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Factors That Allow Polyolefins To Form Miscible Blends: Polyisobutylene and Head-to-Head Polypropylene

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ABSTRACT: Solid-state CODEX NMR experiments directly probe chain dynamics in pure polyisobutylene (PIB), head-to-head polypropylene (hhPP), and their binary blend. The conclusions we draw from the results of the CODEX experiments, which are conducted over a temperature range of 210−300 K and which probe frequencies of 5−10 Hz, indicate that the overall chain dynamics of the blend system exceeds that of the two unmixed polymers. This is in agreement with our previous work on miscible PIB/polyethylene-*co*-butene blends [*Macromolecules* **2003**, *36,* 4844−4850], in which configurational entropy was shown to increase for miscible polyolefins. The CODEX experiments on PIB/hhPP, which offer the advantage of *direct* and *simultaneous* observation of *both* chains in the blend, show that conformational reorientation in hhPP increases significantly upon blending with PIB, while PIB chain dynamics are relatively unchanged. Rotating frame spin−lattice relaxation experiments support this conclusion. The benefits of direct chain observation of both polymer blend components at mechanically relevant frequencies (hertz) are compounded by the lack of any isotopic labeling requirements. These results on PIB/hhPP further support an entropically driven miscibility as a general phenomenon in nonpolar polyolefins.

Introduction

Beginning students in basic chemistry, physics, and biology are often taught that "like dissolves like" as a way of understanding mixing in liquid solutions.[1] This rule works very well for common cases involving mixtures of small molecule liquids. Familiar examples involve phase separation of water from any of a variety of nonpolar hydrocarbon oils or the obvious lack of intimate contact in vinegar and oil mixtures. We know from everyday experience with oil-based paint and thinners that simple hydrocarbons (oils or waxes) dissolve other oils. The extension of this principle to nonpolar saturated hydrocarbon macromolecules (polymers like polyethylene/polypropylene with molecular weights > 5000 g/mol) predicts that they obey the "like dissolves like" rule and form intimate mixtures. Surprisingly, molecular-level mixing is not observed for almost all binary hydrocarbon polymer mixtures.[2−4] Only a few cases of miscibility between hydrocarbon macromolecules (polyolefins) have been reported.[5−10] The reason for this unexpected phase behavior in polyolefins is unknown, given that amorphous hydrocarbon polymers have essentially identical molecular and bulk properties. Here, we show by direct experimental evidence that miscibility in bulk polyolefin mixtures can be described by configurational entropy contributions, in which a miscible blend of two polyolefins exhibits a measurable increase in its total conformational "freedom" relative to the unmixed polymers over a range of temperatures. Increased conformational dynamics in a polymer chain corresponds to a reduction in the size of cooperatively rearranging regions in the polymer mixture, which in turn corresponds to a positive configurational entropy of mixing.[11−13] These polyolefins are amorphous, and our findings are relevant to the emerging field of amorphous mixtures. From a fundamental perspective, our results provide some of the first chain-level evidence for the thermodynamics of mixing in large, weakly interacting molecules, which is pertinent to both the multibillion dollar polyolefin industry and the beginning science student.

Polypropylene (PP) and polyisobutylene (PIB) are common polyolefins composed of three- and four-carbon monomers, respectively. A bulk mixture of these two polymers, either in their melt state or generated by dissolution in a mutual solvent, followed by drying, is not intimately mixed at the molecular chain level.[14] Just as with polyethylene, polypropylene phase separates from C_4-based polymers including polyisobutylene and poly-1-butene. However, Krishnamoorti and co-workers made the startling find several years ago that if the regio-sequence in the polypropylene chain is altered in a regular fashion, this new polypropylene was miscible with polyisobutylene.[5] Scheme 1 represents a miscible blend of polyisobutylene with this head-to-head, tail-to-tail polypropylene (hhPP), the latter made by anionic polymerization techniques.[15] Our group later demonstrated that amorphous hhPP/PIB blends are intimately mixed at the chain level (25 Å) using solid-state NMR methods.[16]

However, no experimental evidence exists at to why the hhPP/PIB blend, which exhibits a lower critical solution temperature (LCST) of 170−200 °C, is miscible while blends of most other polyolefins phase separate (including the PIB/head-to-tail PP blend). Solid-state NMR methods are ideally suited to the problem of mixing in polyolefins, since the bulk, amorphous blends may be examined without additional complicating solvents. Therefore, the experimental results are directly transferable to real materials. More importantly, the data probe local, molecular, and segmental details. Here we use a combination of traditional chemical shift and relaxation methods along with a recently developed exchange technique called CODEX (for Centerband Only Detection of Exchange)[17] to show that there is an increased configurational entropy in the mixed PIB/

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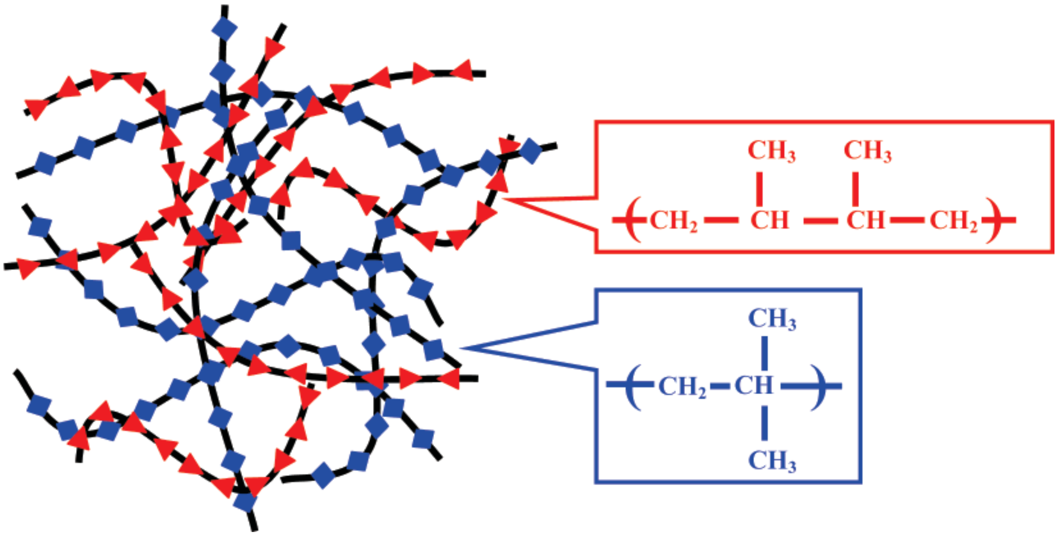
Scheme 1



hhPP blend relative to the unmixed polymers, rather than an increased intersegmental contact between dissimilar polymer chains. This latter possibility, which might be expected to drive mixing enthalpically, has already been addressed in previous publications, in which Xe NMR unequivocally showed a lower chain packing density in the miscible hhPP/PIB blend than in the pure PIB polymer itself.[18] The time scale of local chain phenomena probed by the experiments in this paper ranges from 5 Hz to 75 kHz.

Recently, Krygier and co-workers have published a detailed analysis of segmental dynamics in PIB/hhPP.[29] We note that our work is distinctly different from that publication in that our CODEX measurements probe the mechanically relevant hertz time scale, instead of kilohertz to megahertz, and that we *directly* measure the dynamics of *both* polymer chains in the blend *simultaneously* over a wide temperature range and without isotopic labeling.

Experimental Section

Polyisobutylene (M_w = 1 000 000) was purchased from ExxonMobil Chemical, atactic polypropylene ($M_w = 200\,000-500\,000$) was purchased from PolySciences, and hhPP was prepared by hydrogenation of poly(2,3-dimethylbutadiene) obtaining a $M_w = 50\,000$. The 50:50 wt % PIB/hhPP blend was prepared by dissolution in toluene over 2 days followed by evaporation and vacuum-drying for 4 days. DSC measurements indicated glass transitions for PIB, aPP, and hhPP of −68, −15, and −20 °C, respectively. Polycrystalline bisphenol A (T_g = 156 °C) was acquired from Aldrich and used without additional modification.

Because of limited sample amounts, most experiments were performed on the 4 mm CPMAS probe, except for the BPA measurements which were completed on the 7 mm probe. The temperature on the 4 mm probe was calibrated using $PbNO_3$ to within ±1. All ^{13}C and ^{1}H measurements were collected on a Bruker DSX-300 with a field strength of 7.05 T. The spinning speeds at the magic angle varied between 3 and 6 kHz with radio-frequency field strengths of 73 kHz. Cross-polarization times ranged between 300 μs for the relaxation experiments to 1 ms for the CODEX experiments. As a precaution, CODEX measurements were altered between the CODEX and reference signal every 256 scans to eliminate spectrometer drift, and typical experimental times were between 8 and 12 h.

Results and Discussion

Figure 1 shows a selected subset of 12 spectra collected over a 30 K temperature range (from a total of 27 acquired over a 100 K temperature range) for pure PIB with a molecular weight M_w = 1 000 000 (a), the miscible hhPP/PIB blend (b), and pure hhPP with M_w = 50 000 (c). The solid brackets identify the peak from backbone CH_2 group of PIB, while the dotted brackets denote the CH_3 peak from hhPP. Note that in each case these peaks are broad due to the combined effects of a distribution of chain conformations in each type of polymer, and differential chain packing environments in amorphous macromolecules, as expected for these heterogeneous polymers.[19] The PIB CH_2 peak (solid bracket, 50−70 ppm region) width varies across the four temperatures due to interference between chain dynamics and the 75 kHz decoupling frequency,[20] but in both the pure PIB (Figure 1a) and the blend (Figure 1b), the changes are essentially identical, suggesting that PIB chain dynamics are relatively unchanged in the blend.

Comparison of the broad hhPP CH_3 peak (dotted bracket) in Figure 1c vs Figure 1b, however, shows that this peak shape is significantly different in the blend at these temperatures, as it is narrower in breadth and with a unique intensity distribution. This difference was observed at all temperatures examined (213−313 K) in our experiments. The differential CH_3 shapes obtained in this simple experiment suggest a significant change in chain conformation, chain packing arrangements, and chain dynamics with a characteristic frequency of 500−1000 Hz for hhPP in the blend, while the PIB chains appear relatively unperturbed.

One way to more quantitatively interrogate the perturbation in the individual PIB and hhPP polymer chains upon formation of the miscible blend is to measure ^{1}H relaxation times in the rotating frame ($T_{1\rho H}$) for individual chemical groups in each polymer via the dipolar coupling to the detected ^{13}C moiety. On the basis of the temperature of the measurement, the measured value will either reflect the molecular dynamics of that specific functional group, e.g., a PIB CH_2 vs a hhPP CH_3, or a single, common “bulk” value due to the averaging effects of ^{1}H spin-diffusion.[21] This latter case will occur for a rigid lattice, where all of the ^{1}H spins in the sample volume are coupled to one another via their dipolar interactions, while the former requires higher temperatures to ensure high chain mobility and therefore elimination of these dipolar interactions. Table 1 presents the results from both limits for the unmixed polymers and the miscible blend, where the two resolved

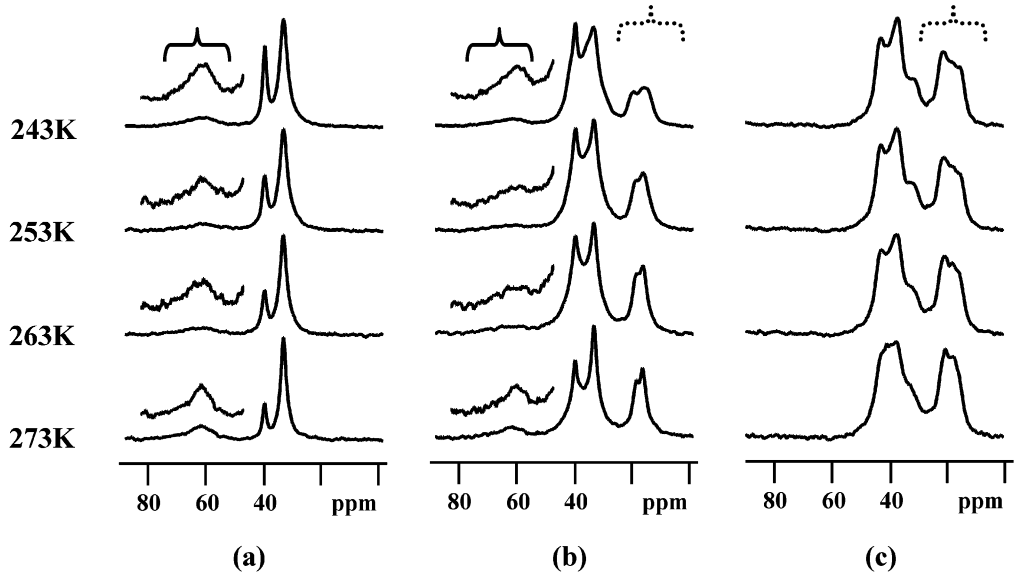


Figure 1. Variable-temperature ^{13}C cross-polarization/magic-angle spinning (CP/MAS) spectra for (a) pure PIB, (b) PIB/hhPP blend, and (c) pure hhPP.

Table 1. ^{1}H Rotating-Frame Spin−Lattice Relaxation Time Constants for the Pure Polymers and Their Miscible Blend

PIB	$T_{1\rho H}$
CH_2 (300 K)	462.4 μs
CH_2 (213 K)	1.847ms
hhPP	$T_{1\rho H}$
CH_3 (300 K)	945.1 μs
CH_3 (213 K)	11.15 ms
PIB/hhPP	$T_{1\rho H}$
PIBCH_2 (300 K)	463.5 μs
hhPP CH_3 (300 K)	600.2 μs
PIB CH_2 (213 K)	3.805 ms
hhPP CH_3 (213 K)	4.21 ms

^{13}C signals from each polymer (see Figure 1) were again used for detection. At 208 K, a temperature near the T_g of pure PIB and well below that of pure hhPP, spin-diffusion is efficient, and a common relaxation value will be observed for spins in close proximity to one another; the essentially identical experimental values of 3.8 and 4.2 ms respectively for the PIB and hhPP chains in the blend confirm intimate mixing. Note that the pure chain values at 213 K are drastically different. Conversely, at 300 K where we know that spin-diffusion is not efficient on the basis of previous measurements of ^{1}H spin-diffusion coefficients,[22] the PIB and hhPP values in the blend do not converge to a common value but still differ by more than 25%.

More importantly, we note that the relaxation time constant for the backbone carbons in PIB is unchanged upon blending (463 μs), while the hhPP value is reduced by more than 50%. Like the result from Figure 1, the data in Table 1 clearly indicate that PIB chain dynamics are essentially unchanged upon forming the miscible blend with hhPP, while chain dynamics for hhPP are dramatically increased. In other words, the density of chain motion with a correlation frequency near 75 kHz, which this relaxation experiment measures, is much greater for hhPP polymer chains in the blend relative to the unmixed state, while that for PIB is unchanged. We further validate this conclusion by quantitatively analyzing the 208 K results: if the polymer chains simply maintained the chain reorientation dynamics characteristic of the pure components, then for this PIB/hhPP blend which has a molar composition of 43% PIB and 57% hhPP, the expected relaxation time for spin-diffusion averaging would be 7.5 ms. The measured relaxation time, from either the PIB or hhPP signal, is smaller by almost a factor of 2 (3.8 and 4.2 ms). Again, this shows that the local chain dynamics in the blend are markedly enhanced relative to the two unmixed components at the same temperature.

Finally, we utilize the recently developed CODEX experiment for detecting slow chain reorientations to independently confirm our conclusions.[17,23] The experiments summarized by Figure 1 and Table 1 probe chain dynamics with characteristic frequencies of ca. 750 Hz and 75 000 Hz, respectively. The CODEX experiment probes much slower motion, e.g., 1−10 Hz, which is a time scale important for physical and mechanical properties in materials. As with the experiments described above, the conformational exchange measured by CODEX will reveal the bulk-average state of the system rather than dilute defect sites that might not be characteristic of the entire polymer mixture. The technical details of the solid-state CODEX experiment and pulse sequence have been recently described as noted above; here it is sufficient to say that the experiment works by obtaining two spectra for each sample at each temperature. In one experiment, a mixing time will be inserted during which chain motion may be detected due to its effect on refocusing the chemical shift during the magic-angle spinning process. The “pure exchange” spectrum, i.e., the trace that shows which parts of the polymer chain or chains move, is obtained by difference and has been shown to be a reproducibly quantitative result. The exchange time scale probed is governed by selection of the mixing time. In our experiments, both 100 and 200 ms mixing times were used. Here, we report only results for the 100 ms experiments since identical conclusions can be drawn from the 200 ms data. We note that these mixing times probe chain conformational rearrangements with a characteristic frequency of 5−10 Hz, i.e., much slower than the previously reported data.

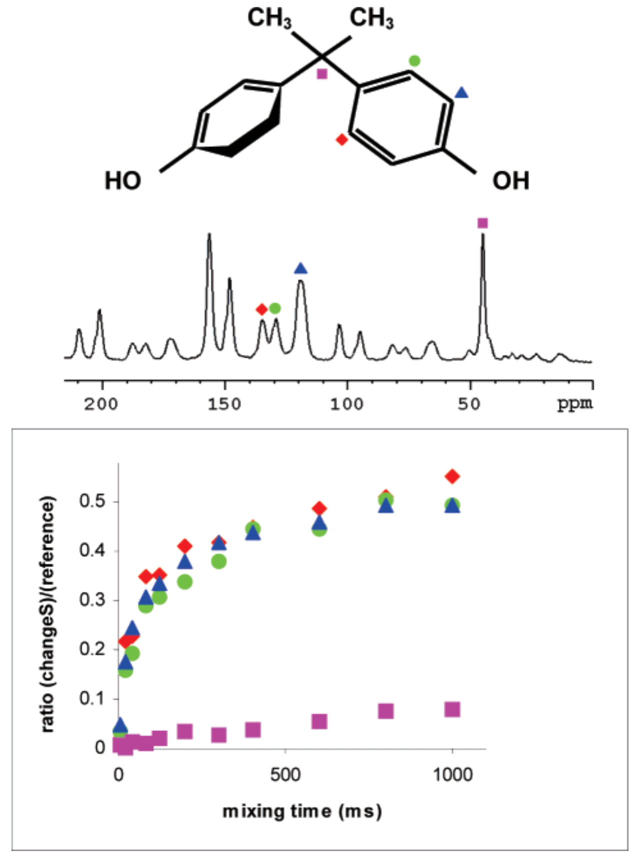


Figure 2. Pure CODEX exchange intensities as a function of mixing time for aliphatic quaternary (■) and protonated aromatic (●, ◆, ▲) carbons in bisphenol A. Structure drawn above contains color-coded scheme with corresponding carbons marked on the 1D CP/MAS plot. Each data point was collected at 308 K with 12 K scans and MAS spinning of 4 kHz.

Before presenting the CODEX results for the PIB/hhPP blend, we demonstrate by suitable control experiments that the CODEX signal arises only from mobile chain segments. Since the results from the CODEX experiment on the blend are central to our final conclusions, a series of experiments on different sample types were completed to span the realm of possible outcomes and eliminate any uncertainty in the blend data. The original CODEX authors used a crystalline organic solid, methylmalonic acid, as a static control sample in which no CODEX difference signal would be expected or observed.[17] We repeated this experiment and obtained an identical result, thereby eliminating the possibility of "false positives". Second, we chose to use a well-known organic solid, bisphenol A or 4,4′-isopropylidenediphenol, which contains aromatic rings that are known to undergo large-amplitude reorientation on a time scale of tens of milliseconds to seconds.[27,28] Since different parts of the structure undergo different motional amplitudes, the CODEX data obtained as a function of exchange mixing time should reflect this behavior. Figure 2 demonstrates that the experiment is indeed sensitive to both the time scale and amplitude of differential molecular reorientation in this organic crystal. The off-axis ring carbons, which have a large chemical shift anisotropy, rapidly "accumulate" a pure CODEX signal, while the quarternary backbone carbon does not.

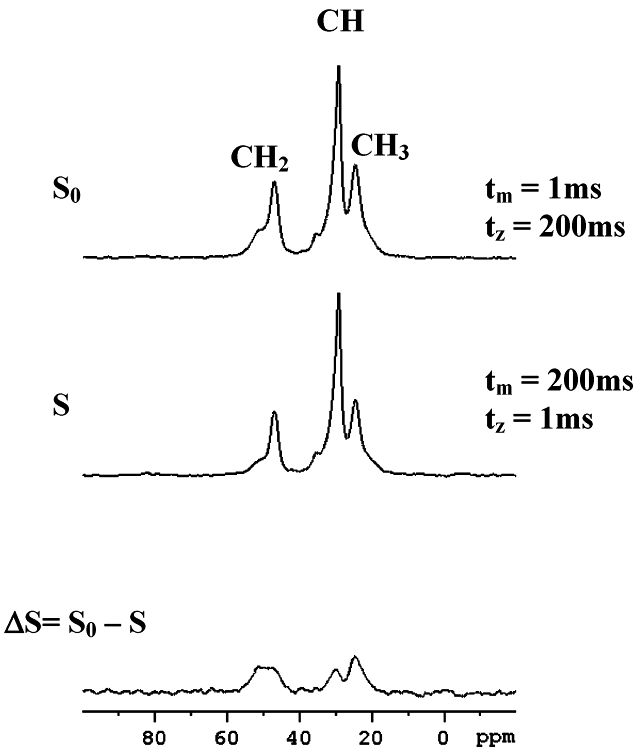


Figure 3. Pure CODEX spectrum (ΔS) is obtained via subtraction of the CODEX (S) from the reference (S_0) as illustrated above. The spectra were obtained with spinning speed of 4 kHz, $Nt_r = 500\ \mu$s, mixing time = 200 ms, scans = 12 K, and line broadening = 75 Hz.

As a final control experiment, Figure 3 shows the discrete steps in obtaining the pure CODEX spectrum for a semicrystalline polypropylene sample. This PP sample (Polysciences) was nominally atactic, but solution NMR revealed significant isotacticity present, in agreement with DSC results. In Figure 3, we observe that the pure CODEX result at 260 K generates a spectrum containing peaks arising only from the conformationally heterogeneous amorphous PP components, as the crystalline fractions are rigid on the 200 ms time scale at this temperature.

Figure 4 shows the pure ^{13}C CODEX spectra obtained after subtraction of the corresponding control spectra for the PIB, hhPP, and blend macromolecules. Again, we span a large temperature range, beginning near the PIB calorimetric T_g (208 K) and ending well higher than the DSC T_g for the blend (230 K). As with all the data presented here, one must understand the limiting effects of low temperature vs high temperature on each experiment. For the CODEX experiment, no pure exchange signal will be observed if there is no motion, i.e., when the polymer chains are truly rigid solids with a time scale for reorientation much longer than 1−10 per second. On the other hand, if local segmental motions become so fast that several events occur during the magic-angle spinning rotor period (200−250 μs), then the ability to detect that event is lost, and again, no signal will be observed. This latter case is shown in Figure 4 for the higher temperature PIB spectra (left column), while the rigid-lattice limit data are observed for the pure hhPP at lower temperatures (right column). For the temperature range shown in Figure 4, the pure CODEX signal is largest for the blend relative to the two unmixed components. Any given signal amplitude would be expected to decrease by a factor of 2 due to the dilution in the blend for a constant exchange function; however, we see that the hhPP signals are preferentially enhanced in the blend relative to their

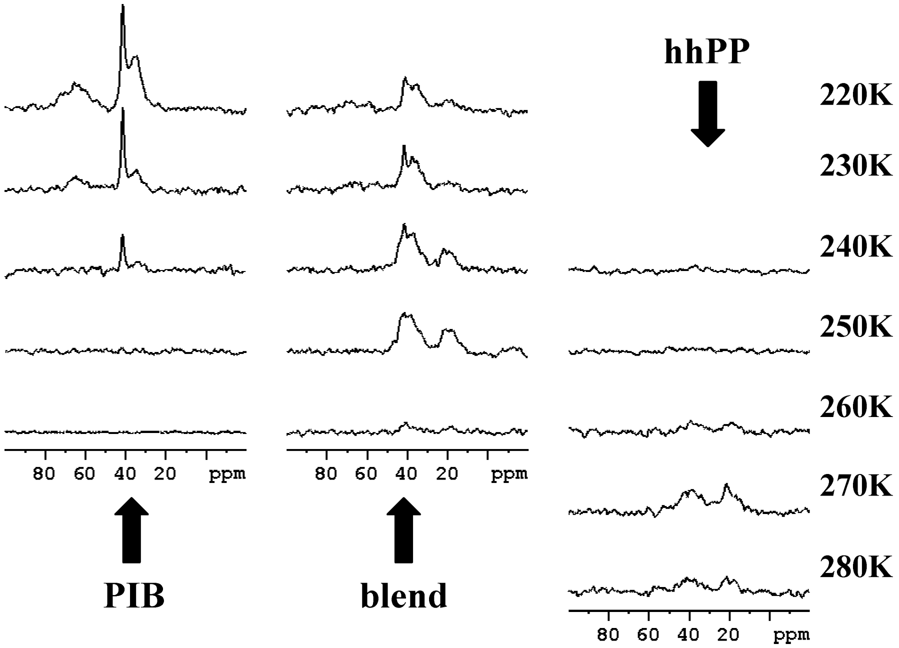


Figure 4. Pure CODEX spectra for neat PIB (left), neat hhPP (right), and the PIB/hhPP blend (middle). All spectra were collected with a 100 ms mixing time.

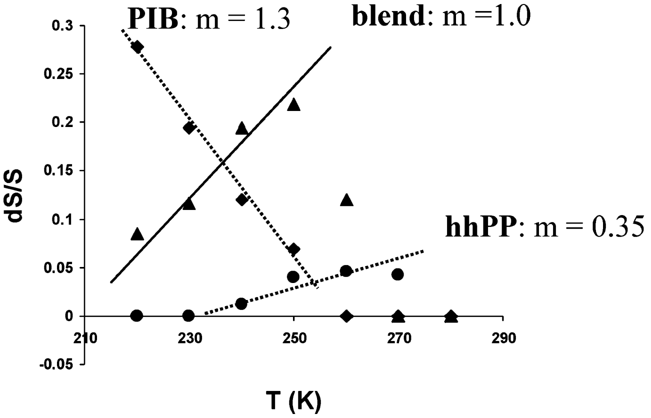


Figure 5. Graph of pure CODEX fraction vs temperature, with the regression slopes through the initial rise/descent (**m**) indicated for pure PIB (◆), pure hhPP (●), and the hhPP/PIB blend (▲).

unmixed state, even at high temperatures. The PIB signals in the blend decrease by approximately a factor of 2, as expected for dilution and a relatively unchanged segmental motion function. Again, these data indicate a dramatic increase in the local segmental motion of hhPP chains upon blend formation, across a large temperature range, while the PIB dynamics appear relatively fixed. One way to examine the system response to blend formation is to integrate the total pure CODEX line shape at each temperature (all peaks in the spectrum) and compare it to the reference spectrum (not shown) for each sample at each temperature. In other words, quantify the total exchange fraction, which we will call **dS/S,** where **dS** is the pure CODEX integrated intensity and **S** is the reference spectrum at the same condition. Figure 5 shows this plot for the data in Figure 4. If the total exchange dynamics in the miscible blend are simply a composition-weighted average of the two components, then we would expect a slope (absolute value) of 0.83 for the regression line through the initial growth of the blend CODEX intensity as the temperature is raised. However, the fact that the observed slope is 1.0, as shown in Figure 5, means that the total chain dynamics increases in the blend relative to the weighted sum of its components. Again, this is in agreement with the low-temperature relaxation data from Table 1, in which the density of chain motion at the necessary frequency to stimulate efficient relaxation was much larger in the blend than the weighted sum of its components. In all three experiment types described by Figure 1, Table 1, and Figure 4, we see that the majority of the extra motion comes from the more rigid (higher T_g) hhPP component, while the more flexible PIB chain segments exhibit an almost unchanged segmental motion upon blend formation.

Conclusions

We can conclude using Adams−Gibbs theory, relating structural dynamics and configurational entropy $S_\mathbf{c}$, given by eq 1, which is particularly applicable to this heterogeneous system of amorphous polymer chains (τ_0 and c are constant).[24]

$$\tau_{ex} = \tau_0 \exp(c/TS_c) \qquad (1)$$

Here, τ_{ex} is the characteristic exchange or relaxation time for a specific chain segment, as measured by either the relaxation data of Table 1 or the CODEX experiment in Figure 3. Using this well-known model with our experimental data, one realizes that the physical picture emerging from the data is consistent with our knowledge of entropy. As the amount of local segmental motion increases, and τ_{ex} decreases, the diameter of the cooperatively rearranging regions of the polymer mixture decreases; i.e., one chain's motion no longer depends as strongly on its neighbor's as before, and individual monomer units no longer behave as part of a much larger single, cooperative chain segment.[12,25,26] Since these amorphous mixtures have a heterogeneous distribution of many closely spaced conformational energy levels, the reduction in packing barriers increases the number of configurations a given chain segment can access per unit of energy kT. Therefore, the configurational entropy S_c increases as the experimentally measured τ_{ex} decreases. This is expected from the fundamental relationship $S = k_B(\ln W)$, where the number of configurational microstates accessible (W) is increased in the blend relative to the pure materials at a given temperature. We conclude that the few cases where these nonpolar hydrocarbon "macromolecular liquids" form intimate mixtures must correspond to an overall positive increase in the configurational entropy of the system.

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