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Observation of polymer interface instability

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Abstract

We observed with a confocal scanning laser microscope the interface between a liquid crystalline polymer (LCP) and polydimethylsiloxane (DMS) after they made contact. The initially flat interface became corrugated and the characteristic length of the corrugation increased gradually. The coarsening rate was found to be controlled by the viscosity (the molecular weight) of the DMS; as the viscosity was increased the rate became slower. The present interfacial instability may be related to the diffusion of the low molecular weight DMS into the LCP.

Keywords: Interface; Instability; Polymer blend

1. Introduction

Several polymer blends have been found to demonstrate a large electrorheological (ER) effect [1]. They are usually composed of two mutually immiscible polymers. We mainly use two kinds of liquid crystalline polymers (LCPs) and polydimethylsiloxane (DMS), where the LCPs are isotropic at temperatures at which the ER effect appears. These blends are classified into two types [2,3]. In both types there are small droplets dispersed in the matrix; in Type I the droplets consist of the LCP, while in Type II they consist of DMS. So far it has been found that the ER effect is related to the morphological change of the blends under an electric field and shear flow [2–6]. The LCPs used have different fractions of mesogen and different molecular weights, designated as the LCP(A) and LCP(B) (Fig. 1). Intriguingly, the LCP(A) forms a Type I blend while LCP(B) forms a Type II blend, when mixed with DMS at a ratio of LCP:DMS = 2:1 in weight. In order to investigate the difference, we observed the temporal evolution of the interface between them [7]. We put each LCP on a glass slide and then added DMS and observed the temporal evolution of the interface between them with an optical microscope. There was no change in LCP(B), but in LCP(A), after the contact between the LCP and DMS, the interface became corrugated—the characteristic length of the corrugation increased gradually and finally droplets began to take off. This phenomenon may indicate that interfacial instability took place.

Interfacial instability has also been found in polymer bilayer films when they were annealed at temperatures above the glass transition temperatures. Jiao et al. [8]

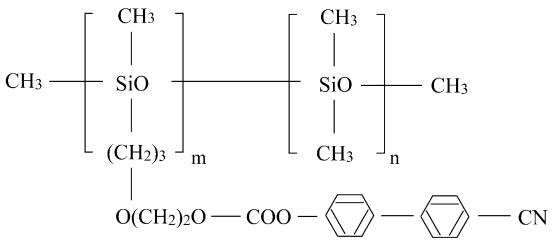

Fig. 1. Chemical structures of LCP(A) ($m + n = 50$, $m/(m + n) = 0.2$) and LCP(B) ($m + n = 30$, $m/(m + n) = 0.4$).

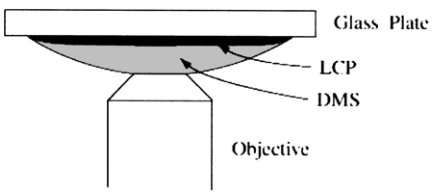

Fig. 2. Schematic illustration of CSLM observations. A matching oil is DMS for objective × 100.

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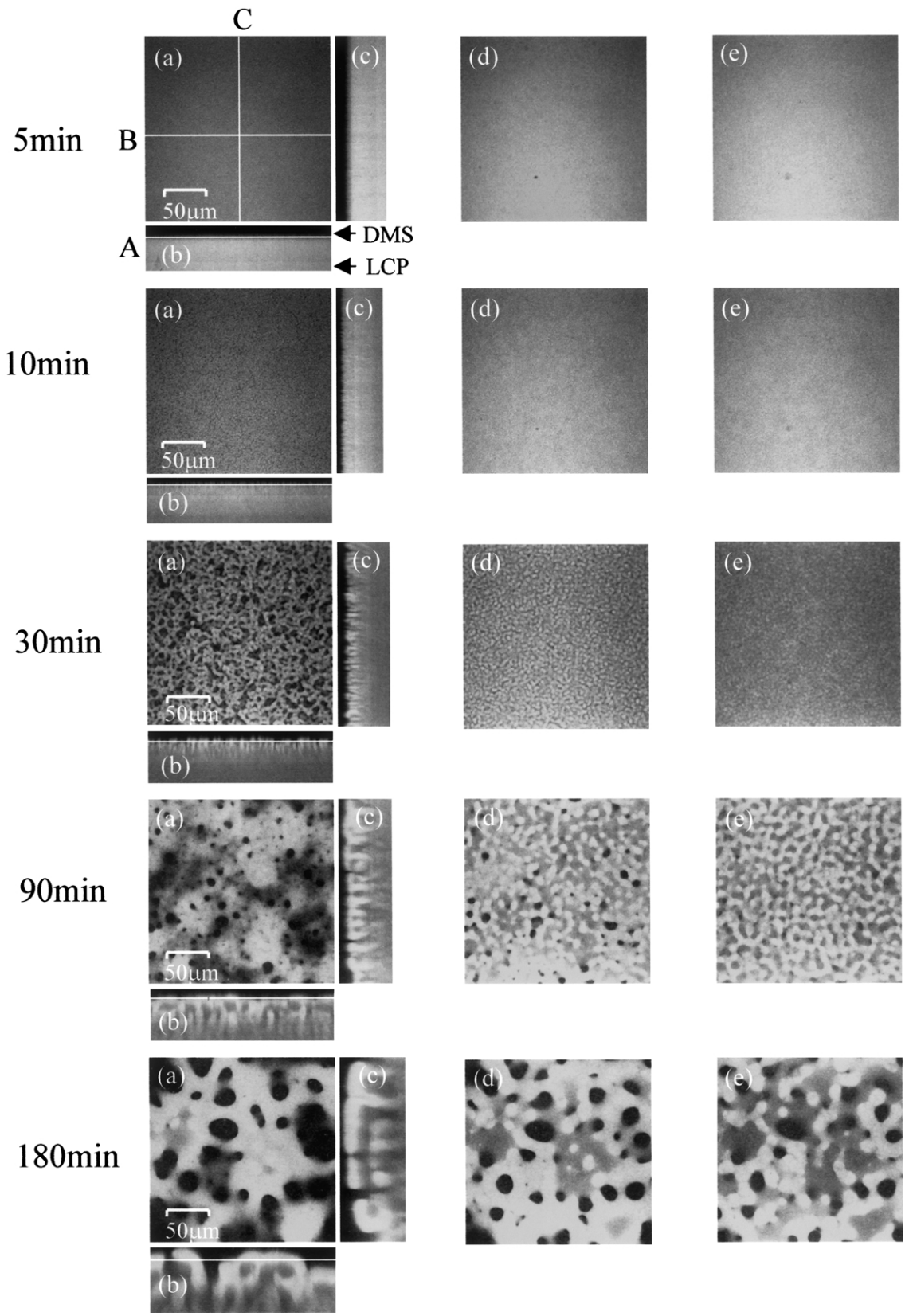

Fig. 3. Cross-sections observed with a CLSM for LCP/DMS(20 cSt) at 5, 10, 30, 90 and 180 min. (b) and (c) are, respectively, cross-sections along line B and C in (a), which is a cross-section along line A in (b), and (d) and (e) are, respectively, those 5 and 10 μm above (a).

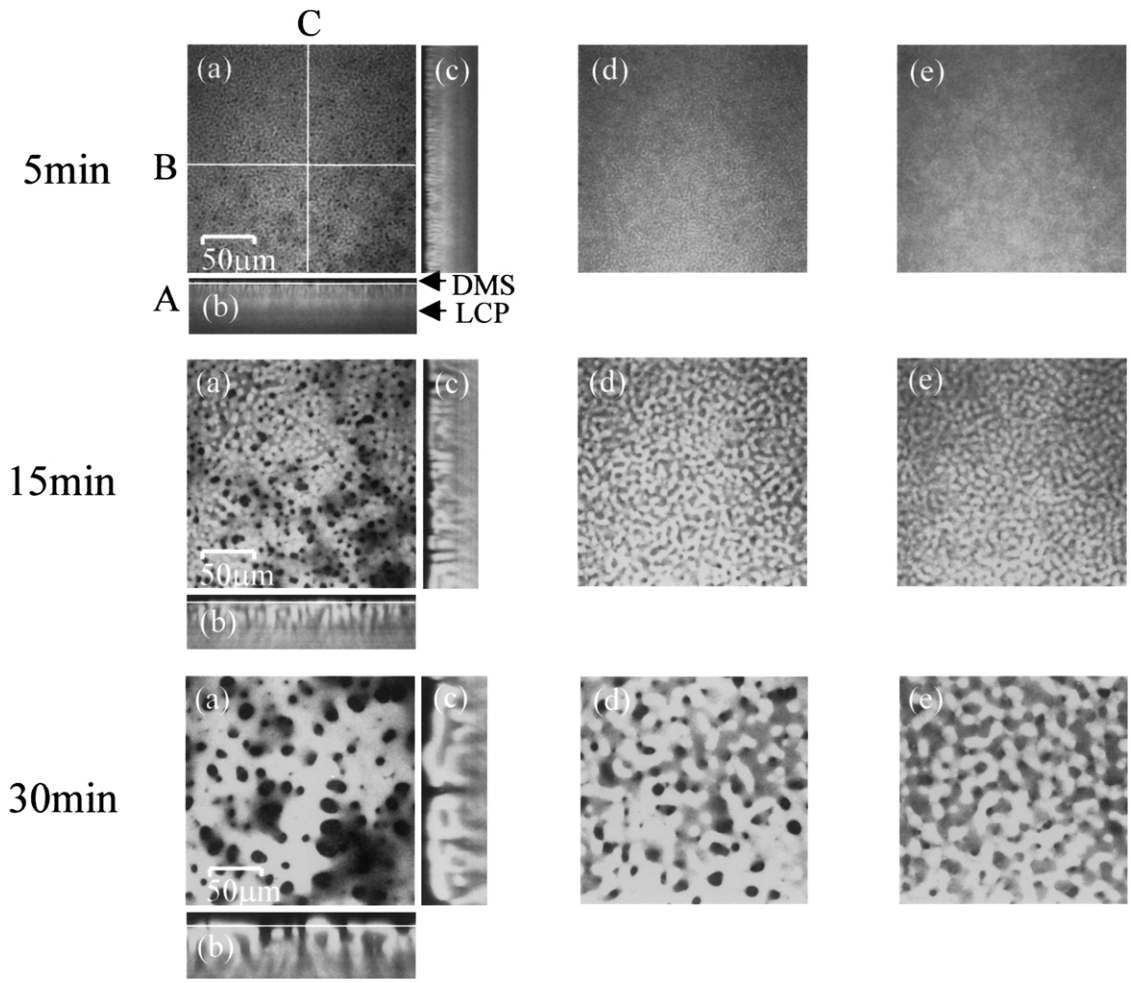

Fig. 4. Cross-sections observed with a CLSM for LCP/DMS(10 cSt) at 5, 15 and 30 min. Conditions for images are the same with Fig. 3.

observed a corrugated interface with a scanning force microscope and concluded that this instability is caused by the reduction of the interfacial tension due to graft copolymer formation at the interface. However, Hayashi et al. [9] observed a transient increase in the effective interface width by neutron reflectivity, which was conjectured to originate in an interfacial undulation due to the diffusion of low weight molecules from one layer to the other. The corrugation appearing in our system is much larger than these, but some kind of instability may take place in our interface also. For this paper, we observed three-dimensionally the interfacial instability with a confocal scanning laser microscope and obtained the time dependence of the characteristic length of the corrugation.

2. Experiment

In the present experiments, we used LCP(A) (supplied by Asahi Chemical Industry), the viscosity of which is about 80 Pa s at 20 °C, and three kinds of DMS (Shin-Etsu Chemical) with different viscosities (different molecular weights), 10, 20 and 30 cSt at 25 °C. To observe the interface between the LCP and DMS clearly, a small amount of fluorescent dye, IANBD amide (Molecular Probes), was doped to the LCP. It was confirmed that the dye did not dissolve in DMS. The experiments were made at room temperature as follows: First, we put the LCP on a glass plate, heated it up so that the interface of the LCP became smooth and then allowed it to cool back down to room temperature. The thickness of the LCP layer was about 20 μm. Then, we dropped each kind of DMS onto the LCP layer, inverted the glass plate and set it on the stage of an inverted microscope (IX70/FV300, Olympus), as shown in Fig. 2. The instrument used was a 100 × oil lens with a numerical aperture of 1.3 and an excitation wavelength of 488 nm.

3. Results and discussion

The temporal evolution of the three-dimensional structure of the interface was observed. Fig. 3 shows 3D images at 5, 10, 30, 90 and 180 min for the interface of LCP/

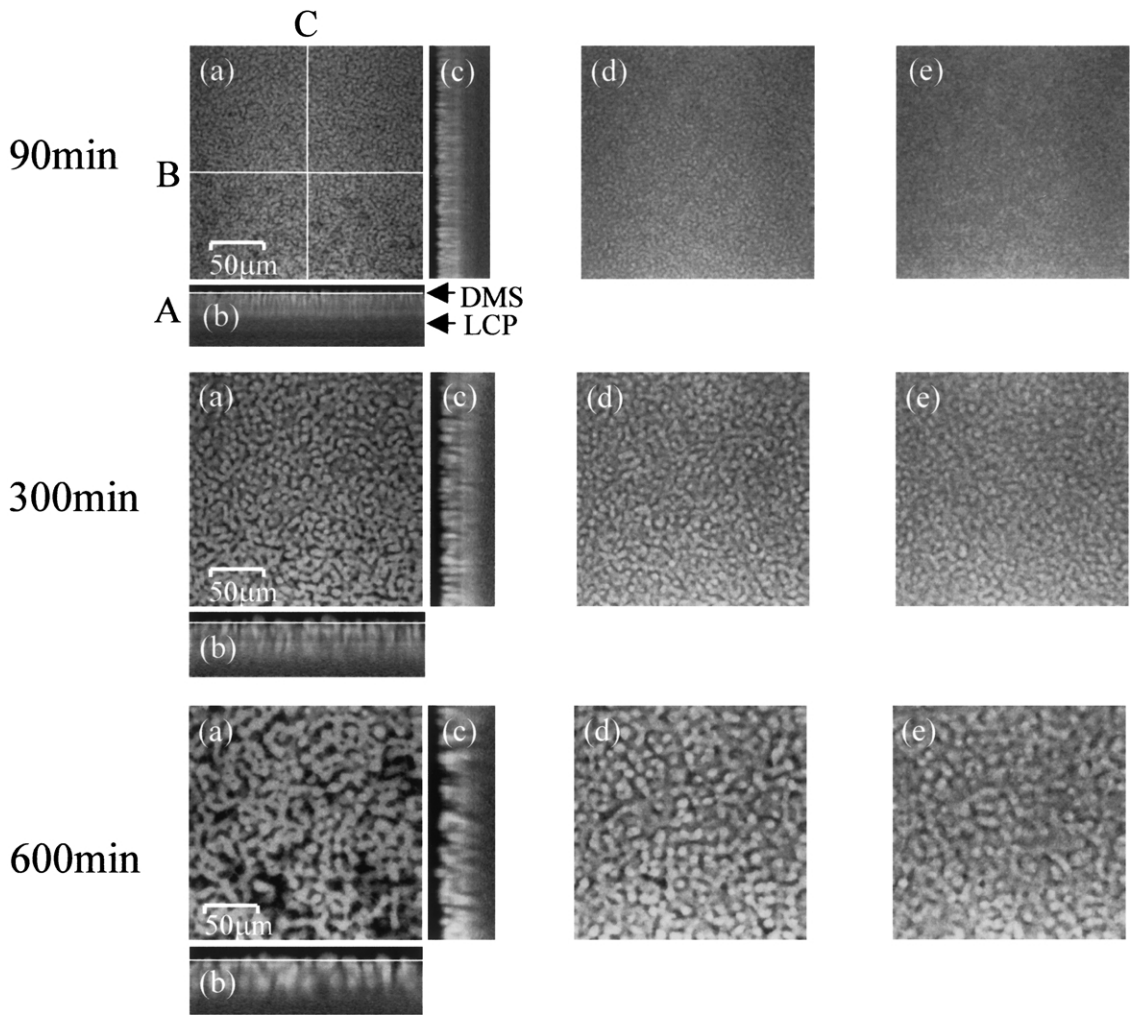

Fig. 5. Cross-sections observed with a CLSM for LCP/DMS(30 cSt) at 90, 300 and 600 min. Conditions for images are the same with Fig. 3.

DMS(20 cSt). At 5 min we show five cross-sections; (b) and (c) are, respectively, cross-sections along line B and C in (a), which is a cross-section along line A in (b), and (d) and (e) are, respectively, those 5 and 10 μm above (a). Note that the vertical direction is inverted in (b), i.e. the upside in (b) is the bottom in the real system. At 5 min the interface is almost flat, but at 10 min the interface becomes slightly rough. At 30 min a corrugated interface is clearly formed and is considerably rougher, as shown in (b) and (c). From (a) it is seen that the LCP is linked in this cross-section while the DMS is not linked, though the DMS is naturally three-dimensionally linked. When we go deeper into the LCP, the fraction of DMS decreases, (d) and (e). From these observations, DMS appears to penetrate the LCP. At 90 min the structure becomes coarse and the tips of LCP coalesce to form roofs. On the other hand, inside the LCP the fraction of DMS increases and so it can be linked as well as LCP, (d) and (e). At 180 min the interface becomes more complicated along the depth direction by the coalescence, and a network-like structure appears.

Similarly, Figs. 4 and 5 show the evolution of the interface of LCP/DMS(10 cSt) and LCP/DMS(30 cSt), respectively. The structural changes in these samples are almost the same as that in the above LCP/DMS(20 cSt) except for the change rate. As the viscosity of DMS is larger, the rate is slower. This fact implies that the diffusion of DMS into the LCP should play a crucial role in the interfacial instability. Therefore, the LCP and DMS are not completely immiscible.

In order to obtain the characteristic length of the corrugation, we calculated the two-dimensional power spectra of cross-sections parallel to the glass surface. Fig. 6 shows the radial power spectra, obtained by circularly averaging the two-dimensional power spectra, for LCP/DMS(20 cSt) at several times. The images used for this analysis were obtained in another run, where the focusing plane was set in place 5 μm from the tip of the LCP, because a series of images with a short interval for a long time was needed. There is a distinguishable peak for each time, indicating that the corrugation should be periodic to some degree, and the peak position shifts to a lower wavenumber, i.e. the characteristic length increases as time passes. The

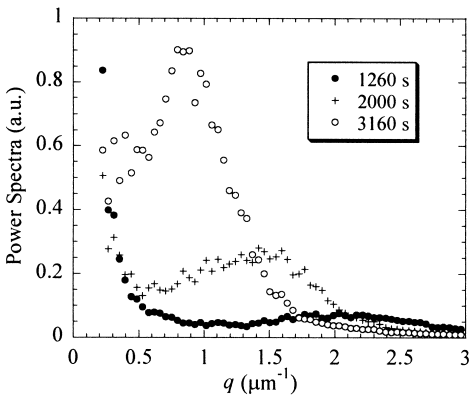

Fig. 6. Power spectra for LCP/DMS(20 cSt) at several times.

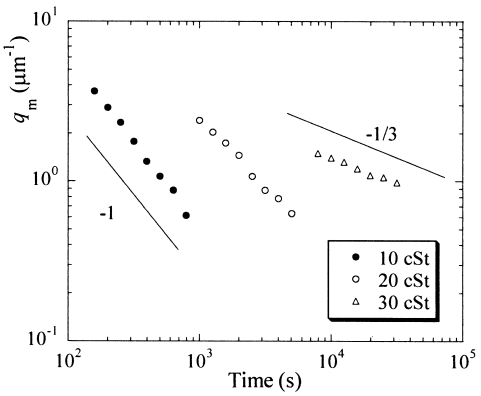

Fig. 7. Time dependencies of the peak position q_m for the three samples.

time dependencies of the peak position q_m are plotted in Fig. 7 for three samples with different viscosities, 10, 20 and 30 cSt. For all the samples the q_m decreases with time, but the rate is slower as the DMS viscosity is larger. Note that a slight change in viscosity brings about a great change in the growth rate, implying the presence of large nonlinearity. In addition, the slope becomes gentler and the exponent of the characteristic length with respect to time ranges between 1 and 1/3. The exponents 1 and 1/3 for the characteristic length are well known in the dynamics of the phase separation processes [10]. The former exponent originates in the diffusion and the latter in the hydrodynamic effect. Strictly speaking, however, the ratio of the bright area to the dark one in our images is not constant and so the image intensity is not a conserved order parameter. Therefore, it may be not proper to discuss the above exponents on the analogy of the phase separation. In addition, our system is not, needless to say, a usual phase separating one in which a structure consisting of complicated fine domains changes into a simply separated domain structure. On the contrary, in our system a flat interface becomes complicated. However, we believe that the diffusion and the hydrodynamic effect should play roles to some degree in the coarsening process of our system.

In conclusion, we have succeeded in observing three-dimensionally an occurrence of interfacial instability with a confocal scanning laser microscope. The corrugation formed became coarse-grained and the coarsening rate depended on the molecular weight of the DMS. The instability may be related to the diffusion of DMS into the LCP, which has not yet been confirmed.

Acknowledgements

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