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Polymer 40 (1999) 1459–1463

polymer

Spinodal decomposition and succeeding crystallization in PCL/SAN blends

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Received 23 March 1998; revised 27 April 1998; accepted 27 April 1998

Abstract

For a binary blend of poly(ε-caprolactone) (PCL) and poly(styrene-co-acrylonitrile) (SAN) containing 27.5 wt% of acrylonitrile, the lower critical solution temperature (LCST) type of phase boundary was determined by thermo-optical analysis. A critical mixture, 80/20 PCL/SAN blend, initially underwent spinodal decomposition (SD) above the LCST and then crystallized at a lower temperature (40°C). Isothermal crystallization was analyzed by differential scanning calorimetry. The longer the SD duration the higher the rate of crystallization. An optimum SD time yielding the highest degree of crystallization was found to exist at a relatively early stage of SD (ca. 5 min). The blend via the optimum time of SD showed the highest melting point. In the blend, a very long and straight crystal lamella was observed by transmission electron microscopy. Thus, the effect of the degree of demixing on the succeeding crystallization was revealed.

Keywords: Crystallization; Spinodal decomposition; Polymer blend

1. Introduction

Miscible polymer blends containing one crystallizable component and exhibiting liquid–liquid phase separation at elevated temperatures (lower critical solution temperature, LCST, behaviour) offer an excellent possibility of controlling morphology and thus mechanical properties. For instance, if a homogeneous mixture of dissimilar polymers is allowed to undergo a rapid temperature jump from below LCST to above LCST, spinodal decomposition takes place and a highly interconnected two-phase morphology with uniform domain size (so-called 'modulated structure') develops. By quenching the demixed system below the glass transition temperature after an appropriate time of demixing, one is able to fix this characteristic morphology [1]. By quenching the demixed blend below the melting point of the crystallizable component, crystallization will proceed and will be highly affected by the degree of demixing.

It is well known that poly(ε-caprolactone) (PCL) and poly(styrene-co-acrylonitrile) (SAN) are miscible only in a limited range of copolymer composition, i.e. the blends display a window of miscibility in the temperature–copolymer composition plane (from about 8 to 28 wt% acrylonitrile in SAN) [2]. Near the borderline of miscibility/immiscibility, LCST behaviour is observed [3,4]. In this study, the blend near the borderline was selected, i.e., SAN containing 27.5 wt% AN was used.

In this paper, the phase behaviour is investigated by the cloud point method using thermo-optical analysis (TOA) and optical microscopy. A single-phase mixture of PCL and SAN is forced to undergo demixing above LCST and the demixed sample is quenched below the melting point T_m of PCL to be isothermally crystallized. The crystallization kinetics are investigated by differential scanning calorimetry (DSC) and the resulting morphology is observed under transmission electron microscopy (TEM). Special attention is paid to the effects of the degree of demixing on the crystallization kinetics and the crystalline morphology.

2. Experimental

The PCL was a commercial polymer of Union Carbide Corp. (PCL-767; $M_w = 40\,400$ g mol^{-1}, $M_w/M_n = 2.61$).

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0032-3861/98/$ - see front matter
PII: S0032-3861(98)00370-X

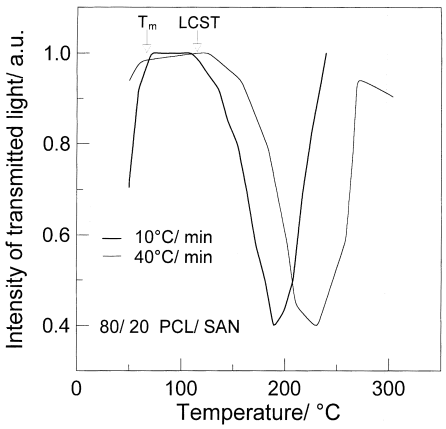

Fig. 1. Transmitted light intensity vs temperature in thermo-optical analysis at two heating rates (10 and 40°C min^{-1}) for 80/20 PCL/SAN sample.

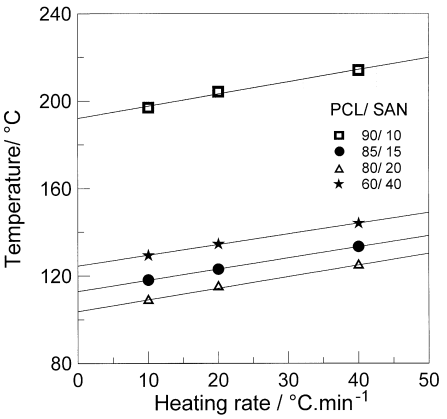

Fig. 3. Evaluation of LCST phase boundary by extrapolating to zero heating rate.

SAN containing 27.5 wt% of acrylonitrile (SAN-27.5) was synthesized at 60°C using ethylbenzene as a solvent and azoisobutyronitrile (AIBN) at a concentration of 0.02 mol l^{-1} as an initiator; $M_w = 169\,000$ g mol^{-1}, $M_w/M_n = 2.09$.

The solution cast method was used to prepare PCL/SAN blends with compositions containing 0, 10, 15, 20, 30 and 40 wt% of SAN. PCL and SAN-27.5 were dissolved at 5 wt% of total polymer in 1,2-dichloroethane. The solution was cast onto polyethylene plates and the solvent was allowed to evaporate for 5 min at 60°C and then 24 h at room temperature.

For the differential scanning calorimetry (DSC) analysis, the specimen was packed into an aluminium pan. The DSC measurements were performed in nitrogen atmosphere (50 bar) on a Perkin-Elmer IV system. For each sample at least two experiments were performed and the results averaged.

By thermo-optical analysis (TOA), the LCST border in the phase diagram was measured. With TOA it is possible to follow changes of the intensity of the transmitted light through the film specimen during programmed heating.

The specimen was annealed on a hot stage at the desired temperature. The melted specimen was placed onto a hot stage of the microscope. Structural development during the isothermal and also during the constant temperature increase was observed under both the optical and the polarizing microscope (Olympus BH-2) equipped with a video recording system and exposure control unit (Olympus PM-20).

For the TEM analysis, the specimens were microtomed to a ultrathin section of 70 nm thickness using a Reichert–Jung ultracryomicrotome with a diamond knife at −70°C and then they were stained with RuO_4 vapour at room temperature for 2 h. The structure in the section was observed under an electron microscope, JEM 100CX (100 kV).

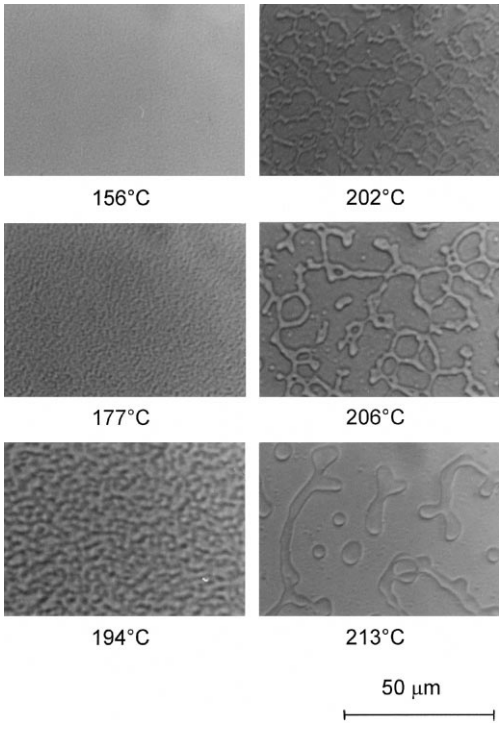

Fig. 2. Optical micrographs of 80/20 PCL/SAN blend during heating run (10°C min^{-1}).

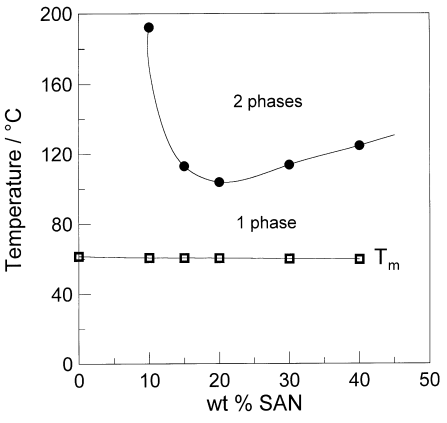

Fig. 4. Phase diagram of PCL/SAN-27.5 system. The melting point T_m was measured by DSC after crystallization at 40°C for 14 h.

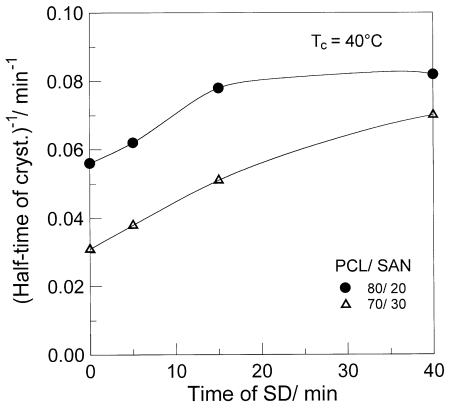

Fig. 5. Effect of SD on crystallization rate.

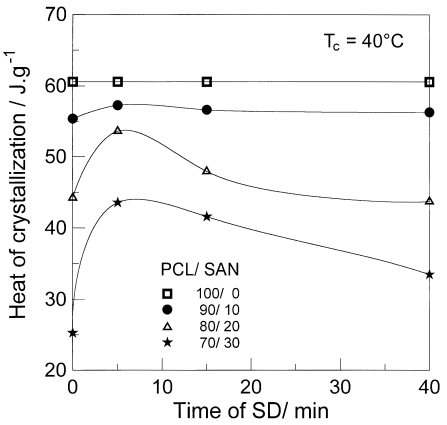

Fig. 7. Effect of SD on the heat evolved by crystallization.

3. Results and discussion

All specimens of PCL/SAN-27.5 blends were optically clear and no structure was observed under a microscope at 80°C (above the melting temperature of PCL). When the specimens were heated at a constant heating rate, e.g., 10°C min^{-1}, they became opaque and a two-phase structure was observed. The change from clear to opaque is represented by the change of intensity of transmitted light with increasing temperature in the thermo-optical analysis (TOA). Two examples are shown in Fig. 1. The intensity of transmitted light increases first due to the crystal melting at approx. 60°C, and then starts to decrease. The decrease may be caused by the onset of spinodal decomposition (at about 125°C). In fact, after the transmitted light intensity started to decrease, a highly interconnected two-phase structure developed and then grew up self-similarly, as shown in Fig. 2. This is very characteristic of spinodal decomposition. The temperature at which the intensity started to decrease is plotted as a function of the heating rate in Fig. 3. The position of LCST was determined as the intercept of the temperature axis (zero heating rate). The position of the LCST boundary obtained by this method is shown in Fig. 4.

A 80/20 PCL/SAN blend in the DSC pan was annealed at 80°C for 5 min and also at 150°C for 5, 10, 15 and 40 min. Then the temperature dropped to 40°C and DSC measurement was carried out to follow the isothermal crystallization. From the exothermic peak, the half-time of crystallization was calculated. The results are shown in Fig. 5 as a function of the annealing time at 150°C, i.e. the time of spinodal decomposition (SD). One can see that the crystallization is accelerated by SD. That is, the longer the SD time, the faster the crystallization. In other words, the higher degree of demixing provides faster crystallization. This may be caused simply by a chain mobility effect. That is, SAN will be segregated out from a PCL-rich region to yield a higher PCL concentration, and this is favourable for crystallization because the PCL-richer region will have higher chain mobility by the exclusion of a high T_g (glass transition temperature) component, SAN. In fact, the effect of SAN content is significant as shown in Fig. 5 (compare 80/20 and 70/30). Such a T_g effect is more systematically shown in Fig. 6.

The heat evolved by the isothermal crystallization at 40°C is shown in Fig. 7 as a function of time of SD. The heat of crystallization is assumed to be proportional to the overall degree of crystallization, X_C. In the blends, the highest X_C is attained after the demixing for a certain time (ca. 5 min).

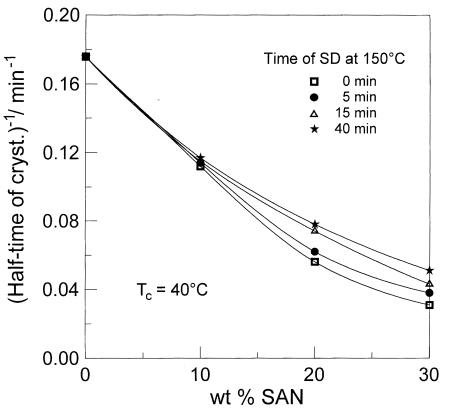

Fig. 6. Crystallization rate vs blend composition.

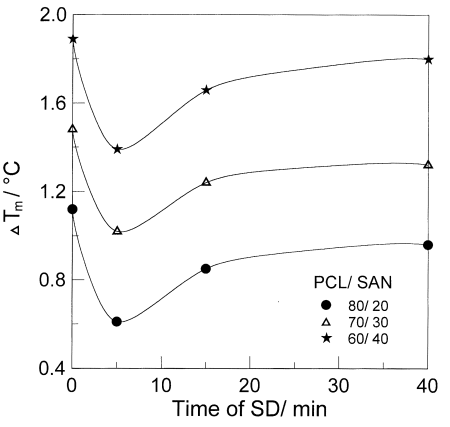

Fig. 8. Effect of SD on the melting point: $\Delta T_m = (T_m$ in neat PCL) − (T_m in blend).

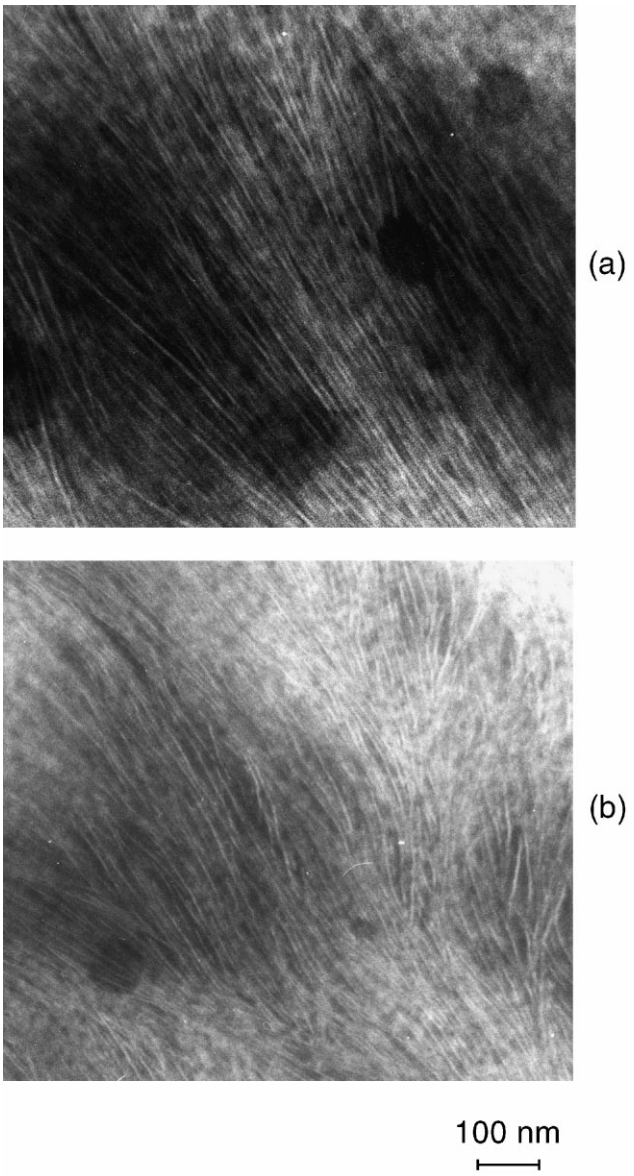

Fig. 9. TEM micrographs of 80/20 PCL/SAN blends crystallized after different SD times: (a) 2.5 min; and (b) 7 min.

After too much demixing, the X_C becomes lower. A higher X_C is expected for the higher level of demixing in which a more favourable situation is provided for the crystallization, as discussed above for the kinetics (Figs 5 and 6). However, when demixing proceeds further, the crystallizable PCL chains in SAN-rich regions will be arrested by the high T_g effect there to render a lower X_C. Thus, there should exist an optimum degree of demixing for the crystallization.

The better situation for the higher X_C may imply the formation of more perfect crystals. The less perfect crystals, e.g., the smaller crystallites with defects, may show the lower melting point T_m. The difference in T_m between neat PCL and the blend, ΔT_m, is shown in Fig. 8. One can see that ΔT_m has a minimum at the optimum time of SD (ca. 5 min), as expected.

Two TEM pictures are shown in Fig. 9. Both samples

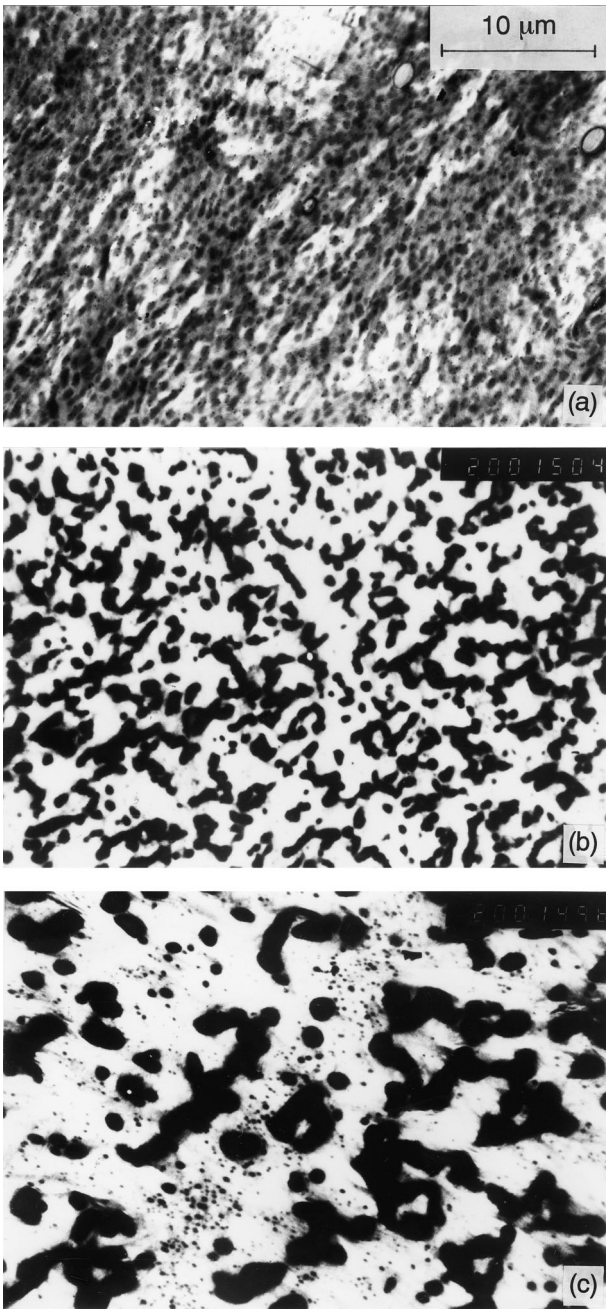

Fig. 10. TEM micrographs of 80/20 PCL/SAN blends crystallized after different SD times: (a) 2.5 min; (b) 15 min; and (c) 40 min.

were crystallized after the SD times near the optimum point. One can see long and straight stripes in Fig. 9a. The bright stripes can be assigned to PCL crystal lamellae, while dark area between stripes to the amorphous region which contains SAN to be stained by RuO_4. This implies that SAN is segregated out between PCL lamellar crystals. In Fig. 9b, the upper right part is rather bright and the left part is mainly dark. The dark part may be a SAN-rich region. One can see that, even in the SAN-rich region, lamellar crystals are formed. Of course, lamellae are seen in the PCL-region, although the phase contrast is poor (probably caused by

less stainable SAN). In any case, the most interesting observation is the formation of very long and straight lamellar crystals in Fig. 9a. At present, this cannot be interpreted conclusively. The segregation of polymer impurity (SAN) at the lamellar level, however, might reduce the surface free energy of lamellar crystals to prevent twisting of lamellar crystals and yield straight and long lamellae.

So far, we have discussed the effect of SD on crystallization. It is also interesting to investigate how the phase-separated structure by SD is affected by crystallization. Then, it is interesting to investigate whether or not the structure developed during SD can be maintained after crystallization.

Fig. 10 shows TEM pictures of the demixed-and-crystallized blends (the demixing time was varied). In the blend with short duration SD (Fig. 10a), SAN domains are very small, reflecting the early stage of SD, and they are dispersed quite regularly. For the blend after long duration SD (Fig. 10b), SAN domains become larger, reflecting the progress of SD, and some aggregate with each other to yield less ordering in the arrangement of domains. The trend becomes more obvious for the blend after much longer duration SD (Fig. 10c). In Fig. 10c, one can see also the presence of small SAN particles of ca. 0.1 μm diameter. SAN chains seem to be segregated out not only to the interlamellar region of 10 nm level, but also to a garbage space of 100 nm level to generate SAN particles. Thus, the crystallization seems to disorder the SD structure and the degree of disordering depends on the degree of demixing by SD.

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