

Cocrystallization and Miscibility in Blends of Vinylidene Fluoride–Tetrafluoroethylene and Vinylidene Fluoride–Hexafluoroacetone Copolymers

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(Received February 23, 1993)

ABSTRACT: Differential scanning calorimetric and dynamic mechanical analyses were carried out to investigate the melting behavior and miscibility of blends of vinylidene fluoride–tetrafluoroethylene and vinylidene fluoride–hexafluoroacetone copolymers, both polymers being crystalline. Blends showed a different melting behavior with the annealing temperature; single or double melting peaks were observed on annealing over an entire blend composition. They were ascribed to the cocrystallization or separate crystallization of blends, respectively. On the other hand, annealing of quenched samples affected the glass transition behavior of blends; single or double glass transition temperatures were observed depending on the annealing condition in the dynamic mechanical measurements. It was well explained with the miscibility of amorphous phases of blends at annealing temperature. Consequently it was found that the cocrystallization in the blends could be occurred in the miscible amorphous phases. Particularly this blend system showed the upper critical solution temperature (UCST) behavior in both the crystalline and amorphous phases; it was almost rare phenomenon that the polymer blends showed UCST behavior.

KEY WORDS Cocrystallization / Miscibility / Melting Temperature / Glass Transition Temperature / Blend / Vinylidene Fluoride–Tetrafluoroethylene Copolymer / Vinylidene Fluoride–Hexafluoroacetone Copolymer /

Many studies have been devoted to the understanding of miscibility of polymer blends which are composed of amorphous/amorphous polymers, amorphous/crystalline polymers or crystalline/crystalline polymers. The nature and characteristics in the amorphous/amorphous or amorphous/crystalline polymer blends are now well accepted to some extent on the theoretical background and experimental observations.^{1–6} However the miscible crystalline/crystalline polymer blends are not only almost rare but also are never clearly understood. They contain the crystal–crystal interaction or cocrystallization as well as amorphous–amorphous interaction. Crystal–crystal

interaction may create the cocrystallization or mixed crystals in blends and it is known to be possible only in the case that blends have the very similar unit cell dimensions between crystals of two polymers. It severely limits the cocrystallization in the crystalline/crystalline blends in spite of discovery of many pairs of miscible amorphous polymer blends. However an effort has been devoted to find the polymer pairs having cocrystallization for past few decades.^{7–13} Blend of poly(vinylidene fluoride) (PVDF) and poly(vinyl fluoride) (PVF)⁷ had been recognized to demonstrate the typical cocrystallization since 1965. It had been explained with the presence of only one major

peak in X-ray diffraction of blends and with the existence of single melting temperature in blends. However it was recently¹² reported that there exists no miscibility in both crystalline and amorphous phases of blend of PVDF and PVF. It may suggest that the similar crystal structure of two crystalline components is not a sufficient condition for the cocrystallization. Recent reports such as in poly(aryl ether ketone) blends¹³ and poly(vinylidene fluoride)/copoly(chlorotrifluoroethylene–vinylidene fluoride) blends¹¹ have also showed that the cocrystallization could be occurred even in blends having small differences in structure in spite of absence of any specific interactions. Moreover Tanaka *et al.*,⁹ insisted that cocrystallization is favored not only when the crystal structures of two components are very similar but also when they already contain some disorder which should render them more tolerant of slight additional mismatch. However the nature of cocrystallization is still controversy and difficult to be resolved.

The polymer pair to be studied here is vinylidene fluoride copolymers, that is, vinylidene fluoride–tetrafluoroethylene (VDF–TFE) copolymer/vinylidene fluoride–hexafluoroacetone (VDF–HFA) copolymer. They are both crystalline polymers; VDF–TFE copolymer^{14,15} readily crystallizes and VDF–HFA copolymer¹⁶ crystallizes slowly because of the existence of bulky side group. This pair of polymers may have a high potential of cocrystallization by introducing other fluorocarbon comonomers into vinylidene fluoride units. Therefore in this study, the possibility of cocrystallization will be investigated by analyzing the melting and glass transition behaviors of blends of VDF–TFE copolymer/VDF–HFA copolymer.

EXPERIMENTAL

VDF–TFE copolymer was the random copolymer of 80 mol% vinylidene fluoride and 20 mol% tetrafluoroethylene and was supplied

from Daikin Kogyo Co., Ltd. VDF–HFA copolymer was the random copolymer of 92 mol% vinylidene fluoride and 8 mol% hexafluoroacetone and was supplied from Central Glass Co., Ltd.

Homogeneous mixtures of VDF–TFE and VDF–HFA copolymers were obtained by dissolving their copolymers at various weight percent in the solvent of tetrahydrofuran at room temperature. From the homogeneous mixtures, films were cast and maintained at room temperature for 12 h. To remove the solvent remained in the film completely, the samples were dried in a vacuum drying oven for 24 h at 100°C.

Quenched samples were prepared by melt-pressing the cast films at 200°C which was above the melting temperature of the samples and subsequently by quenching them into the mixtures of ice and water. The thickness of samples obtained so was about 50 μm .

The thermal properties were measured by differential scanning calorimetry (Rigaku TG-DSC) with the sample of weight of approximately 6 mg and the peaks of melting and crystallization curves were taken as melting and crystallization temperatures, respectively.

The dynamic mechanical properties were measured at 10 Hz using the dynamic viscoelastic mechanical apparatus developed by Furukawa *et al.*¹⁷ at a heating rate of 2°C min⁻¹. Particularly in order to investigate the temperature dependence of miscibility of blends, the quenched films were annealed at a fixed temperature (T_a) and then very immediately quenched into liquid nitrogen bath. Thermal program at this time is shown in Figure 1. In this case, a particular attention was required in order for the sample to reserve in a flat state without distorting during quenching. Those samples were placed in the dynamic measuring apparatus of which the temperature was kept below -100°C and then the dynamic mechanical properties were measured. Sample treated so was called an 'annealed/quenched' sample in this study.

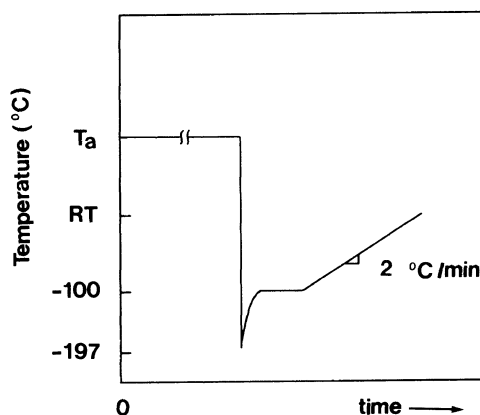


Figure 1. Thermal program used for dynamic mechanical measurement of samples annealed/quenched at a fixed annealing temperature (T_a).

RESULTS AND DISCUSSION

Melting Behavior and Cocrystallization

Figure 2 shows the DSC thermogram of quenched samples measured at a heating rate of $20^\circ\text{C}\text{min}^{-1}$. Pure VDF-TFE copolymer exhibits a higher melting temperature than that of pure VDF-HFA copolymer. Melting peak of pure VDF-HFA copolymer is very broad in comparison with that of pure VDF-TFE copolymer, which is due to the poor crystallization on quenching from the melt because of bulky molecular structure of VDF-HFA copolymer. Even the blend samples also show the single melting peak over an entire composition of blends and their melting temperatures increase continuously with the increase of VDF-TFE copolymer in blends. It indicates that both two polymers crystallize together within the same crystals on quenching as they are almost universally observed during rapid crystallization of crystalline/crystalline polymer blends.^{18,19} Since such a cocrystallization on quenching is metastable, the crystals may be separated in other thermal treatment, depending on the miscibility of blends. Figure 3 shows DSC result of the blends cooled slowly from the melt, and two separated exotherms and two separated endotherms of blends are

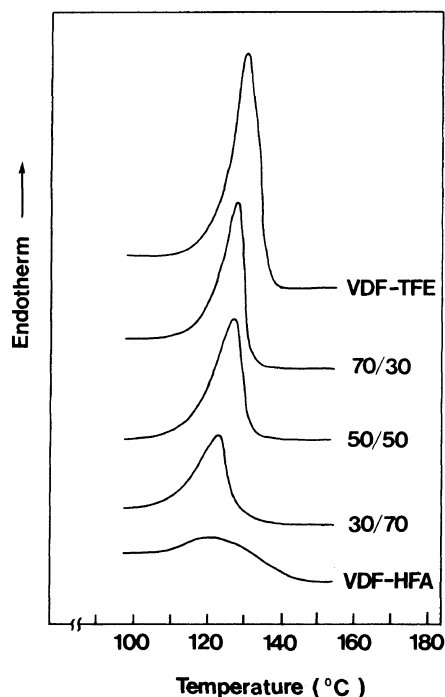


Figure 2. DSC thermograms of quenched samples with the various blend ratios of VDF-TFE/VDF-HFA copolymers blends.

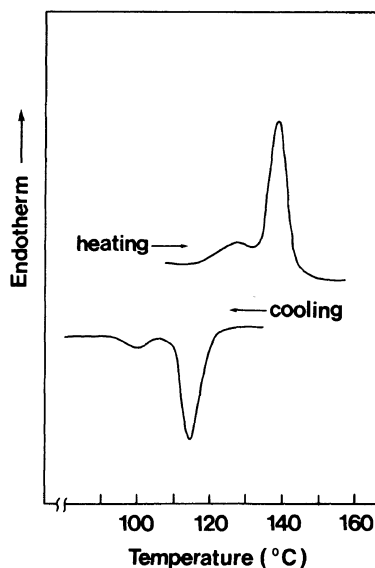


Figure 3. DSC thermograms of 50/50 blend which was cooled at a rate of $20^\circ\text{C}\text{min}^{-1}$ from the melt to room temperature and then reheated at the same rate.

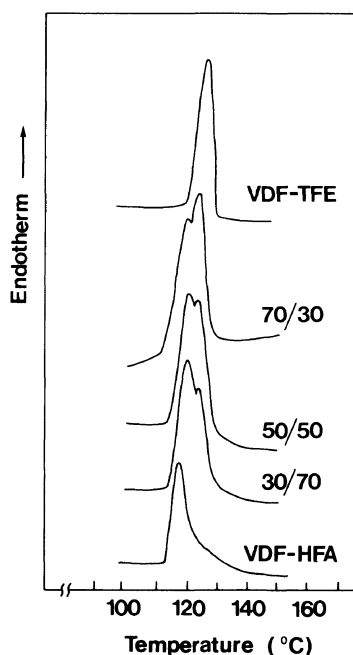


Figure 4. DSC thermograms of the samples annealed at 100°C for 6 h.

represented, respectively. The higher melting temperature of VDF-TFE copolymer in the reheated blend sample than that in the quenched VDF-TFE copolymer is considered to result in difference of size of crystallite due to the different thermal history. The crystallization curve of blend has two exothermic peaks at 114.5°C and 100°C and such two crystallization temperatures are nearly corresponded to the respective crystallization temperature of VDF-TFE and VDF-HFA copolymers. These double peaks also appear in its reheated melting curve; they have two melting temperatures at 138°C and 127°C which are corresponded to each of melting temperatures of two pure polymer components. It means that on crystallization of blend sample, VDF-TFE copolymer crystallizes firstly and then VDF-HFA copolymer does, and therefore on the melting of the blend sample crystallized so, crystals of VDF-HFA copolymer melt firstly and then the crystals of VDF-TFE copolymer do.

The quenched samples with various blend

compositions were annealed at the fixed temperatures for 6 h. Figure 4 shows the DSC melting curve of the samples annealed at 100°C. Melting temperatures of pure VDF-TFE and VDF-HFA copolymers annealed at 100°C are 125.5°C and 116.5°C, respectively and the difference between their melting temperatures becomes about 9°C. For the blend samples annealed at 100°C, the melting curve exhibits double endotherms and the intensity of their endothermic peaks changes corresponding with the blend ratio of VDF-TFE and VDF-HFA copolymers. It means that two polymer components of blend crystallize separately at 100°C similarly as in the case of cooling from the melt. A slight shift of two melting peaks of blend sample toward each melting temperature of two pure polymer components may be regarded as the existence of partial interaction of two polymer components.

However thermograms of blend annealed at 110°C never show the double melting peaks and show the single melting peak over all the entire blend ratios as shown in Figure 5. They vary continuously with the blend composition and have no maximum or minimum as shown in Figure 6. The enthalpy for melting endotherm was also changed continuously with blend composition. That is, the melting enthalpy was increased with the increase of content of VDF-TFE copolymer in the blend. Moreover the shape of melting curve of samples annealed at 110°C never changed with the heating rate, while the samples annealed at 100°C or below show larger difference of melting temperature between double peaks as the heating rate decreased. An attention should be given to this fact that the blend sample annealed at 110°C shows the single melting temperature over all the blend ratios of blend regardless of change of the heating rate. It should be ascribed to the formation of cocrystallization of two polymer components. That is, the cocrystallization in the blend of two crystalline polymers can be regarded to be generally evidenced by the single melting

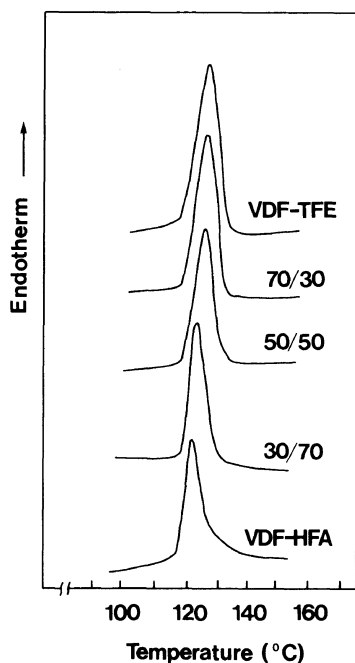


Figure 5. DSC thermograms of the samples annealed at 110°C for 6 h.

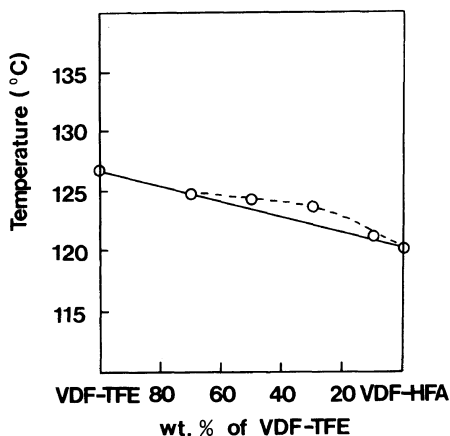


Figure 6. Melting temperature versus the blend ratio of the samples annealed at 110°C.

temperature. The phase diagram showing the crystal-crystal interaction of blends is shown in Figure 7. It represents a typical upper critical solution temperature (UCST) behavior.^{20,21} It is very peculiar and interesting that such a type

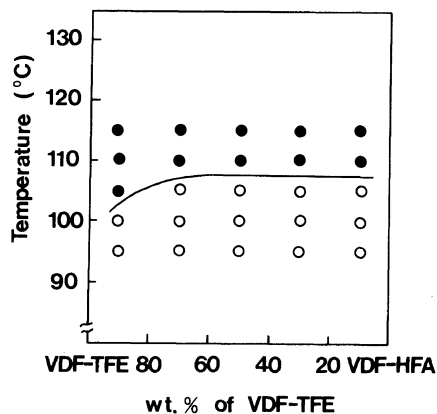


Figure 7. Phase diagram showing single (●) or double (○) melting temperatures on DSC thermograms of annealed samples.

of phase diagram is observed in this blend.

Wide angle X-ray diffraction measurements were carried out in order to elucidate the structural change of crystals on cocrystallization of blends. However it was impossible to ascertain the cocrystallization from the separate crystallization of two polymer components because of very close value of X-ray diffraction angle in two polymer components; all the samples showed almost invariable Bragg spacing around $20.0^\circ 2\theta$ indicating all trans molecular conformation²² similar to form I of PVDF. Crystal structures of blends were revealed to exist only in form I regardless of annealing temperature, while those with rich VDF-HFA copolymer showed a weak X-ray diffraction intensity due to existence of form II crystals besides X-ray peaks of form I. Here it should be noted that the blends annealed at 100°C showed only the form I crystal structure in spite of the separate crystallization. It might be perhaps ascribed that the blends form a kind of epitaxial crystallization.²³

Miscibility in the Amorphous Phases

Figure 8 shows the dynamic mechanical properties of quenched blend samples in terms of $\tan \delta$ versus temperature. For pure VDF-TFE copolymer,²⁴ two relaxational peaks are

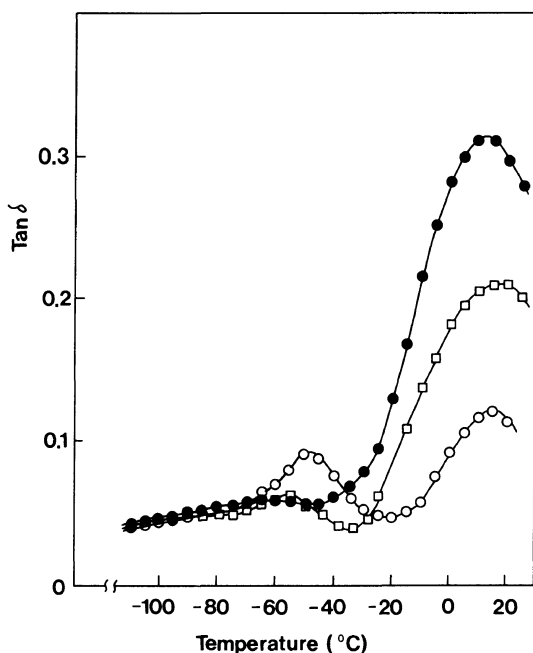


Figure 8. Temperature dependence of $\tan \delta$ in the quenched samples: \circ , VDF-TFE; \square , 50/50; \bullet , VDF-HFA.

exhibited near -52°C and 12°C . They are due to the glass transition of amorphous phase and the molecular motion in crystalline phase, respectively. Pure VDF-HFA copolymer has also two peaks in the curve of $\tan \delta$ versus temperature. The small peak near -60°C is ascribed to the secondary transition which is related to the molecular motions of side chains of amorphous phase or crystal defects and the large peak at 15°C is associated with the glass transition temperature (T_g). The intensity of maximum $\tan \delta$ at 15°C for the sufficiently annealed sample was lowered than that of quenched sample due to the increase of crystallinity, whereas the intensity of maximum $\tan \delta$ near -50°C was increased with annealing. Therefore VDF-TFE and VDF-HFA copolymers have T_g at -52°C and 15°C , respectively. For the quenched blend sample containing VDF-HFA copolymer of 50 wt%, two relaxational peaks are shown in the neighborhood of -52°C and 15°C , which are

corresponded to each T_g of two polymer components. Absence of the crystalline relaxational peak in the quenched blend is likely to come from the relatively large effect of the peak at T_g of pure component with comparison to the crystalline relaxation of the other pure component. Such two glass transition temperatures appeared in all the quenched blend samples over an entire blend composition. As well, value of maximum $\tan \delta$ at each T_g varies relatively with the blend ratio of blends. It indicates that the amorphous phases of quenched blend sample are not miscible on the molecular scale. At this point, if the previous melting behavior of blends are recalled, it might seem to be mismatched with the immiscibility of amorphous phases because it is regarded that blends hardly cocrystallize in the immiscible amorphous phases. Therefore in order to clear it, the temperature dependence of miscibility in the amorphous state, *i.e.*, dynamic mechanical properties of annealed/quenched samples was investigated.

The annealed/quenched sample at 100°C or below for 6 h showed the similar relaxational pattern as that of quenched sample, indicating the immiscibility of blends at this temperature. However dynamic mechanical behavior of annealed/quenched sample at 110°C was different from the annealed/quenched sample at 100°C or below. Figure 9 shows temperature dependence of $\tan \delta$ of annealed/quenched blend sample; the relaxational pattern changes with the annealing time. The annealed/quenched blend sample at 110°C for 20 min shows the main relaxational peak at -25°C and another peak at -52°C . The former is located at an intermediate position of glass transition temperatures of two polymer components, and the latter is corresponded to T_g of VDF-TFE copolymer. Further annealing for 6 h makes the relaxational peak at -52°C disappear and shows only a peak at -25°C . It suggests that there can exist two kinds of amorphous phases in annealed/quenched blend, that is, rich VDF-TFE amorphous

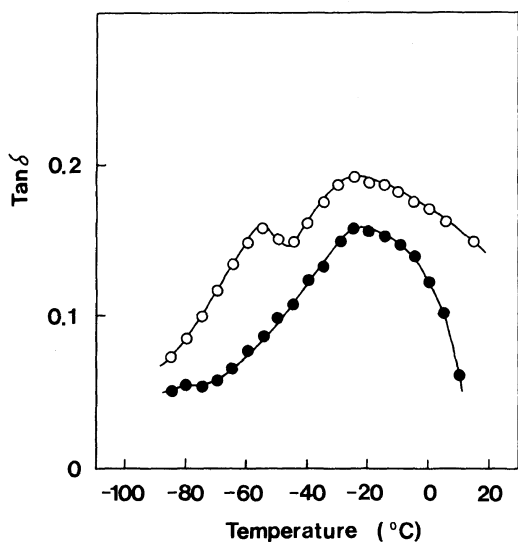


Figure 9. Temperature dependence of $\tan \delta$ in annealed/quenched 50/50 blend at 110°C for 20 min (○) or 6 h (●).

phase and miscible phase of two amorphous molecules. The former is likely to be primarily due to the interphase located between crystalline and amorphous phases, considering that this peak disappears on annealing at 110°C for 6 h. Hahn *et al.*²⁵ reported the existence of crystal-amorphous interface in blends of PVDF and poly(methyl methacrylate) by observing their dielectric properties and Flory *et al.*²⁶ suggested the concept of interphase in the crystalline polymer blends. Such a interphase concept could be also applicable to blends consisting of two crystalline polymers. In this study, it can be explained as follow; the peak at -52°C is ascribed to the amorphous phase of rich VDF-TFE copolymer located at the interface of crystals because of richness of VDF-TFE copolymer in crystals owing to faster crystallization of VDF-TFE copolymer than VDF-HFA copolymer even if they are cocrystallized on quenching. But annealing for a long time results in the development of the cocrystallization with the similar concentration of each polymer component in the crystals and therefore the relaxational peak at -52°C

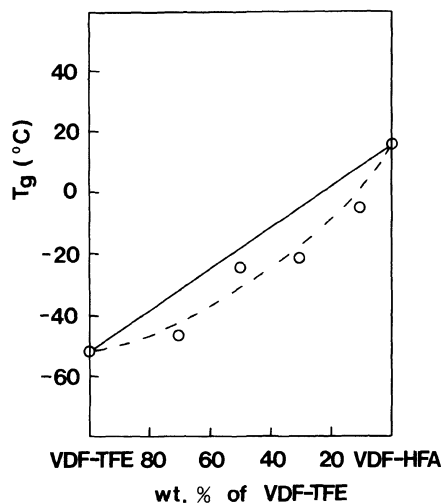


Figure 10. Glass transition temperature versus the blend ratio of the sample annealed/quenched at 110°C for 6 h.

disappears. Consequently this is ascribed to the result of the cocrystallization formed on annealing at 110°C . The main peak at -25°C in the annealed/quenched blend at 110°C reflects the miscibility in the amorphous phases of two polymer components. Value of maximum $\tan \delta$ at -25°C was lowered as the increase of annealing time. It is attributed to the increase of crystallinity as it is almost observed in the dynamic mechanical measurement of many crystalline polymers.

The blend samples show only a single T_g on annealing/quenching at 110°C for 6 h over all the blend ratios. Figure 10 shows T_g versus blend ratio of samples annealed/quenched at 110°C for 6 h, in which T_g varies continuously with the blend ratio. These facts are sufficient to say that the amorphous phases of blends are miscible at 110°C . On the other hand, even if the single T_g appeared in the sample annealed/quenched at 110°C , its second dynamic measurement showed two relaxational peaks. It means that the reversible phase separation appears through heating and cooling above or below 110°C . Now it is mentioned that the blend system of VDF-TFE and VDF-HFA copolymers shows UCST behavior in the

amorphous phase as well as in the crystalline phase as described previously. It is not usual and is very contrasted with the blend system of PVDF or its copolymers with other amorphous polymers showing the lower critical solution temperature (LCST) behavior.

CONCLUSIONS

Melting of blends of VDF-TFE and VDF-HFA copolymers had a different behavior with the annealing temperature; annealing at 100°C showed double melting temperatures in blends but annealing at 110°C showed single melting temperature over an entire blend composition. It was ascribed to the facts that cocrystallization or separate crystallization was formed on annealing. Such a cocrystallization was in a close relationship with the miscibility of amorphous phase, which could be explained by observing the dynamic mechanical properties of annealed/quenched samples. That is, cocrystallization was possible only in the miscible state of amorphous phases of blends. Particularly it was very interesting that this blend system showed UCST behavior not only in the crystalline but also in the amorphous phases.

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