Crystallinity and Miscibility of Poly(vinyl isobutyl ether)/Poly(ε-L-lysine) Blends by Solid State $^{13}$C NMR Study

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Abstract The relation between crystallinity and miscibility of semicrystalline polymer blends of poly(vinyl isobutyl ether) (PVIBE) and poly(ε-L-lysine) (ε-PL) is investigated by $^{13}$C cross-polarization with magic-angle-spinning (CPMAS) NMR (nuclear magnetic resonance) and DSC measurements. Analysis of the $^1$H spin-lattice relaxation curves observed from both PVIBE and ε-PL signals, which are indirectly obtained from well-resolved $^{13}$C CPMAS NMR spectra, suggested that the domains of ε-PL in the blends are in the range of 50–100 nm scale. Two-spin or three-spin models were used to simulate the $^1$H relaxation curves taking into account the contribution of a $^1$H spin-diffusion rate between PVIBE and ε-PL. Furthermore, it was found that blending ε-PL largely influences the crystallinity of PVIBE but that of ε-PL is little affected by blending PVIBE except for 10/1 composition. The observed melting point of ε-PL shifted towards lower temperature accompanied by PVIBE content. This shift was explained by the Gibbs-Thomson effect that the decrease of thickness of crystalline phase causes the depression of the melting point.

Keywords Miscibility, Crystallinity, Poly(vinyl isobutyl ether), Poly(ε-L-lysine), $^1$H spin-lattice relaxation, $^1$H spin diffusion, High-Resolution Solid-State $^{13}$C NMR.

Introduction

A thermoplastic or an elastic polymer is used widely for engineering purposes. To improve physical or chemical properties of polymers for some purposes, we often made use of mixing another polymer to these kinds of engineering polymers. Therefore, instead of synthesize a brand-new polymer with all the properties we want, we try to mix two polymers together to form a blend that we hopefully have some properties of both. Recently, with a raise of public awareness to ecology, engineering polymers tend to be required to have properties of eco-friendliness, especially when out of use.

Poly(ε-L-lysine) (ε-PL) has attracted an attention as a novel biodegradable material$^{1-3}$. Microbial produced ε-PL is safe for human beings, a water-soluble semicrystalline polymer, and has an antibacterial activity. Some kinds of foods contain it as preservatives. Since the ε-PL has a good biodegradable/biocompatible property, ε-PL can be used as a new environmental-compatible polymer. ε-PL is, however, too brittle and low degree of polymerization to use engineering purposes as it is, so that it may be used as an additive for a synthetic polymer to give biodegradability or antibacterial activity.

Poly(vinyl isobutyl ether) (PVIBE) is a thermoplastic, elastic, and semicrystalline polymer, and used as a plasticizer. The blending of PVIBE and ε-PL makes it possible to become a new biodegradable material or plasticizer. Furthermore, a PVIBE/ε-PL blend consists of semicrystalline/semicrystalline polymers. It is interesting to study the morphology of such a semicrystalline polymer blend, because both crystallinity and miscibility largely influence a mechanical property of a polymer blend.

In this study, we study the relationship between the crystallinity and the miscibility of the semicrystalline polymer blends, PVIBE/ε-PL, by solid-state $^{13}$C NMR technique. The crystallinity is estimated from a solid-state $^{13}$C NMR spectra obtained with cross-polarization and magic-angle-spinning (CPMAS) technique. The miscibility is discussed from the $^1$H spin-lattice relaxation curves indirectly obtained from the $^{13}$C CPMAS NMR spectra. The relation between the domain size and
crystallinity is also discussed with DSC results.

**Experimental**

**Sample preparation**

Poly(epsilon-L-Lysine) (epsilon-PL, repeating unit, RU, is -NHCH2CH2CH2CH2CH(NH)CO-) was provided from Chisso Corporation as a solid powder. The relative weight-average molecular weight \(M_w\) is approximately 4,700, the glass-transition temperature \(T_g\) is ca. 323 K, and the melting point \(T_m\) is ca. 445 K. Poly(vinyl isobutyl ether) (PVIBE, RU is \(-CH_2CH(OCH2CH(CH_3)_2)-\)) was obtained from Scientific Polymer Products, Inc., and its \(M_w\) is 600,000. The values of \(T_g\) and \(T_m\) are ca. 253 K and ca. 316 K, respectively. They were used without further purification. PVIBE and epsilon-PL were dissolved in chloroform/methanol mixed solvent, which the volume fraction is 9/1, at a concentration of 15 w/v\%. The mixed ratios of PVIBE/epsilon-PL blends were 10/1, 10/2, 10/3, 10/4, and 10/5 by weight. The opaque and elastic films of the PVIBE/epsilon-PL blends were obtained from casting the respective chloroform/methanol=9/1 solutions on a Teflon plate at 313 K and further dried under vacuum at 313 K for 1 or 2 days. A blend with high content of epsilon-PL more than PVIBE/epsilon-PL=10/5 showed to be macroscopic heterogeneous, so that we studied only 10/1 to 10/5 blend compositions in this study.

**NMR measurements**

\(^{13}\)C NMR measurements were made using a Bruker DMX500 spectrometer operating at 125.76 MHz for \(^{13}\)C and 500.13 MHz for \(^{1}H\). High-resolution solid-state \(^{13}\)C NMR spectra were obtained by the combined use of cross polarization (CP) and magic-angle spinning (MAS) with \(^{1}H\) high-power dipolar decoupling. The radio-frequency field strengths for \(^{1}H\) was 55.6 kHz and for \(^{13}\)C 50.0 kHz. The \(^{1}H\) decoupling frequency was chosen to be 3 ppm downfield from tetramethylsilane (TMS) and the two-pulse-phase-modulation decoupling method\(^{4}\) was used. The MAS frequency was chosen to obtain a clear spectrum at the aliphatic region without overlapping of the artificial spinning side bands of the CO carbons. The MAS frequency of 10 kHz did not show the side bands on the peaks at the aliphatic region. At such a much higher speed, the efficiency of CP enhancement between \(^{1}H\) and \(^{13}\)C nuclei is steeply getting worse. In order to overcome the decreased CP efficiency, the ramped-amplitude CP method was used\(^{5,6}\). \(^{13}\)C Chemical shifts were measured relative to TMS using the methine carbon signal at 29.47 ppm for solid adamantane as an external standard. The \(^{1}H\) spin-lattice relaxation time in the laboratory frame (\(T_1^H\)) was indirectly measured from well-resolved \(^{13}\)C signals enhanced by CP of 800 \(\mu\)s applied after the \(^{1}H\) \(\pi\) pulse.

**DSC measurements**

The differential scanning calorimetry (DSC) was examined by using a Perkin-Elmer 7 system with increasing temperature at rate of 2 K·min\(^{-1}\) from 233 K to 473 K.

**Results and Discussion**

**Crystallinity**

Figure 1 shows the observed \(^{13}\)C CPMAS NMR spectra...
of pure PVIBE, pure ε-PL, and the PVIBε/ε-PL=10/1, 10/3, and 10/5 blends. The peak assignments are also depicted in the figure. The real contents of PVIBε/ε-PL blends were ascertained by $^1$H dipolar-decoupling (DD) with MAS spectra, and the obtained weight ratios were equaled the mixing weight ratios of 10/1 to 10/5, respectively. The $^{13}$C spectrum of ε-PL is similar to the previously observed one in ref. 2. The doublet of carbonyl peaks at 178.5 and 177.0 ppm are observed more clearly in the current solid-state $^{13}$C CPMAS NMR spectrum. There are also small differences in the chemical shifts between the previous and the current spectra. These may be due to a difference of sample preparation. The present ε-PL is cast from a methanol solution, while the previous ε-PL is from a water solution.

In order to dissolve both PVIBE and ε-PL in the same solvent, it was necessary to use a chloroform/methanol mixed solvent. The crystallinity of PVIBE cast from the chloroform/methanol mixed solution is largely affected by the mixing ratio of methanol in the solvent, because methanol is a poor solvent for PVIBE. Therefore, the $^{13}$C NMR spectrum of PVIBE shows the methanol content dependence. For example, the $^{13}$C NMR spectrum of PVIBE cast from a pure chloroform solution shows a broad-line $^{13}$C peak of CHOCH$_2$ at 75 ppm: similar spectrum can be seen in Figure 2(d). For PVIBE cast from a chloroform/methanol=9/1 solution, a doublet $^{13}$C peak of CHOCH$_2$ appears at 76 and 74 ppm on the broad-line peak as shown in expanded spectra in Figure 1. These observations clearly indicate that the doublet peak is attributed to the crystalline phase. We carefully controlled the chloroform/methanol solvent ratio to be 9/1.

The $^{13}$C chemical shifts of both PVIBE and ε-PL in the PVIBE/ε-PL blends show the same values that observed for each pure sample. This indicates that there is no interaction, which influences the $^{13}$C NMR spectra, between PVIBE and ε-PL in the blends. However, Figure 1 shows that the peak shape of C$_{\alpha}$H signal of ε-PL observed at 57.8 ppm is largely affected by blending of PVIBE, especially in the PVIBE/ε-PL=10/1 blend. The sharp peak on a broad line disappears mostly. Furthermore, for the PVIBE/ε-PL=10/5 blend, the intensity of the doublet peak at 76 and 74 ppm of PVIBE decreases as compared to those of pure PVIBE or PVIBE/ε-PL=10/1 and 10/3 blends.

Signal intensity via the CP experiment differentiates the difference of molecular motion, so that these observations strongly indicate that the crystallinity of both PVIBE and ε-PL is affected by blending each other. This implies that the miscibility will be also influenced by the change of crystallinity or mixing ratio.

To investigate the crystallinity, we obtained the $^{13}$C CPMAS NMR spectra separated into contributions arising from the crystalline (CR) and non-crystalline (NC) phases by basing on the differences in the intrinsic $^1$H spin-lattice relaxation time in the rotating frame ($T_{1\rho}^H$), that characterize the CR and NC phases$^{7,8}$). Figure 2 shows the expanded and separated spectra for the PVIBE/ε-PL=10/5 blend based on $T_{1\rho}^H$ difference into the NC and the CR phases: the CHOCH$_2$ peaks of PVIBE are on the left and C$_{\alpha}$H peak of ε-PL on the right. Spectra (a, e) and (b, f) are the CP contact time of 1 $\mu$s and 3 ms, respectively. Spectra (c, g) and (d, h) are the CR phase and the NC phase, respectively.

![Figure 2](image_url)

**Figure 2.** Expanded and separated $^{13}$C CPMAS NMR spectra for the PVIBE/ε-PL=10/5 blend based on $T_{1\rho}^H$ difference into the NC and the CR phases: the CHOCH$_2$ peaks of PVIBE are on the left and C$_{\alpha}$H peak of ε-PL on the right. Spectra (a, e) and (b, f) are the CP contact time of 1 $\mu$s and 3 ms, respectively. Spectra (c, g) and (d, h) are the CR phase and the NC phase, respectively.
greater in Figure 2(b), because the $T_{1\text{H}}$ is much shorter in the NC phase than in the CR phase. Figures 2(c) and (d) are linear combinations of Figures 2(a) and (b) where we have attempted to null the NC and CR signal contributions, respectively. Similar criterion holds on Figure 2(e) to (h). The linear combinations for PVIBE and $e$-PL are achieved individually, because the $T_{1\text{H}}$ value characterized the NC phase for PVIBE is extremely faster than that for $e$-PL; this means that the decrease of the peak intensity after 3 ms $^1$H spin locking for PVIBE is different from that for $e$-PL. The sum of Figures 2(c) and (d) reproduce the whole spectrum of Figure 2(a). Similarly, Figure 2(e) is also reproduced by (g) and (h).

The crystallinity is estimated from the relative contribution of the CR component of the whole $^{13}$C CPMAS spectrum after a CP time of 800 $\mu$s. The relative CR contribution is obtained from the integral of Figure 2 (c) or (g). The relative NC contribution is similarly given. Since both integrals are distorted during the 800 $\mu$s CP time, the peak areas were corrected by using an individual CP efficiency. The values of the CP efficiency were determined by the experiments of various CP contact periods. The obtained crystallinity for pure PVIBE is ca. 20% and for pure $e$-PL is ca. 54%. These values have an experimental uncertainty of 5%. The value of 54% for pure $e$-PL is smaller than the previous value of 63% obtained by Maeda, et al. This may be due to a difference between the current and previous sample preparations as mentioned above, and also a difference in the estimation method. The previous method is based on the difference in $T_{1\text{C}}$. For the method based on $T_{1\text{C}}$ difference, the CR region will be included some amounts of an interface that has the similar molecular motion as that of the CR. While for the current method based on $T_{1\text{H}}$ difference, the spectrum of the NC region will contain the interface region, because the narrower peak, which is attributed to the CR phase, is usually caused by the higher order and the lower molecular motion. In any case, the absolute value of the degree of crystallinity is not so important in this study. Both methods can trace the change of crystallinity by blending. The discussion on the difference of the absolute value of the crystallinity between both methods will be published elsewhere.

The values of crystallinity of PVIBE in the PVIBE/$e$-PL blends were estimated as 10–13%, except for that in the PVIBE/$e$-PL=10/5 blend. The degree of PVIBE crystalline phase in the PVIBE/$e$-PL=10/5 blend is approximately 7%. After blending with $e$-PL, the crystallinity of PVIBE become roughly half as compared to that of pure PVIBE. On the other hands, the crystallinity of $e$-PL in the PVIBE/$e$-PL blends were not so much influenced by blending with PVIBE, the values are 55–59%, except for the PVIBE/$e$-PL=10/1 blend: the degree is approximately 30%. These observations suggest that the growth of crystalline phase of PVIBE is largely affected by blending with $e$-PL, while the crystallization of $e$-PL is not significantly hindered by the blending with PVIBE. However, for the PVIBE/$e$-PL=10/1 blend, the crystallization of $e$-PL is impeded by much amounts of PVIBE. The miscibility will, thus, depend on the compositions of $e$-PL in the blend.

Figure 3 shows the observed and expanded DSC curves of pure PVIBE, PVIBE/$e$-PL=10/1, 10/2, 10/3, 10/4, 10/5 blends, and pure $e$-PL at the temperature range of 240 to 340 K (A) and 400 to 460 K (B). The glass transition of PVIBE is observed at around 253 K for every blend and the neat PVIBE. Similarly, the melting points of PVIBE for neat and every PVIBE/$e$-PL blend are observed at around 316 K. These values are not affected by blending with $e$-PL. The melting point of the crystalline phase of $e$-PL showed, however, a gradual change from 445 to 431 K with increase of PVIBE content. The value of melting point $T_m$, which is obtained at the maximum peak top, of pure $e$-PL is observed at approximately 445 K. The shape of the endothermic peak is not simple but apparently a doublet peak: another peak appears at 438 K. At this time, we do not have any idea to explain the reason why the doublet peak is apparently observed. Maeda et al. have pointed out the possibility of two kinds of crystalline phases from the observation of the $^{13}$C NMR doublet peak for carbonyl group at 178.5 and 177.0 ppm as shown in Figure 1 (b). The values of $T_m$ of $e$-PL for the PVIBE/$e$-PL...
PVIBE/
approximately 60%. The calculated values for the
measured 1H spin-lattice relaxation decays in the
content. The
shifts towards lower temperature with increase of PVIBE
Miscibility
diffusion phenomenon.

However, if the obtained values of crystallinity from NMR
for the PVIBE/e-PL blends are independent of the actual
measurements will not be achieved.

Both estimated values from DSC and NMR have an
experiment error of about 5%. These values coincide
with each other within an experimental error. Of course,
the value of 60% that we assumed here for the degree of
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However, if the obtained values of crystallinity from NMR
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crystallinity, the agreement between DSC and NMR
measurements will not be achieved.

It is well known that the shift of $T_m$ peak towards lower
temperature relates the thickness of crystalline phase. Figure 3(A) shows that the $T_m$ value of PVIBE in the
blends is not altered even at PVIBE/e-PL=10/5, while the
decrease of $T_m$ value of e-PL drastically occurs with
increase of PVIBE. This indicates that PVIBE acts as a
polymeric diluent for e-PL, but e-PL does not show dilute
effect for PVIBE. Therefore, the existence of PVIBE
inhibits the growth of crystalline phase of e-PL, and the
crystalline thickness decreases with the amount of PVIBE
for the PVIBE/e-PL blends. Next, we discuss the domain
size of the crystalline phase by means of the $1H$ spin-
diffusion phenomenon.

**Miscibility**

To study the miscibility, that is the domain size, we
measured the $1H$ spin-lattice relaxation decays in the
laboratory frames ($T_1^H$) through the well resolved $13C$
NMR. A CP from $1H$ to $13C$ enables us to detect the $1H$
decays for both PVIBE and e-PL independently.

Figure 4 shows the observed $T_1^H$ relaxation curves for
PVIBE ($\circ$, $\bullet$) and e-PL ($\triangle$, $\blacksquare$) in the PVIBE/e-PL=10/1 blend. The open and solid symbols represent the $T_1^H$
curves of the CR and the NC phases, respectively. For pure
PVIBE and pure e-PL, the observed $T_1^H$ curve of the CR
phase was in excellent agreement with that of the NC
phase; broken and dotted broken lines depict the respective
relaxation curves, respectively.

If the PVIBE/e-PL blend is homogeneous, the fast $1H$
spin diffusion averages spin temperature of almost all the
protons between PVIBE and e-PL. Thus, we will observe
the same $1H$ magnetization decay from both PVIBE and e-
PL; the intermediate relaxation decay between the broken
and dotted broken lines are observed. In such a case, we
can conclude that the blend is homogeneous on a scale of
20–50 nm$^3$). On the other hand, if the $1H$ magnetization
decays observed from the blends are the same as those
obtained from pure PVIBE and e-PL, respectively, the
blend is concluded to be immiscible. To realize the
agreement between the $1H$ relaxation curves of PVIBE and
e-PL, it is necessary for the $1H$ spin-diffusion rate to be 10
to 100 times faster than the $1H$ relaxation rate of PVIBE$^{10}$; the
relaxation rate of PVIBE is faster than that of e-PL. If the
$1H$ spin-diffusion rate is slower by a factor of 4 than the
$1H$ relaxation rate of e-PL, on the contrary, the observed $1H$
relaxation curves for the blends show similar
decays of pure PVIBE and e-PL$^{10}$. The lower limit
estimated from the slow $1H$ spin-diffusion rate is
approximately 100 nm: this means that the maximum
domain size which $1H$ spins can flip-flop mutually is ca.
100 nm.

When the blend is partially miscible, that is, domain size
is 50 to 100 nm scale, the $T_1^H$ values do not agree with
each other and the $T_1^H$ relaxation curves become
characteristic non-exponential decays with an insufficient
$1H$ spin-diffusion rate$^{11}$. In this case, we can obtain

![Figure 4. Observed $T_1^H$ relaxation curves of the PVIBE/e-PL blend. The symbols $\bullet$ and $\circ$ represent the $T_1^H$ relaxation curves for the non-crystalline and crystalline phases of PVIBE, and $\triangle$ and $\blacksquare$ those of e-PL. Each solid line represents the calculated curve from equation (1). The broken and dotted broken lines represent the $T_1^H$ relaxation curves for pure PVIBE and e-PL, respectively.](image-url)
information of repeating unit length, L, using the relation of \(L=2(D/\pi k_h)^{1/3}/(f_{\text{PVIBE}}/f_{\text{e-PL}})\) by estimating the \(^1\text{H}\) spin-diffusion rate \(k_h\) and assuming the simple lamella-structure model: \(D\) is the \(^1\text{H}\) spin-diffusion coefficient and \(f_i\) is the proton molar fractions of polymer \(i\). Therefore, the observation of both \(^1\text{H}\) magnetization decays (\(T_{1e}\) relaxation curves) gives useful information on miscibility qualitatively and quantitatively.

The observed \(T_{1e}\) relaxation decays on a semi-log plot as shown in Figure 4 are clearly non-simple-straight lines, and especially the initial several data points of \(\varepsilon\)-PL (△, ▲) show curved lines. Furthermore, the \(T_{1e}\) curve of the CR is different from that of the NC, while that of CR for PVIBE (○) is the same as that of NC (●). This observation indicates that the insufficient \(^1\text{H}\) spin diffusion occurs between PVIBE and \(\varepsilon\)-PL during the \(T_{1e}\) measuring period, and similarly even between the CR and NC phases of \(\varepsilon\)-PL. In this case, we can deal with the observed \(T_{1e}\) curves as a three-spin system; these spin species are protons of both CR and NC phases of PVIBE, protons of NC phase of \(\varepsilon\)-PL, and protons of CR phase of \(\varepsilon\)-PL. In the three-spin system, the \(^1\text{H}\) spin-diffusion rate is divided to three kinds of the rates, between PVIBE and CR of \(\varepsilon\)-PL, \(k_{AC}\) between PVIBE and NC of \(\varepsilon\)-PL, \(k_{AB}\), and between CR and NC of \(\varepsilon\)-PL, \(k_{BC}\).

To simulate the observed \(T_{1e}\) relaxation curves for the PVIBE/\(\varepsilon\)-PL=10/1 blend and estimate the effect of \(^1\text{H}\) spin diffusion on the relaxation curve more quantitatively, we used the equation of the three-spin systems which the three proton species exchange the magnetization via \(^1\text{H}\) spin diffusion as:

\[
\frac{d}{dt} \begin{pmatrix}
    -\xi_A f_A k_{AB} f_A k_{CA} \\
    -\xi_B f_B k_{AB} f_B k_{BC} \\
    -\xi_C f_C k_{CA} f_C k_{BC}
\end{pmatrix}
= \begin{pmatrix}
    M_A(t) \\
    M_B(t) \\
    M_C(t)
\end{pmatrix}
\]

(1)

where \(M_i(t)\), \(f_i\), and \(K_j\) \((j=A, B, C)\) denote, respectively, the magnetization, the proton molar fraction, and the intrinsic relaxation rate \(=1/T_{1e}\) of species \(i\). The quantity \(k_{ij}\) \((i, j=A, B, C; i \neq j)\) is the \(^1\text{H}\) spin-diffusion rate between species \(i\) and \(j\) \((k_{ij}=k_{ji})\). Here, A, B, and C denote both CR and NC phases of PVIBE, NC phase of \(\varepsilon\)-PL, and CR phase of \(\varepsilon\)-PL, respectively. The initial magnetizations ratio \(M_{CA}^0:M_{CB}^0:M_{AC}^0\) is assumed to be \(f_A:f_B:f_C\), and the degree of crystallinity of \(\varepsilon\)-PL for the PVIBE/\(\varepsilon\)-PL=10/1 blend is used to divide into \(f_B\) and \(f_C\).

The simulated ‘best-fit’ curves are depicted as colored solid lines in Figure 4. The simulated lines are in good agreement with the observed data points. The obtained values are \(K_A=1.12\text{ s}^{-1}\), \(K_B=0.39\text{ s}^{-1}\), \(K_C=0.25\text{ s}^{-1}\), \(k_{AB}=0.57\text{ s}^{-1}\), \(k_{BC}=2.0\text{ s}^{-1}\), and \(k_{CA}=0.33\text{ s}^{-1}\). The uncertainty is approximately 10%. For the PVIBE/\(\varepsilon\)-PL=10/1 blend, the \(^1\text{H}\) spin-diffusion rate between PVIBE and the NC phase of \(\varepsilon\)-PL \((k_{AB})\) is more than twice as fast as that between PVIBE and the CR phase of \(\varepsilon\)-PL \((k_{CA})\). It is noted again that the crystallinity of \(\varepsilon\)-PL in the PVIBE/\(\varepsilon\)-PL=10/1 blend is low and roughly half as compared to the other blends. These results suggest that the NC phase of PVIBE is in close proximity to that of \(\varepsilon\)-PL, and then the crystallization of \(\varepsilon\)-PL is deeply hindered by the NC phase of PVIBE. Since the \(^1\text{H}\) spin diffusion occurs from PVIBE NC region to the CR phase of \(\varepsilon\)-PL, the value of \(k_{CA}\) relates the domain size of PVIBE and \(\varepsilon\)-PL.

When we assume that the domain is a lamellar structure, the repeating unit length (sum of each domain length of PVIBE and \(\varepsilon\)-PL) can be estimated to be 570 nm with the \(^1\text{H}\) spin-diffusion coefficient of 380 nm² s⁻¹ for PVIBE/\(\varepsilon\)-PL blends, which is estimated by \(^1\text{H}\) spin–spin relaxation rate of the NC protons of PVIBE. By multiplying the proton molar ratio of \(\varepsilon\)-PL in the PVIBE/\(\varepsilon\)-PL=10/1 blend to the length, we attain the domain size of \(\varepsilon\)-PL to be 41 nm. This relatively small domain size of \(\varepsilon\)-PL in the PVIBE/\(\varepsilon\)-PL=10/1 blend causes the growth of crystalline phase of \(\varepsilon\)-PL to be hindered by large amount of PVIBE. Furthermore, by multiplying the value of crystallinity, we can estimate the total thickness of CR phase of \(\varepsilon\)-PL domain to be 12 nm: “total” means the sum of each CR phase thickness.

For the other blends, we simulated the observed \(T_{1e}\) relaxation curves using the two-spin system with a \(^1\text{H}\) spin-diffusion rate \((k_{ij})\) between PVIBE and \(\varepsilon\)-PL domains, because the \(T_{1e}\) relaxation of CR phase is completely coincide with that of NC phase for both polymers in the blends; two spin species are protons of PVIBE and protons of \(\varepsilon\)-PL. For the two-spin system, the six parameters in Eq. (1) are reduced to three. Thus, we can similarly estimate the total thickness of CR phase of \(\varepsilon\)-PL domain by using the value of \(^1\text{H}\) spin diffusion rate between PVIBE and \(\varepsilon\)-PL. The estimated values are 24, 35, 46, and 57 nm for PVIBE/\(\varepsilon\)-PL=10/2 to 10/5 blends, respectively. Although these values are not real thickness of each CR phase of \(\varepsilon\)-PL but the total value, it is very interesting that the thickness decreases with increase of the content of PVIBE. This phenomenon coincides with the \(T_m\) shift towards lower temperature with increase of the content of PVIBE. According to the Gibbs-Thomson effect, the depression of \(T_m\) is inversely proportional to the
between the NC regions of PVIBE and CR thickness of.

From the NMR analysis, we cannot obtain each intrinsic size of thinning of the intrinsic CR thickness, the amount of CR phase becomes decreases without contribute the change of the thickness of each CR phase, Consequently, the obtained CR thickness by solid-state DSC measurement does not suggest this phenomenon. For the other compositions, the homogeneity is inferior to that of the PVIBE/e-PL=10/1 blend and the crystallinity of e-PL does not change by blending PVIBE. This is ascribed to that the amount of NC region of e-PL is too small to interact with the NC phase of PVIBE satisfactorily. With increase of PVIBE, however, the domain size of e-PL becomes relatively small so that the 1H spin diffusion from PVIBE to e-PL works effectively. For the PVIBE/e-PL=10/5 blend, the domain size of PVIBE is 250 nm and that of e-PL 100 nm. For the PVIBE/e-PL=10/2 blend, on the contrary, the NC region of PVIBE is still over 200 nm but the domain size of e-PL is ca. 40 nm, including the CR phase of 20 nm. Such a decrease of domain size of e-PL results in the gradual increase of the 1H spin–diffusion rate from 0.1 s\(^{-1}\) to 0.4 s\(^{-1}\) from PVIBE/e-PL=10/5 to 10/2.

The \(T_m\) decrease of e-PL is caused by the decrease of CR thickness, which is induced by dilute effect of PVIBE. Such a dilute effect for semicrystalline polymers has been found in a lot of semicrystalline/amorphous polymer blends, such as poly(ethylene oxide)/poly(methyl methacrylate)\(^{14, 15}\). The polymeric diluent does not always work as an inhibitor of the growth of crystalline phase but sometimes acts as a propagator. In the PVIBE/e-PL blends, PVIBE works as an inhibitor of the growth of crystalline phase of e-PL.

**Conclusions**

We showed that the miscibility of the PVIBE/e-PL blends is affected by the crystallinity. Blending of e-PL influences the crystallinity of PVIBE. However, the degree of crystallinity of pure PVIBE is only 20% and the miscibility is not affected by a rich component of PVIBE. On the other hand, the crystallinity of e-PL is not affected by blending PVIBE except for the PVIBE/e-PL=10/1 blend. However, the poor but high crystallinity component of e-PL largely affects the miscibility of the PVIBE/e-PL blends. For the PVIBE/e-PL=10/1 blend, in particular, the NC regions of both PVIBE and e-PL become rather intimate condition than the other blends. This is attributed by the decrease of crystallinity of e-PL from 60% to 30%. At first glance, the crystallinity of e-PL is not changed from the compositions of 10/5 to 10/2, however, the CR thickness of e-PL decreases by blending PVIBE. The decrease occurs accompanied by increase of PVIBE. This also causes the blends to be homogeneous. The decrease of CR thickness is also supported by DSC measurement: the

![Figure 5](image)

Figure 5. Plot of \(T_m\) and the total CR thickness of e-PL, \(d\), for the PVIBE/e-PL blends. The blue solid line is obtained from the least-square fitting of equation (2).
$T_m$ of $\epsilon$-PL shifts towards lower temperature.

The estimated values in this study are not checked by another analysis, such as X-ray diffraction, although we have measured X-ray of the PVIBE/$\epsilon$-PL blends. The much amount of PVIBE gives large and broad signal coming from the NC region and then obscured the important diffraction pattern from the CR region. However, it has been explained that the $^1$H spin-diffusion analysis gives accurate length of several block copolymers\(^{16}\) or layered distance of nylon6/clay nanocomposites\(^{17}\) by comparing with X-ray based analyses such as TEM, SAXS, or WAXD. Therefore, the estimated values in this paper will be correct and have not tremendous large error.

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References