Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 7264–7270

polymer

www.elsevier.com/locate/polymer

Electro-rheological effect and dynamic rheological properties of a blend composed of two liquid crystalline materials with different molecular weight

Kosuke Kaneko*, Yusuke Miwa, Naotake Nakamura

Department of Applied Chemistry, College of Science and Engineering, Ritsumeikan University, 1-1-1, Nojihigashi, Kusatsu, Shiga 525-8577, Japan

Received 25 June 2007; received in revised form 8 October 2007; accepted 14 October 2007

Abstract

Electro-rheological (ER) effect of a blend composed of two liquid crystalline materials with different molecular weights is described in this article. The results indicated that ER effect of the blend was observed at the temperature range where each neat sample did not show ER effect. Furthermore, both storage modulus (G') and loss modulus (G'') decreased drastically at the temperature range for the blend in dynamic viscoelastic measurements. We show that steady ER effect could be obtained by using a blend made up of two liquid crystalline components, whereas remarkable increment in shear stress was not observed for each component under applied electric field.

Keywords: ER effect; Blend; Liquid crystal

1. Introduction

Electro-rheological (ER) fluids whose viscosity is controlled by an applied electric field strength have been widely studied as smart materials for industrial utilities since the ER effect was first discovered by W.M. Winslow in 1949 [1]. ER fluids are divided into two types on the basis of component of the fluids and the mechanism of appearance of the effect. One of them is called heterogeneous type in which dielectric particles are dispersed in insulating oil such as silicone. The ER effect in this system is caused by formation of clusters and chains built up by polarized dielectric particles between electrodes under electric field. Another one is called homogeneous type which consists of single fluid such as liquid crystal materials. The mechanism of the latter case is assumed to be that anisotropic domains made by oriented moieties within the molecules generate resistance to shear flow, resulting in change in shear stress.

In general, side chain liquid crystalline polymers especially show relatively large change in shear stress under electric field, because the motion of terminal mesogens is free from that of polymer backbone [2–6]. Although the magnitude of generated shear stress is too large in comparison with that of low molar weight liquid crystalline materials, the response time for applied electric field is low, which is one of the problems in homogeneous ER fluids composed of liquid crystalline polymers. To solve this problem, dilution by silicone with low viscosity is widely accepted. In this case, the fluid is characterized as blend system or immiscible fluids. The polymer with high inherent viscosity is dispersed as droplets in other fluid with low viscosity in the system. Other researchers, Orihara et al., reported that liquid crystalline droplets with high viscosity could change their shape and size, and observed an elongation of the droplets along the direction of applied electric field by microscopic measurement [7]. This contributes to form a bridge structure between electrodes and as a result, it increases the viscosity of the fluid. In addition, it has been known that the ER effect was observed at a temperature above its clearing point. As an explanation to the fact that the ER effect of the immiscible fluid was observed at a higher temperature range than the clearing point, it was assumed that the phase transition behavior near the clearing point changed under electric field in the presence of shear flow.

---

* Corresponding author. Tel.: +81 77 561 2779; fax: +81 77 561 2659.
E-mail address: rc003987@se.ritsumei.ac.jp (K. Kaneko).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.10.034

In our laboratory, we have studied ER effect of liquid crystalline materials such as side chain liquid crystalline polymer composed of siloxane backbone and liquid crystalline oligomer composed of cyclic-siloxane chain. Using these samples, their phase transition behavior and electrorheological properties were investigated [8–10]. The introduction of siloxane chain into the polymer and the oligomer was due to the high flexibility which is expected to induce smooth orientation for mesogenic groups to electric field. However, the polymer did not show attractive ER effect because of its high inherent viscosity which obstructed the orientation of the mesogens, leading to the slow response. On the other hand, the oligomer showed small changes in shear stress only in the range of low shear rate with good response time.

In this study, we attempted to measure a rheological property of a blend of a polymer and an oligomer, and found that the blend showed remarkable ER effect at a temperature range where each neat sample did not show the effect. Then, phase transition behavior of the blend was also investigated by DSC and POM.

2. Experimental

2.1. Samples

Structures of the polymer and the oligomer are shown in Fig. 1. Both the polymer and the oligomer were prepared by a typical hydrosilylation according to the literatures [8–10]. Their phase transition behavior obtained from DSC measurements is summarized in Table 1. The two samples were mixed in a ratio of 1:2 (polymer/oligomer) by weight. Prior to all measurements done in this study, the blend was kept in full isotropic state at 120 °C for 10 min.

2.2. Characterization

Thermal properties were measured with Diamond DSC (Perkin–Elmer) with heating and cooling rates of 5 °C/min. The textures of the liquid crystalline phases were observed with a Nikon Eclipse E600 polarizing optical microscope equipped with a Mettler Toledo FP-82HT hot stage and a Mettler Toledo FP-90 central processor.

Table 1
Phase transition behavior of the polymer and the oligomer on cooling (5 °C/min)

Sample		T_g (°C)		T_{cl} (°C)	
Polymer	G	−8	SmA	48	I.L.
Oligomer	G	−11	SmA	109	I.L.

G: glass state; SmA: smectic A and I.L.: isotropic liquid.

2.3. Rheological measurements

The rheological properties were measured by a rotational rheometer (Rheosol-G2000, UBM Ltd.) equipped with an electric field controller (Matsusada Precision Devices high-voltage supply). All measurements were performed using parallel plates with a diameter of 15 mm and a gap of 0.1 mm. First, the sample mounted between the parallel plates was heated to a temperature in the isotropic state, and kept for 10 min. Then, it was cooled step by step to the measuring temperature or well inside the smectic A phase. After each cooling step, the sample was kept at the measuring temperature at least 45 min to make an equilibrium state before the measurements were started. The electric field of 2, 4 and 6 kV/mm was applied between upper plate and lower one under steady shear flow at a constant shear rate (50 s^{-1}). Generated shear stress was defined as the difference between the measured shear stress in the presence and absence of the application of the electric field. Shear rates reported in this paper have been defined as the shear rates at the edge of the plates, because the fixtures did not provide a uniform shear strain.

Dynamic viscoelastic behavior in oscillatory shear mode was investigated by using the rotational rheometer with shear strain of 5% and constant vibration frequency of 5 Hz. The linear response under the shear strain of 5% was identified by shear strain dependence in the measuring temperature range.

3. Results and discussion

3.1. Phase transition behavior

Fig. 2 shows an evolution of morphology of the blend observed on cooling. On the cooling process from the isotropic liquid phase, the appearance of bâtonnet texture was observed at 103 °C (Fig. 2(a)). A temperature at which the bâtonnet texture appeared was in agreement with the clearing point of neat cyclic-siloxane compound. On decreasing, the bâtonnet

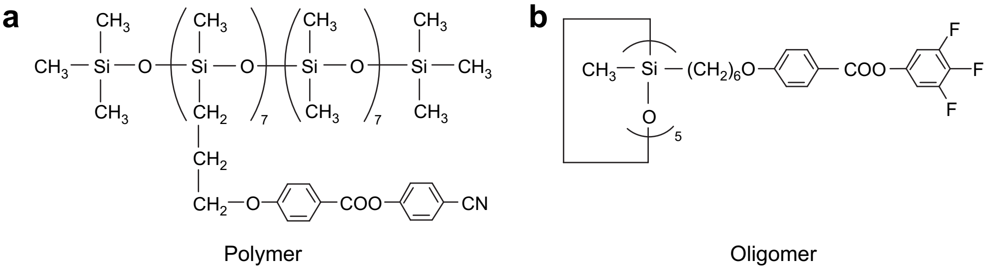

Fig. 1. Structures of neat liquid crystalline materials: (a) side chain liquid crystalline polymer; (b) cyclic-siloxane oligomer.

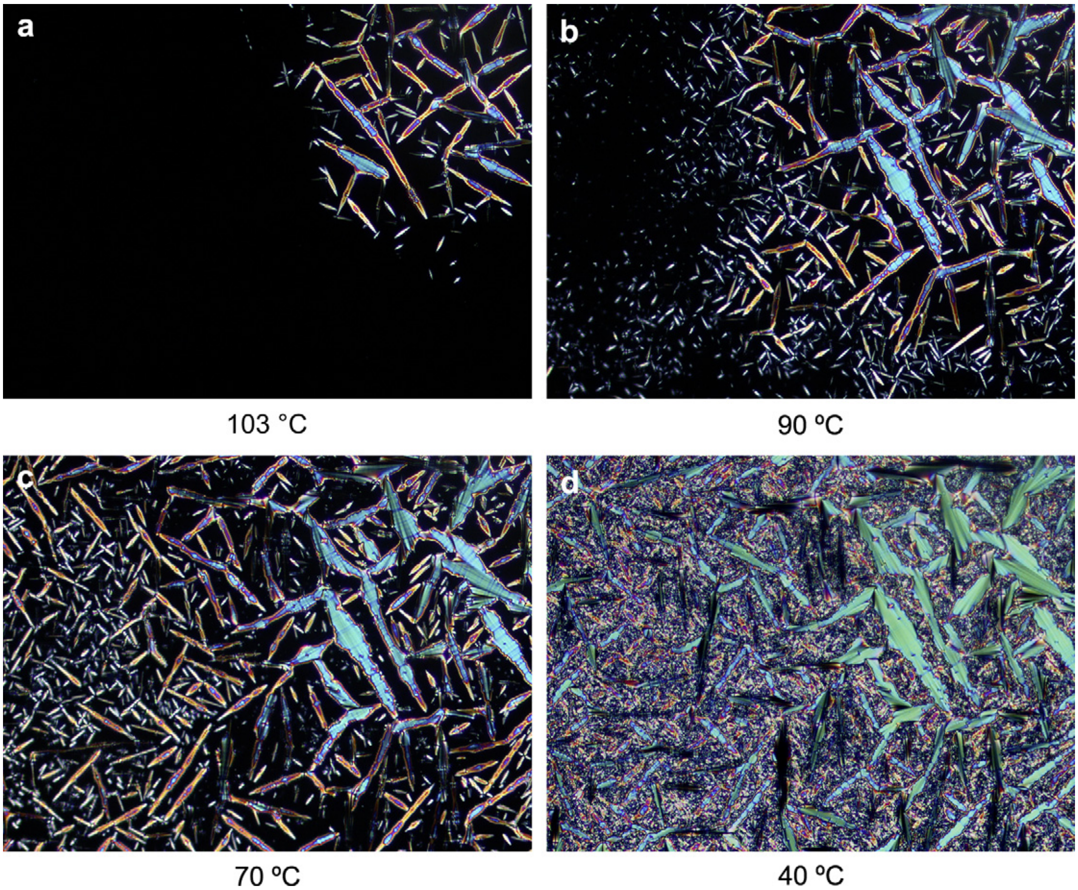

Fig. 2. Evolution of morphology of the blend on cooling, taken at (a) 103 °C; (b) 90 °C; (c) 70 °C and (d) 40 °C.

texture continued its growth and a number of the needles increased at the same time (Fig. 2(b)). Then, a coalescence of them advanced significantly at lower temperature range (Fig. 2(c)). It should be noted that dark area under POM was not caused by homeotropic orientation of smectic A. When passing through the clearing point of neat polymer, the dark area was filled with anisotropic domain by formation of liquid crystalline phase (Fig. 2(d)). Comparing a phase transition behavior of the blend with that of each compound, two components in the blend formed their liquid crystalline phases independently. This indicated that they were immiscible with each other and micro phase separation occurred in the blend.

In DSC diagram of the blend, as shown in Fig. 3, an exothermic peak was detected at 103 °C that was in good agreement with the temperature at which the bâtonnet texture by the cyclic-siloxane appeared. An exothermic peak at 48 °C corresponded to the clearing point of neat polymer. Baseline shift at −11 °C was attributed to a glass transition of both components.

3.2. Rheological properties

3.2.1. ER effect of the blend

Temperature dependence on the ER effect of the blend is shown in Fig. 4(a)–(d). Electric field of 2, 4, 6 kV/mm was applied to the blend for 100 s under a constant shear rate of 50 s^{-1}. As seen in these figures, ER effect obtained was drastically influenced by given temperature. The ER effect became recognizable from 90 °C. With decreasing temperature, the

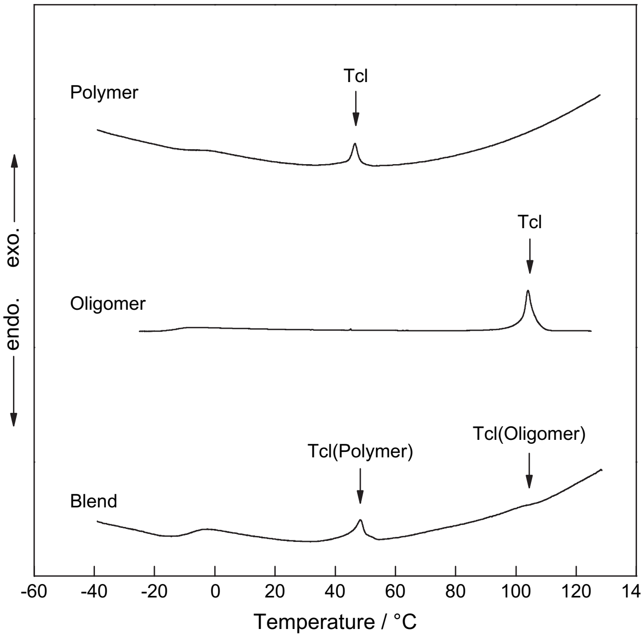

Fig. 3. DSC diagram on cooling (scanning rate: 5 °C/min).

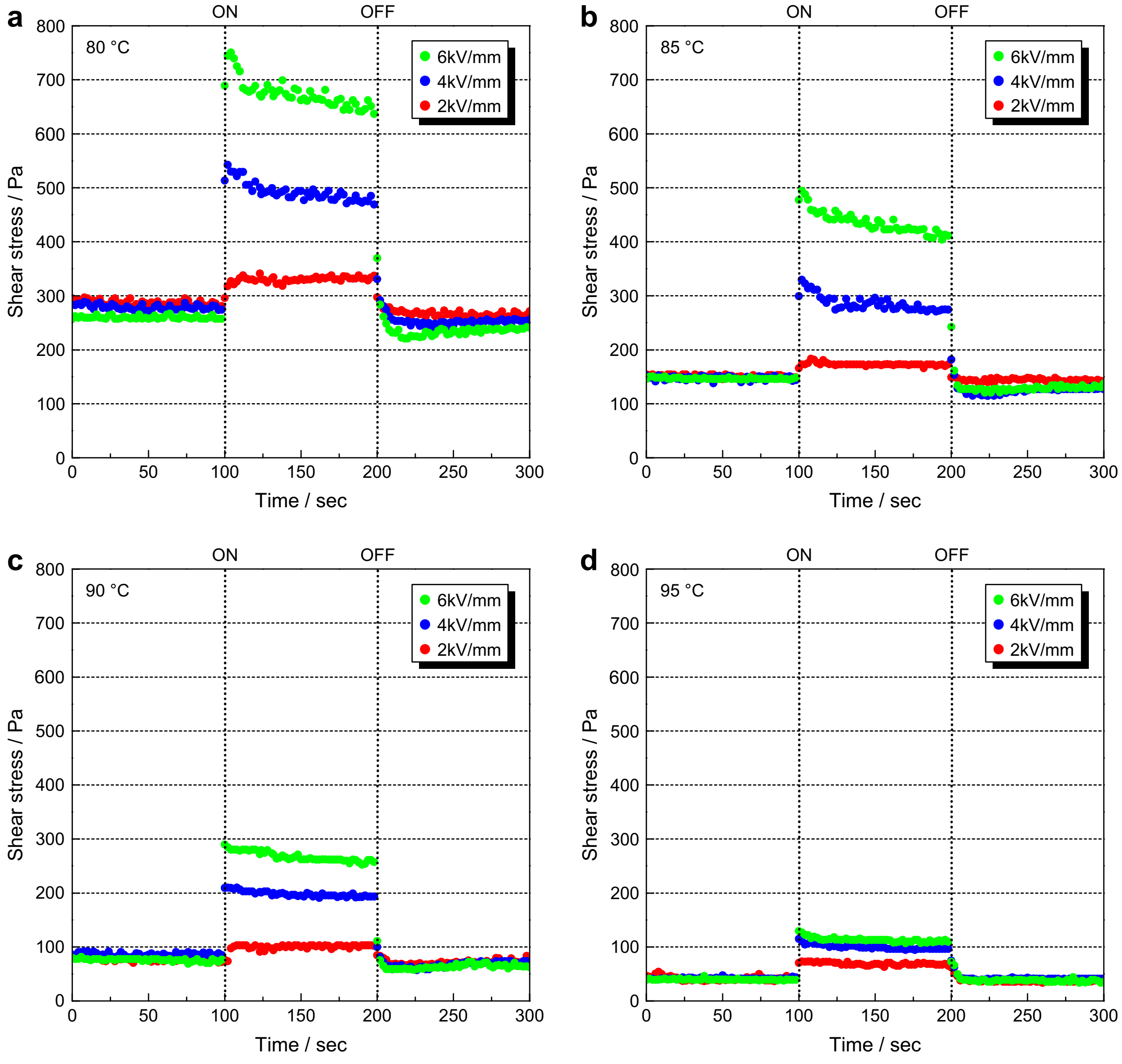

Fig. 4. Temperature dependence on the ER effect of the blend: (a) 80 °C; (b) 85 °C; (c) 90 °C and (d) 95 °C.

changes in shear stress by applied electric field apparently increased at each magnitude of electric field. At 80 °C, largest ER effect was observed, resulting in variation of shear stress from 260 Pa under no electric field to 680 Pa under 6 kV/mm. It is essential to note that shear stresses increased immediately after the application of electric field, which is able to solve the problem of slow response in ER fluids composed of polymers with high viscosity. Moreover, recovery of shear stress after removal of electric field was also very fast. It is assumed that the cyclic-siloxane was dispersed in the mixed polymer. These domains consisted of the cyclic-siloxane could elongate and form bridge structure in the polymer in isotropic phase between electrodes [7]. Below 80 °C, effective ER effect was not obtained because of unstable shear stress under no electric field. This was because the cyclic-siloxane formed specific smectic order and then polydomain can be made around this temperature.

In general, fluids used for dilution such as silicones do not have intrinsically the role of appearance of ER effect. However, the polymer studied in this measurement might have a possibility to show the enhancement in shear stress under electric field. The terminal mesogens in the polymer are supposedly arranged under electric field in the isotropic phase, which would be negligible to show the enhancement in shear stress. The orientation of the mesogens attached with polymer backbone via flexible spacer in isotropic phase may assist to make stable domains formed with cyclic-siloxane. Fluids with low viscosity used for the dilution may generate a slip and flow of domains, resulting in the weakness of interaction between the domains.

A correlation between generated shear stress and ratio of ER effect obtained under 4 kV/mm at each temperature is represented in Fig. 5. The ratio of ER effect shows a ratio of the shear stress under applied electric field to that in absence of the electric field. With decreasing temperature, shear stress under no electric field increased progressively due to decrement of molecular motion. Thus, even if the generated shear stress was large at lower temperature range, such as 300 Pa obtained

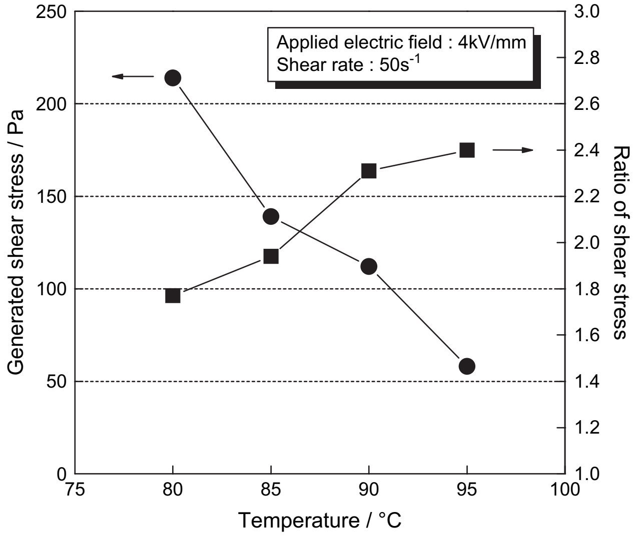

Fig. 5. Correlation between generated shear stress and ratio of ER effect under 4 kV/mm.

at 80 °C, consequently the ratio of the ER effect became small. At higher temperature, shear stress under no electric field was small compared with that at lower temperature, the ratio indicated large value (2.8 times).

3.2.2. ER effect of the polymer

Shear stress of the neat polymer under 6 kV/mm at different temperatures is shown in Fig. 6. Given shear rate was 50 s^{-1}. As shown in this figure, no change in shear stress by applied electric field was observed. No ER effect was observed either in the case of 2 and 4 kV/mm.

The polymer exhibited isotropic phase in the temperature range where the rheological measurement was performed. It is known that side chain liquid crystalline polymers, such as this polymer, show ER effect above its clearing point, because anisotropic domains composed of mesogenic moieties aligned by applied electric field can form. In the case of the polymer, its clearing temperature determined by DSC was 48 °C, thus the temperature at which the ER effect measurement was performed was too high from its clearing point. It is assumed that influence of domains formed by mesogenic moieties of the polymer in isotropic phase would be negligible for enhancement in shear stress.

3.2.3. ER effect of the oligomer

ER effect of the neat oligomer under 6 kV/mm measured in smectic phase is shown in Fig. 7. It can be seen that stable shear stress in the absence of electric field was not obtained especially at lower temperature, thus resulting in few ER effect. It is considered that the formation of domains and its disorganization by strain occurred at the same time due to the increase in smectic order with decreasing temperature. Transient rearrangement of smectic layers by the applied electric field occurred, and the shear stress increased by only few times just after the application. However, the sample was sheared and the smectic layers slipped, leading to the gradual decrease in shear stress under electric field. After the removal of electric field, the slips between smectic layers stopped and the disorganization of the domains by strain occurred again. As a consequence, an increase in shear stress due to friction between domains is observed. This behavior was apparently seen with decreasing temperature toward smectic phase though it could not be observed just below its clearing temperature.

3.2.4. Shear rate dependence on ER effect for the blend

Fig. 8 shows shear stress under electric field at various shear rates. Changes of shear stress upon application of electric field are particularly pronounced in a given shear rate range. Higher strengths of applied electric field resulted in considerable increase in shear stress. Generated shear stress

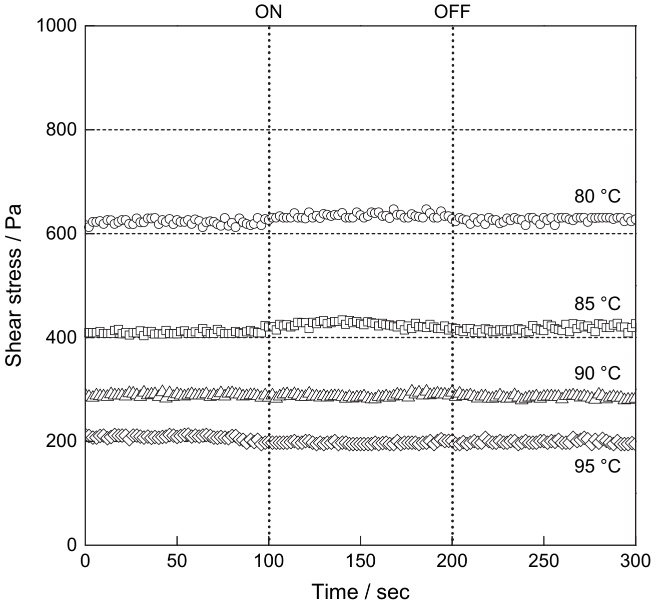

Fig. 6. Shear stress of the neat polymer under 6 kV/mm.

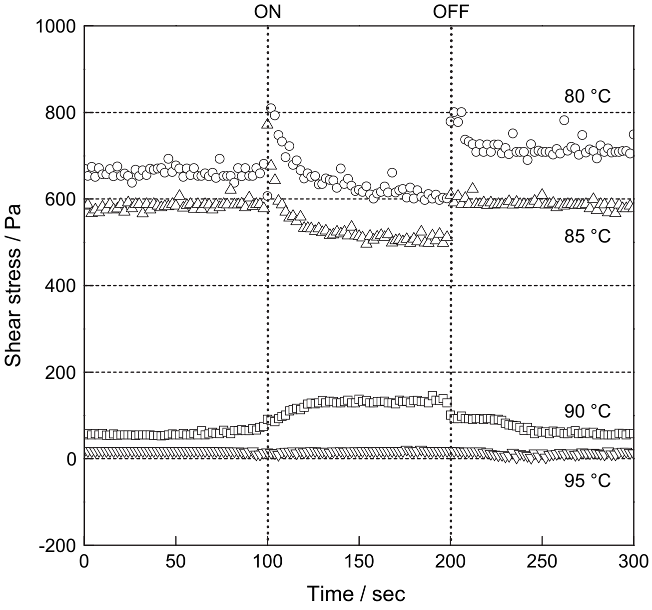

Fig. 7. Shear stress of the neat oligomer under 6 kV/mm.

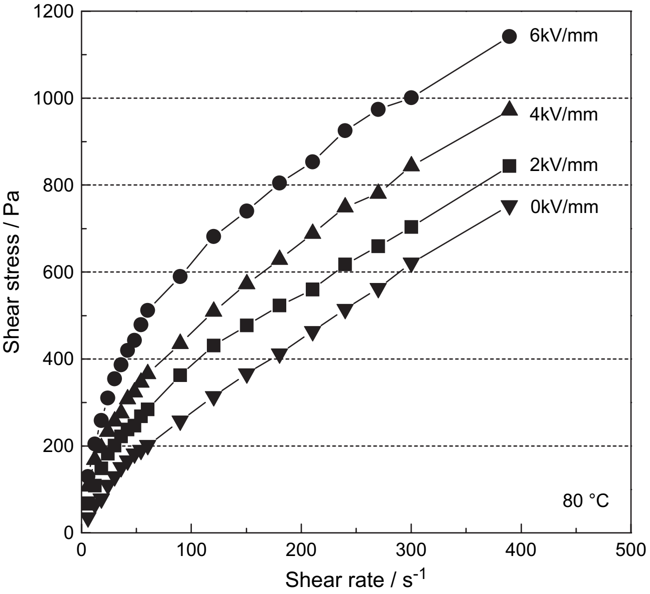

Fig. 8. Shear rate dependence on ER effect of the blend.

of 400 Pa was constantly obtained over 100 s^{-1} under 6 kV/mm though shear thinning behavior was seen. These curves resembled a behavior of Bingham fluids, which is characterized as ER fluids of heterogeneous type.

3.2.5. Dynamic viscoelastic measurement

A result of dynamic viscoelastic measurement for the blend is shown in Fig. 9. The blend was cooled from isotropic melt where both a storage modulus (G') and a loss modulus (G'') were relatively unstable. Interesting behavior occurred just after the clearing point determined by DSC, which was mainly due to the phase transition of the cyclic-siloxane component. As seen in Fig. 9, both G' and G'' drastically decreased until 90 °C, and they were lower than those in isotropic phase.

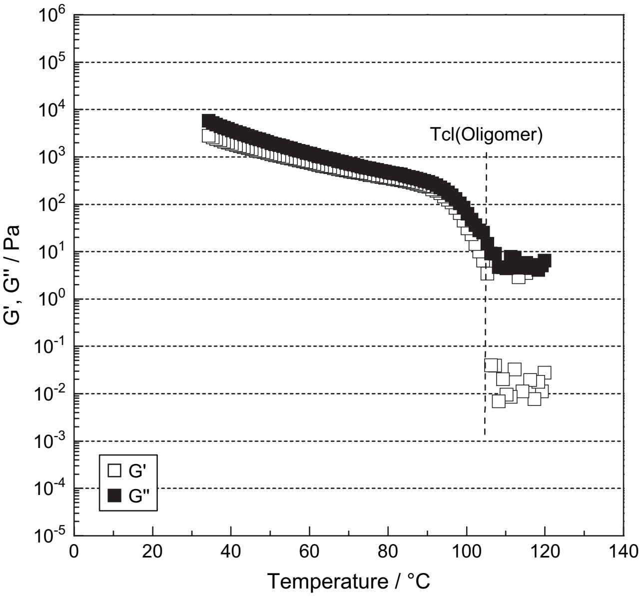

Fig. 10. Dynamic viscoelastic behavior of the neat oligomer.

Then, they increased again until ~77 °C. Below the temperature, both G' and G'' gradually increased and their slopes changed at the phase transition temperature (48 °C) of the polymer. This unexpected behavior of G' and G'' may be due to facial slip between the cyclic-siloxane forming smectic domain and the polymer in isotropic phase. However, the blend showed large ER effect interestingly at a temperature range where a sudden drop in both G' and G'' was observed. To put it concretely, the ER effect became larger on increasing G' and G'' from 90 °C to 80 °C.

Dynamic viscoelastic behavior of each component was also investigated in order to compare with that of the blend, as shown in Figs. 10 and 11, respectively. For the neat cyclic-siloxane, G' increased drastically with difference of magnitude

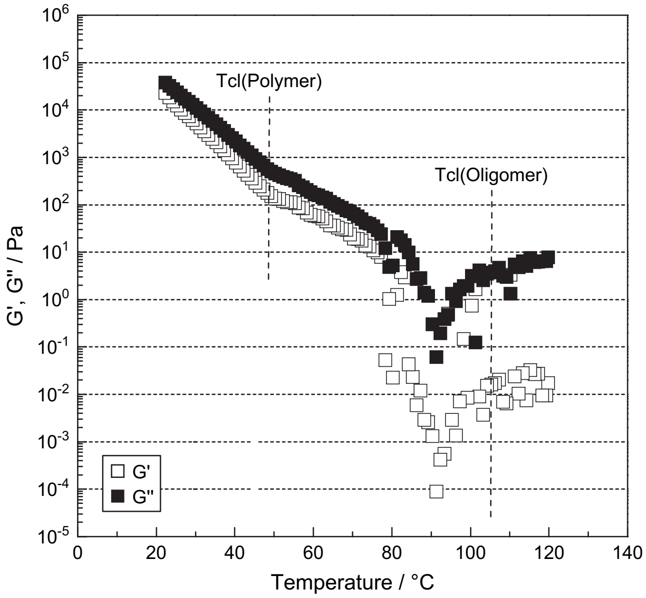

Fig. 9. Dynamic viscoelastic behavior of the blend.

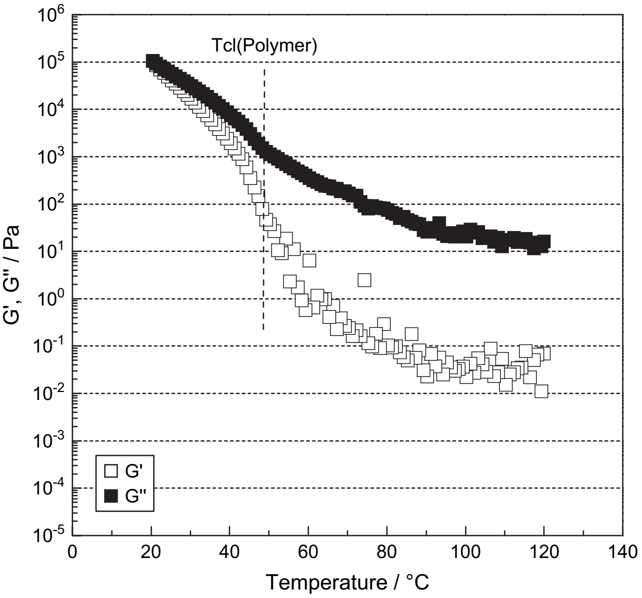

Fig. 11. Dynamic viscoelastic behavior of the neat polymer.

of 10^2 order at 103 °C, while G'' also increased slightly. This change corresponded well to a formation of smectic domain. Both G' and G'' showed a gradual increase after the clearing temperature on cooling.

Irregularity in G' and G'' was observed at a clearing temperature (48 °C) for the neat polymer in Fig. 11. This slight change is attributed to slow formation of smectic phase due to its high viscosity. This is supported by the fact that a typical smectic texture appeared after annealing under POM.

4. Conclusion

We have studied the ER effect of the blend composed of liquid crystalline materials as a function of temperature under varied electric field. We observed that the ER effect of the blend increased with decreasing temperature from 95 °C to 80 °C, whereas each component did not show the effect at all in the temperature range. In the dynamic viscoelastic measurements, a drastic decrease in G' and G'' was observed for the blend in the temperature range in which considerable ER effect was obtained, contradictory for each component. This behavior suggests that facial slip between the oligomer forming smectic domain and the polymer in isotropic phase occurred. In this case, the oligomer dispersed in isotropic melt of the polymer plays intrinsically an important role for increment in shear stress under an applied electric field. Blending with the melt is likely to generate a suitable condition for organization of smectic domain formed by the oligomer, which restricts both the slip between smectic layers and excessive weakness of interaction between the domains. From these observations, it is concluded that the condition when G' and G'' of the blend were smaller than those of each component due to the slips was favorable for the appearance of ER effect in blend system.

Acknowledgement

The authors are indebted to Associate Professor T. Hanasaki of Ritsumeikan University (Japan) for his helpful advice and discussion. A High-Tech Research Center Project for Private Universities matching fund subsidy from Ministry of Education, Culture, Sport, Science and Technology is gratefully acknowledged for partial support of this work (2006).

References

[1] Winslow WM. J Appl Phys 1949;20:1137–40.
[2] Inoue A, Maniwa S. J Appl Polym Sci 1995;55:113–8.
[3] Inoue A, Maniwa S, Ide Y. J Appl Polym Sci 1997;64:303–10.
[4] Inoue A, Ide Y, Oda H. J Appl Polym Sci 1997;64:1319–28.
[5] Tanaka K, Oiwa Y, Akiyama R, Kubono A. Polym J 1998;30:171–6.
[6] Ning Y, Alex MJ. Macromolecules 1997;30:5822–31.
[7] Orihara H, Kawasaki T, Doi M, Inoue A. J Appl Polym Sci 2002;86:3673–80.
[8] Kaneko K, Nakamura N. Liq Cryst 2007;34:229–34.
[9] Kaneko K, Miwa Y, Nakamura N. J Appl Polym Sci 2007;105:2474–81.
[10] Kaneko K, Miwa Y, Nakamura N. Mol Cryst Liq Cryst 2007;473:43–55.