# Notes

## Polyolefin Blend Miscibility: Polarization Transfer versus Direct Excitation Exchange NMR

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### Introduction

Relatively simple chemical constituents in polyolefin macromolecules belie the fact that their phase behavior in mixtures can be complex.[1] Polyolefins are obviously important economically as commodity polymers, but many specialty applications require unique formulations of multiple polyolefins with slightly different chemical structures. Predicting the details of the ultimate phase mixing is difficult and nonintuitive, and experimental verification of chain level behavior is challenging due to similar chemical and physical properties among varying polyolefin chain structures. Many investigators have approached this problem through multiple theoretical and experimental avenues in recent years.[2−7] We have recently described aspects of binary polyolefin blend phase behavior, relying extensively on advanced solid-state NMR methods to show that configurational entropy is an important thermodynamic parameter in controlling miscibility between different polyolefin structures.[8−10] Important general conclusions based on these advanced NMR experiments are often complicated by complex pulse sequences that employ an initial polarization transfer step. CODEX NMR experiments have proven particularly powerful for direct chain level interrogation of mixing and dynamics in amorphous polyolefin blends, but to date, all work has involved polarization transfer from protons to carbons (cross-polarization or CP) to generate the initial signal in the CODEX experiment.[11,12] Concerns about nonrepresentative sampling of a subset of polymer chains by polarization transfer steps can arise in cross-polarization solid-state NMR methods; differential polymer chain dynamics may lead to nonuniform polarization transfer efficiency in that step, often preferentially emphasizing the more spatially constrained or rigid regions of the sample which preserve larger heteronuclear dipolar couplings.[13,14] To address this in the context of amorphous polyolefin blend miscibility, we have devised a modified version of the experiment employing only direct carbon polarization as the initial step in the experiment. On the basis of quantitative comparisons of the modified direct polarization versus CP-based CODEX results over a wide temperature range (including $T_g$) for atactic polypropylene (aPP), we demonstrate that results representative of all polymer chains in the sample are obtained here as well as in previously published polarization-transfer-based results. Our work shows that CODEX-based exchange methods can provide chain-level information representative of the bulk mixing and miscibility in amorphous polyolefin blends.

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### Experimental Section

Atactic polypropylene (aPP) was a commercial sample acquired from Eastman, characterized by a DSC $T_g = -11$ °C and $M_n = 2600$. Solid-state NMR measurements were collected on a Bruker DSX-300 with field strength equal to 7.05 T and using a 4 mm double-resonance magic-angle spinning probe with the probe temperature calibrated to within ±1 K using $Pb(NO_3)_2$. All CODEX exchange data were acquired with active MAS speed control and rotor synchronization, and as a precaution, measurements were altered between the CODEX and reference signal every 256 scans to eliminate spectrometer drift. Slow exchange data were acquired using a 50 ms exchange time, unless otherwise noted. Total experiment times typically ranged between 8 and 12 h for a single measurement, depending on the temperature.

The modified direct-excitation CODEX experiment devised for this work is shown in Figure 1, and as stated earlier, a single $^{13}C$ 90° pulse is used to directly excite the carbon signals from the polymer chains. While this experiment obviously suffers from sensitivity loss relative to the original CP-based sequence, it eliminates any possibility of selection of subsets of polymer chains based on differential cross-polarization dynamics.[13,14] In acquiring data for the aPP sample used in this study, $^{13}C$ $T_1$ time constants were measured using the Torchia method[15] and found to equal 0.77 s for the $CH_3$ carbons at 274 K. Since we previously reported data on the aPP $CH_3$ carbons in polyolefin blends via the CP CODEX approach, this is the relevant structural moiety to consider here. In acquiring data using the direct excitation CODEX experiment, 4 s repetition times were used to ensure adequate relaxation of $^{13}C$ methyl group polarization.

### Results and Discussion

Polypropylene (aPP) has been discussed as a key component in many polyolefin blends, is economically important, and was included in recent work by us involving blends with polyethylene copolymers.[10] For these reasons, we have selected atactic polypropylene (aPP) as a relevant test material in this work. Figure 2a,b shows a comparison of direct excitation $^{13}C$ MAS and direct excitation CODEX for aPP with their respective CP-based counterparts in Figure 2c,d. The data were acquired at 274 K, since this corresponds to the previously published exchange intensity maximum for aPP.[10] Relative peak intensities differ dramatically in the normal Bloch decay (i.e., direct or single-pulse excitation) and CP/MAS spectra (Figure 2a,c) due to the combined differences in heteronuclear dipolar couplings and concomitant CP efficiency as well as simple $^{13}C$ $T_1$ effects.[13,14] For example, the relative height of the backbone $CH_2$ group compared to the more mobile $CH_3$ side group is enhanced in the CP/MAS spectrum (Figure 2c) compared to that observed in the Bloch decay spectrum (Figure 2a).

As expected, the different excitation methods produce different reference spectra $S_0$ in the CODEX results of Figure 2b,d. The key question is whether the details of polymer chain

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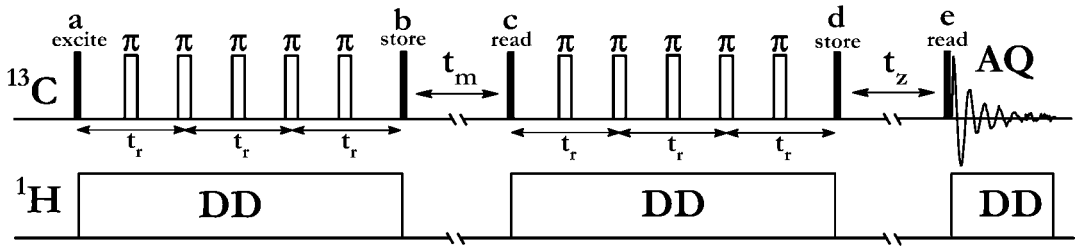


**Figure 1.** Pulse sequence diagram for direct excitation $^{13}C$ CODEX experiment, based on a modified version of the original sequence.[11,12] The modified phase cycling scheme for all $\pi/2$ pulses, which includes required changes in the receiver phase due to elimination of the CP step, is shown in Table 1. The phase alternation for the $\pi$ pulses in the first and second evolution windows follows the *xy*-8 phase cycling scheme.[16] The exchange mixing time $t_m = 50$ ms in this work, and the relationship between the exchange signal intensity measured by CODEX and the length of the evolution/refocusing windows ($Nt_r$) has been presented earlier for aPP.[10] DD denotes dipolar decoupling.

**Table 1. Modified Phase Table for the $\pi/2$ Pulses Used in the Direct-Excitation CODEX Experiment Shown in Figure 1**

| $\pi/2$ excite | first $\pi/2$ store | first $\pi/2$ read | second $\pi/2$ store | second $\pi/2$ read | receiver |
|---|---|---|---|---|---|
| $y\ -x\ -y\ x$ | $-y\ x\ y\ -x$ | $y\ -x$ -y x | $-y\ x\ y\ -x$ | $y\ -x\ -y\ x$ | $-y\ x\ y\ -x$ |
| | $-y\ x\ y\ -x$ | $-y\ x\ y\ -x$ | | | $y\ -x\ -y\ x$ |
| | $-x\ -y\ x\ y$ | $x\ y\ -x\ -y$ | | | $-y\ x\ y\ -x$ |
| | $-x\ -y\ x\ y$ | $-x\ -y\ x\ y$ | | | $y\ -x\ -y\ x$ |
| | $y\ -x\ -y\ x$ | | | | $y\ -x\ -y\ x$ |
| | $y\ -x\ -y\ x$ | | | | $-y\ x\ y\ -x$ |
| | $x\ y\ -x\ -y$ | | | | $y\ -x\ -y\ x$ |
| | $x\ y\ -x\ -y$ | | | | $-y\ x\ y\ -x$ |

reorientation as measured during the 50 ms exchange time manifest themselves in a quantitatively similar way independent of the initial excitation method. This question cannot be answered by direct inspection of the $S_0$ and S spectra in Figure 2b,d, as this is only a single result at one temperature. Since we previously published a detailed analysis of the CP CODEX results on the methyl group of pure aPP and aPP in blends over a wide temperature range, including the glass transition temperature,[9,10] new data were acquired using the modified direct excitation CODEX experiment over an identical temperature range for the same aPP polymer.

Figure 3 shows comparative data for the direct excitation CODEX and the CP-based CODEX for the aPP $CH_3$ group over its complete temperature range, beginning slightly below $T_g$ and increasing to temperatures high enough to eliminate (via motional averaging) the chemical shift anisotropy interaction which is required to monitor exchange during the evolution and refocusing windows of the CODEX experiment. Since the overall sensitivity decreases for the direct excitation version, we have plotted only the temperature-dependent response of the $CH_3$ group here, instead of the much weaker backbone $CH_2$ signal. However, we showed earlier that identical results are obtained for both $CH_2$ or $CH_3$ groups in aPP.[10] As previously discussed, the fact that the detectable CODEX exchange intensity coincides with the $T_g$ by DSC shows that each experiment is probing the onset of slow chain dynamics in polyolefins in the 1−100 Hz frequency range. The advantage of the CODEX approach for polyolefin blend work is site resolution which allows chain-specific information before and after blend formation, instead of an averaged response. In Figure 3, we observe a negative 1−2 K per point shift in the direct excitation data relative to the CP-based CODEX results. While there is a ±1 K uncertainty in the temperature calibration using $PbNO_3$ chemical shift thermometry, the systematic low-temperature shift here arises from the use of a much larger heat exchanger in the variable temperature equipment for acquisition of the direct excitation data. This change was necessary due to the factor of 3 longer data acquisition time per point for the direct excitation CODEX results compared to the CP-based

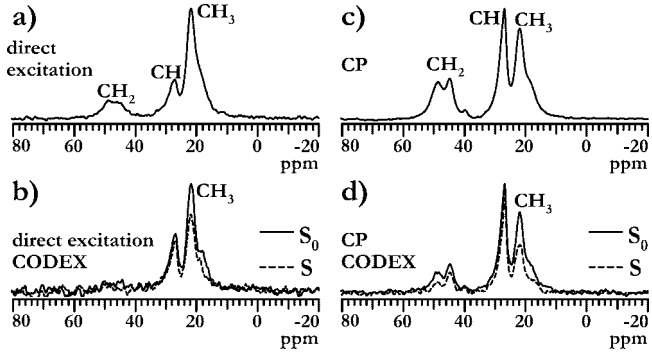


**Figure 2.** $^{13}C$ NMR MAS spectra of aPP at 274 K: (a) single-pulse spectrum, 128 scans; (b) corresponding direct excitation CODEX spectra with 50 ms exchange time and 4096 scans; (c) CP spectrum with 1 ms polarization transfer time and 128 scans; (d) corresponding CP CODEX spectra with 50 ms exchange time and 4096 scans. $S_0$ is the reference spectrum in each of the two CODEX results, and S is the exchange spectrum.

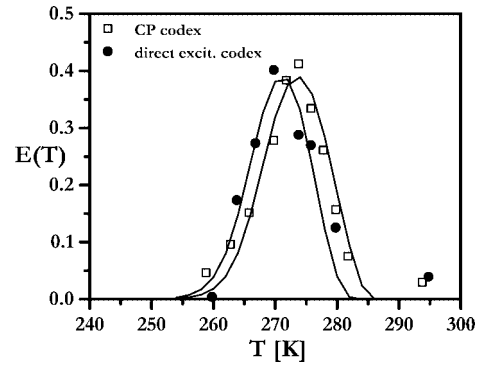


**Figure 3.** Normalized exchange intensities $E(T)$ for the methyl carbon signal of pure aPP obtained by cross-polarization CODEX (□) versus direct excitation CODEX (●). The smooth lines are fits to the data using the same isotropic rotational diffusion/Arrhenius model (as described in detail previously in refs 9 and 10) for either experiment. For reference, the $T_g$ by DSC occurred at 262 K. The 1−2 K low-temperature shift observed for the direct excitation points relative to the CP CODEX points is attributed to the use of a much larger heat exchanging coil in the variable-temperature setup for the former; this was required since the experimental acquisition time per point was 3 times longer for the direct excitation data.

CODEX data. Even with this small temperature offset, one observes that the exchange intensity representative of slow chain dynamics with central correlation time constants ranging from 1 s to 1 ms, i.e., the $E(T)$ vs $T$ curve in Figure 3, is essentially identical. Quantitative analysis of each curve using either an Arrhenius or KWW/WLF model gives the same activation energies, central correlation time constants, correlation time distributions, $\beta$ values, etc., for chain reorientation as previously reported for aPP using the CP-based CODEX.[10] Given the reduced sensitivity in the direct excitation CODEX results (compare spectra b and d of Figure 2), the absolute error in each measurement is higher than the CP CODEX results; the fact that the same exchange intensity curve is reproduced from the individual pure exchange difference spectra at each temperature indicates that results are representative of the behavior of aPP polymer chains, irrespective of excitation method. As mentioned earlier, 4 s repetition times allowed uniform sampling of all aPP methyl carbon groups in the direct excitation experiment. Also, the CP CODEX results were obtained using a 1 ms cross-polarization time, which is near the maximum in a $T_{CH}$ experiment and therefore should provide the most uniform sampling of all polymer chains. One could use the polarization method as a more discriminating initial selection method in the CODEX approach, if desired, by employing well-known adjustments in either experimental method. For example, the direct excitation method used in conjunction with a short repetition time (e.g., 0.5−1 s) between each transient would select for the most mobile regions, while the CP CODEX approach with a very short polarization transfer time (e.g., 50−100 $\mu$s) would skew the response to the most constrained subset of chains. Sensitivity losses would ultimately limit the degree to which either type of severe polarization discrimination was practical, even though the level of selectivity could prove especially informative for semicrystalline blends or polyolefin nanocomposites.

In conclusion, we have devised a modified CODEX experiment employing direct $^{13}C$ excitation as the first step in the experiment to show that the CODEX strategy does provide information on slow chain dynamics and miscibility in polyolefin blends which is representative of the bulk polymer behavior. Detailed comparison of amorphous polypropylene exchange data obtained with either the direct excitation CODEX or the original CP CODEX method gives essentially identical results over a wide temperature range, including $T_g$.

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