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An Immiscibility Loop in Isotactic Polypropylene/Partially Hydrogenated Oligo(styrene-*co*-indene) Blend

Chang Hyung Lee, Hiromu Saito, Graciela Goizueta,[†] and Takashi Inoue*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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ABSTRACT: We found an immiscibility loop in isotactic polypropylene/partially hydrogenated oligo(styrene-*co*-indene) blend by the cloud point method; the blend had a lower critical solution temperature-type phase boundary at low temperatures and an upper critical solution temperature-type boundary at high temperatures. The existence of the immiscibility loop was justified by the kinetic analysis of the liquid−liquid phase separation, that is, the apparent diffusion coefficient of spinodal decomposition, obtained by the time-resolved light-scattering method, increased and then decreased with increasing temperature inside the immiscibility loop, suggesting the presence of two spinodal temperatures. The existence of the immiscibility loop was also supported by the kinetics of the crystallization around the lower spinodal temperature and the observation of spherulite formation inside the immiscibility loop.

Introduction

Most pairs of high molecular weight polymers are immiscible. Miscible polymer/polymer blends tend to phase separate at elevated temperatures. This LCST (low critical solution temperature)-type phase behavior is typical of miscible blends. About 180 pairs of dissimilar polymers have been found to exhibit the LCST behavior.[1] Some miscible polymer blends also phase-separate at low temperatures. This UCST (upper critical solution temperature)-type phase behavior is often observed when one or both components have a relatively low molecular weight. An immiscibility loop, consisting of LCST- and UCST-type phase boundaries, is known in low molecular weight systems, e.g., water/nicotine.[2] In this paper, we deal with the loop-type phase behavior which is very rare in polymer blends.

In the previous article,[3] we investigated the spherulite formation in a single-phase mixture of isotactic polypropylene (iPP) and partially hydrogenated oligo(styrene-*co*-indene) (HSI) by time-resolved light-scattering at relatively low crystallization temperatures (110−75 °C). At higher temperatures, we found strange results in both spherulite morphology and crystallization kinetics. These results motivated us to study the phase behavior of the iPP/HSI blend which was believed to be a totally miscible system. Later, we found that Cimmino et al.[4] had dealt with a similar system, iPP/hydrogenated oligo(cyclopetadiene). They investigated the immiscibility loop by the cloud point method using a constant heating rate procedure. In this paper, we first used the cloud points after long annealing (~24 h) to determine the equilibrium phase boundary and then carried out time-resolved light-scattering studies of the kinetics of the phase separation after a temperature jump from a single-phase to a two-phase region to confirm the phase behavior. The light-scattering studies inside the immiscibility loop are particularly interesting; one can expect a peak in the temperature dependence of the apparent diffusion coefficient D_{app} for phase separation because, with increasing temperature inside the loop, D_{app} will first increase above the LCST and then decrease on approaching the UCST.

Experimental Section

The iPP used was a commercial polymer supplied by Mitsui Toatsu Chemicals, Inc. (J3HG); $M_w = 3.5 \times 10^5$, $M_n = 5.0 \times 10^4$. HSI was supplied by Arakawa Chemicals, Ltd. (ARKON); $M_w = 770$, styrene content = 60 wt %, degree of hydrogenation (indene) = 70%.

The blends of high-iPP content (>10 wt %) were melt-mixed at 200 °C by using a Mini-Max Molder (CS-183 MMX, Custom Scientific Instruments, Inc.). The single-phase melt was extruded and chopped into pellets. A thin film (ca. 15 μm thick) was prepared by pressing the pellets between two cover glasses at 200 °C. When the iPP content was <10 wt %, the viscosity was too low to be melt-mixed in the Mini-Max Molder. Then, iPP and HSI were dissolved in xylene at a concentration of 5 wt % of total polymer. The solution was cast onto a cover glass. The cast film was dried under vacuum (10^{-4} mmHg) at 100 °C for 1 day to prepare a film of 15 μm thickness.

For the cloud point measurements, the films were heated for 3 min at 210 °C (above the melting temperature, T_m, of iPP and at the single-phase region). Then they were rapidly transferred to another hot stage and annealed for 24 h at various temperatures. When the films were clear and the two-phase morphology could not be detected under an optical microscope, we judged that the blends were in the single-phase region. In the two-phase region the films became opaque, and a liquid−liquid phase-separated structure was observed under the microscope.

Using a light-scattering photometer equipped with a CCD (charge-coupled device) camera,[5] the kinetics of phase separation were investigated. This light-scattering apparatus facilitates the time-resolved measurement of a two-dimensional angular distribution of scattered light with 576 × 382 data points in a time slice of 10 s and a one-dimensional one with 576 data points in a time slice of 0.14s. The film specimen was held at 210 °C (in the single-phase region) for 3 min and then rapidly transferred into a light-scattering hot-stage set at a desired annealing temperature, and the scattering profile was recorded as a function of time during isothermal annealing. A polarized He-Ne gas laser of 632.8 nm wavelength was applied perpendicularly to the film specimen. The scattered light was passed through an analyzer. We employed the V_v geometry in which the optical axis of the analyzer was set parallel to that of the polarizer. The crystallization kinetics were also studied by time-resolved light-scattering, employing the H_v geometry with a perpendicular set of the two optical axes.

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* To whom correspondence should be addressed.

[†] Present address: PLAPIQUI, Universidad Nacional del Sur, 12 de Octubre 1842, 8000-Bahia Blanca, Argentina.

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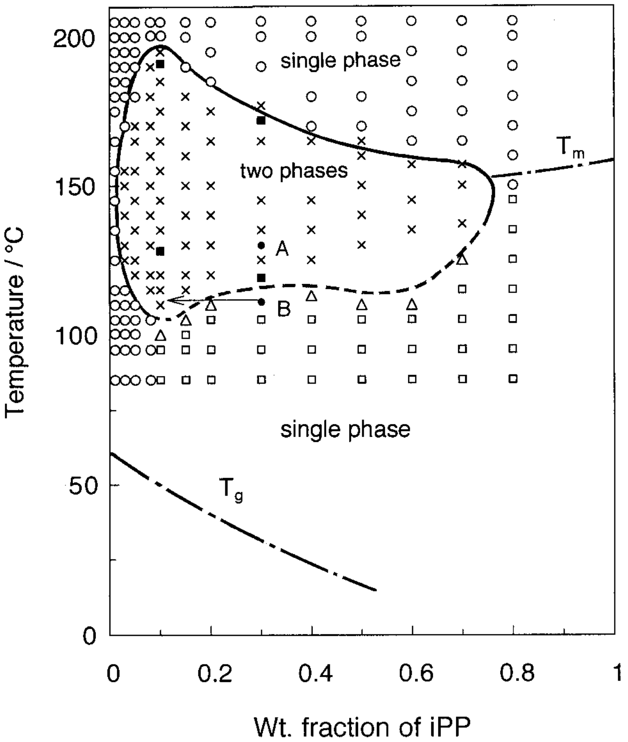

Figure 1. Phase diagram of the iPP/HSI system: (○) clear and no structure development after a 24 h anneal, (×) opaque and structure development by liquid–liquid phase separation, (□) spherulite formation, and (△)ambiguous by cloud point but single-phase nature confirmed by the H_v and V_v time-resolved light-scattering studies.

During the isothermal annealing, the time variations of the texture of iPP spherulite were also observed under an optical microscope (Olympus BH-2) equipped with a TV video recording system.

Results and Discussion

After annealing for 24 h, some films were transparent and no indication of liquid–liquid phase separation could be seen under an optical microscope. This behavior is indicated by open circles in Figure 1. Some films became translucent, and the bicontinuous two-phase morphology with a periodic distance of a few micrometers, characteristic of spinodal decomposition, was observed. This is indicated by crosses in Figure 1. One can clearly see an immiscibility loop in the phase diagram. It consists of LCST and UCST phase boundaries. The LCST-type phase boundary was somewhat arbitrary (by broken line), since the crystallization of iPP at the lower temperatures made it difficult to locate the cloud point. The margin of error is indicated by triangles in Figure 1. However, the LCST behavior was justified by the time-resolved light-scattering study of the spinodal decomposition which dominated the crystallization for a short time after the temperature jump from the single-phase region so that a time window was provided to determine the LCST-type spinodal temperature. The following analysis was used.

In the early stage of spinodal decomposition, the scattered intensity I is expected to increase exponentially with time:[6]

$$I(q,t) = I(q,0)\exp[2R(q)t] \tag{1}$$

where q is the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, θ and λ being the scattering angle and the wavelength of light in specimen, respectively. The amplification factor $R(q)$ is given by

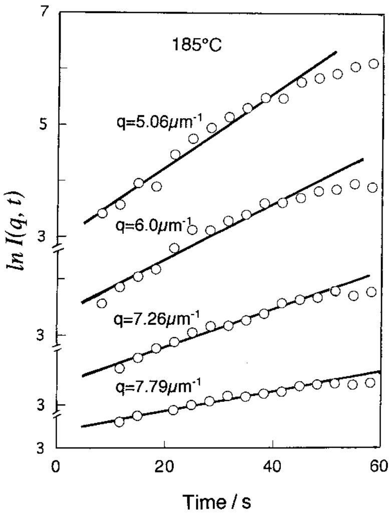

Figure 2. Change of the scattered light intensity at various q's with time for a 10/90 iPP/HSI mixture at 185 °C.

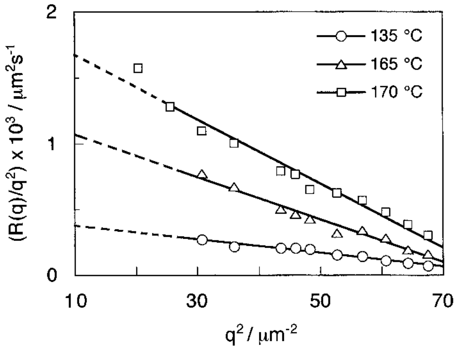

Figure 3. $R(q)/q^2$ versus q^2 plot in a 10/90 iPP/HSI mixture at 185 °C.

$$R(q) = -Mq^2(\partial^2 f/\partial c^2 + 2\kappa q^2) \tag{2}$$

where f is the local free energy of mixing, c is the concentration, κ is the concentration-gradient energy coefficient, and M is the mobility. According to eq 1, a plot of $ln\ I$ versus t at a fixed q should yield a straight line of slope $2R(q)$. The linear relationship is realized for the liquid–liquid phase separation in a 10/90 iPP/HSI mixture after a temperature jump into the immiscibility loop as shown in Figure 2, indicating that the initial stage can be described by the linearized theory.

Figure 3 shows $R(q)/q^2$ versus q^2. As expected from eq 2, the plot yield is linear, indicating again that the initial stage can be described within the framework of the linearized theory. From the intercept of $R(q)/q^2$ at $q^2 = 0$, one can obtain the apparent mutual diffusion coefficient D_{app} given by[7]

$$D_{\mathrm{app}} = -M(\partial^2 f/\partial c^2) \propto D_c[|\chi - \chi_s|/\chi_s] \tag{3}$$

where D_c is the self-diffusion coefficient for translational diffusion, χ is the interaction parameter and χ_s is the χ at the spinodal temperature.

Values of D_{app} were obtained at various temperatures inside the immiscibility loop. The results are shown in Figure 4 as a function of temperature. One can see that with increasing temperature D_{app} first increases, attains a maximum, and then decreases. The increase of D_{app}

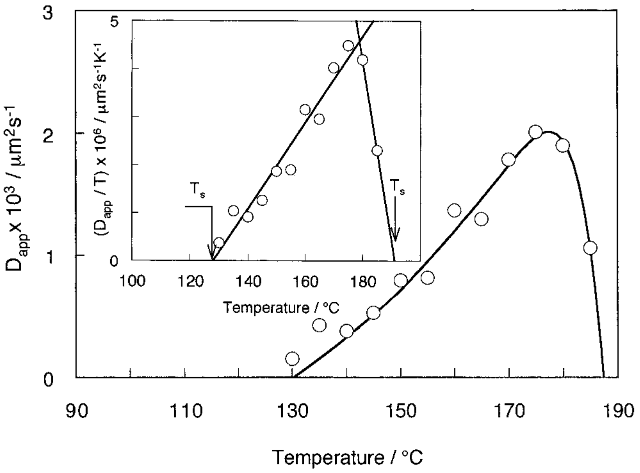

Figure 4. Temperature dependence of apparent diffusion coefficient D_{app} in a 10/90 iPP/HSI mixture. Spinodal temperature T_s is obtained from the intercept of the T axis of D_{app}/T vs T plots.

with increasing temperature is expected in a system with a LCST system, since the quench depth $|T - T_s|$ increases with temperature (see eq 4). On the other hand, in a system with an UCST, a decrease of D_{app} is expected with increasing temperature on approaching UCST with a decrease of the quench depth. Both the increase and the decrease of D_{app} have been observed in systems with LCST and UCST, respectively.[7,8]

The spinodal temperature T_s can be estimated by employing the relation $D_c \propto T$ from the Stokes–Einstein equation and $|(\chi - \chi_s)/\chi_s| \propto |T - T_s|$. Equation 3 leads to

$$D_{app} \propto T|T - T_s| \tag{4}$$

Equation 4 implies that plots of D_{app}/T versus T should be linear, and the T_s is estimated by the intercept on T axis. Typical examples are shown in the inset in Figure 4. Four T_s's estimated are shown by closed squares in Figure 1.

Additional evidence for LCST behavior at low temperatures was given by observing structure formation at point B in Figure 1. The point B is located in the single-phase region just outside the immiscibility loop so that only the crystallization is expected to take place. However, after the crystallization proceeds to a certain level, the remaining melt is expected to attain the compositions inside the immiscibility loop as indicated by an arrow.

To discuss the crystallization process, it is convenient to employ the integrated intensity, invariant Q, defined by

$$Q = \int_0^{\infty} I(q) q^2 \, dq \tag{5}$$

The invariant in the H_v mode, Q_{H_v}, is proportional to the mean-square optical anisotropy $\langle\delta^2\rangle$

$$Q_{H_v} \propto \langle\delta^2\rangle = \phi_s \delta_s^{\,2} \tag{6}$$

where ϕ_s is the volume fraction of spherulites and δ_s is the spherulite anisotropy.[9]

On the other hand, the invariant in the Vv mode, Q_{V_v}, is ascribed to both $\langle\delta^2\rangle$ and the mean-square density fluctuation $\langle\eta^2\rangle$. The $\langle\eta^2\rangle$ is given by

$$\langle\eta^2\rangle = \phi_s(1 - \phi_s)(\alpha_s - \alpha_0) \tag{7}$$

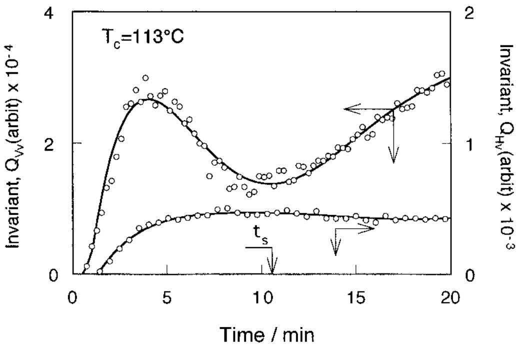

Figure 5. Time variation of the invariants Q_{V_v} and Q_{H_v} in a 30/70 iPP/HSI mixture.

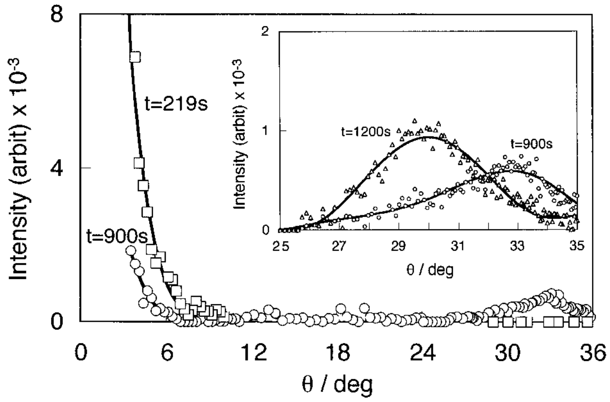

Figure 6. Change in V_v light-scattering profile of a 30/70 iPP/HSI mixture during isothermal annealing at 130 °C, after temperature drop from 200 °C.

where α_s is the polarizability of the spherulite and α_0 is the polarizability of the melt.

The time variation of the invariants Q_{V_v} and Q_{H_v} after the temperature drop from 210 to 113 °C for a 30/70 iPP/HSI mixture (point B) is shown in Figure 5.[10] Q_{H_v} increases with time and then levels off, as expected from eq 6, i.e., ϕ_s increases and attains a maximum when spherulites fill the whole space. This is quite natural for polymer crystallization. Q_{V_v} increases with time, attains a maximum, and then decreases. This is also expected from eq 7, since $\langle\eta^2\rangle$ should have a maximum at $\phi_s \approx 0.5$. However, after attaining a minimum at t_s, Q_{V_v} starts to increase again. This is unexpected from eq 7. The increase after t_s should be ascribed to a new density fluctuation which is not related to crystallization, since there is no time variation in Q_{H_v} after t_s. The new fluctuation can be assigned to the spinodal decomposition by investigating the V_v scattering profile and its time variation.

Figure 6 shows the change in the V_v scattering profile at an azimuthal angle of 45° with time. At $t = 219$ s ($<t_s$), the scattering intensity decreases monotonously with increasing scattering angle θ. However, at $t = 900$ s ($>t_s$), a scattering peak appears at a wide angle ($\theta >$ 33°). The peak position shifts to smaller angles with time as shown in the inset of Figure 6. Both the scattering peak and its time variation are very characteristic of the spinodal decomposition. This suggests that the remaining liquid phase has been diluted (less polymer content) by the crystallization of iPP and is thrust into the two-phase region of the phase diagram (see arrow in Figure 1). Actually, under the optical microscope, we observed the bicontinuous structure with a unique periodicity between the spherulites. Thus, the results support the existence of the LCST-type phase

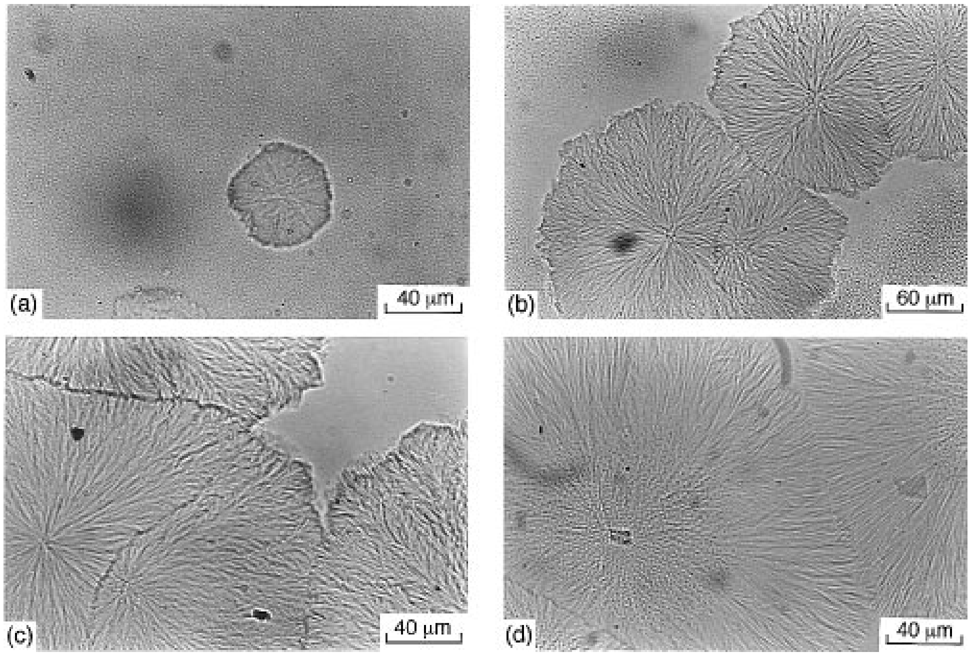

Figure 7. Optical micrographs of a 30/70 iPP/HSI mixture: (a) 12 min, (b) 43 min, (c) 71 min, and (d) 180 min after temperature drop from 200 to 130 °C.

boundary around the point B in Figure 1. We carried out a similar experiment at various points indicated by open triangles in Figure 1 and observed similar behavior of the crystallization and the following spinodal decomposition. Open squares in Figure 1 show that the spinodal decomposition could not be detected but that only the crystallization was observed.

From the microscopic observation on crystallization in the two-phase region inside the immiscibility loop, other evidence for the loop phase diagram was obtained. A 30/70 iPP/HSI mixture underwent a temperature drop from 200 to 130 °C (point A in Figure 1), and structure development was observed under the optical microscope. The results are shown in Figure 7. As expected from the light-scattering results (Figures 2−4), the spinodal decomposition proceeds to develop a regularly phase-separated bicontinuous structure followed by the spherulite formation (Figure 7a). Note that the memory of spinodal decomposition (the bicontinuous structure) is preserved in the spherulite (Figure 7a). When the spherulites increase in size, the bicontinuous structure disappears around the growing front (Figure 7b), i.e., dissolution of the bicontinuous structure takes place. This may be caused by the segregation of the impurity HSI from the spherulite to render a highly diluted mixture with the composition of the single-phase region outside the immiscibility loop. Thus, crystallization should proceed from the single-phase mixture. Actually, there is no memory of spinodal decomposition far from the center of the spherulite (Figure 7b). It is interesting that a single-phase mixture is trapped between truncated spherulites (Figure 7c) and that the final spherulite (Figure 7d) reflects the change from the crystallization from the liquid−liquid phase-separated system in the early stages (center of spherulite) to the crystallization from the single-phase mixture in the late stages of the spherulite growth.

Conclusion

An immiscibility loop was found to exist in the iPP/HSI system by cloud point method, and it was supported by time-resolved light-scattering. A supplemental evidence for the loop was provided by the structure formation at low temperatures just below the loop, i.e., crystallization proceeded, and it induced the spinodal decomposition. Other evidence was given by a series of phase transitions inside the loop: Spinodal decomposition proceeded, the crystallization from the decomposed state followed, and then the crystallization from the single-phase state took place.

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(10) Integral to get Q was carried out over a wide q range: from $q = 0.5$ ($\theta = 2°$) to 9.2 ($\theta = 36°$). Scattering intensity at $\theta >$ 35 was nearly zero. Then, the integral can be recognized to be a nice approximation of Q integrated in the q range of $0-\infty$.

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