Investigation of Miscibility between iPP and Propylene−Butene Random Copolymer by Small-Angle Neutron Scattering

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ABSTRACT: The degree of miscibilityof (iPP)/atactic propylene−butene random copolymer (a(P/B)) blends has been evaluated by using χ parameters obtained from a series of SANS experiments. It was found that the observed χ value decreased with increasing the butene content in a(P/B) from approximately zero in iPP/aPP. It showed a relatively larger negative value when the butane content was high. The temperature dependence of χ for this blend system was also measured. The sign of the slope of χ vs $1/T$ plot was apparently affected by butene content. It changed from positive to negative with an increase of butene content in a(P/B), indicating switching of the phase behavior from a UCST to an LCST system. SANS results were analyzed with the lattice cluster (LC) theory. It is estimated that the enthalpic interaction between a propylene and a butene monomer unit is negative. The value of trans−gauche exchange energy obtained from the LC theory is found to be associated with the segment length evaluated from SANS.

Introduction

It is well-known that miscibility control of polyolefin polymer blends is very important for both industrial applications and its inherent scientific interest.[1−3] To understand the miscibility between polyolefins, many researchers have performed various experiments such as morphology observation by TEM,[4−6] observation of phase diagrams by small-angle light scattering (SALS),[7,8] and estimation of χ by small-angle neutron scattering (SANS),[9−14] pressure−volume−temperature diagrams (PVT),[15] solubility parameters,[13,14] etc. Among them, SANS is one of the most powerful experiments which can quantitatively estimate the degree of miscibility between polyolefins, and many SANS studies for polyolefin blend systems have been reported. These SANS results have been often utilized to construct theories of miscibility in order to explain the experimental data.[10,11,16−18] Until now, various theories have been proposed such as the segment matching (SM) theory,[10,11] the lattice cluster (LC) theory,[16−19] the solubility parameter (SP) theory,[13,14] etc. In the case of the SM theory, the key issue is in matching the segment length of polymers. That is, the degree of matching is proportional to the extent of miscibility due to nematic structure formation. The SM theory was successful in explaining the miscibility behavior of isotactic PP (iPP)/ethylene−ethyl ethylene random copolymer (E_xEE_{1-x}) and syndiotactic PP (sPP)/E_xEE_{1-x} blends when the ethylene to ethyl ethylene ratio was changed.[10,11] On the other hand, the LC theory expresses the monomer structure using lattice approximation, and it precisely describes the entropic term based on the monomer structure. The LC theory has successfully explained the miscibility of iPP/head-to-head PP blend,[18] iPP/EHR blend,[9] ethylene−norbornene (E_xN_{1-x})/E_yN_{1-y} blend,[19] etc. In general, dominant interactions between polyolefins without polar groups are dispersive forces, and hence the interaction parameters (χ) between components are usually positive. These theories assume that the interaction between the same species is most preferred and χ values between different species are always positive except for blends with specific interactions.

In the material shown in this paper, negative χ values were observed by SANS even though the polymer components were nonpolar. We performed SANS experiments for an iPP/atactic propylene−butene random copolymer (a(P/B)) blend system, which showed relatively larger negative χ values with increase of the butene content in a(P/B). In this paper, we will show SANS results for iPP/a(P/B) and discuss the origin of negative χ values and the decrease of χ with an increase of butene content in conjunction with the temperature dependence of χ by applying the SM theory and the LC theory.

Experimental Section

Materials. iPP used was polymerized with propene by an isospecific metallocene catalyst system; dimethylsilyl bis(2-methyl-4-naphtylindenyl) zirconium dichloride and methyl aluminoxane with H_2 in toluene at 50 °C. C_3D_6, purchased from Junsei-Kagaku Co., was used as a monomer in synthesizing deuterated iPP. Synthesized crude iPPs were, at first, roughly fractionated by the Soxlet method, and the boiled-heptane soluble part was removed from the sample. The molecular weight distribution was measured by GPC with standard polystyrene calibration, and M_w/M_n values determined were all around 1.6. Second, polymers extracted by the Soxlet method were further fractionated with trichlorobenzene and 2-ethoxyethanol mixed solvent to obtain a sample with a narrower molecular weight distribution. For the fractionated iPP, weight-averaged molecular weights of two iPPs were measured by high-temperature GPC-MALLS in trichlorobenzene as a solvent. The molecular characteristics of iPPs used for SANS are shown in Table 1. For the hydrogenated iPP sample, the mesopentad ([*mmmm*]), which shows the degree of isotacticity of iPP, was measured to be around 0.97 by NMR. a(P/B)s were polymerized with hydrogenated

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propene and butene by a metallocene catalyst system. As-polymerized polymers were fractionated with *ortho*-dichlorobenzene and 2-ethoxyethanol. The a(P/B) samples used in this study are also listed in Table 1. The microstructure of aPP was also measured with NMR, and its diad ratio was $[mm]/[mr]/[rr] = 13{:}48{:}39$. The M_w's of the fractionated a(P/B)s were measured by MALLS in trichlorobenzene as a solvent. The blend samples from the deuterated iPP (d-iPP) and a(P/B)s were prepared by dissolving polymers in *meta*-xylene at 130 °C, followed by precipitation into methanol. The precipitate was filtered and vacuum-dried at 80 °C for 1 day. Samples were melted into the sample cells in a vacuum oven to complete them without forming air bubbles.

Small-Angle Neutron Scattering (SANS) Measurements. SANS measurements were performed on the instrument SANS-U at the Institute for Solid-State Physics, The University of Tokyo, installed in the research reactor JRR-3 located at Japan Atomic Energy Research Institute, Tokai, Japan.[20] A flux of cold neutrons with a wavelength of $\lambda = 7.0$ Å was irradiated to the sample, and the scattered intensity profiles were collected with an area detector of 128 pixels × 128 pixels. The sample-to-detector distances were set to be 2 m and 8 m, which covered the accessible q range, being 0.006−0.1 Å^{-1}. Here, q is the scattering vector defined as $4\pi \sin \theta/\lambda$ and 2θ is the scattering angle. Scattered intensities were circularly averaged by taking into account the detector inhomogeneities, corrected for cell scattering, transmission, and incoherent scattering, and then scaled to the absolute intensities with a polyethylene standard sample (Lupolen).[20,21]

Analysis of SANS Profiles. The coherent cross section of a blend of deuterated and hydrogenated polymers is given by eq 1

$$\frac{d\Sigma}{d\Omega} = \left(\frac{b_D}{v_D} - \frac{b_H}{v_H}\right)^2 \cdot S(q) \qquad (1)$$

where b_D and b_H are the scattering lengths of monomers of the deuterated and hydrogenated PP, which have the specific molar volumes v_D and v_H, respectively. v_H at the temperatures of SANS experiments was calculated from the empiric formula of temperature dependence of specific volume (cm^3/g), $v_{gH} = 1.152 + 0.0078 \cdot T$ (°C), which is described in the literature.[22] Though this is the formula for polyethylenes, we used this equation for the analyses due to the reasonable agreement with the coefficient of thermal expansion and the density of iPP reported in other literatures.[23,24] v_H is calculated from v_g by the following formula: $v_H = M_{mH} \cdot v_{gH}/N_A$ (M_{mH}: molecular weight of hydrogenated monomer unit, N_A: Avogadro number). The specific molar volume of deuterated sample, v_D, is same with that of hydrogenated sample under the supposition that the volume per monomer unit is the same between deuterated and hydrogenated samples and only the molecular weight of monomer unit is different.

The structure factor $S(q)$ in eq 1 is given by eq 2a based on the random phase approximation (RPA),[25,26]

$$S(q)^{-1} = [v_D N_{w,D} \phi_D P_D(q^2 R_{g,D}{}^2)]^{-1} + [v_H N_{w,H} \phi_H P_H(q^2 R_{g,H}{}^2)]^{-1} - 2\chi_{DH}/v_0 \qquad (2a)$$

$$P(q^2 R_g{}^2) = \frac{2[(1 + U\xi)^{-1/U} + \xi - 1]}{(1 + U) \cdot \xi^2} \qquad (2b)$$

$$U = Q - 1 \qquad (2c)$$

$$\xi = q^2 R_g{}^2/(1 + 2U) \qquad (2d)$$

$$v_0 = \sqrt{v_H v_D} \qquad (2e)$$

where ϕ_D is the volume fraction of the deuterated component and $R_{g,D}$, $R_{g,H}$, $N_{w,D}$, and $N_{w,H}$ denote the radii of gyration and the weight-averaged number of segments per chain of the deuterated (subscript D) and the hydrogenated (subscript H) species, and Q is the molecular weight distribution (M_w/M_n), respectively, while χ_{DH} is the Flory−Huggins interaction parameter between deuterated and hydrogenated polymers. $P_i(q^2 R_{gi}{}^2)$ (i = D or H) in eq 2b denotes the form factor of component i, and it is assumed to be represented by the Debye function. The molecular weight distributions of all the present polymers were taken into account by assuming a Shultz−Zimm distribution.[27,28]

Table 1. Characteristics of the Fractionated Polymer Samples

sample name	M_w	M_w/M_n	M_z
D-iPP	15 000	1.44	20 000
H-iPP	16 000	1.38	21 200
aPP	35 000	1.34	44 600
a(P/B) (P/B = 80:20)[a]	32 600	1.30	42 900
a(P/B) (P/B = 60:40)	32 000	1.50	47 000
a(P/B) (P/B = 37:63)	37 000	1.34	47 000
a(P/B) (P/B = 13:87)	34 000	1.42	44 300
aPB	26 000	1.44	35 100

[a] The ratios between propylene and butene in a(P/B)s are molar ratios.

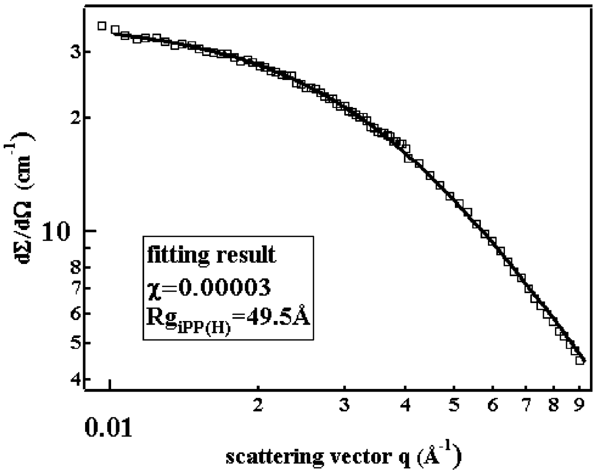


Figure 1. SANS profile for a d-iPP/h-iPP (50:50) blend at 190 °C (□) and its fitting results (bold line) with eq 2.

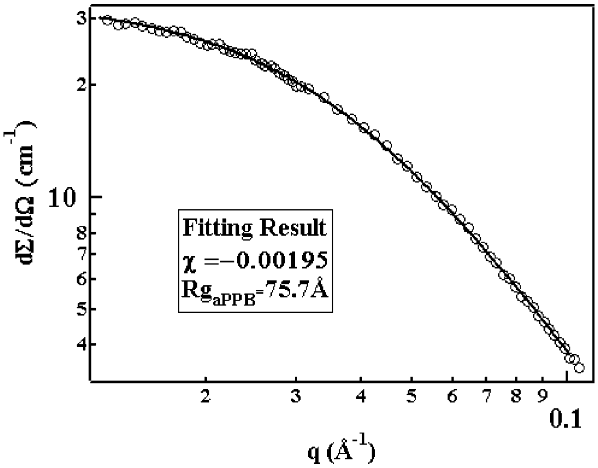
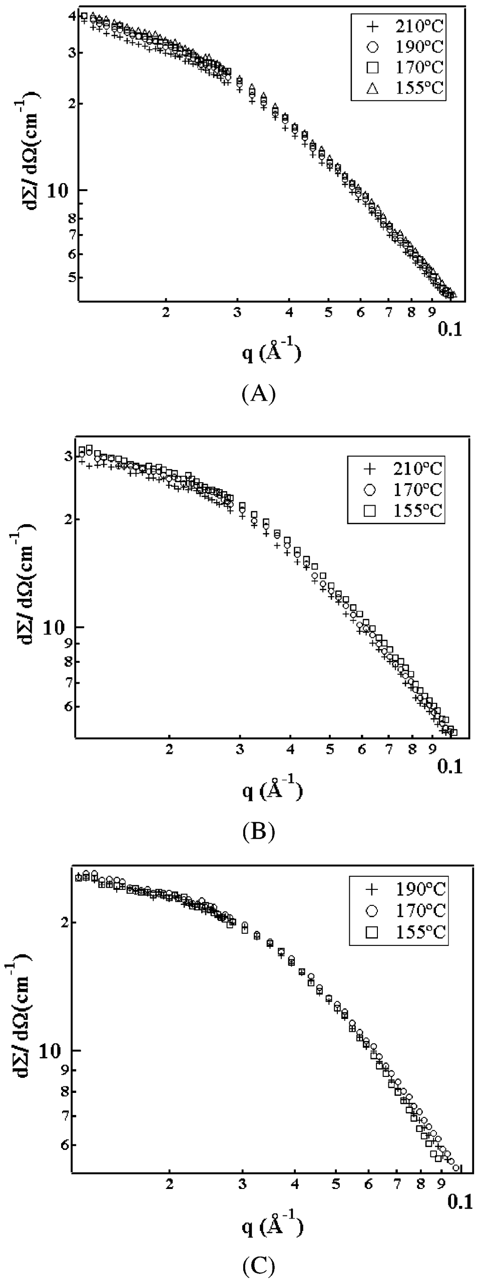


Figure 2. SANS intensities obtained from d-iPP/a(P/B) (P/B = 60:40) blend at 190 °C and their fitting results with eq 2.

Results

In Figure 1, the SANS profile from the d-iPP/h-iPP (50:50) blend at 190 °C and its fitting result with eq 2a is shown. Free parameters in eq 2a are $R_{g,D}$ and χ_{DH} under the supposition that the segment length of a monomer unit b $(= (6R_g{}^2/N_z)^{1/2})$ of d-iPP and h-iPP are the same. We obtained $R_{g,H} = 49.5$ Å for the hydrogenated iPP and a small χ_{DH} value ($<10^{-4}$) by applying a least-mean-square method as a fitting procedure. The ratio of R_g to $M_w{}^{1/2}$ ($R_g/M_w{}^{1/2}$) obtained in this experiment is 0.40 and is almost consistent with the value obtained from iPP (0.37−0.40) with narrow molecular weight distribution ($M_w/M_n \sim 1.7$)



(A)

(B)

(C)

Figure 3. SANS profiles for three d-iPP/a(P/B) blends at various temperatures. a(P/B) materials are aPP (A), a(P/B) (P/B = 60:40) (B), and aPB (C).

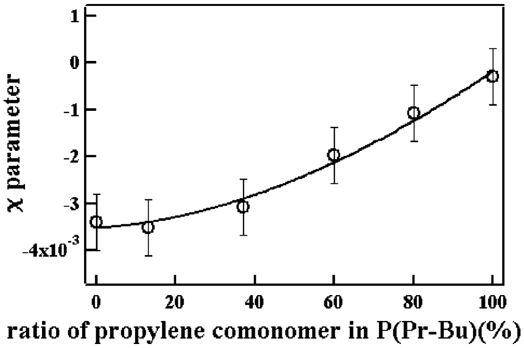


Figure 4. χ_{DH} plotted against propylene content in a(P/B). With decreasing the propylene content, χ_{DH} value becomes small and negative. Solid line shown in this figure is the result of fitting procedure based on the formula of LCT described in eq 3. Error bars are estimated from the uncertainty of molecular weight, fitting procedure, and thicknesses of the samples.

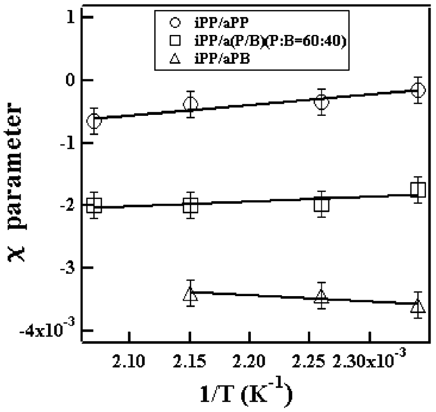


Figure 5. χ_{DH} values for d-iPP/aPP, d-iPP/a(P/B) (P/B = 60:40), and d-iPP/aPB plotted against 1/*T*. Solid lines are eyeguides.

previously reported by other authors.[9,29] The very small χ_{DH} value means that d-iPP and h-iPP can be recognized as equivalent species, as is also already reported.[9,11]

We measured SANS data for various d-iPP/a(P/B) blends with different compositions in the molten states at 155, 170, 190, and 210 °C. The measuring temperature was always lowered from 210 to 155 °C stepwise in each sample. Although 155 °C was near the nominal melting point of deuterated iPP, it never crystallized within several hours at the temperature after complete melting and annealing. We obtained χ value and segment length *b* from fitting procedure using eq 2, where free parameters were R_g of a(P/B) and χ. In Figure 2, a typical fitting result of SANS profile for d-iPP/a(P/B) is shown. The curve excellently fits to the experimental data. In Figure 3, the variations of SANS profiles with temperature are compared among three blend series, i.e., (A) d-iPP/aPP, (B) d-iPP/a(P/B) (P/B = 60:40), and (C) d-iPP/aPB. These profiles show smooth curves and their slopes become smaller with decreasing *q*, which are typical scattering patterns for miscible polymer blends under the measured condition. In Figure 4, the estimated χ values for d-iPP/a(P/B) (50:50 by weight) blends are plotted against the propylene content in the copolymers. It can be easily recognized that χ decreases with decreasing propylene content in a(P/B) while remaining negative. In Figure 5, the temperature dependence of d-iPP/aPP, d-iPP/a(P/B) (P/B = 60:40), and d-iPP/aPB is compared, and it is clearly recognized that temperature dependence between d-iPP/aPP and d-iPP/aPB is quite different and the slopes of χ vs 1/*T* plots show opposite signs. The change of sign of this slope was already reported in iPP/EHR blend system by Seki et al.,[9] where the increase of hexene content in ethylene−hexene random copolymer (EHR) made the sign of slope negative. It should be noted that an increase of the content of the longer branch comonomer component in the blends commonly makes the slope negative. The hexene segment in EHR may play the same role as that of butene in our present blend system.

Discussion

The χ value variations depending on butene content in a(P/B) and on temperature are validated by the theories in detail and are interpreted. Before getting into detailed discussion, it should be noted that the deuterium switching effect previously reported may be also effective in the present blend systems to some degree and that absolute χ value is sometimes different as much as $1-20 \times 10^{-4}$ by switching the deuterium labeled component.[13] However, even if we take the labeling effect into consideration, χ value of iPP/a(P/B) would still be negative with increasing the ratio of butene monomer in a(P/B).

We will now attempt to compare the measured variation of χ with the predictions of existing theories in the literature. At first, to check the SM theory, segment lengths were estimated for iPP, aPP, aPB, and a(P/B)s from the formula $b = (6R_g^2/N_z)^{1/2}$ by applying R_g values obtained by fitting procedure, and they are plotted in Figure 6. From our experiment, the value of the segment length of iPP for three-carbon reference volume is 5.3 Å. By comparing Figures 4 and 6, it is considered that SM theory qualitatively explains the lowering of the interaction parameter χ between iPP and a(P/B) with increasing butene content in a(P/B). As is seen in Figure 6, the segment length of aPP used here is larger than that of iPP or that of aPP previously reported because the [*rr*] rich structure like the present aPP sequence has a larger segment length than the [*mm*] rich structure,[10] and the value becomes smaller with increasing butene content in a(P/B) and a matching with the value for iPP segment length is accordingly attained at around 60% propylene content. However, the SM theory cannot explain the further decrease of χ value with increasing the butene content, namely decreasing the propylene content for iPP/a(P/B) blends having apparently negative values. This must be the limitation of the SM theory, so this theory cannot correctly reflect the dominant factor of miscibility in the case that attractive interaction works between polymers. Therefore, we have to adopt another theory to interpret our results.

Second, applicability of the LC theory was examined for our SANS results. By using the following formula of the LC theory introduced by Dudowicz et al.,[30] we can estimate the value of the enthalpic term and the conformation energy.

$$\chi = \chi_{\rm h}/T + \chi_{\rm s}$$

$$= \frac{\epsilon}{kT}\cdot\frac{z}{2}\cdot\sqrt{s_{\rm iPP}\cdot s(P/B)}(1-x)^2 + \sqrt{s_{\rm iPP}\cdot s(P/B)}\cdot \frac{1}{z^2}(r_{\rm iPP} - r(P/B)^2) \quad (3)$$

$$s_{\rm iPP} = 3 \qquad s_{\rm iPP}^{\rm tri} = 1 \qquad s_{\rm iPP}^{\rm tetra} = 0 \qquad s_{\rm aPP} = 3 \qquad s_{\rm aPP}^{\rm tri} = 1 \qquad s_{\rm aPP}^{\rm tetra} = 0$$

$$s_{\rm aPB} = 4 \qquad s_{\rm aPB}^{\rm tri} = 1 \qquad s_{\rm aPB}^{\rm tetra} = 0$$

$$s_{\rm a(P/B)} = 3x + 4(1-x)$$

$$r_i = \left(1 - \frac{2}{s_i} - \frac{s_i^{\rm tri}}{s_i}\right)\cdot g_i + 2\,\frac{s_i^{\rm tri}}{s_i}$$

$$g_i = \frac{z}{z - 1 + \exp(E_b^i/kT)}$$

$$r_{\rm (P/B)} = x r_{\rm aPP} + (1-x) r_{\rm aPB}$$

where s_i and $s_i^{\rm tri}$ (i = iPP, aPP, aPB, a(P/B)) are parameters determined from lattice structures of monomers, x is the molar ratio of propene in a(P/B), and E_b^i (i = iPP, aPP, aPB) denotes trans−gauche conformational exchange energy, whereas the lattice condition number z equals 6 for three-dimensional space. In our case, $r_{\rm iPP}$ was fixed as 1.20, which was the value adopted in the previous paper and was calculated from $E_b/k = 300$ K. From the excellent curve fitting result for χ values between iPP and a(P/B) (solid line shown in Figure 4) using the above formula, we obtain the following results, $\epsilon/kT = -0.0003$, $r_{\rm aPP} = 1.02$ ($E_b/k = 412$ K), $r_{\rm aPB} = 1.20$ ($E_b/k = 160$ K). These fitting results show that enthalpic interaction between propylene and a butene monomer units is negative. Furthermore, the trans−gauche conformational exchange energies for three different polymers give the following relationship: $E_{\rm aPP} > E_{\rm iPP} > E_{\rm aPB}$. It is easily understood that the conformational exchange energy of aPB is smaller than that of iPP because of its small segment length. Moreover, the present aPP has a [*rr*] sequence-rich structure, and hence it is reasonable that conformational free energy of aPP is larger than that of iPP.

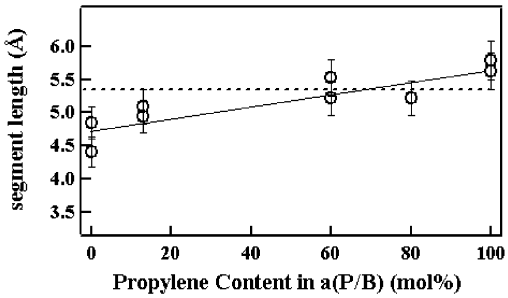


Figure 6. Segment lengths of various a(P/B)s calculated from R_g and N_z. The dotted line shows the segment length of iPP. The segment length of aPP is larger than that of iPP, which is caused by the [rr] rich microstructure in aPP.

However, in principle, the LC theory cannot explain the experimental data by monomeric or segmental structure without an attractive “enthalpic” interaction, which is the “temperature-dependent” attractive interaction, and we also have to discuss the entropic interaction that can contribute to the temperature-dependent attractive interaction. As for the contribution of entropic interaction to the attractive interaction, some authors reported experimental results, which indicate the existence of an attractive “entropic” interaction.[31−33] For example, in the head-to-head polypropylene (hhPP)/polyisobutylene (PIB) blend system, which is a miscible polyolefin blend system having the negative χ value by SANS, it was reported that the dynamics of hhPP is strongly affected by the addition of PIB in spite of little change in PIB dynamics, indicating the entropically driven attractive interaction.[31] Furthermore, the theoretical approach using the simple lattice model had clarified that the entropically driven mixing between the squares with different size occurs due to the more effective packing between different sized monomers although it has no temperature dependence.[34] In our case, we should also consider the local stabilization effect like local stable packing as a sort of temperature-dependent attractive interaction. The reason why the temperature-dependent local packing structure occurs could be attributed to the chain branch of aPB, which can deeply penetrate into a random coil of iPP rather than iPP itself and has an advantage with respect to the effective local packing. In the previous report by Seki et al.,[9] $1/T$ dependence of χ parameter for d-iPP/aPH has a slope with a large negative value and it ensures the contribution of longer side chains to the miscibility of blends due to better “temperature-dependent” attractive interaction. In this aspect, we can suppose that copolymerization of propylene with the monomers having longer branches such as butene, hexene, and octene will contribute to generate better interaction owing to local deeper penetration. However, we also have to take into account that the existence of longer chains affects the local structure such as segment length of a copolymer and the “temperature-independent” entropy term, which is well expressed by the coarse-grained models in miscible blends in molten state. Long side chains could also strongly affect the dynamics of blends due to its faster segmental motions compard with that of the main chain.

In future work, we should proceed to the dynamical experiments like quasielastic neutron scattering and neutron spin−echo spectroscopy to clarify the existence of local packing structure and the effect of dynamics on the miscibility between iPP and a(P/B) for deeper understanding of miscibility between polyolefins.

Conclusion

SANS experiments have been performed in order to evaluate the degree of miscibility for iPP/a(P/B) system by using the χ parameter. It has been found that the χ value decreases with increasing the butene content in a(P/B) and shows a relatively larger negative value. SANS results obtained were analyzed by the lattice cluster (LC) thory, The analysis indicated that the temperature-dependent attractive interaction exists between propylene and butene. Furthermore, trans−gauche conformational exchange energy estimated from the LC theory could be associated with the segment length evaluated by SANS.

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