Immiscible Polymer Blend Electrorheological Fluids: Composition Dependence

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ABSTRACT: We investigated the composition dependence of the electrorheological properties of immiscible polymer blends which consist of liquid crystalline polymers (LCPs) and polydimethylsiloxane (DMS). We used two different kinds of LCPs, designated as A and B polymers. We observed that for a fixed ratio of an LCP and DMS (LCP: DMS = 2:1) the electrorheological properties change from type I to type II as the fraction of the A polymer is reduced. Microscopic observations indicate that the change in the electrorheological properties is associated with the structural change; in type I, LCP droplets are dispersed in DMS, while in type II, DMS droplets are dispersed and, furthermore, that the structural change is associated with the miscibility between DMS and the LCPs; the A polymer is partially miscible with DMS, while the B polymer is hardly miscible with DMS. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3673–3680, 2002

Key words: blends; interfaces; liquid-crystalline polymers (LCP); networks; rheology

INTRODUCTION

A large electrorheological (ER) effect in immiscible polymer blends was found by Inoue and Maniwa.[1] These blends are composed of liquid crystalline polymers (LCPs) and polydimethylsiloxane (DMS), where the LCPs have a larger viscosity, permittivity, and conductivity than those of DMS.[2,3] It should be noted that these blends have an ER effect in the isotropic phase of the LCPs, so that the origin of the ER effect is not an orientational change of the molecules, which plays an essential role in low molecular liquid crystalline ER fluids,[4] but a change of the morphology of the blends. These blends have been classified into two types, called types I and II.[5] In both types, the structure is of small droplets dispersed in the matrix, but in type I, the droplets consist of LCP, while in type II, they consist of DMS.

The fundamental mechanism of the ER effect for these fluids was studied by rheological measurement and microscopic observations,[2,3,5–9] and the following conjecture was proposed: In the type I blend (Fig. 1), the apparent viscosity without a field is low because the droplets can flow easily, sliding over each other in the matrix of DMS which has a low viscosity [Fig. 1 (a)]. Under an electric field, the droplets of LCP with a high viscosity are elongated along the field by the electrostriction exerted on the interface between the LCP and DMS and link up together to form bridges between the electrodes. This results in an increase of the apparent viscosity [Fig. 1 (b)] since the high-viscosity phase is now connected.[2,6,7] Furthermore, under a strong electric field and shear rate, phase inversion may take place as shown in Figure 1(c).[8] In the type II blend (Fig. 2), on the other hand, it was found that, under a shear flow and no electric field, thin layers of DMS are formed between the plates (b). These layers may be formed by the shear flow, which makes the DMS droplets stretch and coalesce with each other so that the layers grow. The area of the thin layers increases as the shear rate is increased. These DMS layers reduce the apparent viscosity. By application of an electric field, the layers become unstable and are destroyed (c), resulting in the ER effect.[9]

In previous articles,[5] we reported that the above two types of behaviors are found in the blends of LCPs shown in Figure 3. Type II behavior was observed for the blends in which only the B polymer is used as the LCP component, while type I behavior was seen for the mixture of the A and B polymers with a ratio of A:B = 1:2 in weight. The difference between the type I and II blends in the electrorheological properties should come from the composition of the LCP. In this article, we investigated how the blend type changes as
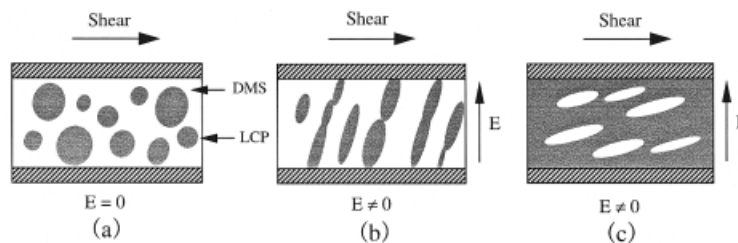
Figure 1 Schematic change in the type I blend.

the ratio of A and B polymers is gradually changed, and the results are discussed on the basis of the miscibility property of DMS and LCPs.

EXPERIMENTAL

We used blends of LCP and DMS, where the composition of the LCPs are changed continuously: The mixture ratio, defined by $x = w_A/(w_A + w_B)$, is changed as $x = 0, 0.06, 0.1, 0.14, 0.18, 0.24, 0.28, 0.33$, and 1. The mixture ratio of the LCP and DMS was always kept at LCP:DMS = 2:1. The blends with $x = 0.33$ and $x = 0$, respectively, correspond to the conventional type I and II blends. Polymers A and B were synthesized by Asahi Chemical Industry (Shizuoka, Japan) and DMS (KF-96-20cSt) was purchased from Shin-Etsu Chemical (Tokyo, Japan).

The rheological measurements were performed with a parallel-plate rotational viscometer (RS-50, HAAKE), which was modified so that electric fields can be applied to the sample using a synthesizer (Model 1940, NF Electric Instruments) and a high-voltage amplifier (Model 609C-6, Trek). In our experiments, we applied ac fields because the stability of fluids or the experimental reproducibility was better than that in dc fields. The diameter of the top plate and the gap between the two parallel plates were 20 and 0.25 mm, respectively. The shear stress at the edge of the top plate was calculated from the torque by assuming that the fluids are Newtonian, although it is a crude approximation in our fluids. Microscopic observations were also made under electric fields without flow.

RESULTS AND DISCUSSION

Rheological properties

Figure 4 shows the flow curves of LCPs at 52°C, where A and B denote the pure A and B polymers, respectively, and A + B denotes the mixture of them with A:B = 1:2 ($x = 0.33$). Both the A and B polymers are almost Newtonian, while the mixture shows shear thinning at high shear rates. As will be shown later, the shear thinning may originate from the change in the domains of immiscible A and B polymers. The viscosities of A, B, and the mixture ($x = 0.33$) at 52°C are 7.0, 28.2, and 14.1 Pa s, respectively. DMS is Newtonian, and the viscosity is 0.012 Pa s at 52°C.

Figure 5 shows the results for the conventional type I ($x = 0.33$) and type II ($x = 0$) blends. As has been reported earlier, the type I and II blends show quite different rheological properties. Under no electric field, the flow curve of the type I blend ($x = 0.33$) curve under no field is simple, while the flow curve of the type II blend ($x = 0$) shows a peak in the low shear rate region. The peak in the flow curve in the type II blend can be explained by the model described in the Introduction (Fig. 2); above a certain shear rate, thin layers are formed and the shear stress decreases. Note that the threshold depends on the increasing of the shear rate and the viscosity of LCP. By an application of the electric field, the shear stress increases both in the type I and II blends. In the type I blend, the shear stress increases anomalously in the low shear rate region. This anomalous increase may be caused by the phase inversion shown in Figure 1, from (b) to (c).[8] In the type II blend, on the other hand, the ER effect is
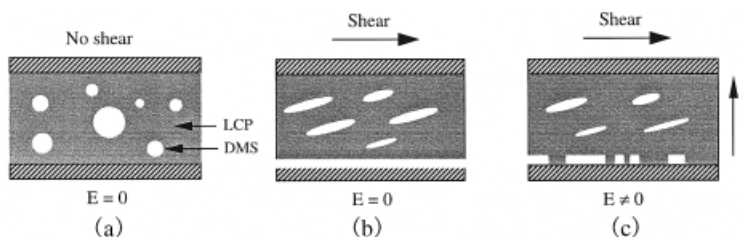

Figure 2 Schematic change in the type II blend.

A polymer : m/(m+n) = 0.2, m+n = 50
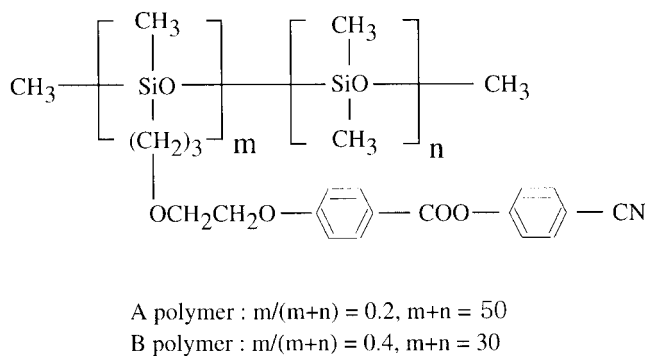B polymer : m/(m+n) = 0.4, m+n = 30

Figure 3 Molecular structures of the A and B polymers.

not observed in the low shear rate region, where no DMS layer is formed without the electric field.

Figure 6 shows the flow curves of the blends under no electric field where the composition of LCP is changed continuously. The temperature is 52°C. With increasing x, the characteristic peak of the type II blend first becomes broad and shifts to the right. With further increase of x, the peak disappears around $x = 0.24$, where the DMS layers are perhaps not formed any more. At $x = 0.28$, the viscosity suddenly decreases, indicating that the phase inversion takes place, that is, the DMS-droplet-dispersed structure changes to an LCP-droplet-dispersed one. In all these blends, the shear stress was observed to increase when subjected to an electric field.

In Figure 7, we show the composition dependence of the viscosity, where the viscosities at shear rates 10 and 70 s^{-1} are shown for $E = 0$ and $E = 0.8$ kV/mm. At a shear rate of 10 s^{-1} and $E = 0$, the viscosity decreases suddenly as a function of the composition x around $x = 0.25$, indicating that the blend changes from type II to type I. At 70 s^{-1}, the viscosity becomes very small in the absence of an electric field, but remains large in the presence of the field. Figure 8
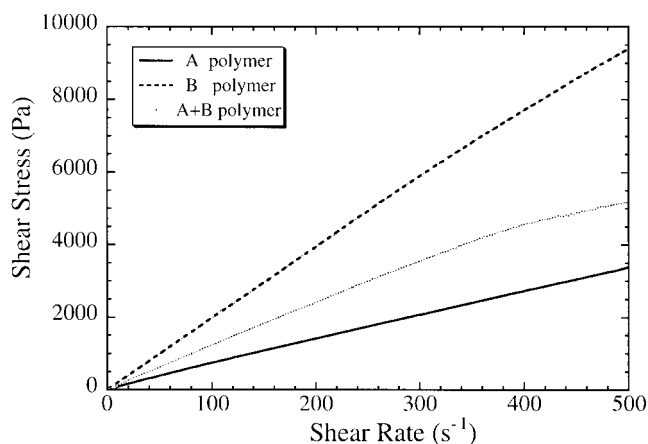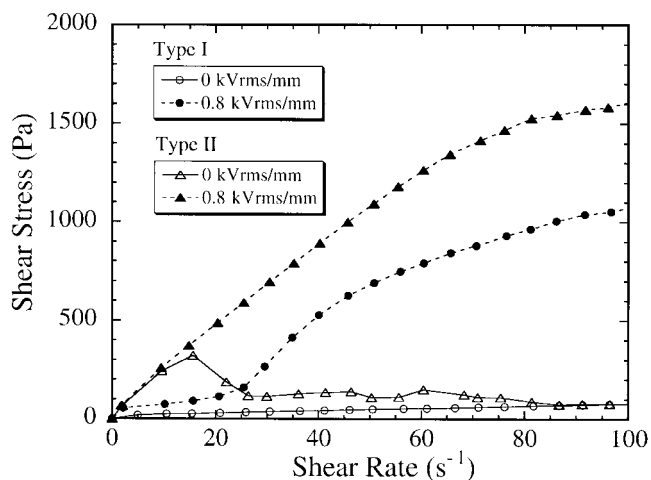

Figure 5 Shear stress curves for the typical type I and II blends with and without an electric field at 52°C.

shows the composition dependence of the electrorheological effect, where we have plotted x versus the viscosity at $E = 0.8$ kV$_{rms}$/mm, η_E, divided by the one without the field, η_0. For small x except $x = 0$ (the conventional type II blend), the ER effect is small. At $x = 0.28$ and 0.33 (the conventional type I blend), the ER effect suddenly increases, but at $x = 1$, it decreases again. In the x range from $x = 0.06$ to 0.24, the viscosity under no field is considerably high as seen in Figure 6, resulting in the small ER effect. This means that the A polymer prevents the formation of DMS layers. On the other hand, the blend of $x = 1$, which will be shown to be the type I blend by microscopic observations later, has a small ER effect compared with the blends of $x = 0.28$ and 0.33. This small ER effect is also due to the large viscosity without the field. However, in this case, the large viscosity under no field is not related to the
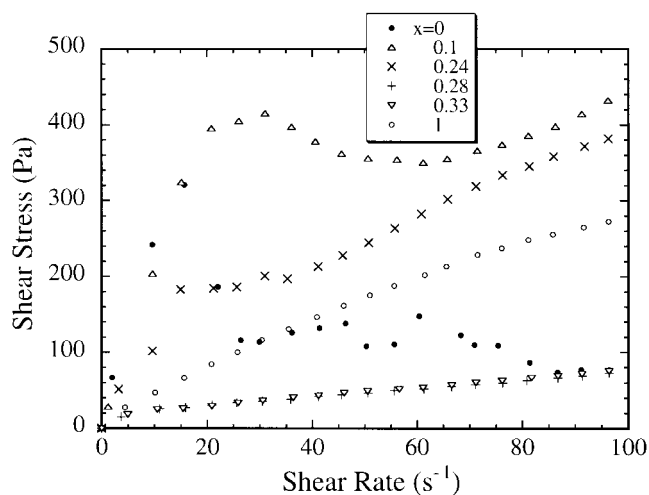

Figure 4 Shear stress curves for the A and B polymers and the mixture of them with A:B = 1:2 at 52°C.

Figure 6 Shear stress curves for several blends of $x = 0, 0.1, 0.24, 0.28, 0.33$, and 1 under no field at 52°C.
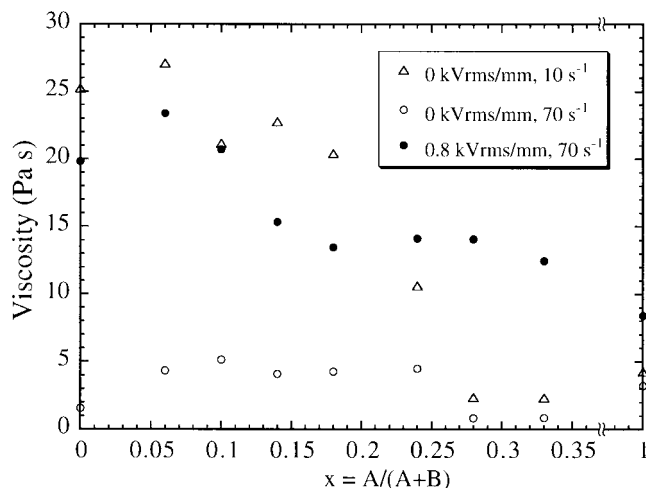
Figure 7 Composition dependence of viscosity at 52°C.

Figure 9 Experimental procedure for investigating the miscibility of LCPs and DMS.

layer formation, because this is the type I blend in which the LCP droplets are dispersed in the DMS matrix. The details will be discussed later.

Microscopic observation

As described in the previous section, the blend changes from type II to type I with increase of the A component. To clarify the mechanism of this change, we observed the interface between the LCP and DMS. We dropped LCP onto a glass slide and then DMS and observed the temporal evolution of the interface between them with a TV camera (Fig. 9). Figure 10 shows the result obtained for the A polymer at 59°C. Several seconds later after the contact between the LCP and DMS, the interface became wrinkled and the characteristic size of the wrinkle increased gradually. The droplets, finally, began to take off and become dispersed into the DMS. For the B polymer, on the con-
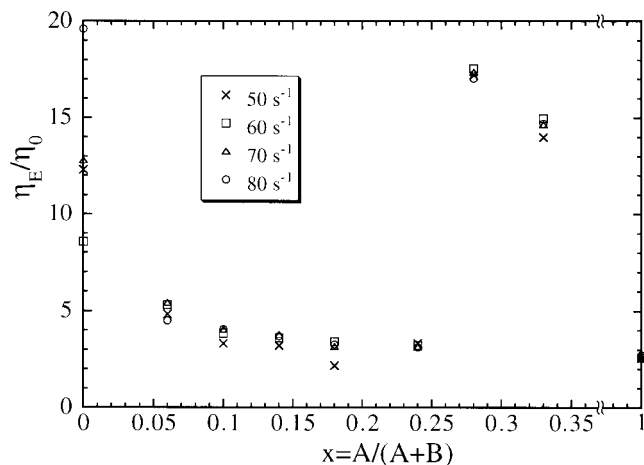
trary, no change was observed, as shown in Figure 11. Figure 12 shows the results for the blend of the A and B polymers (A:B = 1:2 in weight). Before contact (a), it is clearly seen that the A and B polymers are immiscible. At 20 s (b), the image becomes clearer than that of (a), but this may be just due to the index matching of the LCP and DMS. The increase in the characteristic size of the wrinkle is not remarkable compared with that in Figure 10 because the B polymer prevents the A polymer from making contact with the DMS. Finally, droplets were formed in the DMS.

The observation for the A polymer (Fig. 10) indicates that the polymer and DMS are partially miscible and the instability is caused on the interface. This partial miscibility may be related to the spontaneous formation of LCP droplets in the type I blend. Figure 11 shows that the A and B polymers are immiscible. From these results, it is possible to explain why the viscosity of the blends of $x = 0.28$ and 0.33 (the typical type I blend) is quite low without the field compared with that of $x = 1$. In these blends, the adhesion force between the A and B polymers may not be so strong that they are easily separated in DMS. In the blend of $x = 1$ (A:DMS = 2:1), on the other hand, there is no interface in the LCP, and so it may be difficult to separate the A polymer itself and, furthermore, droplets can easily coalesce to increase the apparent viscosity.

As for the difference between the A and B polymers in miscibility, it may be due to the difference in the molecular structure. The fraction of mesogen in the A polymer is smaller than that in the B polymer, as shown in Figure 3, and so the B polymer is greater in difference from DMS than is the A polymer in structure, leading to the strong immiscibility with DMS for the B polymer.

Last, we show the results of the observation for ER blends under no shear flow both with and without a field. In the experiments, we used a glass plate with two parallel thin indium tin oxide (ITO) strip electrodes prepared by evaporation. The distance between the electrodes was 100 μm. In this cell, the electric field was applied parallel to the glass plate. Figure 13 shows photographs taken before and after applying an ac field of 0.8 kV$_{rms}$/mm and 10 Hz at 59°C for

**Figure 8** Composition dependence of the ER effect for several shear rates at 52°C.
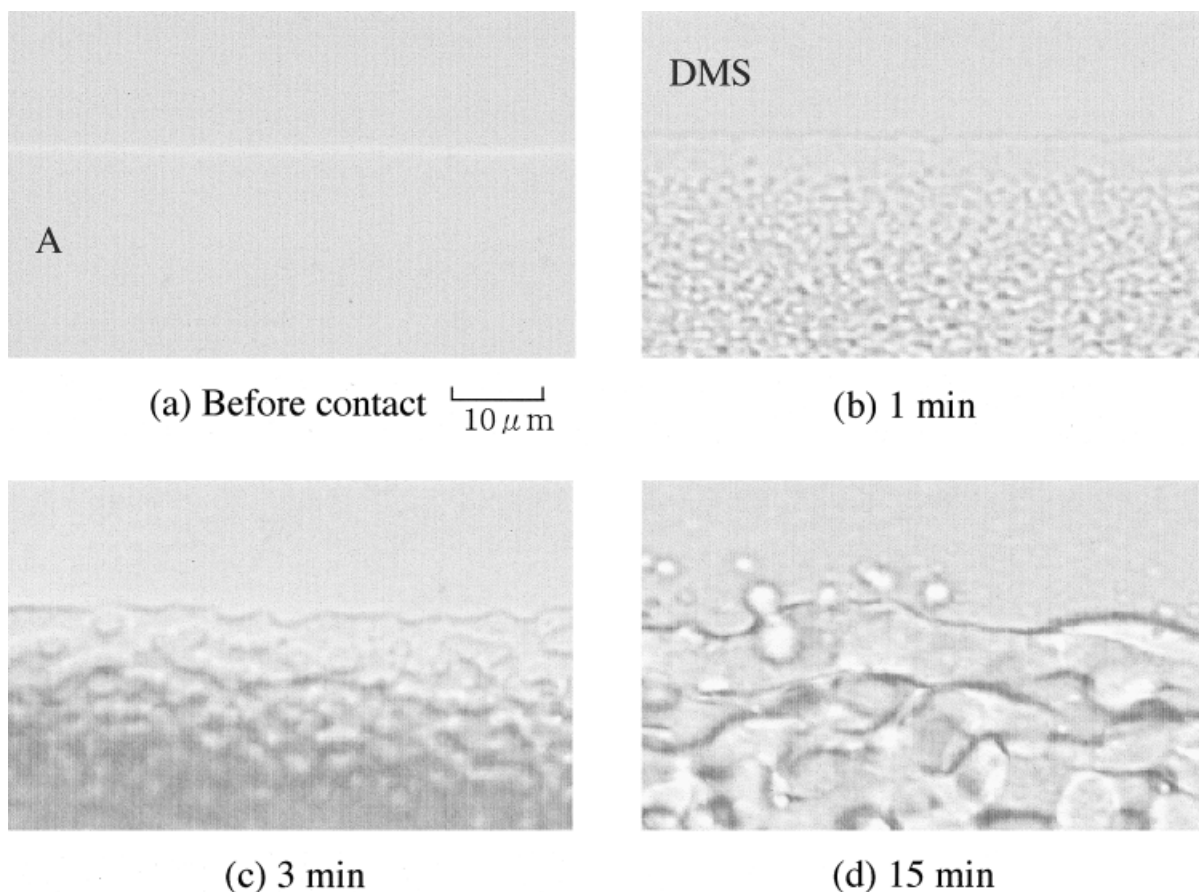
Figure 10 Temporal evolution of the interface between the A polymer and DMS at 59°C.

several compositions (x = 0, 0.06, 0.1, 0.33, 1). For the typical type I blend of x = 0.33 (d), LCP droplets are dispersed in the DMS matrix without the field. After applying the field, the droplets are elongated along the field and linked to make bridges between the electrodes. The driving force to stretch the droplets is the electrostriction exerted on the interface between the LCP and DMS. Torza et al. calculated the defor-

mation of a droplet under an ac electric field.[10] According to their results, the deformation of a droplet consists of both dc and ac components; the former is constant and the latter has a frequency twice of that of the applied field. In our experiments, the oscillatory component was very small compared with the stationary component. The stationary deformation depends on the permittivities, the conductivities, and the vis-
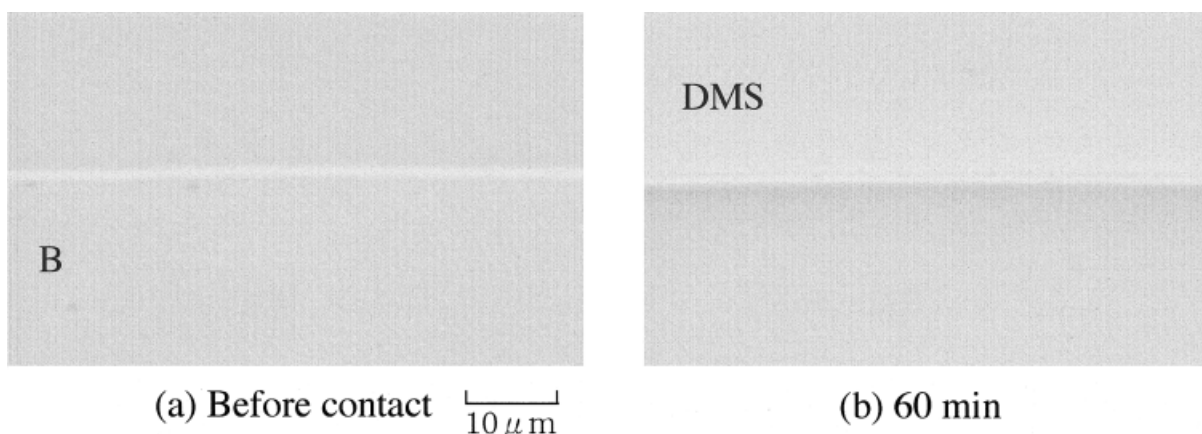
Figure 11 Temporal evolution of the interface between the B polymer and DMS at 59°C.

(a) Before contact   10 μm

(b) 20 sec

(c) 5 min

(d) 25 min
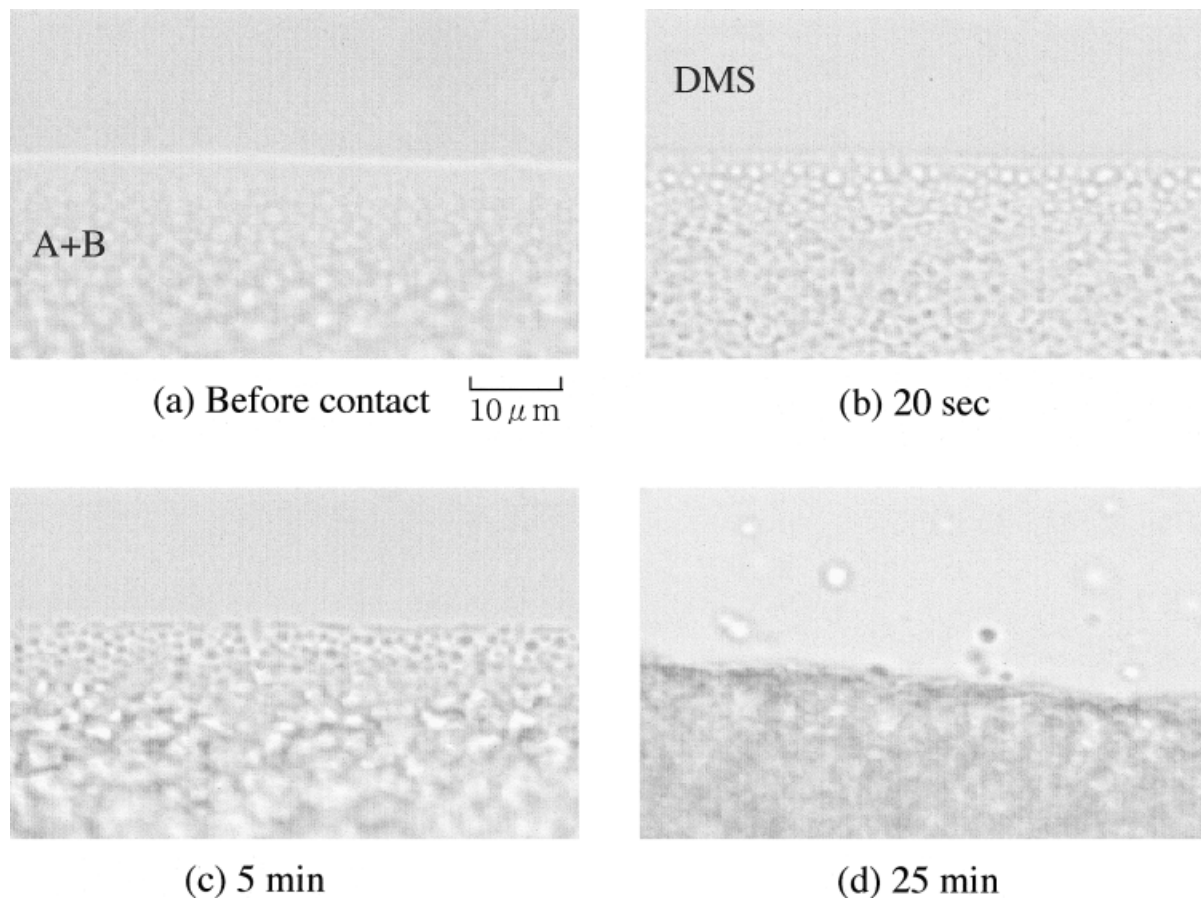
Figure 12   Temporal evolution of the interface between the mixture (A:B = 1:2) and DMS at 59°C.

cosities of LCP and DMS and the surface tension between them as well as the frequency and the amplitude of the applied field.

We need a difference between LCP and DMS in permittivity or conductivity to have electrostriction exerted on the interface between them. In our blends, the LCP has larger permittivity and conductivity than those of DMS. In the typical type II blend of $x = 0$ (a), on the contrary, droplets of DMS are dispersed in the matrix of the LCP under no field and almost no deformation takes place under a field. The difference between these two types in the response to a field may be due to the differences in permittivity and/or conductivity of the LCP. Here, it should be noted that, even if the A and B polymers have the same permittivity and conductivity, the corresponding blends should be different in the strength of electrostriction because one is obtained by the phase inversion of the other.

In addition, the difference in the surface tension may be important. Since the A polymer is partially miscible with DMS, the surface tension of the A polymer is considered to be smaller than that of the B polymer, that is, the droplet in type I may be elon-gated more than is the one in type II. To clarify the origin of the difference, we need to measure the permittivities and conductivities of the A and B polymers and the surface tensions and calculate the deformations by using the theory by Torza et al. From Figure 13(b,c), it is seen that the change from type I to II blends should take place between $x = 0.06$ and 0.1. From Figure 7, on the other hand, the type changes around $x = 0.24$. This difference may be due to whether there is shear flow or not. Our results suggest that the type II blend may become more stable than will the type II blend under shear flow, although the reason is not yet clear.

CONCLUSIONS

We observed the change from type I to type II both in rheological properties and structure by changing the ratio of the A and B polymers. It was found that the A polymer is partially miscible with DMS and tends to disperse into DMS spontaneously. Furthermore, by adding the B polymer, which is immiscible with the A polymer and DMS, the A and B polymers are more easily dispersed in DMS under a shear flow, leading to the type
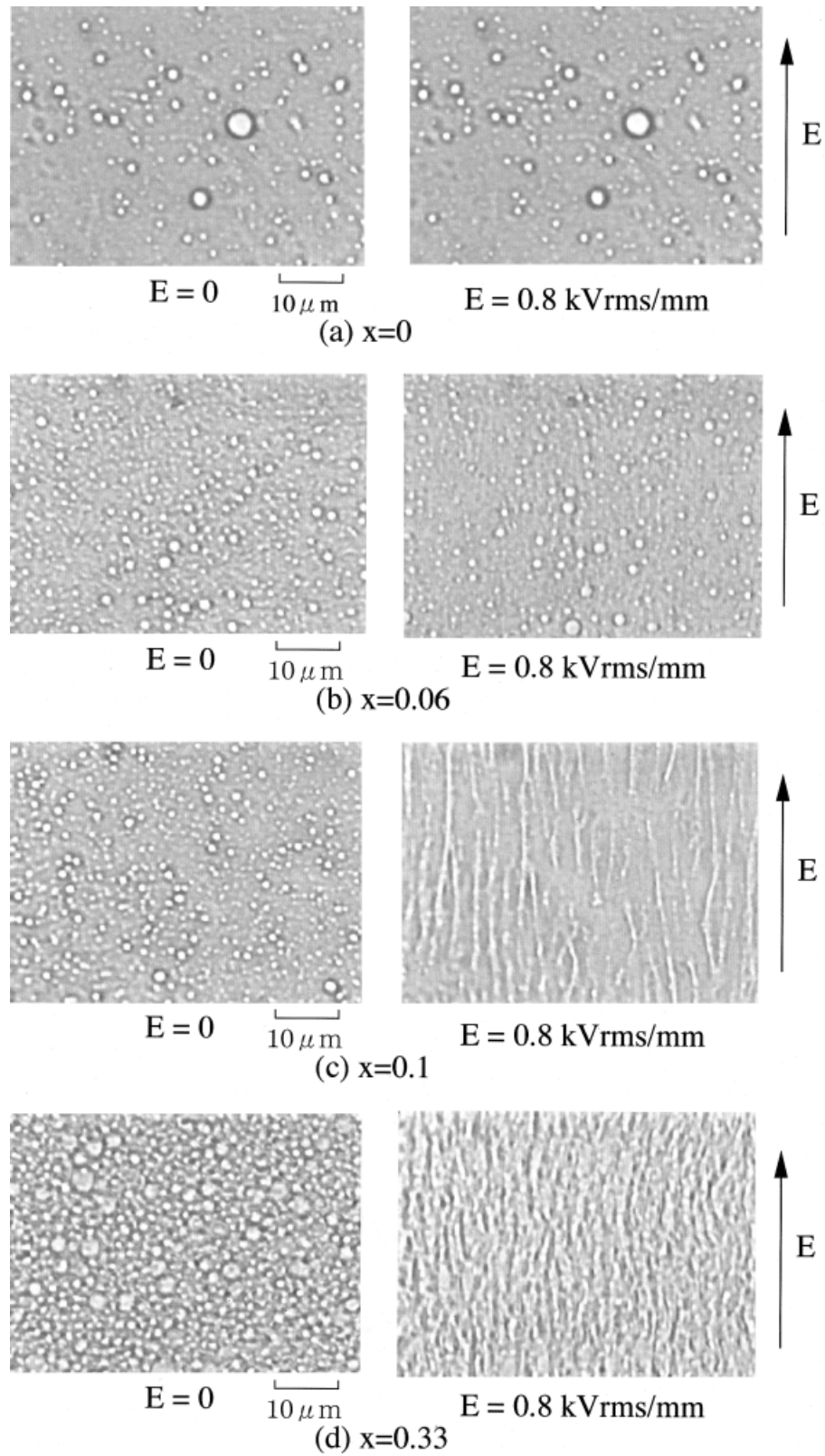
Figure 13   Influence of electric field on the structure for several blends.

I blend. On the other hand, the type II blend consists of the B polymer (and a small amount of the A polymer) and DMS, which are almost immiscible. These results indicate that the miscibility is crucial in our blends and may give a guiding principle for designing blends.

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