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Carbon-13 Rotor-Driven Spin Diffusion in a Polymer Blend

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Rotor-driven spin diffusion is being developed as a tool for structure determination in systems which are not readily amenable to traditional techniques.[1-5] So far the prospective systems include polycrystalline samples of large or insoluble proteins, membrane proteins, self-assembling proteins, and other complex biological systems with some examples already studied. In this paper, rotor-driven spin diffusion is applied to an amorphous, glassy polymer blend in order to ascertain the magnitude of the effect and the prospects for measurement of intermolecular distances in such systems.

Rotor-driven spin diffusion is typically applied to rare spins where well-resolved spectra are produced by magic angle spinning (MAS). Spin exchange between two resolved lines can be enhanced by fulfilling the rotational resonance condition, i.e., matching an integer multiple of the rotor speed ($n\omega_r$) to the frequency separation ($\Delta\omega$) of the lines, $\Delta\omega = n\omega_r$. The presence of this type of spin exchange has been demonstrated for carbon-13 in natural-abundance systems[2] and in doubly labeled systems.[1,3-5] The technique has been shown to lead to quantitative distance information in a doubly labeled small molecule[1] where a simulation[6] of the time dependence of spin exchange leads to a value for the spatial separation of the two labeled carbons. Subsequently, distances in doubly labeled biological systems[3-5] have also been determined by a similar procedure.

A variation of the approach is considered here where spin exchange between a labeled carbon on one polymer repeat unit and natural-abundance carbons on another type of polymer repeat unit in a miscible blend will be observed. Proton-driven spin exchange[7] in this type of system has been studied before, but the expectation is that the rate of rotor-driven spin diffusion will be much larger, providing a better basis for quantitative information. Rotational resonance restricts spin diffusion to the pair of carbons satisfying the condition while proton-driven spin diffusion involves all resonances simultaneously. Also, the successful determination of distances from rotor-driven spin diffusion in complicated biological systems is encouraging.

The polymer blend selected for study is poly(2,6-dimethyl-1,4-phenylene oxide) and polystyrene where one methyl group in every repeat unit of the former polymer is carbon-13 labeled.[7] To keep carbon-13 as a rare spin, the ratio of polystyrene (PS) to poly(2,6-dimethyl-1,4-phenylene oxide) (PXE) is chosen to be 10 to 1 or higher. The polymer repeat unit structures and a typical MAS spectrum is shown in Figure 1.

The rotational resonance experiments were performed on a Bruker MSL 300 NMR spectrometer. To enhance the effects of spin exchange, one line of the pair of lines under rotational resonance is inverted with a DANTE sequence.[8] The full pulse sequence for the experiment is shown in Figure 2, and the amount of spin exchange is monitored as a function of the mixing time. To separate spin–lattice relaxation from spin diffusion, the experiment is performed with and without decoupling during the mixing time.[2] With decouping, the resonance lines are sharp and the rotational resonance condition will be met. Without decoupling, the lines are dipolar broadened, thereby obviating the effect of the rotational resonance condition.

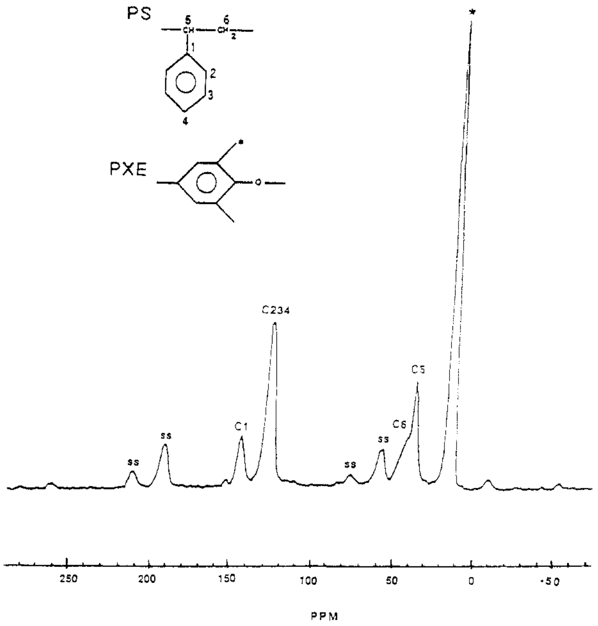

Figure 1. Carbon-13 MAS spectrum of the PS/carbon-13-labeled PXE (5 wt %) blend. The peaks are labeled according to the structures. First-order side bands of the aromatic peaks are denoted by "ss".

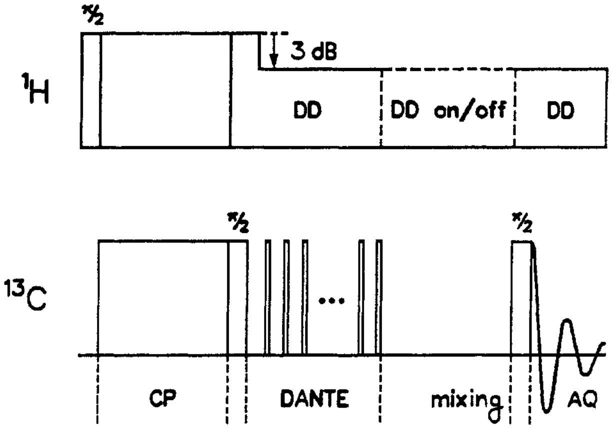

Figure 2. Pulse sequence for observation of carbon-13 spin exchange under rotational resonance conditions using a DANTE sequence to invert one of the participating carbon resonances. Typical parameters are a $\pi/2$ pulse width of 4 μs and a cross-polarization time of 2 ms. The DANTE sequence consists of 23 0.6-μs pulses separated by 76-μs intervals.

Figure 3 shows the change in intensity of the protonated phenyl carbons of PS in rotational resonance ($n = 2$) with the inverted methyl resonance of PXE with and without decoupling. In the presence of decoupling, the decay of intensity is more than an order of magnitude faster, indicating the presence of rapid spin exchange produced by rotational resonance. The apparent time constant for rotor-driven spin exchange is much shorter than that for proton-driven spin diffusion measured previously.[7]

Because of the choice of a labeled PXE unit at a concentration of 10 wt % and unlabeled PS units, only

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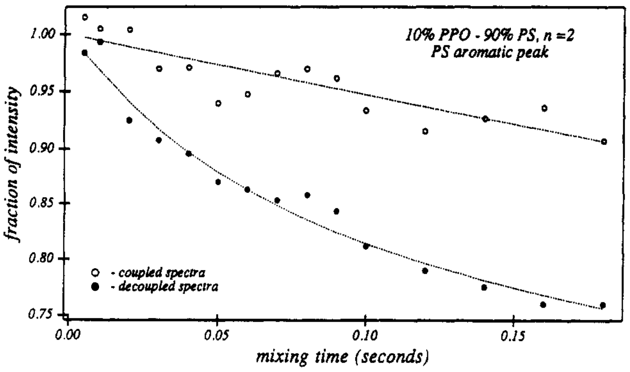

Figure 3. Intensity of the phenyl carbons versus time for 10 wt % PXE in PS. The filled and open circles are data taken with and without proton decoupling during the mix time, respectively. In both cases the labeled methyl peak of the PXE is inverted by the DANTE sequence and n is set to 2 ($\omega_r/2\pi$ = 4187 Hz). The lines represent fits to eqs 1 and 2.

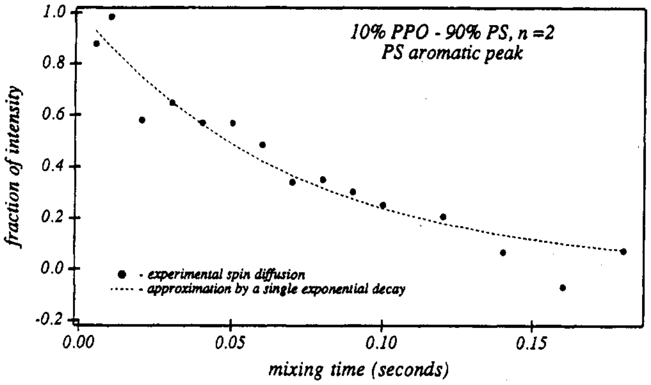

Figure 4. Fraction of the phenyl carbons' signal intensity affected by rotor-driven spin diffusion versus time.

Table I. Decay Times

composition (% PXE)	site	n	T_1 (s)	SD (s)
5	C234	2	1.3	0.014
5	C5	1	2.0	0.032
5	C6	1	1.1	0.071
10	C234	2	1.9	0.060

some fraction ϕ of the PS units is in close contact with PXE units. If the PS intensity decays as a function of mixing time t with the time constant T_1 in the coupled experiment,

$$A(t) = A_0 \exp(-t/T_1) \qquad (1)$$

then the decay of intensity during the decoupled experiment would be given by

$$A(t) = (1 - \phi)A_0 \exp(-t/T_1) + \phi A_0 \exp[-(t/T_1 + t/\mathrm{SD})] \qquad (2)$$

where an exponential time constant SD is assumed to describe the change in intensity with time from the spin diffusion process. If eq 1 weighted by the factor $1 - \phi$ is subtracted from eq 2, only the fraction of PS units influenced by spin diffusion is considered. A plot of the time dependence of this portion of the intensity is shown in Figure 4 for the aromatic PS carbons.

The same experiment and analysis were carried out for the partially resolved aliphatic backbone carbons of PS under rotational resonance produced by $n = 1$ ($\omega_r/2\pi$ = 1750 and 2000 Hz for C5 and C6, respectively). Table I summarizes the time constants obtained for the phenyl carbons and the aliphatic carbons. The SD values have an uncertainty of less than 10%. In all cases, rotor-driven spin diffusion produces more rapid intensity decay than spin–lattice relaxation, which is desirable if a quantitative interpretation is to be attempted.

Qualitatively, the rotor-driven spin diffusion observed here is in agreement with the proton-driven spin diffusion previously observed on these samples. Stronger proton-driven spin diffusion was observed to the phenyl carbons of PS than to the backbone carbons. In the simplistic analysis just presented, rotor-driven spin diffusion to the phenyl carbons with $n = 2$ is comparable to that to the backbone carbons with $n = 1$. Simulation of intensity changes with mixing time developed by Griffin et al.[6] shows that spin diffusion for $n = 1$ is expected to be greater than that for $n = 2$ if distance and orientation factors are comparable. Rotor-driven spin diffusion could be comparable for $n = 1$ to the backbone and $n = 2$ to the phenyl group if the phenyl group were closer to the methyl group of PXE as was concluded in the proton-driven spin diffusion study.

A quantitative evaluation using the simulation approach of Griffin et al.[6] is being developed to interpret the results obtained on this blend. Key parameters in the simulation are the order of rotational resonance n, internuclear distance r, relative orientation of the shielding tensors, and the zero quantum dephasing time constant T_{2ZQ}. For shorter distances and longer T_{2ZQ}, oscillations in the intensity with mixing time are expected and observed in simple cases.[1] There is some evidence of oscillatory behavior present in the decay curves (Figures 3 and 4), but in an amorphous blend intermolecular distances will be given by a distribution rather than a single value and this will presumably dampen the oscillatory behavior. This aspect is still under consideration. Thus far, the simulation efforts lead to distances around 5 Å, which is again consistent with the proton-driven results and modeling of the blend.[7]

At this stage there is sufficient promise in the rotor-driven spin diffusion results obtained here to motivate the pursuit of a more complete interpretation in spite of the isotopic labeling requirement which appears desirable. The ideal outcome would be the development of a structure-determining procedure for glasses comparable to that now on hand for determining protein structures in solution using two-dimensional NMR. This aspiration was initially expressed by the developers of the rotational resonance technique in regard to carbon-13-labeled biological systems,[1,2] and it can now be extended to include polymeric glasses.

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