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C−H to O Hydrogen Bonding: The Attractive Interaction in the Blend between Polystyrene and Poly(vinyl methyl ether)

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While low-molecular-weight liquids are miscible with each other even when the mixing is endothermic, polymers frequently do not mix, even when they have very similar structures, arising from the fact that mixing of long chain molecules involves a negligible change of entropy. The lower critical solution temperature exhibited by the blend of polystyrene (PS) and poly(vinyl methyl ether) (PVME) demonstrates an exothermic mixing of these polymers. The source of this exotherm, which accounts for the compatibility of the blend of PS and PVME, which has long been of interest, is shown here to involve a weak C−H to O hydrogen bond[1] between the aromatic hydrogens on the PS and the oxygen of the PVME.

NMR studies carried out more than 20 years ago first in the solid-state blend[2,6] and then in concentrated solution of PS and PVME[3−5] suggested a correlation between the aromatic meta and para hydrogens in PS and the methyl hydrogens in PVME. Here we report new NMR data for the PS/PVME blend in the solid state, which fully confirms specific interactions between the aromatic hydrogens of PS and the methoxyl group of the blended PVME, and as well solid-state NMR data using regiospecifically monodeuterated PS, allowing comparison among ortho, meta, and para hydrogens in the PS blended with PVME.

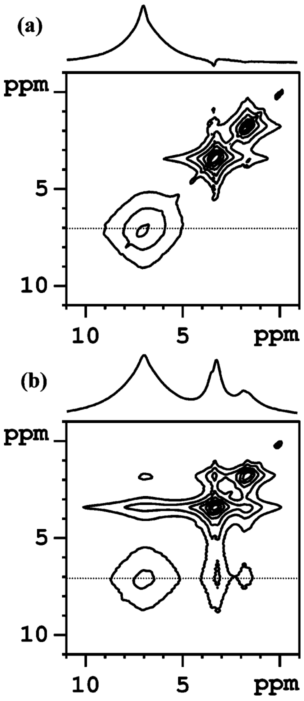

Figure 1. 2D MAS exchange plots for a solid PS/PVME blend, acquired with a 29 kHz MAS frequency. The blend was prepared at equimolar monomer ratio by casting a film from the homogeneously mixed solution in toluene. In **(**a**)**, the mixing time is 0 ms, and in **(**b**)**, 10 ms. Following solvent evaporation, the film was dried in a vacuum oven at 60 °C for 3 days. The dashed line denotes the position from which the slices were extracted to generate the ^{1}H spectra on the top of each contour plot.

Figure 1 shows a two-dimensional (2D) solid-state NMR exchange experiment for a PS/PVME blend prepared from toluene by solution casting in the standard way. The experiment is the standard three-pulse exchange sequence of the bulk solid-state blend undergoing magic-angle spinning (MAS) with an unusually high rotation rate of 29 kHz. Such high speeds have not been used to investigate the PS/PVME blend, allowing some relatively important distinctions compared to the previous work.[2] Figure 1a shows the expected autocorrelation diagonal, with no cross-peaks, for the case with a 0 s mixing time. In contrast, strong interchain cross-peaks connecting the PS aromatic ring hydrogens at ca. 7 ppm to the PVME methoxyl group hydrogens at 3.2 ppm are evident after 10 ms (Figure 1b) of polarization transfer, indicating the close proximity of these two functional groups. Control experiments indicate that at least 15 kHz of MAS is required to transform the homogeneous proton line width for the solid blend (i.e., a single broad peak) to the resolved spectra similar to those shown on the top of each contour plot in Figure 1. Compared to the exchange data previously published[2] for this blend, the MAS frequency during the polarization transfer period for the data in Figure 1 is an order of magnitude larger (29 kHz vs 2.8 kHz), and the exchange mixing time is an order of magnitude shorter (10 ms vs 100 ms). Since the homogeneous proton line width is preserved at the lower 2.8 kHz spinning speed, resulting in the maximum overlap integral for zero-quantum energy transfer, spin diffusion is extremely efficient in transferring polarization over large distances quickly.[7] At the much higher spinning speed of 29 kHz used for Figure 1, the static dipolar interaction through the energy-conserving zero-quantum spin flips is greatly attenuated, as demonstrated by the near-solution-like spectrum of three well-resolved peaks. However, even at 29 kHz MAS the ortho, meta, and para hydrogens could not be distinguished, a distinction gained in another way as shown below. Polarization propagates via spin diffusion, albeit more slowly due to the much smaller overlap integral, and this gives rise to the cross-peaks connecting the PS aromatic ring and the PVME methoxyl group in Figure 1b after only 10 ms, indicative of intimate arrangement of these polymer segments.

The early NMR results[3−5] pointing to the meta and para hydrogens rather than the ortho hydrogens as predominating for the interaction with PVME were taken in concentrated solution, which is necessary to gain the resolution to distinguish these hydrogens. The critical importance of this finding stimulated our synthesis of specifically monodeuterated ortho, meta, and para polystyrene.[8] Such selectively labeled blends (50% monodeuterated-PS:50% PVME) are amenable to the previously described solid-state ^{1}H−^{13}C NOE experiments for

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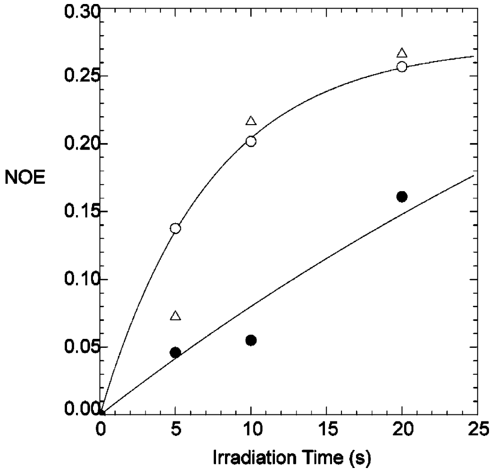

Figure 2. Intensity of the deuterated aromatic carbon signal as a function of NOE irradiation time for PVME blends with (●) ortho, (○) meta, and (△) para deuterated polystyrene. The deuterated carbon signals were selectively detected using a 60 μs dipolar dephasing time.

distinguishing these sites on the aromatic ring of PS.[6] As explained in detail by the papers in ref 6, intermolecular NOE enhancement rates are increased for carbons closest to the methyl hydrogens of the PVME OCH_3 group, as C_3 rotation/tunneling generates the necessary fluctuating dipolar fields required to stimulate cross-relaxation and generate the Overhauser effect. Figure 2 shows the plot of the NOE buildup for the three blends. Increased resolution in the aromatic region of the ^{13}C spectrum (see ref 6a), arising from the selection of only the deuterated carbons via controlled periods of ^{1}H$-^{13}$C dipolar dephasing, allowed cross-relaxation rate measurements rather than the intensity as a single point giving increased confidence in the results[9] and demonstrates that the preference for the meta and para hydrogens in PS participating in the interaction with PVME can be confirmed in the solid-state blend.

Consider now the existing literature on the blend between PS and PVME:

(1) Early reports demonstrated that the compatibility of the blend has a curious solvent dependence,[10] which was later confirmed by NMR work as well.[2] Miscibility of PS and PVME is encountered in films cast from benzene, toluene, and perchloroethylene, but not from chloroform, methylene chloride, or trichloroethylene.[10]

(2) Deuteration of the PS, carried out to increase the scattering cross section in a neutron diffraction study, led to another surprise in an enhanced compatibility of the blend reflected by an ~40 °C increase in the lower critical solution temperature.[11] However, the same effect on the lower critical solution temperature was attained by only deuterating the aromatic hydrogens.[12,13] Deuterium substitution of the aliphatic backbone hydrogens had little effect on the blend.[13]

(3) Infrared spectroscopy experiments showed vibrational changes in both the aromatic hydrogens of polystyrene and the methoxyl group of PVME in the blend. Hsu and co-workers[14] pointed out the necessity of a "favorable intermolecular interaction" in the PS/PVME blend (there are known exceptions to this rule in other blends)[15] and that understanding the nature of this interaction "represent important areas of study."

The essential characteristics defining the presence of a C$-$H to O hydrogen bond have been well summarized in small molecules.[16] Consistent with general observations for this kind of weak hydrogen bonding, the frequency of the C$-$H bending mode should decrease,[16] which was precisely found in the early infrared spectroscopic work.[14] Another characteristic is that participation in the C$-$H to O hydrogen bonding increases in moving from sp^3 to sp^2 hybridization of the carbon to which the hydrogen is bonded so that weak hydrogen bonds, hardly perceptible from aliphatic carbon, are found for aromatic bound carbon.[16,17] This hybridization dependence is in line with the observations on deuteration of the polystyrene where only deuterium substitution of the aromatic hydrogens affects the blend properties.[11-13]

The solvent dependence of the blend is especially revealing in that chloroform, methylene chloride, and trichloroethylene but not benzene, toluene, and tetrachloroethylene are known to form C$-$H to O hydrogen bonds.[1] PS and PVME only form a compatible blend when these polymers are mixed in the latter three solvents. Solvents capable of forming the same kind of weak hydrogen bond necessary for the compatibility of the PS and PVME could be expected to interfere with similar hydrogen-bonding interactions between the blending polymers during the mixing process. Support for a C$-$H to O hydrogen bond is further confirmed by the data in Figure 2, which leave no question that steric effects are playing a role. Approach of the ortho deuteron, adjacent to the backbone of the PS, would be difficult, as reflected by the slower rise of the NOE effect for the ortho deuteron (Figure 2).

We can now define with precision the insight expressed in 1990 that there are "many weak interactions...that are small compared to hydrogen-bonding and electrostatic interactions."[5] The para and meta aromatic hydrogens on the aromatic ring of the PS and to a lesser extent the ortho hydrogen on that ring are involved in a weak C$-$H to O hydrogen bond[1] with the oxygen of the methoxyl group of PVME.

Comparison of the historical development of the concept of the weak hydrogen bond with the literature on the PS/PVME blend outlined above demonstrates a parallel but entirely separate development.[18] A critical paper published in 1982[19] stimulated acceptance[18] of the concept of the weak hydrogen bond and has led to a literature growing increasingly more extensive across a wide spectrum of chemistry and biochemistry.[20] The polymer literature, although focused on the PS/PVME blend as discussed above, failed to connect the experimental observations concerning the blend to the developing work with small molecules, which arises to some extent from the absence of a focus on the molecular basis of χ parameters.[21]

Weak interactions, observable with difficulty in small molecules,[1,16,18] must play larger roles in macromolecules arising from the cooperativity$-$amplification properties of polymers.[22] This is beautifully demonstrated in the blend between PS and PVME where the cooperative characteristics of the blend amplify the per unit weak effect into a very large effect, allowing two polymers to form a blend with a large structural isotope effect on the lower critical solution temperature of the blend. Rather than being left out of the story, polymers with their cooperative$-$amplification characteristics should be central players in advancing the study of the chemical basis of nonclassical hydrogen bonding and weak effects in general. Increased connection between polymer phenomena and ongoing structural research in chemistry and biochemistry is likely to be valuable.[23] For one example, the results reported here could stimulate the search for other blends dependent on this kind of weak per unit interaction or even modification of polymers to enhance such weak interactions, allowing new blend opportunities.

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