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Intermolecular Proton–Deuterium Polarization Transfer in Magic Angle Spinning NMR Spectra: A New Spectroscopic Tool for Interfaces

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The combination of cross-polarization (CP) and magic angle spinning (MAS)[1] is a well-established method for obtaining high-resolution NMR spectra of solids and has been used primarily in recording the spectra of spin $^1/_2$ nuclei such as ^{13}C, ^{29}Si, and ^{31}P. Some results involving the central transition of half-integer quadrupolar nuclei such as ^{17}O and ^{29}Al ($I = {}^5/_2$) have been reported,[2,3] and the underlying theory has been discussed by Vega.[4] Deuterium, on the other hand, is an integer spin nucleus ($I = 1$), and its NMR spectrum has been used extensively to characterize the dynamics and orientation of polymers[5,6] and biological macromolecules. These studies are based on the detailed analysis of the powder patterns (Pake doublets) obtained from nonspinning samples using one- and two-dimensional NMR. In this communication we report for the first time an approach that combines deuterium NMR with cross-polarization and magic angle spinning. In the systems we have studied, cross-polarization is an intermolecular process. Hence, it gives rise to novel experimental opportunities for studying both the miscibility of polymer blends and polymer–diluent or guest–host interactions and for selectively accessing the interfacial region between protonated and deuterated phases by solid-state NMR.

The broad, so-called Pake doublet observed in the static ^{2}H 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 give rise to rotational echoes in the ^{2}H free induction decay.[7,8] Several recent papers have investigated ^{2}H MAS spectra both theoretically[9,10] and experimentally for the purpose of solids imaging,[11] sensitivity enhancement,[12] resolution of inequivalent deuterium sites,[13] and ^{2}H–^{13}C internuclear distance determinations via rotational echo double resonance (REDOR).[14] With the exception of the latter, these experiments were run in the absence of proton spin decoupling, and in the case of spin imaging studies,[11] the predicted dephasing[15] of the rotational echoes due to proton–deuteron dipolar interactions has been observed.

We have observed cross-polarization between protons and deuterium under MAS conditions in several partially deuterated materials, solid solutions, and polymer blends. In the following, we report our results on a 20% blend of perdeuterated atactic poly(methyl methacrylate) (PMMA-d_8) in protonated atactic PMMA (PMMA-h_8). The characterization of the PMMA samples has been previously reported.[16] The ^{2}H free induction decay obtained by a standard ^{1}H–^{2}H cross-polarization sequence using spin–temperature alternation and a contact time of 1.5 ms is shown in Figure 1a. It consists of a series of rotational echoes

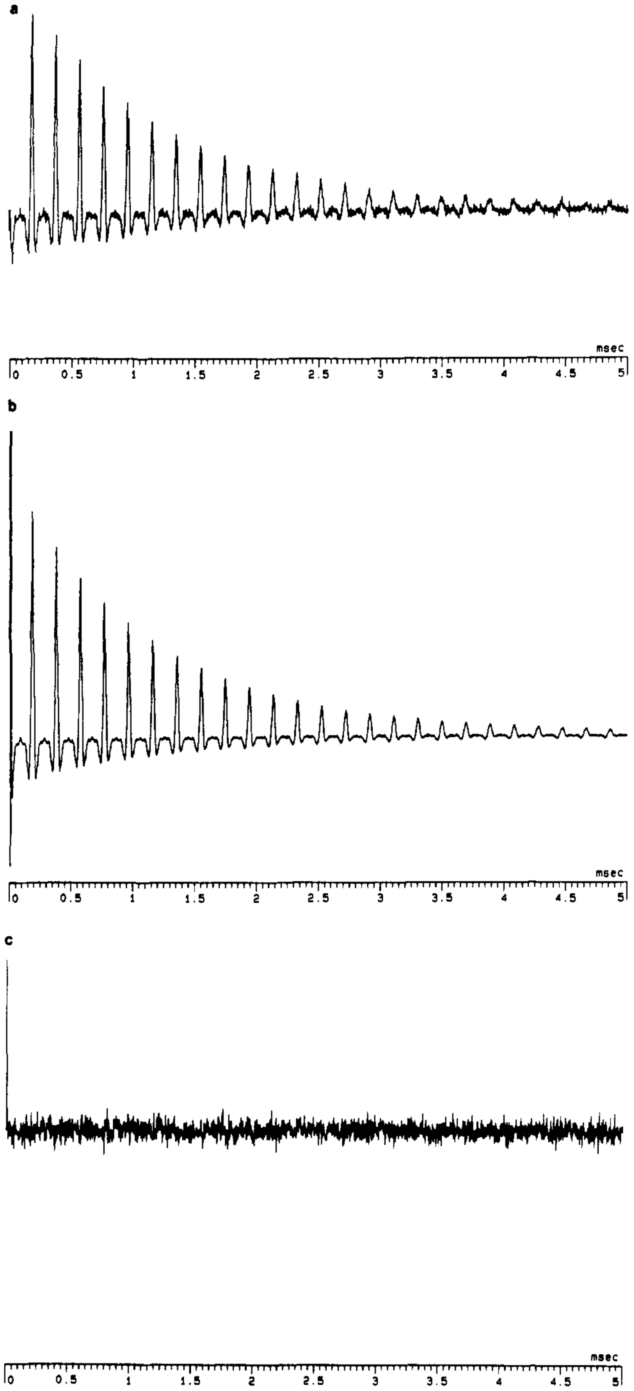

Figure 1. Deuterium MAS spectra of a blend of PMMA-d_8 (20%) in PMMA-h_8. (a) ^{2}H time domain spectrum following cross-polarization from protons with a contact time of 1.5 ms and a 46-KHz spin-lock radiofrequency field. The rotational echoes are separated by the rotor period (~191 μs) and persist for over 6 ms. Average of 13 000 transients. (b) ^{2}H time domain spectrum following a 5.4-μs 90° pulse. Average of 2300 transients. (c) No signal is observed in pure PMMA-d_8 after averaging 6376 transients. The delay between pulses was 5 s for all spectra.

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(1) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976,** *98,* 1031.

(2) Blackwell, C. S.; Patton, R. L. *J. Phys. Chem.* **1984,** *88,* 6135.

(3) Walter, T. H.; Turner, G. L.; Oldfield, E. *J. Magn. Reson.* **1988,** *76,* 106.

(4) Vega, A. *Solid State Nucl. Magn. Reson.* **1992,** *1,* 33.

(5) Spiess, H. W. *Chem. Rev.* **1991,** *91,* 1321.

(6) Jelinski, L. W. *Annu. Rev. Mater. Sci.* **1985,** *15,* 359.

(7) Maricq, M. M.; Waugh, J. S. *J. Chem. Phys.* **1979,** *70,* 3300.

(8) Ackerman, J. L.; Eckman, R.; Pines, A. *Chem. Phys.* **1979,** *42,* 423.

(9) Ye, C.; Sun, B.; Maciel, G. E. *J. Magn. Reson.* **1986,** *70,* 241.

(10) (a) Clayden, N. J. *Chem. Phys. Lett.* **1986,** *131,* 517. (b) Kristensen, J. H.; Bildsoe, H.; Jakobsen, H. J.; Nielsen, N. C. *J. Magn. Reson.* **1992,** *100,* 437.

(11) Günther, E.; Blümich, B.; Spiess, H. W. *Chem. Phys. Lett.* **1991,** *184,* 251.

(12) Schadt, R. J.; Dong, R. Y.; Günther, E.; Blümich, B. *J. Magn. Reson.* **1992,** *96,* 393.

(13) Kim, A. J.; Butler, L. G. *J. Magn. Reson.* **1992,** *99,* 292.

(14) Schmidt, A.; McKay, R. A.; Schaefer, J. *J. Magn. Reson.* **1992,** *96,* 644.

(15) Gruwel, M. L. H. *Chem. Phys. Lett.* **1992,** *191,* 621.

(16) O'Reilly, J. M.; Teegarden, D. M.; Wignall, G. D. *Macromolecules* **1985,** *18,* 2747.

0002-7863/93/1515-4407$04.00/0

spaced by the sample rotation period (~191 μs). It is identical to the single pulse excitation spectrum (Figure 1b), only weaker due to inefficiencies in the cross-polarization process. No cross-polarization was observed in a sample of PMMA-d_8 (Figure 1c) because of the very low concentration and long spin–lattice relaxation time of any residual protons. It has been our experience that the spin–lattice relaxation of residual protons in perdeuterated glassy and crystalline systems is longer than that in the corresponding protonated materials. In polystyrene-d_8, for example, the residual proton T_1 is longer than 15 s (Zumbulyadis and O'Reilly, unpublished results). Thus, ^{1}H–^{2}H cross-polarization in such systems showed be viewed as a primarily *intermolecular* process unless the spectrum of the perdeuterated material by itself points to the contrary.

We have measured the cross-polarization rate in the PMMA/PMMA-d_8 blend system by monitoring the dependence of the third, fourth, and fifth rotational echo on contact time (cf. Figure 2). A value of 2.3 ms was determined for the cross-polarization time constant T_{CP}.

We have determined that protonated and deuterated PMMA are miscible, as was assumed in the interpretation of small-angle neutron scattering experiments.[16] Previous NMR determinations of polymer miscibility by intermolecular cross-polarization have relied on polarization transfer from the protons of one polymer to the ^{13}C nuclei of another, perdeuterated, component.[17] Such studies presume, however, that the typically weak ^{13}C signals of the deuterated component are sufficiently resolved and can be distinguished from the stronger and potentially overlapping signals of the protonated species. This problem cannot be always allayed by a simple delayed decoupling experiment, since quaternary carbons and carbonyls and their associated spinning sidebands cannot be effectively suppressed in this manner. Our approach circumvents this difficulty. The lack of an interfering deuterium background allows miscibility or, stated more generally, molecular proximity studies in systems where one of the components is present in very low concentrations. Such a situation arises in the technologically important case of block copolymer compatibilizers or in the biochemically important case of studying small amounts of a host in a guest matrix. While some of these experiments may also be possible through ^{1}H–^{13}C cross-polarization coupled with double isotopic labeling, e.g., simultaneous deuteration *and* ^{13}C enrichment, our approach eliminates the need for such cumbersome syntheses. Finally, the well-known spectral editing potential of CP/MAS experiments could lead to improvements in solid-state deuterium NMR imaging.[11]

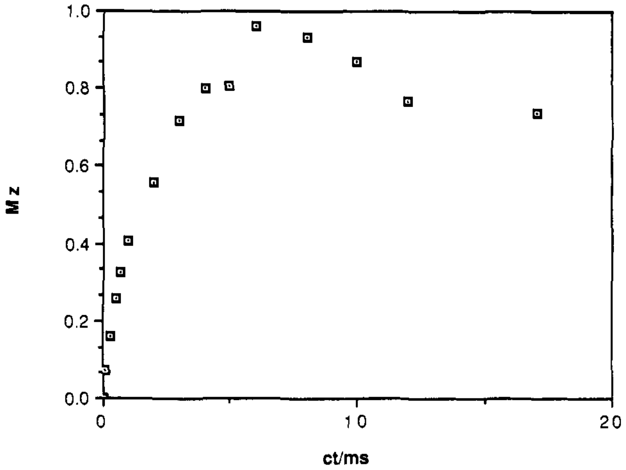

Figure 2. Proton–deuterium cross-polarization dynamics of 20% PMMA-d_8 in PMMA-h_8. The average of the normalized intensities of the third, fourth, and fifth rotational echo is plotted as function of CP contact time.

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[17] (a) Parmer, J. F.; Dickinson, L. C.; Chien, J. C. W.; Porter, R. S. *Macromolecules* **1987**, *20*, 2308. (b) Gobbi, G. C.; Silvestri, R.; Russell, T. P.; Lyerla, J. R.; Fleming, W. W. *J. Polym. Sci. Polym. Lett.* **1987**, *25*, 61.