate was 10 sec^{-1}. The applied electric field was fixed at 1.67, 3.33, and 6.67 kV mm^{-1} for each measurement of the ER effect.

RESULTS AND DISCUSSION

Phase Transition Phenomenon

Figure 3 shows the DSC curves of TCAD-5. During the cooling process, a small but sharp peak (A) was observed at 94°C, and a base line shift (B) appeared at about 20°C. A fine schlieren texture was identified in the cooling process at around 94°C by observation with a polarizing microscope. The schlieren texture is shown in Figure 4. Therefore

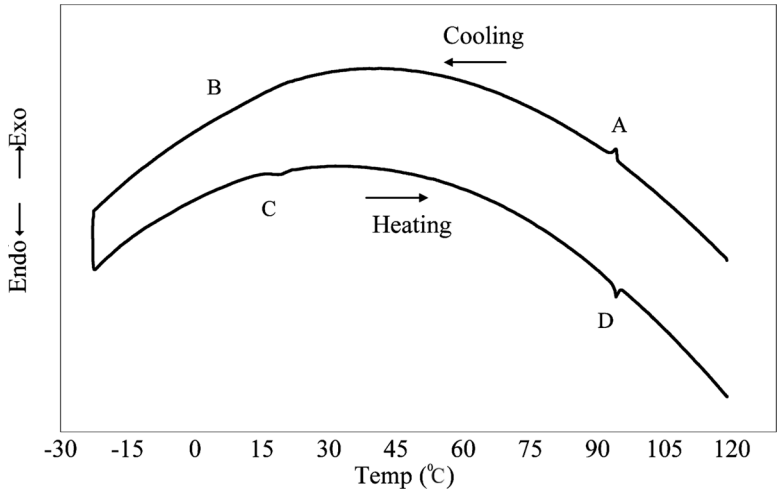

FIGURE 3 DSC curves of TCAD-5. Scanning rate: 2.0°C min^{-1}.

peak A was identified as a clearing point. The fine schlieren texture gradually grew with decreasing temperature, and finally the texture changed to homogeneous gray accompanied by the absence of peaks in the DSC curve. Although this gray texture did not vary around 20°C, the base line shift (B) was identified as a glass transition point because of the typical shape.

During the heating process, the base line shift (C) was observed at about 17°C, and a small sharp peak (D) was detected at 94°C. The former corresponded to the glass transition point as explained previously. The latter was the clearing point, because the gray texture was changing to the schlieren one with increasing temperature, and the schlieren texture became dark around 94°C. This result shows that TCAD-5 has the liquid crystalline phase between 94°C and 20°C on cooling and between 17°C and 94°C on heating. The liquid crystalline phase was identified as a nematic one since a schlieren texture was observed as well as perceptible fluidity. A quite similar phase transition phenomenon was observed in the case of TCAD-4. The liquid crystalline phase exists between 106°C and 19°C on cooling and between 22°C and 106°C on heating.

Dynamic Viscoelasticity

The dynamic viscoelastic behavior of TCAD-5 on cooling is shown in Figure 5. The storage modulus (G′) values obtained from 100 to about

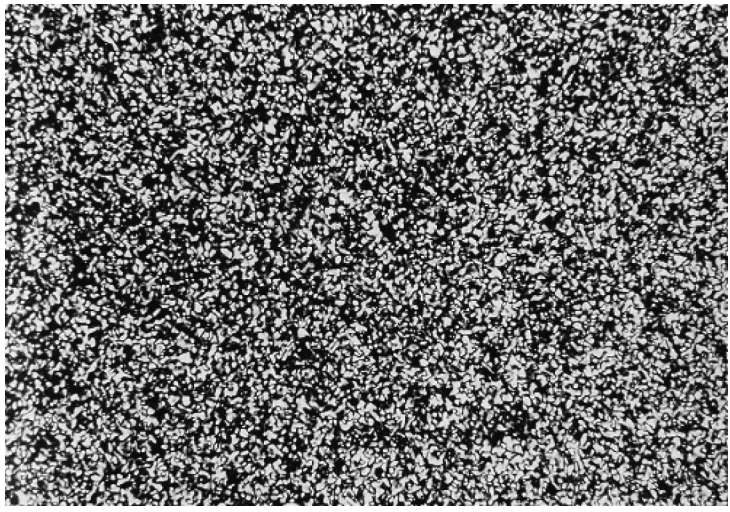

FIGURE 4 Schlieren texture appeared just below the clearing point.

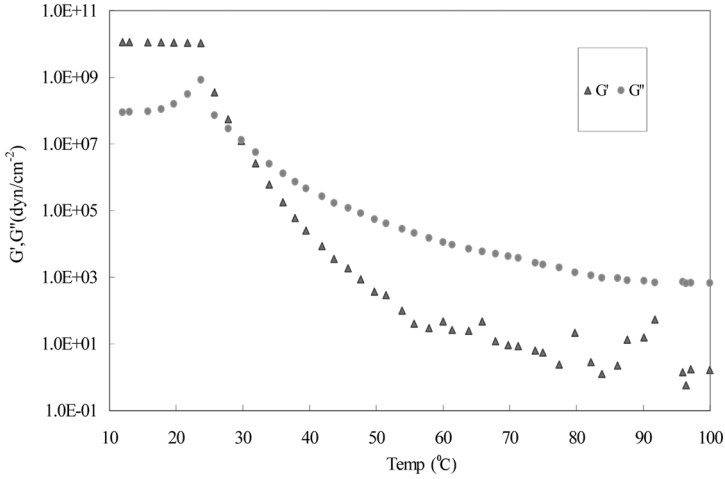

FIGURE 5 Temperature dependence of the storage modulus(G′) and the loss modulus(G″) of TCAD-5. Cooling process.

60°C drifted a little. This result might be attributed to a limitation of the torque detector of the apparatus. Therefore, the clearing point could not be clearly observed around 94°C. In addition, the loss modulus (G″) values did not show any drastic change at the clearing point, because the phase transition from the isotropic liquid to nematic phase is not accompanied by a dramatic structural change. In other words, there is no significant difference between the nematic structure and that of the isotropic liquid. In the liquid crystalline phase, the values of G′ and G″ increased gradually with decreasing temperature. This fact suggests that the degree of ordering of the liquid crystalline molecules in the phase increases with decreasing temperature. As mentioned earlier, the texture was gradually changed from a fine schlieren texture to a gray one with decreasing the temperature. Therefore, the texture change is attributed to the increment of the degree of arrangement of the molecules. Throughout the liquid crystalline phase, G″ values were higher than the G′ ones. This means that the liquid crystalline phase has viscoelastic properties. Below 20°C, the value of G′ was constant, while the value of G″ decreased with decreasing the temperature. This phenomenon is commonly observed below the glass transition point, though the glass transition temperature is a little higher than that obtained by DSC. This discrepancy is due to the different measuring methods. That is to say, the glass transition point is defined as a point corresponding to half the value of the

change in heat capacity obtained by DSC, whereas in viscoelastic measurements it is detected when the micro-Brownian motion freezes.

Upon heating, the viscoelastic measurements of TCAD-5 strongly resembled those observed on cooling. Similar results were obtained on cooling and heating for TCAD-4.

In general, G′ and G″ values of the low molecular weight liquid crystals remain constant in the liquid crystalline phase and change abruptly at the melting point. The results obtained from TCAD-5 and 4 are different from the behavior observed for the low molecular weight liquid crystals. However, the results obtained here resembled those of the liquid crystals which showed a glass transition such as oligomeric liquid crystals.

ER Effect

The results of ER effect measurements obtained at 40, 60, and 80°C for TCAD-5 are shown in Figures 6, 7, and 8, respectively. The values of the applied electric field are indicated in the figures. In each measurement, no electric field was applied for the first 300 sec. After that, the electric field was applied at 1.67 kV mm^{-1} for 120 sec, and with the same interval, the electric field was adjusted to 3.33 and 6.67 kV mm^{-1} The electric field was manually applied; therefore, a few time lags were observed in the figures, but this is not a serious problem because the response time was estimated as the interval of time observed from

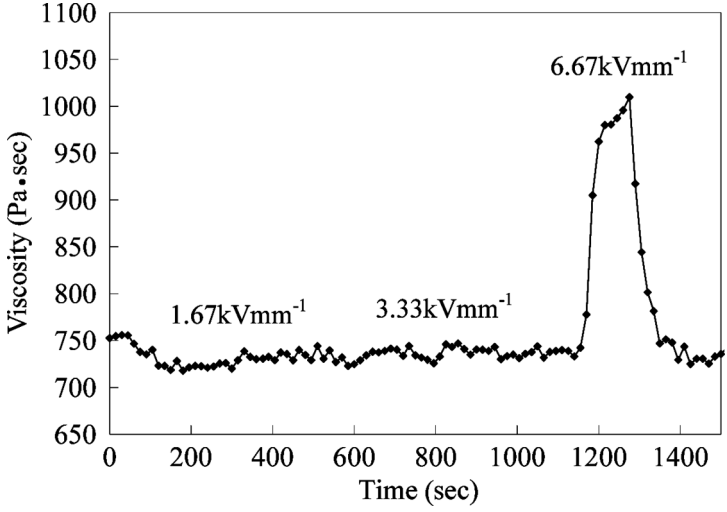

FIGURE 6 ER effect of TCAD-5 (40°C).

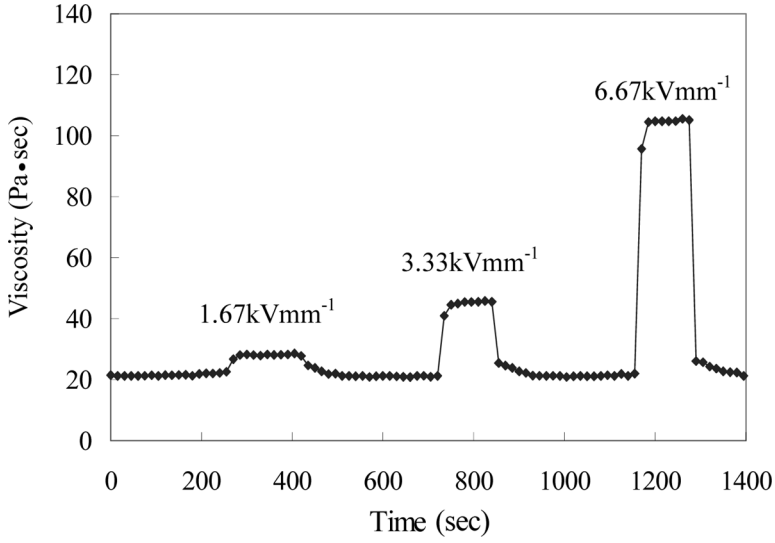

FIGURE 7 ER effect of TCAD-5 (60°C).

the point of application of the electric field to the point at which the viscosity reached its maximum.

In the case of the measurement at 40°C, a slight ER effect was observed only below 6.67 kV mm^{-1} as is shown in Figure 6. A ratio of

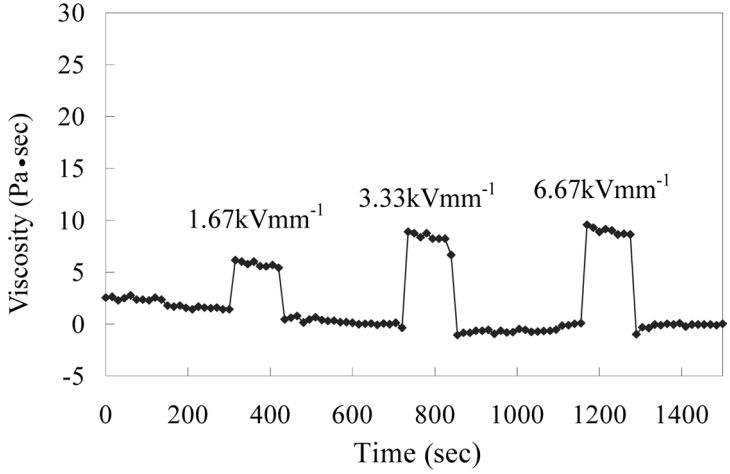

FIGURE 8 ER effect of TCAD-5(80°C).

the increment viscosity, that is, the ratio between the viscosity reached and the inherent one, is about 1.3 and not enough for any application. In the cases of 1.67 and 3.33 $kV\,mm^{-1}$, no effect was detected. These results may be attributed to the high inherent viscosity (around 730 Pa·sec). This value is several decades or hundreds of times higher compared with those at 60 and 80°C, as we can see in Figures 7 and 8.

As is shown in Figure 7, the ER effects were clearly observed at 60°C under each applied electric field. The ratio of the increment increases with increasing electric field, that is, about 1.4 times for 1.67 $kV\,mm^{-1}$, about 2.0 times for 3.33 $kV\,mm^{-1}$, and about 5.0 times for 6.67 $kV\,mm^{-1}$. In TCAD-5, we have to note that the response time is estimated to be a few seconds, and this value is very short compared with that of polymer liquid crystals for which the response time is more than 25 sec [10]. The response time is one of the most important points for commercial applications of materials as ER fluids. Therefore, TCAD-5 is an excellent ER fluid, because the increment ratio is reasonably large, and the response time is short enough for some applications.

A similar result, quick response and some degree of ER effect, was obtained by the measurement at 80°C, but the absolute value of the final viscosity is relatively low compared with that at 60°C. This lower value may be attributed to a flow which disturbs the arrangement of

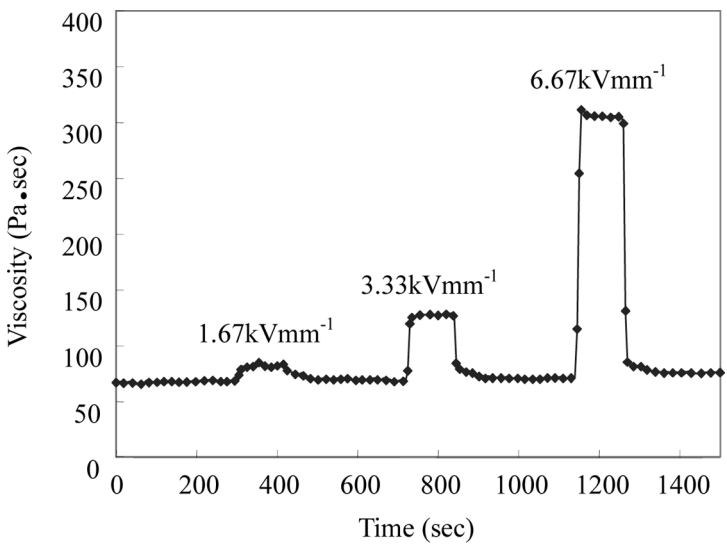

FIGURE 9 ER effect of TCAD-4 (60°C).

the mesogens caused by the applied electric field in addition to the lower inherent viscosity at such a higher temperature.

The measurements of the ER effect were made at 40, 60, and 80°C on TCAD-4, and quite similar results were obtained. The best result was obtained at 60°C, the same temperature as that of TCAD-5 and the result is shown in Figure 9. An increment ratio of about 4.2 for the viscosity was obtained under 6.67 $kV\,mm^{-1}$ combined with a quick response time.

Based on the results obtained, oligomeric liquid crystals such as TCAD-5 and 4 can be considered promising ER fluids due to their moderate inherent viscosity combined with a quick response. Consequently, it is considered that the oligomeric liquid crystals studied here will be useful for many industrial purposes [11].

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