Polyolefin Miscibility: Solid-State NMR Investigation of Phase Behavior in Saturated Hydrocarbon Blends

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ABSTRACT: Chain-level mixing in polyolefins is investigated for blends of polyisobutylene (PIB) and polyethylene-*co*-1-butene (PEB). Previous reports suggest that PIB exhibits unusual mixing behavior in certain saturated blends relative to other polyolefins, even though it is immiscible with most. Variable-temperature ^{1}H, ^{2}H, ^{13}C, and ^{129}Xe NMR experiments are used to characterize local PIB chain dynamics in blends with PEB in which the concentration of 1-butene comonomer units is 23 or 66 wt %. Results from 1D and 2D solid-state ^{13}C exchange experiments, ^{1}H relaxation measurements, and ^{2}H line shape analysis indicate that local conformational dynamics of the PIB CH_2 group in the polymer backbone increase significantly in blends with PEB copolymers containing 66 wt % butene comonomer (PEB-66). Even though the PEB-66 is a higher T_g polymer than PIB, PIB exhibits a lower effective T_g when the blend is formed relative to its pure state. Similar perturbations are not observed in the PIB/PEB-23 blend, indicating that this blend is not miscible at the chain level. These results are directly relevant to the length scale of glass transitions in polyolefins, indicating that local interchain packing plays an important role in the conformational dynamics that occur *within* a chain, and are suggestive of local configurational entropy contributions to mixing. Although ^{1}H spin-diffusion experiments could not reveal quantitative length scales of mixing in the these blends due to insufficient contrast between the constituents, ^{129}Xe NMR experiments showed that the PIB/PEB-66 blend was homogeneous on a 50 nm length scale. In agreement with the heterogeneous morphology indicated by the dynamic NMR experiments, ^{129}Xe NMR showed two resolved peaks for the PIB/PEB-23 blend, indicative of phase separation on a 50 nm length scale. The compilation of all the data, most of which was obtained at natural abundance, indicates that the PIB/PEB-66 blend exhibits intimate chain-level mixing on a length scale much shorter than R_g (ca. 8 nm). More importantly, the data show that reduced chain packing constraints occur in the miscible blend and suggest that local entropic contributions are the driving force for miscibility.

Introduction

Polyolefins and their blends are a commercially important class of materials, and new polymer architectures now accessible via metallocene catalysis ensure that a growing number of novel blend compositions are forthcoming.[1−3] These synthetic advances have revitalized the structure−property investigations of polyolefins and their copolymers by virtue of the improved control of traditional comonomer incorporation and the increased flexibility in copolymerizing bulky monomers.[1] The relative number of possible polyolefin blends now routinely accessible has clearly increased, and the prospect of "engineering" phase behavior in polymer/copolymer blends by rational comonomer incorporation is a realistic target for lighter weight, higher strength, and lower cost materials. However, questions remain as to how mutual solubility in polyolefin blends depends on polymeric microstructure, tacticity, comonomer incorporation, and chain dynamics and, further, how each of these architectural and physical characteristics contributes to the interplay between enthalpy and entropy that ultimately determines bulk phase behavior. Following the seminal work in the area of polyolefin miscibility by the Graessley, Lohse, and Bates groups,[4−14] we have pursued magnetic resonance investigations of microscopic miscibility and dynamics in polyolefin blends using solid-state NMR methods.[15−17] We are particularly interested in polyolefin blends that contain polyisobutylene (PIB) as one component, not only due to our long-standing interest in this polymer[18,19] but also due to reports that it exhibits negative χ (negative enthalpy) behavior with certain other polyolefins.[6] Such behavior is unusual for blends of completely saturated polymers, as no obvious chemical interactions exist that might drive mixing. In particular, we have shown that PIB exhibits chain-level mixing with head-to-head polypropylene (hhPP),[15] while others have reported that it phase separates in blends with normal atactic head-to-tail PP.[8] Given the unique chain-packing properties of PIB (which give rise to its barrier properties), we feel that this apparent regioselectivity might arise from differential interchain packing geometries. On the basis of previous reports by Graessley, Lohse, and coworkers,[4−11] we are studying blends of PIB with poly(ethylene-*co*-1-butene) copolymers (PEB), in which the relative comonomer concentration in the PEB is either 23 or 66 wt % (13 and 49 mol %, respectively). Our goals in this work are to interrogate length scales of mixing in the absence of extensive deuterium labeling as well as determine the relationship between local backbone conformational barriers and miscibility.

Experimental Section

Commercial polyisobutylene (M_w = 1 000 000) was obtained from ExxonMobil Chemical. The PEB-66 (M_w = 114 000) is

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the same polymer previously referenced as HPB66 by Graessley and co-workers and is a monodisperse ethylene−butene copolymer obtained by anionic polymerization of butadiene, followed by hydrogenation. The degree to which the diene polymerizes 1,2 vs 1,4 addition determines the butene and ethylene concentrations, respectively, as has been extensively discussed in previous papers.[6] The PEB-23 sample is a commercial ethylene−butene copolymer made via metallocene polymerization (M_w = 79 000) and sold as Exact 4041 by ExxonMobil. The 50:50 wt % blends were prepared from dissolution in toluene for 24−48 h, followed by solvent evaporation, and then vacuum-drying to 10^{-2} Torr for 4 days or longer. DSC measurements indicated that PIB, PEB-66, and PEB-23 polymers had glass transition temperatures of −68, −48, and −45 °C, respectively.

^{13}C and ^{1}H NMR measurements on bulk polymers/blends were acquired on a Bruker DSX-300 instrument, operating at a field strength of 7.05 T. Unless otherwise stated, magic-angle-spinning (MAS) speeds were 3−5 kHz, and radio-frequency field strengths were 73 kHz. Cross-polarization contact times were 300 μs, chosen to enhance the relative intensity of the PIB backbone CH_2 group, which has a short $T_{1\rho H}$ at all temperatures used in this investigation. Pure-phase 2D ^{13}C−^{13}C exchange experiments were acquired using the simple three-pulse sequence, modified for cross-polarization excitation, and with mixing times synchronized with the rotor period.[20,21] A 16-step phase-cycling routine with TPPI was used to achieve absorption line shapes in each dimension. Typically, 64−128 t_1 increments were acquired using 64, 96, or 128 scans per increment, with subsequent zero-filling to generate a 1K × 1K data matrix prior to Fourier transformation. ^{1}H spin−lattice and rotating-frame spin−lattice measurements were done using standard methods in which the carbons were observed as a function of the ^{1}H saturation recovery and spin-locking times prior to cross-polarization, respectively.

^{129}Xe NMR experiments were performed on a Bruker AVANCE 500 MHz spectrometer with an Oxford narrow bore magnet. A 10 mm i.d. 1H/BB probe (BB500-10EB, Nalorac Cryogenic Corp.) was used for all measurements. All spectra were acquired at 298 K. The line from free xenon gas was used as the internal standard (0 ppm). The instrumental parameters for acquisition of the one-dimensional, single-resonance ^{129}Xe NMR spectra are as follows: spectrometer frequency = 138.365 MHz; spectral width = 83 333 Hz (equivalent to 602 ppm); number of data points = 16K; relaxation delay = 2 s; acquisition time = 0.098 s; pulse width = 16 μs (tip angle = 60°); number of transients > 1K. The silhouette of the sample container duplicates that of the ordinary 10 mm NMR tube installed in the sample spinner. In place of the glass tube, there is an Ultem tube (o.d. = 10 mm, i.d. = 6.35 mm). Ultem does not absorb a significant amount of xenon under the conditions of these studies. A specially designed valve is housed in the spinner so that the polymer sample can be charged with xenon gas. Typically 120 psig (equivalent to 9.287 bar, total pressure) of xenon was used. Equilibration was almost instantaneous.

Variable-temperature static ^{2}H NMR data were obtained at a frequency of 30 MHz using standard quadrupolar echo sequences. All data were acquired on a Bruker CXP-200 instrument, which had been upgraded with a Tecmag data acquisition package. For the PIB homopolymer data, 512 scans were collected, while 2000 transients were used for the PIB in the PIB/PEB-66 blend.

Results and Discussion

^{1}H Observation and Relaxation. Analysis of morphology in polymer blends may be addressed using solid-state NMR methods. In particular, nondestructive spin-diffusion techniques are attractive since isotopic labeling is not a requirement, and recent developments in the understanding of spin-diffusion data have increased the quantitative accuracy of the method.[22−24] However, as we have previously shown, direct ^{1}H observation of spin-diffusion in amorphous polyolefin blends is problematic due to the lack of resolution between the inhomogeneously broadened lines characteristic of such polymers, even with multiple pulse or fast MAS methods.[16] Figure 1 shows ^{1}H MAS spectra obtained at 8 kHz for the PIB/PEB-66 blend, in which an additional dipolar filter sequence is applied prior to the read pulse in order to introduce spectral resolution based on gradients in the time scale of molecular motion in the two polymers.[25] Comparison of parts A−D of Figure 1, in which the strength of the dipolar filter is increased in subsequent spectra, shows that this is not achieved experimentally, thereby eliminating the possibility of direct observation spin-diffusion methods. Results were identical for experiments without MAS, except that the line width was larger by a factor of 6−7. As one would expect, similar results were obtained for the higher resolution ^{13}C-detected ^{1}H dipolar filter experiments, precluding the use of natural abundance spin-diffusion experiments as a quantitative tool for measuring length scales of mixing in these blends. Of course, the fact that the chain dynamics of the PIB and PEB samples used in this study were too similar to allow contrast based on the dipolar filter, or Goldman−Shen methods[26] (which were also attempted), does not mean this is generally the case for polyolefin blends. Each blend type must be evaluated individually, and indeed, some of our previous work on polyolefin blends has successfully utilized spin-diffusion for measuring domain sizes.[15] Preliminary experiments in which ^{13}C chemical shift filters were used to generate ^{1}H polarization gradients in one polymer, via selective DANTE pulses, suffered from unacceptably poor signal-to-noise and were not pursued further. Such experiments will be investigated at a later time with appropriate levels of ^{13}C labeling.

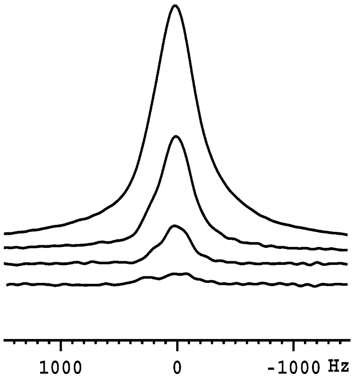

Figure 1. ^{1}H dipolar filter on PIB/PEB-66 blend at 23 °C as a function of the number of 12-pulse dipolar filter cycles,[25] in which the interpulse spacing was 10 μs. From top to bottom, the number of filter cycles was 0, 10, 20, and 30, respectively.

The degree to which $T_{1\rho H}$ data may be used to prove intimate mixing via spin-diffusion is critically dependent upon the motional characteristics of the polymer system. For mobile polymers, it is not a reliable measure of the length scale of mixing, since the values for individual protons *within* a monomer unit vary greatly. This is true for PIB and PEB-66. For neat PIB, the CH_2 and CH_3 groups have values at 298 K of 520 and 1220 μs, respectively. Similarly, in neat PEB-66, the values for CH_2 and CH_3 groups differ by more than a factor of 2. While the pure component polymer values do converge for PIB at 213 K, a more reasonable temperature for interpreting the data due to improved spin-diffusion, they do not reach the same value. These results are in contrast to semicrystalline polyolefins, for example,

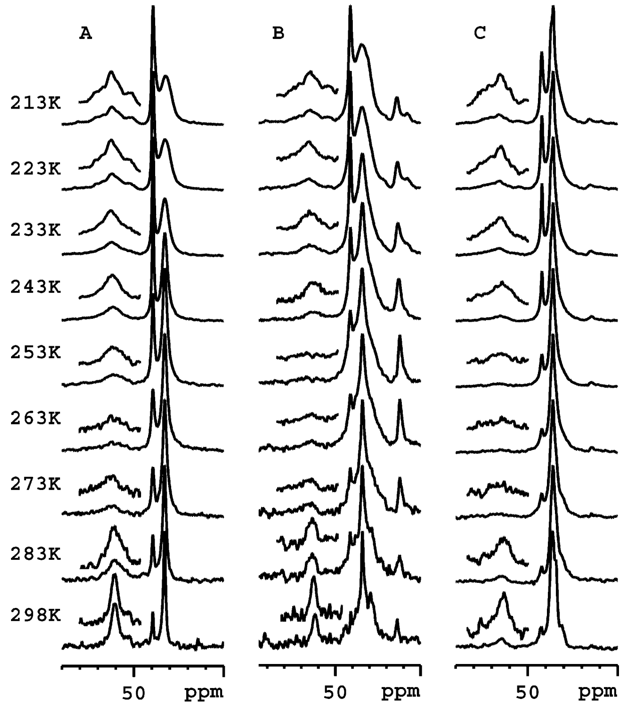

Figure 2. Variable-temeperature CP/MAS stack plot of (A) PIB, (B) PIB/PEB-66 blend, and (C) PIB/PEB-23 blend. Acquisition temperatures are indicated on the figure, and the PIB CH_2 region is expanded in the inset above each spectrum. Note that PIB CH_2 ^1H $T_{1\rho}$ relaxation time constants at 213 K are 810, 498, and 884 μs for the samples in (A), (B), and (C), respectively. These results agree with the line-shape data.

where we find that all protons in the crystallites of isotactic polypropylene (i-PP) have a common $T_{1\rho H} = 20$ ms at room temperature. For the PIB/PEB-66 blend, only the PIB methylene carbons and PEB methyl carbons are well-resolved at 213 K, and their $T_{1\rho H}$ values are 498 and 1100 μs, respectively. We point out these results here since the observation of disparate $T_{1\rho H}$ data is often used to "prove" that blends are not intimately mixed. Obviously, this criterion is not applicable to amorphous polyolefin blends, since the neat polymers themselves have unique values within the monomer unit, even at temperatures near T_g.

Variable-Temperature 1D ^{13}C CP/MAS NMR Data. Results from variable-temperature CP/MAS experiments on PIB and its blends with PEB are shown in Figure 2. Details concerning the relative rates of conformational exchange along the backbone of PIB are revealed by the line-shape changes of the PIB CH_2 signal as the temperature is increased from 213 K (10 deg above the DSC T_g). At 213 K in Figure 2A, the broad CH_2 line for neat PIB, extending from 45 to 80 ppm (see inset expansions), has resolved features corresponding to segments in trans−trans, trans−gauche, or gauche−gauche conformations.[29] As the temperature is increased, the CH_2 lines broaden, become featureless, and reappear as a single line at room temperature. The temperature at which the line for neat PIB is completely broadened is 267 K (spectrum not shown), near the 263 and 273 K data points shown in Figure 2A. The broadening mechanism is the well-known Rothwell−Waugh effect, where incoherent polymer chain motion occurs on a similar time scale as the coherent averaging radio-frequency (rf) field that is applied to decouple the protons.[27] When the frequency of chain motions approaches that of the rf field strength or the MAS rate, line widths in the ^{13}C spectrum may become broad beyond detection. Indeed, this effect is commonly observed in many polymers, but usually for CH_3 carbons. In this case, the results in Figure 2A indicate that the time scale of conformational exchange rates *along* the PIB backbone, i.e., between t−t, t−g, and g−g conformers, is centered about 73 kHz at 267 K. Of course, there is indeed a distribution for motional correlation frequencies, but the fact that a completely flat CH_2 "signal" is observed at 267 K indicates that the majority of the polymer chains satisfy this condition.

In contrast, Figure 2B shows the results from the same experiment for the PIB CH_2 group in the blend with PIB-66. Immediately one observes that the temperature at which the maximum interference of PIB CH_2 motion with the decoupling field occurs is 253 K in the blend, some 10−15 K lower than in the neat PIB. Again, the line shape changes unequivocally indicate that the relevant exchange process is conformational exchange between backbone conformers, a process that, based on the comparison of parts A and B of Figure 2, occurs at significantly lower temperatures for PIB in the blend with PEB-66. For example, one still observes a "rigid" CH_2 line shape for the neat PIB at 233 K, while the CH_2 signal for PIB in the blend at 233 K is superposable with the 253 K signal from neat PIB. Also, complete inspection of PIB/PEB-66 plots in Figure 2B shows that the breadth of the transition as a function of temperature is significantly wider in the blend. By comparison, the CH_2 line shape for the PIB/PEB-23 blend in Figure 2C much more closely mimics the temperature dependence of the neat PIB, e.g., resolved conformer contributions to the line shape persist up to 243 K, and the signal is still observed at 253 K, in contrast to the PIB/PEB-66 blend.

Static ^2H NMR. ^2H solid-state NMR can provide very specific details concerning the nature, the amplitude, and the rates of molecular motions.[28] Figure 3 shows selected results from a complete variable-temperature study on PIB and the two blends, in which the temperature was increased in 10 K increments from 210 K. In Figure 3A−D, the spectrum from neat perdeuterated PIB is shown on top and the PIB/PEB-66 blend on the bottom. Only 20% of the PIB monomer units were perdeuterated in the blend sample. Since the PIB units are perdeuterated, the spectra are dominated by the motionally averaged CD_3 signal; the broad CD_2 pattern (135 kHz splitting) is well-resolved only in the 210 K spectrum. As such, these data on specific CH_3 dynamics provide a compliment to the CH_2-specific results from the ^{13}C experiments. Rapid C_3 rotation of the methyl group provides an anisotropically averaged Pake pattern with a 40 kHz splitting, even at 210 K. Additional reduction of this splitting will only occur if additional modes of motion are present, which reorient the bond vector between the methyl and backbone carbon in space. For the case of PIB, these additional motions will only arise through motions associated with the polymer backbone, since they are attached to quaternary backbone carbons. Therefore, changes in the CD_3 line shape should also be sensitive to conformational dynamics in PIB. Figure 3 shows additional narrowing and, ultimately, collapse of the CD_3 line shape for the neat polymer and the PIB in the blend with PEB-66 at 270 K. Additional temperature increases result in further narrowing of the line, but they are not shown here. More interesting is the marked contrast in the line shape

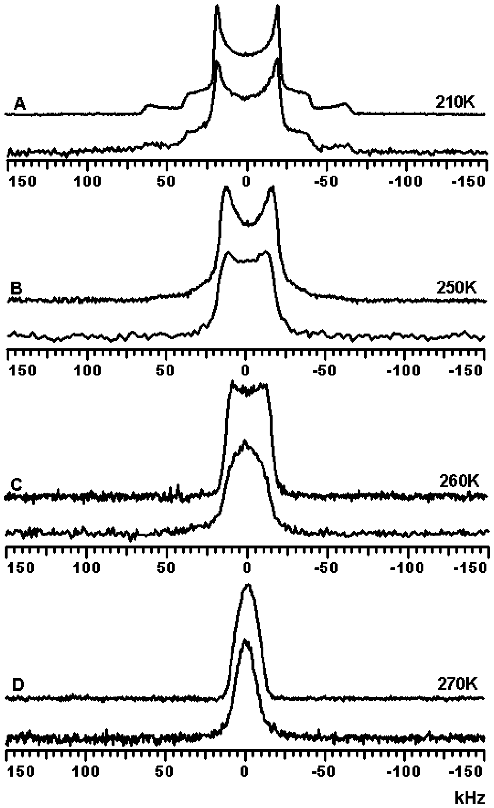

Figure 3. Selected spectra from variable-temperature static ^2H experiments on PIB-d_8 (top) and PIB(18 mol %-d_8)/PEB-66 blend (bottom) at (A) 210, (B) 250, (C) 260, and (D) 270 K. Although only four data points are shown, spectra were collected at 10 K increments from 210 to 300 K. Note the faster motional time scale of the PIB chains in the blend relative to bulk PIB at the three higher temperatures.

between the two samples at each temperature. In particular, at 260 K, the neat PIB line shape is still not coalesced, while the PIB in the blend is past the coalescence point. At 270 K, the PIB line width is 25 kHz at half-height, while that of the PIB in the blend is 15 kHz. Clearly, the motional frequency of backbone dynamics in PIB is increased at a given temperature, relative to the neat polymer. We are currently working on specific motional models for simulating the ^2H line-shape results as well as preparing PIB polymer specifically labeled at the CH_2 position. Even so, we see that there is excellent agreement in the coalescence temperatures from the methyl ^2H spectra in Figure 3 and the methylene ^{13}C spectra in Figure 2. For the blend, that temperature is approximately 253 K and for the neat PIB, 265 K. Although the PIB is an amorphous polymer, with a distribution of chain dynamics, it is satisfying that both the ^{13}C and ^2H NMR results provide a consistent explanation of increased conformational chain freedom for the PIB/PEB-66 blend.

2D ^{13}C Exchange Experiments. One-dimensional line shape experiments, like those in Figures 2 and 3, provide qualitative insights into the differences between PIB chain dynamics. Quantitative analysis of exchange lifetimes, and identification of conformational exchange pathways, requires 2D MAS exchange experiments.[18,19,29] In Figure 4, results from rotor-synchronized 2D ^{13}C homonuclear exchange experiments are shown for PIB and the two blends with PEB. These data were acquired at 213 K, or 8 K above the glass transition for pure PIB as measured by DSC. Figure 4A shows the control experiment on neat PIB with a short 100 ms mixing time, and as expected, there is no off-diagonal intensity. After 1 s (Figure 4B), the diagonal is broadened slightly, and the signal-to-noise decreases slightly due to spin−lattice relaxation during the mixing time ($T_1 = 2.9$ s for PIB in bulk and in blends). However, again we see little off-diagonal intensity that would suggest conformational exchange even after 1 s. Within the limits of the sensitivity, similar results are observed for the PIB CH_2 group in the blend with PEB-23; a well-resolved diagonal dominates the 2D spectrum in Figure 4C after 1.5 s of exchange. In clear contrast to any of these results, the diagonal intensity is completely redistributed among all conformers for the CH_2 group of PIB in the PIB/PEB-66 blend (Figure 4D) after *only 100 ms*. In this blend, the CH_2 carbons of PIB have been labeled with 5% ^{13}C to increase sensitivity. A similar exchange pattern, albeit at lower sensitivity, was obtained for the sample in Figure 4D after a 1 s exchange period (not shown). Comparison of slices from the 100 ms experiment in Figure 4D and the 1 s experiment (not shown) revealed essentially complete exchange in each. More importantly, comparison of Figure 4D with Figure 4A,B shows that exchange rate is much larger for PIB in the miscible blend, relative to the pure PIB. We also note that these results agree with $T_{1\rho H}$ data on PIB and the two PEB blends at 213 K. The CH_2 protons in neat PIB and PIB in the PIB/PEB-23 blend have similar values of 810 and 884 μs, respectively, while the PIB in the PIB/PEB-66 blend has $T_{1\rho H} = 498$ μs. By comparison, we do not observe such a short value of $T_{1\rho H}$ for neat PIB until the temperature is increased to 298 K, at which point the neat PIB $T_{1\rho H} = 516$ μs. The conformational freedom of PIB chains in the blend with PEB-66 is much larger at any given temperature than in neat PIB or the PIB/PEB-23 blend.

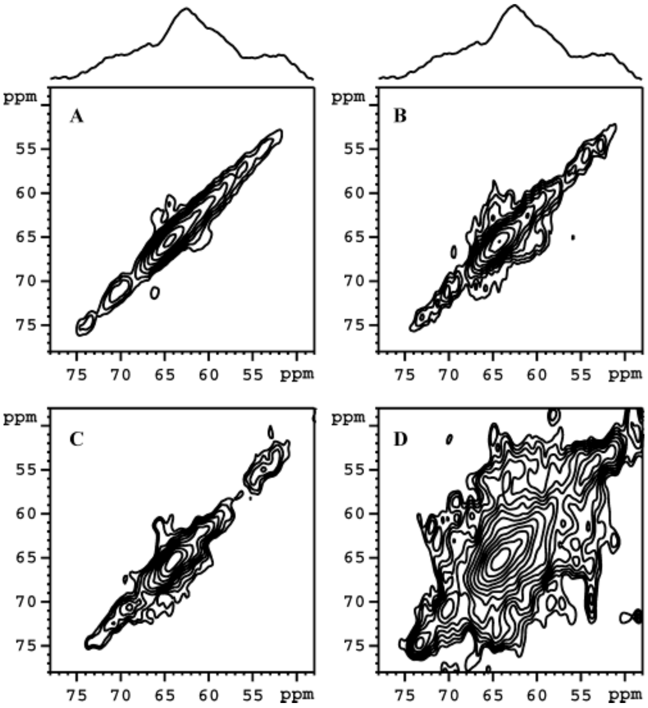

Figure 4. Two-dimensional MAS ^{13}C exchange spectra of the PIB methylene region (50−80 ppm) at 213 K for (A) neat PIB with 100 ms mixing time, (B) neat PIB with 1 s mixing time, (C) PIB/PEB-23 blend with 1.5 s mixing time, and (D) PIB/PEB-66 blend at 100 ms mixing time. ^{13}C T_1 values at 213 K equal 2.9 s for the PIB CH_2 carbons in all samples.

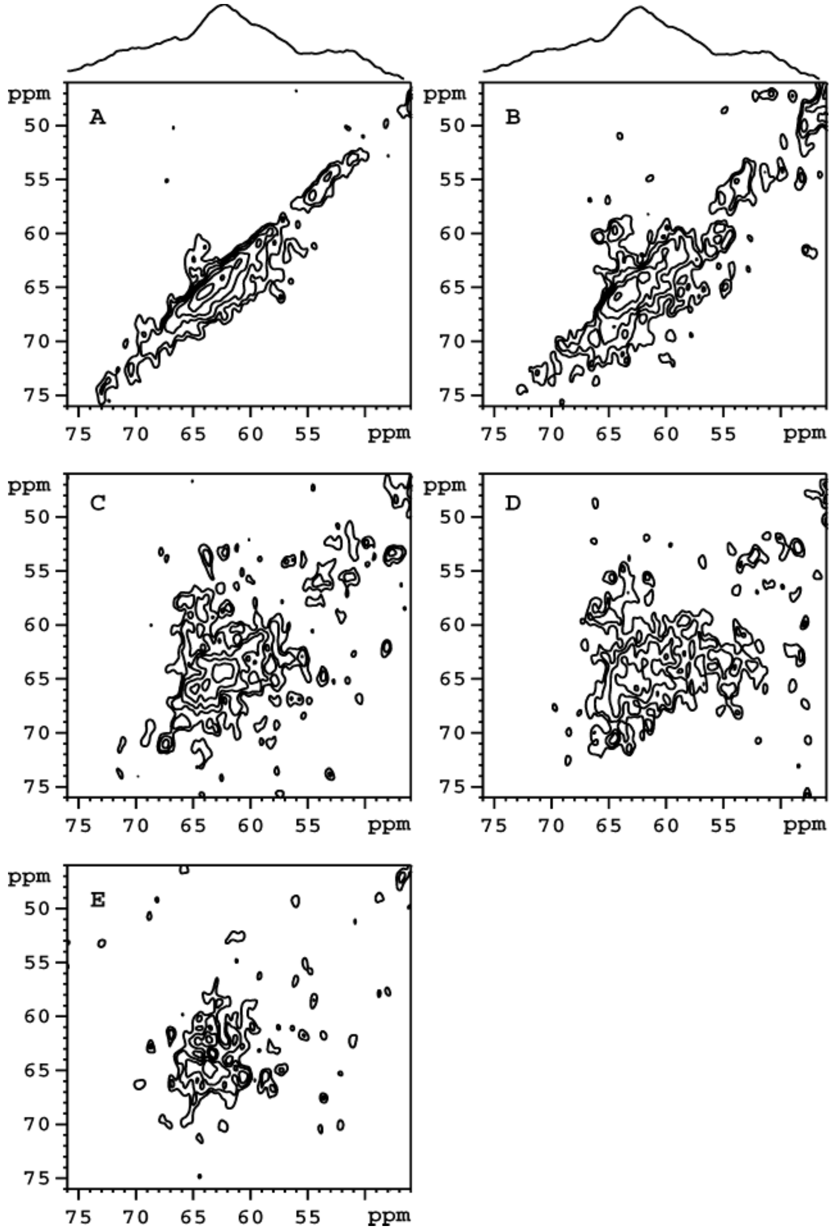

Figure 5. Two-dimensional MAS ^{13}C exchange spectra of the PIB methylene region (50−80 ppm) at 213 K for a PIB/PEB-66 blend in which the PIB contains 5% ^{13}C-labeled CH_2 groups at mixing times of (A) 5 ms, (B) 25 ms, (C) 50 ms, (D) 100 ms, and (E) 1.5 s.

In an effort to verify that the exchange pattern progressed as expected with longer mixing times, PIB/PEB-66 results for the 5% labeled PIB CH_2 moieties (in the blend) are shown in Figure 5. Only 64 scans were collected for each of these, which explains the lower sensitivity relative to the 256 scans used in Figure 4D. In addition to quantitative exchange rates, we are interested in identifying possible pathways for exchange, e.g., if one could observe sequential events in which tt/tg and tg/gg exchange occurred before the detection of tt/gg exchange. This requires running several experiments at relatively short mixing times. Figure 5A shows the results for a short mixing time of 5 ms, in which no exchange is observed, while parts B, C, and D of Figure 5 correspond to mixing time of 25, 50, and 100 ms, respectively. As off-diagonal intensity develops within the tg and between tg/gg peaks, we also observe the loss of the weak diagonal peak corresponding to the tt conformers (67−75 ppm). By 100 ms (Figure 5D), one can discern an approximately fully developed exchange pattern, particularly between the tg/gg regions. Of course, as diagonal intensity is redistributed among all possible off-diagonal elements and spin−lattice relaxation takes place, the overall sensitivity decreases, as shown for the 1.5 s result in Figure 5E.

^{129}Xe of Xenon Gas Absorbed in PIB and PIB/PEB Blends. NMR of Xe gas which is absorbed into a polymer blend has been shown to be a good indicator of whether the polymer is homogeneously mixed on a length scale defined by the Xe gas diffusion coefficient.[30,31] Because of its large, highly polarizable electron density, the ^{129}Xe chemical shift is very sensitive to subtle changes in its electronic environment. In amorphous polymers, the free volume of the polymer largely determines the ^{129}Xe chemical shift. We have used this nondestructive method to provide complementary information to the dynamic NMR data presented above. Figure 6 presents the results of simple ^{129}Xe one-pulse experiments for Xe gas absorbed in PIB and its blends with PEB-66 and PEB-23. Figure 6B shows that

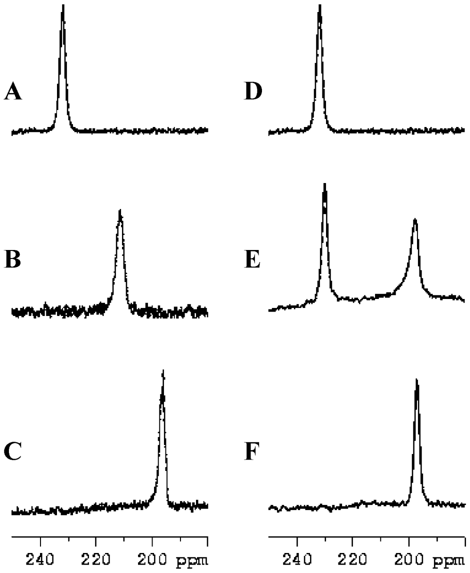

Figure 6. Static ^{129}Xe NMR spectra of Xe gas adsorbed in (A) PIB, (B) PIB/PEB-66 blend, (C) PEB-66, (D) PIB, (E) PIB/PEB-23 blend, and (F) PEB-23. The number of transients vary in each case but are greater than 1K for all. The mass of each sample also varies between experiments.

a single peak with an intermediate chemical shift is observed in the PIB/PEB-66 blend, relative to the neat PIB and PEB-66 in parts A and C of Figure 6, respectively. In contrast, Figure 6E shows two peaks at the chemical shift of the pure polymers for the PIB/PEB-23 blend, as may be observed by comparing its spectrum with those in Figure 6D,F. These data clearly indicate that the PIB/PEB-66 blend is miscible on a length scale defined by the chemical shift difference of the two constituents and the Xe gas self-diffusion coefficient D_{Xe} in these low-T_g polymers. An estimate can be made concerning the upper limit of the length scale of mixing, or domain sizes, in the fast exchange limit shown by Figure 6B. The lifetime of a Xe gas molecule $\tau \ll (1/\Delta\nu)$ for the fast exchange regime, where $\Delta\nu = 4841$ Hz is the difference between the pure component shifts. Therefore, the average distance a Xe gas molecule diffuses in a time τ is

$$x_{\text{rms}} \ll (2D_{\text{Xe}}/\Delta\nu)^{1/2}$$

Since we do not have the experimental capability to directly determine D_{Xe} using PFG methods, values from the literature for similar low-T_g polymers are used in above equation. Following the reports by Walton[30] and Veeman,[31] $D_{\text{Xe}} = 10^{-7}$ cm^2/s is taken as a reasonable upper limit in these polyolefins. Solving, we obtain $x_{\text{rms}} \ll 64$ nm as an upper limit on the domain size of the PIB/PEB-66 blend. However, we point out that this is indeed a maximum limit and remind the reader that the 1D and 2D exchange experiments presented above indicate that the length scale of mixing is actually much shorter. For reference, the 64 nm limit is almost an order of magnitude larger than R_g for these chains, and in order for mixing to induce large changes in the PIB backbone dynamics, the local environment around each chain must be perturbed.

Implications for Thermodynamics of Mixing in Saturated Polymer Blends. The direct experimental evidence presented above indicates that (1), of the two blends, only the PIB/PEB-66 blend is miscible and (2) the barrier to conformational exchange of PIB chains in the miscible blend is significantly lower than in pure PIB. At 213 K, all three conformational states of PIB can freely exchange between one another with a rate larger than 10 Hz, while the pure PIB exchange rates are negligible. (Indeed, we did not observe any conformational exchange in neat PIB or the PIB/PEB-23 blend up to the 2 s maximum exchange time used in this study.) The ^{2}H and ^{13}C 1D line shape, ^{13}C 2D exchange, and $T_{1\rho\text{H}}$ data all indicate that this is the case. In terms of the absolute entropy S of the PIB chains in the PEB-66 blend, in which there are three chain conformations/backbone bond relative to only one in the pure PIB, the ratio of $S_{\text{blend}}/S_{\text{pure}} = \ln(3^N)$, where N is the number of backbone bonds in the PIB chain. However, this only accounts for the entropy change for PIB in the blend. One must also consider the effects of blending on the PEB-66 polymer. Examination of the 10−15 ppm region in Figure 2 shows that the CH_3 groups of the ethyl side chains in PEB-66 are sensitive to conformation, since resolved trans−gauche/gauche−gauche peaks are observed below 243 K. Comparison of the temperature dependence of the CH_3 peaks in the blend with the neat PEB-66 copolymer, over the entire temperature range (223−253 K in particular), indicates that the conformational dynamics are similar in each. The peaks are superimposable at each temperature with those for the neat PEB-66 (not shown). Since the 1D ^{13}C line shape changes with temperature agreed with the detailed 2D exchange data for the PIB methylene carbons, we are confident that similar information for the PEB-66 methyl group indicates little change in its chain dynamics upon blending. Clearly, the PEB-66 is not more “constrained” at a local chain level in the blend relative to its pure state. On the whole, these results suggest that configurational entropy may be the operative driving force in the overall negative ΔG required for miscibility.

Such a result is intuitively satisfying for blends involving PIB, since the chain packing density in pure PIB is higher relative to other simple polyolefins, and it is unlikely that PIB packs more efficiently with dissimilar chain architectures.[32] Indeed, there have been several reports that PIB displays unusual mixing behavior compared to most polyolefins, and qualitatively this could be explained by increases in the absolute configurational entropy $S = k_B \ln W$ upon mixing. Miscibility between macromolecules is rarely attributed to entropic contributions, as Flory−Huggins theory indicates that these will scale to zero with typical polymer molecular weights.[33] However, such arguments are based on consideration of a molecular “size parameter”, such as the degree of polymerization or molecular mass, and fail to recognize the dynamic heterogeneity that exists on a short length scale among the subunits in the chain. Of course at this stage, these are qualitative arguments, but they are in complete agreement with the observed experimental findings for the PIB/PEB-66 blend.

Conclusions

Direct experimental observation of local chain dynamics, and mixing, in blends of PIB and PEB indicates that these polymers are not miscible over the entire butene comonomer range. For 50/50 blends, we observe intimate chain mixing for PIB and PEB containing 66 wt % (49 mol %) butene comonomer but phase separation for a PIB/PEB-23 blend. A variety of site-specific

1D and 2D dynamic solid-state NMR experiments, most in the absence of isotopic labeling, indicated that the conformational exchange rates of the PIB backbone increase significantly upon blending with the PEB-66 blend, while the PEB-66 itself was not affected by blending. Longer range probes of blend structure using Xe gas absorption revealed that the PIB/PEB-66 blend was homogeneous on a length scale ≪64 nm, in agreement with the chain-level NMR results. In addition to demonstrating an experimental strategy by which one can generally probe polyolefin blend mixing at the chain level, our results suggest that local configurational entropy may be the operative driving force for miscibility in polyolefin blends.

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