Determination of Polymer Miscibility by Proton–Deuterium CP/MAS NMR Spectroscopy

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Polymer miscibility has been the subject of numerous solid-state NMR studies. Among them, intermolecular cross-polarization[1,2] methods involving ^1H–^{13}C polarization transfer from protonated to deuterated polymers probe polymer proximity over short distances and, therefore, hold the promise of resolving the geometry of specific interactions between polymer chains that drive miscibility. This technique requires, however, that the weaker ^{13}C resonances of the deuterated species be resolvable from the readily cross-polarized and, therefore, stronger resonances of the protonated polymer. This requirement may stymie the facile and unambiguous detection of minor components, such as compatibilizers, that play a crucial role in the technology of advanced polymer blends.

In this paper, we report a novel intermolecular cross-polarization technique that avoids many of the difficulties. Our technique relies on an intermolecular transfer of nuclear polarization from protons to deuterium. Unlike protons and ^{13}C, deuterium signals are generally free of background interference. Furthermore, since under the influence of cross-polarization only those deuterium nuclei close to protons are detected, our technique is interface-selective and has implications beyond the detection of polymer miscibility.

The broad, so-called Pake doublet observed in the static ^2H NMR spectra (i.e., spectra obtained in the absence of mechanical sample spinning) of solids, micelles, and liquid crystalline materials is inhomogeneously broadened and will upon magic angle spinning (MAS) give rise to rotational echoes in the ^2H free induction decay (fid).[3] Several recent papers have investigated ^2H MAS spectra both theoretically[4,5] and experimentally for the purpose of solids imaging,[6] sensitivity enhancement,[7] and ^2H–^{13}C internuclear distance determinations via rotational echo double resonance (REDOR).[8] *We have observed that under MAS the deuterium spectrum can be readily obtained by cross-polarization from protons.* The spectrum obtained by cross-polarization/magic angle spinning (CP/MAS) is indistinguishable from the MAS-only spectrum, in contradistinction to the one published static ^1H–^2H CP spectrum where only selected crystallite orientations satisfy the Hartmann–Hahn condition and are observed.[9]

We demonstrate this technique using homogeneous and phase-separated blends of perdeuterated *syn*-poly(methyl methacrylate) (*syn*-PMMA-d_8) in poly(vinylphenol) (PVPh) as model systems, containing 18.8% *syn*-PMMA-d_8. The *syn*-PMMA-d_8 was 78% syndiotactic, with a molecular weight of 125 K and a molecular weight distribution of 1.25, and was synthesized as described in the literature.[10] The two polymers are miscible. However, it has been shown[11] that when films of the blend are cast from tetrahydrofuran (THF) as the solvent, they are largely phase-separated, displaying two glass transition temperatures. On the other hand, when the blend is redissolved in methyl ethyl ketone (MEK) and precipitated by addition to an excess of hexane (a nonsolvent for both polymers), a single-phase material is obtained.

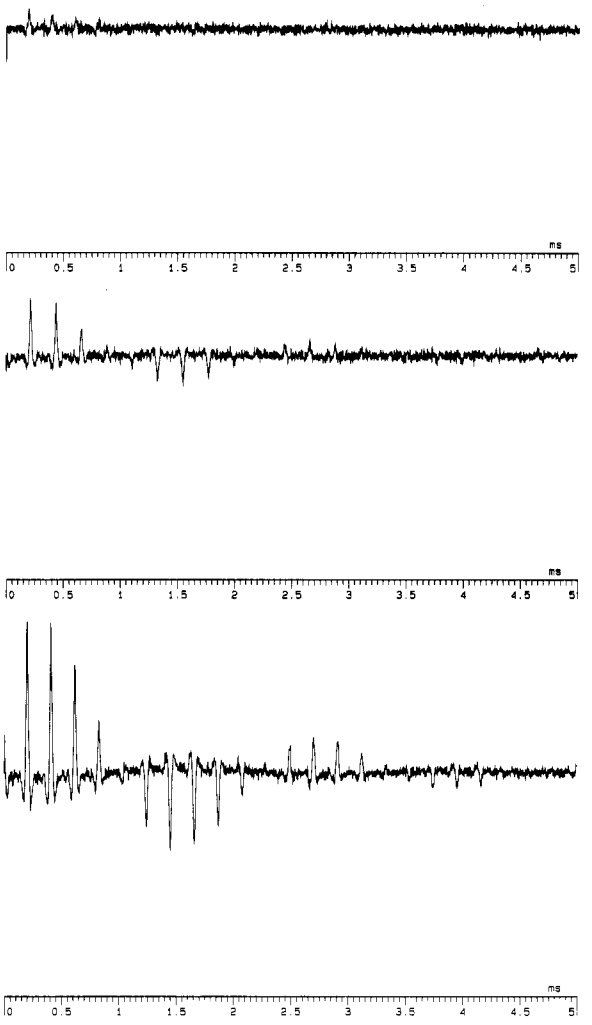

Figure 1. Time domain ^2H CP/MAS spectra of *syn*-PMMA-d_8 and *syn*-PMMA-d_8 (18.8%)/poly(vinylphenol) blends. All spectra were recorded under identical conditions with a 3-ms contact time, a delay of 4 s between pulses, and an average of 20 000 transients. (a) Only a very weak signal due to cross-polarization from residual protons is observed in a 56-mg sample of pure *syn*-PMMA-d_8. (b) ^2H time domain spectrum of a partially phase-separated *syn*-PMMA-d_8 (18.8%)/poly(vinylphenol) blend, solvent cast from THF. The sample contains 49.2 mg of *syn*-PMMA-d_8. (c) ^2H time domain spectrum of the corresponding single phase blend prepared by precipitation from MEK. Note the better signal-to-noise ratio, even though the sample contains only 22.7 mg of the deuterated polymer.

The time domain deuterium CP/MAS spectra for nominally perdeuterated *syn*-PMMA-d_8 and its blends with PVPh are shown in Figure 1, together with the experimental conditions. The time domain spectra (fids) consist of a series of rotational echoes spaced by the MAS rotation period. The pure *syn*-PMMA-d_8 sample (56.2 mg) displays a very weak deuterium signal that originates from cross-polarization from a small amount of residual protons (<2%). This signal can be readily suppressed, however, by taking advantage of the long spin–lattice relaxation of the isolated residual protons.

Figure 1b shows the CP/MAS spectrum of the blend displaying two distinct glass transition temperatures. The sample contained 49.2 mg of deuterated material. Significant cross-polarization intensity is observed, from the interfacial regions of the phase-separated material. The spectrum of the single-phase blend is shown in Figure 1c. A stronger signal is observed compared to Figure 1b, even

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though a smaller sample, containing only 22.7 mg of the deuterated material, was used. Clearly, the bulk of phase-separated *syn*-PMMA-d_8 does not contribute to the signal in Figure 1b.

Unlike the more common CP/MAS experiments involving polarization transfer from ^1H to other spin $^1/_2$ nuclei such as ^{13}C, ^{29}Si, or ^{15}N, the ^1H–^2H CP process does not offer a sensitivity enhancement. That is true in part because the Hartman–Hahn condition is satisfied only during some part of the rotational period. The CP process, however, is a sensitive and versatile gauge of ^1H–^2H proximity.

The absence of a deuterium background enables miscibility studies of minor components present in concentrations of less than 10%. This is particularly important when trying to characterize the fate of block copolymer compatibilizers used to promote interfacial adhesion in immiscible blends. Micellization of the compatibilizer in one of the phases reduces its efficacy. A deuterated compatibilizer molecule at the interface would display cross-polarization, while it would yield no signal in its micellar form with no protons in its immediate environment.

Polarization transfer between protons and deuterium also has implications beyond the simple detection of polymer miscibility. Deuterium MAS spectra are often resolved if the spinning angle is painstakingly adjusted.[12] Furthermore, double quantum techniques can enhance this resolution.[13] Thus, by monitoring the relative cross-polarization rates for the various kinds of deuterons, we can extract information about the mutual orientation of two strongly interacting polymer chains and thus begin to understand the factors that drive miscibility at the molecular level.

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