Macromolecules

Volume 37, Number 6 March 23, 2004

Communications to the Editor

Two-Dimensional ^{13}C NMR with ^{1}H Spin Diffusion for Characterizing Domain Sizes in Unlabeled Polymers

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Received May 19, 2003
Revised Manuscript Received January 16, 2004

In chemically or physically heterogeneous solid polymer materials, ^{1}H spin diffusion solid-state nuclear magnetic resonance (NMR) can provide information on sizes of domains, heterogeneities, and interfaces on a length scale of 0.5−50 nm.[1−3] It can be applied in the absence of long-range order and may be combined with mobility and conformational studies. The approach is based on tagging of ^{1}H magnetization in one-phase, subsequent diffusion of ^{1}H magnetization into other regions during a mixing time t_m and finally observation of the integral magnetization in each phase in terms of peak areas in the ^{1}H or, after cross-polarization, the ^{13}C spectrum.[2] If domains are small, reequilibration will be fast, while for large domains, the signal change as a function of t_m will be slow. Using spin-diffusion coefficients determined in other experiments,[2,4−6] the measured t_m dependence of the peak intensities can be converted into an interfacial area per volume and finally into approximate domain sizes. ^{1}H $T_{1\rho}$ measurements, though also based on ^{1}H spin diffusion, provide a much cruder estimate of domain size, identifying only whether or not component polymers are mixed below a cutoff length scale determined by the intrinsic $T_{1\rho}$ relaxation times of the polymers.

One of the main limitations to an even wider application of detailed ^{1}H spin diffusion experiments has been insufficient contrast between different component polymers.[2,7,8] In particular, for systems consisting of two rigid polymers, only techniques based on proton chemical shift differences have been available. These are of limited use because they require major structural differences between the components; in addition, they are experimentally rather demanding. Therefore, methods with polymer identification by the much better resolvable ^{13}C chemical shifts are desirable for studies of nanocomposites of structurally similar polymers. This requires a two-dimensional experiment with the high site resolution of ^{13}C in both dimensions and fast ^{1}H spin diffusion during the intervening mixing time t_m.[9]

For ^{13}C-enriched samples, triple cross-polarization techniques (^{1}H to ^{13}C, ^{13}C evolution, ^{13}C to ^{1}H, ^{1}H spin diffusion, ^{1}H to ^{13}C, ^{13}C detection) can be used to achieve such a correlation between carbons via ^{1}H spin diffusion.[10,11] However, for ^{13}C in natural abundance (1.1%) and given typical H:C ratios of between two and one, the sensitivity of the triple-CP method is 0.5−1% of the regular cross-polarization/magic-angle spinning (CP/MAS) spectrum. This is insufficient unless the signal for each spectrum is averaged over multiple days. The dramatic sensitivity reduction is due to the second CP step, from one ^{13}C spin to 90−180 ^{1}H spins, which results in a polarization per spin of only 0.5−1% of the thermal equilibrium value.

In this Communication, we introduce a new technique for two-dimensional (2D) $^{13}C-^{13}C$ NMR with exchange by ^{1}H spin diffusion. It is practical for many unlabeled multicomponent polymers due to a more than 4-fold sensitivity enhancement, or 20-fold reduction in measuring time, that is achieved by multiple depolarization of protons.[12] As indicated in the pulse sequence of Figure 1, every ^{13}C spin depolarizes the nearby proton spins multiple times in CP periods that alternate with t_1 evolution periods. The depolarization of these protons depends on the magnetization state of ^{13}C at the end of t_1; thus, the ^{13}C frequency ω_1 modulates the proton magnetization. To yield clean 2D spectra where the signal in ω_1 is exclusively due to the ^{13}C-modulated protons, the pulse sequence uses multiple alternating depolarization (MAD), which was introduced by Khitrin

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10.1021/ma034659b CCC: $27.50
Published on Web 02/19/2004

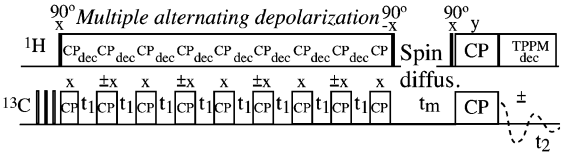

Figure 1. Basic pulse sequence for 2D MAD C(HH)C NMR. The crucial two-scan phase cycle for multiple alternating depolarization is indicated. ^{1}H spin diffusion occurs during the mixing time t_m. CP indicates standard Hartmann−Hahn cross-polarization, "dec" heteronuclear decoupling, TPPM two-pulse phase modulation for improved decoupling.

and Fung[12] in ^{2}H NMR with ^{1}H detection; they showed that multiple alternating depolarization can be combined with undistorted t_1 evolution and effectively suppresses the signal of all protons that are too far from the X nucleus to experience its dipolar field during the CP periods. More details of the spin dynamics in this process will be published elsewhere.[13]

After ^{1}H spin diffusion during the mixing time t_m, the MAD-selected ^{1}H magnetization and its modulation by the ^{13}C ω_1 frequency is transferred, via cross-polarization, to ^{13}C within the range reached by the ^{1}H spin diffusion. The second ^{13}C frequency is recorded in ω_2. A cross-peak at ($\omega_1 = \omega_A$, $\omega_2 = \omega_B$) indicates ^{1}H spin diffusion from a ^{13}C of segment or polymer component A to a ^{13}C of segment or polymer component B. In contrast to ^{13}C spin diffusion,[14,15] which shows complex cluster dynamics, the ^{1}H spin diffusion used here is simple to analyze.[1,2,16] The known ^{13}C density provides an internal size standard on a scale <2 nm: The relative cross-peak intensity can be converted into a volume reached by the magnetization, by adopting an ensemble-average description where each carbon site is labeled by ^{13}C at a level of 1.1%. This is illustrated in examples below.

Figure 2 shows spin diffusion between different segments within the crystallites of annealed iPP as an example of the clean 2D spectra obtained easily with this method. With increasing mixing time t_m, the transfer of magnetization between the various $^{13}CH_n$ groups, which are typically separated by 0.8 nm,[14] results in increasing cross-peaks. Equilibrium has been reached when each row of the spectrum is equal to the regular 1D spectrum. Within this homopolymer, this is the case for spin diffusion times $t_m \geq 3$ ms.

As a nontrivial application, Figure 3 shows MAD C(HH)C spectra of a commercial miscible blend (Noryl) of polystyrene, PS, and poly(xylylene ether), PXE (also known as poly(dimethyl phenylene oxide), PPO, or poly-(1,6-dimethylphenylene ether), PPE). In this system, traditional ^{1}H magnetization selection methods are severely hampered by poor ^{1}H chemical shift contrast,[17] since both component polymers contain aliphatic and aromatic protons. At $t_m = 0$ (Figure 3a), some spin diffusion occurs during the ^{1}H spin lock needed for the various cross-polarization periods. In the spectrum, cross-peaks between PXE signals predominate, which indicates preferred proximity of PXE units to other PXE units. The 1:3 ratio of the total cross-peak area to the diagonal-peak integral, seen most easily in the cross sections shown in Figure 3a, indicates that the probability of finding a second ^{13}C in the volume probed by spin diffusion is ca. $^1/_3$. Given the 1:90 ^{13}C:^{12}C ratio, the probability of finding a ^{13}C among 30 carbons is $^1/_3$. Thus, we conclude that at these cross-polarization times the experiment probes a volume of ca. 30 carbons, or 4 repeat units. The effective diameter of this volume is

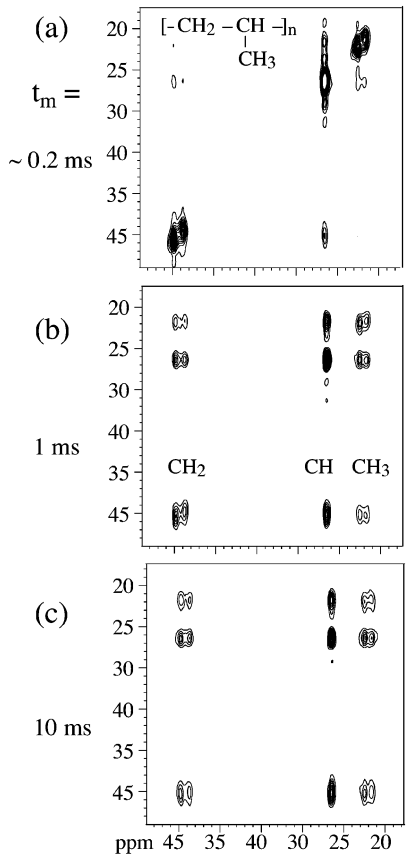

Figure 2. Series of 2D MAD C(HH)C spectra of semicrystalline iPP as a function of mixing time. The three spectra shown were acquired within 9 h total at a spinning frequency of 5 kHz. For (a), we used $n = 5$ depolarization periods with CP times of 0.2 ms each; for (b) and (c) $n = 11$ with CP times of 0.4 ms each.

ca. 1.1 nm. An alternative analysis of the length scale probed by spin diffusion during the CP spin-lock, based on $\langle x^2\rangle^{1/2} = (2D_{eff}t_{eff})$ with an effective $D = 0.07$ nm^2/ms measured independently[6] and with an average mixing time of $t_{CP}/2 = 3$ ms, yields an effective diameter of $2\langle x^2\rangle^{1/2} = 1.3$ nm. It is clear that the magnetization distribution does not have a sharp 1.3 nm cutoff but extends out to somewhat longer distances.

After an additional $t_m = 0.5$ ms (Figure 3b), cross-peaks between both component polymers are detected more clearly, but spin diffusion within PS (see middle cross section) still predominates slightly. On the basis of the >1:1 total cross-peak:diagonal-peak areas, we estimate that the volume probed here corresponds to a sphere of ca. 1.6 nm diameter around the ^{13}C encoded in the ω_1 dimension; this sphere contains ca. 100 carbon atoms, or 12 polymer repeat units, of which a small majority are of the same type as the central unit. This indicates heterogeneities consisting on average of ca. 5 repeat units of one polymer, which shows that PS and PXE are mixed almost homogeneously: In the local environment, three repeat units of one type are always tied together due to polymer connectivity, and a couple of repeat units from other chains of the same type are nearby statistically. This result is in qualitative agreement with the analysis of ^{1}H-detected spin diffusion experiments on a similar PS−PXE blend.[17] After $t_m =$ 2 ms (see Figure 3c), equilibrium has been approached, as indicated by similar relative cross-peak intensities in all slices.

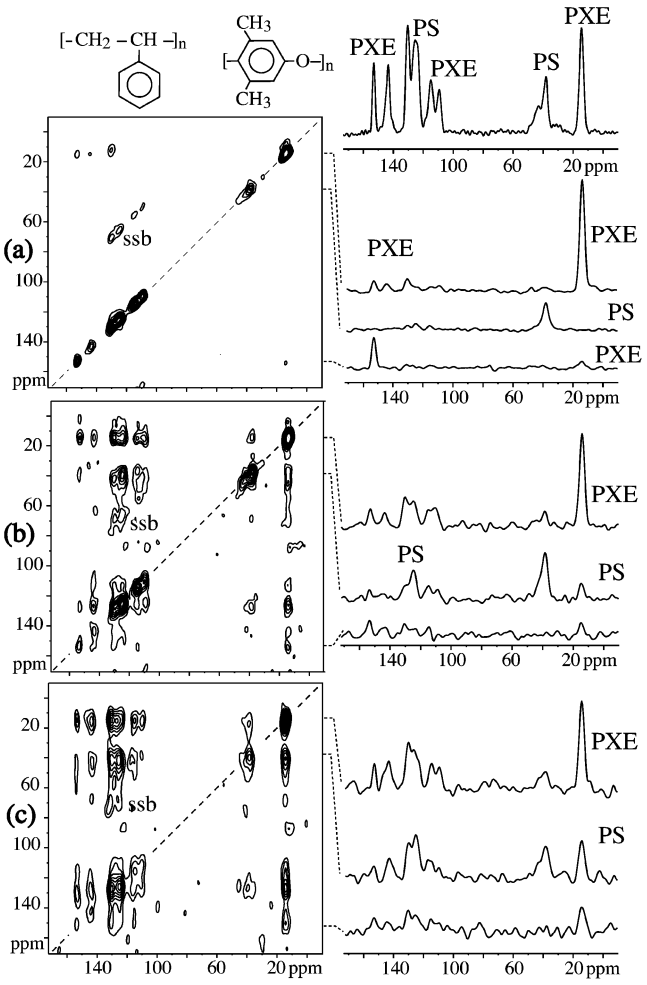

Figure 3. 2D MAD C(HH)C spectra of PS/PXE for different mixing times. The regular 1D CP/MAS spectrum of the blend is shown at the top on the right. (a) Nominal $t_m = 0.01$ ms, (b) $t_m = 0.5$ ms, and (c) $t_m = 2$ ms. Cross sections at the indicated ω_1 positions are shown on the right. We used $n = 11$ depolarization steps of 0.5 ms duration each. The final CP time before detection was 1 ms, and the spinning frequency 6 kHz. The label "ssb" marks spinning sidebands in ω_1, while TOSS (total suppression of sidebands) was used in ω_2. Measuring time: 17 h per 2D spectrum.

The experimental total cross-peak efficiencies, measured with $t_1 = 0$ and $t_m = 10$ ms relative to the standard CP/MAS spectrum, are 2.1% in iPP and 3.2% in PS/PXE, which exceeds the theoretical efficiency of the triple-CP experiment[10,11] by a factor of 4. The difference between iPP and PS/PXE is expected on the basis of their different carbon:proton ratios. The MAD C(HH)C method requires a sufficiently long $T_{1\rho} > 5$ ms in order to allow enough time for the multiple CP and t_1 periods. However, if only low resolution in ω_1 is required, a shorter $T_{1\rho}$ may be acceptable. The experiment is quite simple to set up, requiring only a good Hartmann–Hahn match and ^{1}H pulse length, which are adjusted as part of routine setup for CP/MAS NMR. Spinning sidebands in ω_1 are no different than in traditional exchange spectra at the same spinning frequency. Limited sensitivity is still the main complicating factor, despite the more than 4-fold signal enhancement achieved. A more detailed discussion of multiple alternating depolarization, the phase sequence for the "sine data set" as used for the spectra in Figure 3, the experimental efficiency, optimum CP times, further sensitivity enhancement by multiple-echo detection, and the length scale probed will be given in a technical paper.[13]

Acknowledgment. K.S.R. thanks P. J. Grandinetti for a stimulating discussion and D. L. VanderHart for helpful comments. This manuscript has been authored at Iowa State University and Ames Laboratory under Contract W-7405-ENG-82 with the U.S. Department of Energy.

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MA034659B