Application of 2-D HETCOR NMR to Investigate Polymer Blend Heterogeneity

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Introduction:

Most NMR techniques for determining domain structures in polymeric systems are based upon the classic Goldman-Shen experiment [1]. Domain sizes are calculated from the time for spin diffusion to transfer magnetization from one region of the sample to another. These experiments generally require resolution of the individual components in the proton spectrum, although recent experiments [2] demonstrate that, in some cases where there is inadequate proton chemical shift resolution, it is possible to follow the evolution of spin diffusion when the constituents have significant differences in proton lineshapes.

An alternative approach to analyzing domain structures entails application of heteronuclear $^{13}C-^{1}H$ NMR. Of the several techniques introduced to measure heteronuclear correlated spectra in the solid state, a particularly effective method has been proposed by Burum and Bielecki [3]. In the basic 2-D experiment, crosspeaks occur primarily for carbon-proton distances of less than ~3 Å. By incorporation of a spin diffusion evolution time, crosspeak intensities reflect longer range couplings, thus enabling conformational and domain size analyses [4]. This latter experiment consists (Fig. 1) of an evolution period during which homo- and heteronuclear interactions are suppressed by simultaneous application of BLEW-24 (^{1}H) and BB-24 (^{13}C) pulse sequences, a waiting period without rf during which exchange of magnetization (spin diffusion) takes place, a mixing period for isotropic cross polarization transfer of proton magnetization to carbons utilizing WIM-24 sequences on both nuclei, and finally, carbon acquisition with proton decoupling. In this paper we examine the
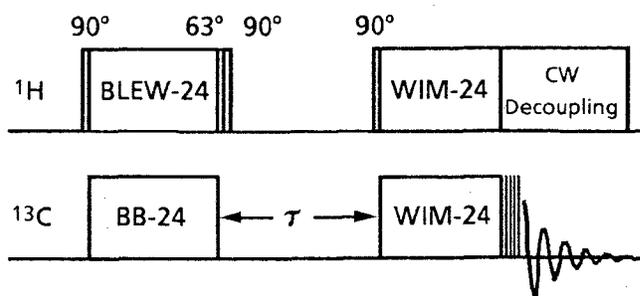

Figure 1. The HETCOR Experiment

applicability of the HETCOR technique to investigate domain sizes in a two component blend.
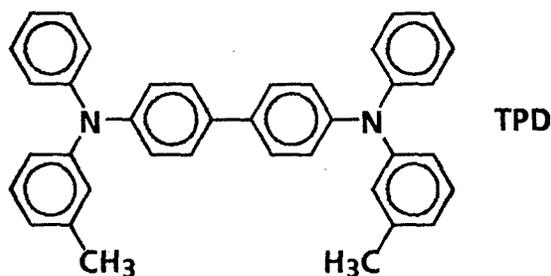
Results and Discussion:

We have chosen for the present study a blend of an aromatic diamine, N,N'-diphenyl-N-

1. Goldman, M.; Shen, L. *Phys. Rev.* 1966, *144*, 321.

2. Campbell, G.C.; VanderHart, D.L. *J. Magn. Reson.* 1992, *96*, 69-93.

3. Burum, D.P.; Bielecki, A. *J. Magn. Reson.* 1991, *94*, 645-652.

4. Simpson, J.H.; Ruggeri, G.; Rice, D.M.; Karasz, F.E., submitted.

N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) in a bisphenol A polycarbonate matrix. Pure TPD is highly crystal-

line, with a melting point of $T_m = 167$ °C and a glass transition temperature of $T_g = 63$ °C [5]. A well mixed 50/50 blend with polycarbonate ($Tg = 137$ °C) cast from methylene chloride is amorphous and shows a single T_g of ~89 °C. Since the aromatic region of the ^{13}C spectrum of the blend has severe overlap, we have focused our analysis on the aliphatic region, where the individual component methyl resonances are resolved.

Figure 2 shows contour plots of the carbon aliphatic region in the two dimensional HETCOR spectra as a function of the spin diffusion mixing time. The ^{13}C peaks at 22 ppm and 32 ppm are from TPD and polycarbonate methyl carbons, respectively. Crosspeaks in the 20 μs mixing time plot are due primarily to short range directly bonded carbon-proton couplings. However, with increasing mixing times, longer range correlations, e.g., between the methyl carbons and aromatic protons, intensify. Ultimately, for very long spin diffusion times, the relative signal intensities for the contours associated with a particular carbon will reflect quantitatively the chemical shift distribution of protons that are within an effective range of spin diffusion from the protons directly bonded to that carbon. Figure 3 shows the volume integral fraction of aliphatic protons for the polycarbonate and TPD methyl carbons as a function of spin diffusion time. Both curves asymptote to an
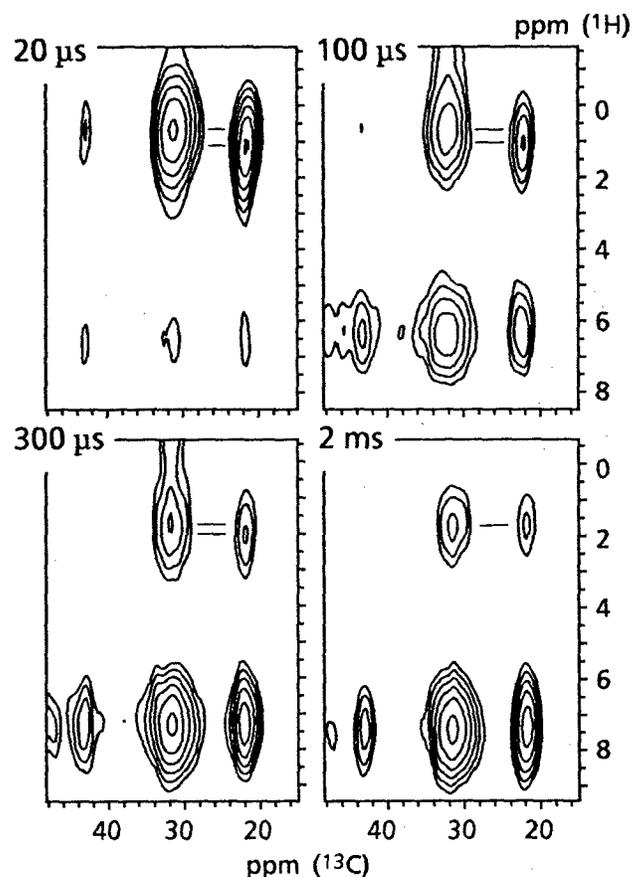

Figure 2. HETCOR contour plots of the aliphatic carbon region of a 50/50 (wt/wt) blend as a function of spin diffusion time.

aliphatic volume fraction of 0.3 (point c), which corresponds exactly to the fraction of protons in the entire sample that are from methyl groups. The results are very different from measurements on a physical mixture of the same components, where separate asymptotes, corresponding to the individual aliphatic proton fractions, are observed for each component (polycarbonate at point a and TPD at point b). Also shown in Figure 2 is the difference response between these two curves. The short term initial rise can be attributed to intramolecular and the long term decay to intermolecular proton spin diffusion. From the ratio of these rates (~10) and the known intramolecular proton-proton distances (0.3 nm) the intermolecular distances can be
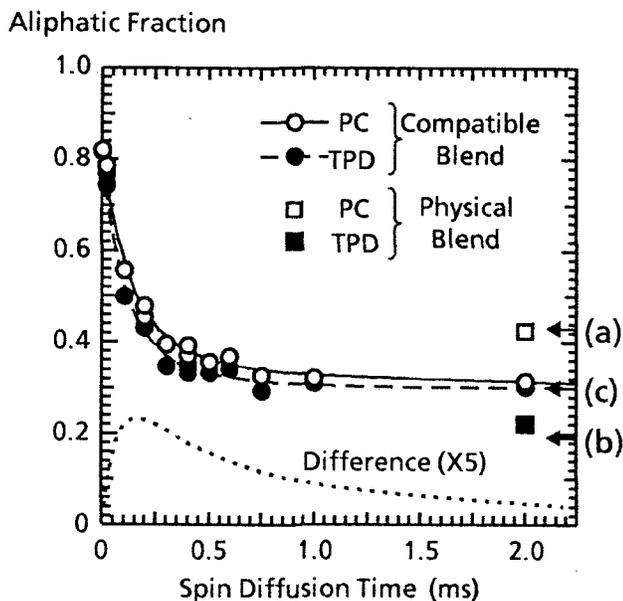
5. Prest, W.M., unpublished data.

Aliphatic Fraction

Figure 3. TPD and polycarbonate methyl carbon correlations with protons.
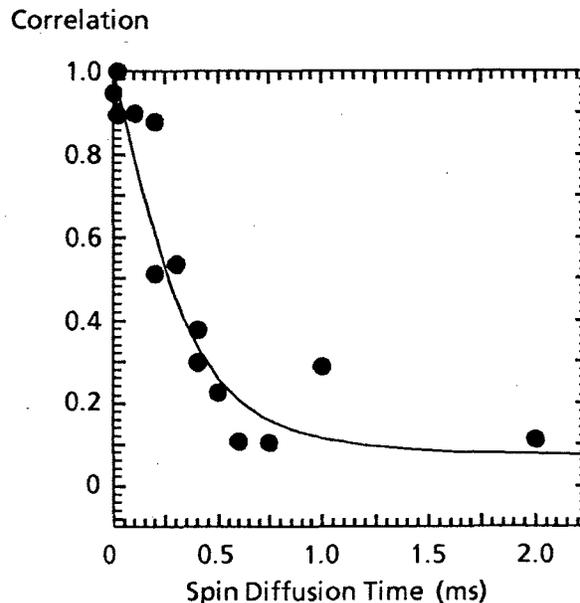
Correlation

Figure 4. Intermolecular correlations between TPD & polycarbonate methyl protons.

estimated to be about 1 nm ($0.3 \times \sqrt{10}$), indicative of intimate molecular level mixing. This treatment of the data permits estimation of interdomain separation without knowledge of the spin diffusion constant, which is only assumed to be equal in both domains.

An alternative approach to analyzing the results of this experiment is shown in Figure 4. Plotted here is a measure of the similarity (mean square difference) of the proton slices for each of the methyl carbon resonances as a function of spin diffusion time. This plot is a direct measure of the diffusion of spin order between the two blend constituents. In spite of scatter, the best fit for the data is a single exponential with a decay rate of 350 ms. Employing the standard equation for determining domain sizes from spin diffusion times, $r = (nDt)^{-1/2}$, where n represents the domain dimensionality, t is the measured spin diffusion time, and D is the spin diffusion constant, typically 5×10^{-12} cm2 sec^{-1}, domain sizes in the range of 0.8-1.4 nm are estimated.

Heating the blend overnight at 110 °C induced some phase separation, as evidenced by a change in appearance from clear to opaque. HETCOR diffusion spectra of this sample showed negligible differences from the data of the clear films. We conclude that a very small amount of phase separation occurred, e.g., near impurities or on the surface only.

In summary, it is shown that the two dimensional heteronuclear correlated spin diffusion experiment is capable of extending the range of applicability of domain size measurements to blends comprised of components that are structurally very similar.