Notes

Heteronuclear Correlation in Solid Polymers: Identification of Hydrogen Bond Donors and Acceptors in Miscible Polymer Blends

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Introduction

Intermolecular interactions can have a profound effect on the phase behavior of polymer blends, and immiscible blends can be converted to single-phase materials with the introduction of low levels of hydrogen bonding or ionic donor and acceptor groups.[1] These systems are often studied by IR[2] or NMR[3,4] spectroscopy, where the frequency and width of the carbonyl resonances are sensitive to the strength and extent of hydrogen bonding. IR spectroscopy has been particularly useful for these studies because the hydrogen-bonding strength and the fraction of hydrogen-bonded groups can be directly measured from the spectra,[2] and a theory has been developed to predict miscibility from these data.[5] However, complex systems containing many types of donors and acceptors may be difficult to study by these methods because the resonances may overlap and the shifts due to hydrogen-bonding interactions may be smaller than the intrinsic line widths, leading to broadened lines and unresolved spectra.

In this report we use two-dimensional (2D) solid-state magic-angle spinning NMR to identify hydrogen bond donors and acceptors in miscible polymer blends. The NMR characterization of polymers has been greatly enhanced with the introduction of two-dimensional NMR methods that improve the resolution and it make possible to assign resonances to specific sites along the polymer backbone and side chains.[6] These methods have been mainly used for the solution characterization of polymers and have only recently been applied to solid materials.[7] One of the most powerful 2D methods for structural analysis is the heteronuclear correlation (HETCOR) of carbon and proton chemical shifts in rotating powdered solids that was first outlined by Ernst and co-workers in 1982.[8] Improved versions of the original experiment have been reported along with the spectra for several crystalline organic solids and polymers.[9–12] Most recently, Kaplan has used a modified HETCOR experiment to measure spin diffusion rates and to probe miscibility in a polymer blend.[13] In this study, we report the first use of solid-state HETCOR experiments for correlating intermolecular interactions in miscible, hydrogen-bonded polymer blends. A potential advantage of this approach is that correlations can be observed between the carbonyl carbon and the hydrogen bond donor, making it possible to identify the interacting groups in complex copolymers and blends.

Experimental Section

The two-dimensional ^{13}C–^{1}H HETCOR data reported here were collected using the pulse sequence described previously.[10] BLEW-12 and BB-12 were applied simultaneously during the evolution period to suppress homonuclear proton dipolar interactions and carbon–proton dipolar interactions, respectively, and the spectra were acquired with one WIM-24 mixing cycle.[9] The WIM-24 (windowless isotropic mixing) sequence differs from normal cross-polarization in that homonuclear proton dipolar interactions are eliminated during the pulsed spin lock period, rather than scaled by a factor of 0.5. This is an important experimental consideration since the proton chemical shift information obtained during the evolution period must not be confounded by proton spin diffusion during the mixing time if the isolated carbon–proton connectivities are to be obtained. The ^{1}H chemical shift scaling factor during the evolution period was 0.41, identical to that previously reported.[12] The data were acquired both with and without quadrature detection in the t_1 dimension, as noted in the figure captions. The 2D spectra were collected with 1024 complex points in the t_2 dimension and 32 points in the t_1 dimension. The data were processed with 50 Hz of line broadening and zero-filled to 256 points in the t_1 dimension prior to Fourier transformation. The carbon and proton $\pi/2$ pulse widths were 4 μs, and the spinning speed was 3.5 kHz. The TOSS sequence was appended to the HETCOR pulse sequence to minimize the spinning sidebands in the carbon dimension.[14] High-resolution proton CRAMPS (combined rotation and multiple pulse spectroscopy) spectra were obtained using the BR-24 pulse sequence.[15,16]

Blends of poly(vinylphenol) and poly(methyl acrylate) (1:1 molar) were prepared from the homopolymers (with molecular weights of approximately 30 000 each) by preparing 2–3 wt % solutions in methyl ethyl ketone, mixing overnight, and casting under a nitrogen atmosphere. The samples were subsequently dried for 24–36 h at 60 °C under vacuum, and optically clear films were obtained.

Results and Discussion

The miscibility of polymer blends is frequently attributed to specific intermolecular ionic, hydrogen bonding, or van der Waals interactions.[1,17] In mixtures of poly(vinylphenol) (PVPh) and polyacrylates the miscibility has been attributed to intermolecular hydrogen bond formation between the phenolic protons of PVPh and the carbonyl oxygen of the acrylates.[2,4] Although hydrogen bonding is a strong interaction that might be expected to have a large effect on the NMR spectrum, only small changes are observed in the chemical shift of the carbonyl resonance upon blend formation. In the 1:1 blends of PVPh and poly(methyl acrylate) (PMA), for example, the induced chemical shift change (1.1 ppm) is smaller than the solid-state NMR line width,[4] making it difficult to determine with accuracy the strength and extent of hydrogen bond formation. For this blend, the extent of hydrogen bonding can be directly analyzed from the IR spectra since separate signals are observed for the free and hydrogen-bonded carbonyl at 1740 and 1710 cm^{-1} (data not shown).

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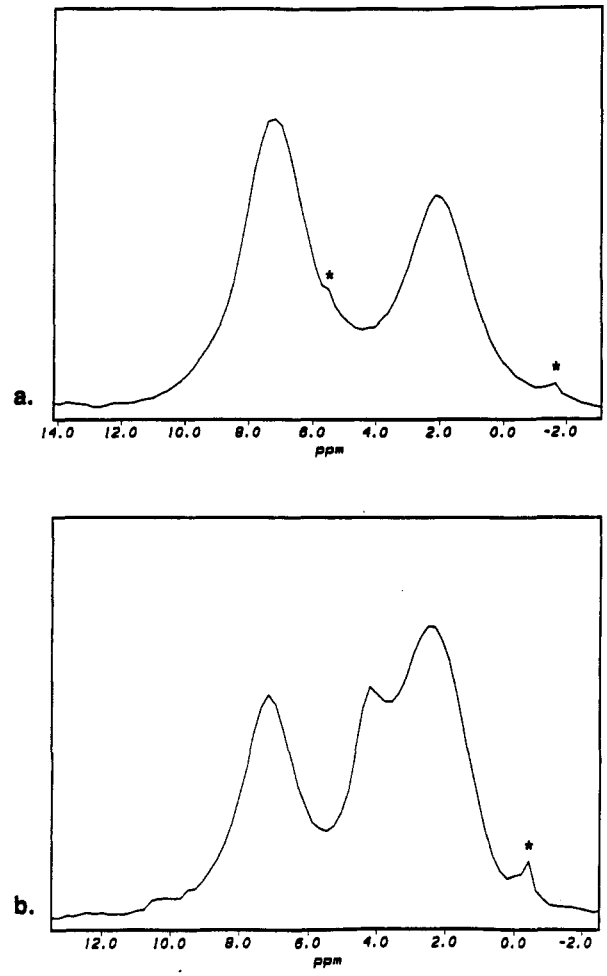

Figure 1. 400-MHz ^{1}H CRAMPS spectra of (a) poly(vinylphenol) (PVPh) and (b) a 1:1 molar blend of PVPh and poly(methyl acrylate) (PMA). In a, the PVPh aromatic proton signal appears at 7.4 ppm and the main-chain CH and CH_2 proton signal is observed at 2.1 ppm. In b, an additional signal at 4.2 ppm is assigned to the methoxyl hydrogens of PMA, and the PMA main-chain protons contribute to the signal near 2.1 ppm. The chemical shift accuracy is estimated to be ±0.3 ppm, and the asterisks donote rotor lines resulting from interference between magic-angle spinning and the multiple-pulse sequence.

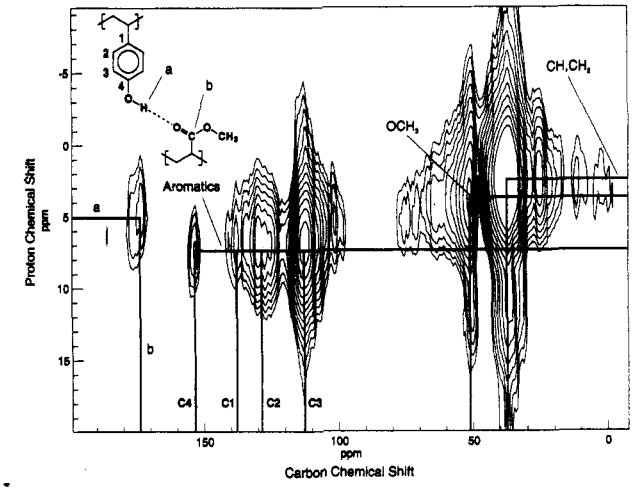

Figure 2. Two-dimensional absolute value solid-state HETCOR/TOSS spectrum for the 1:1 PVPh/PMA sample of Figure 1b. The inset plot shows the chemical structures of the polymers, and the assignments are indicated. The intermolecular correlation between the PVPh hydroxyl protons (a) and the PMA carbonyl carbon (b) are also shown.

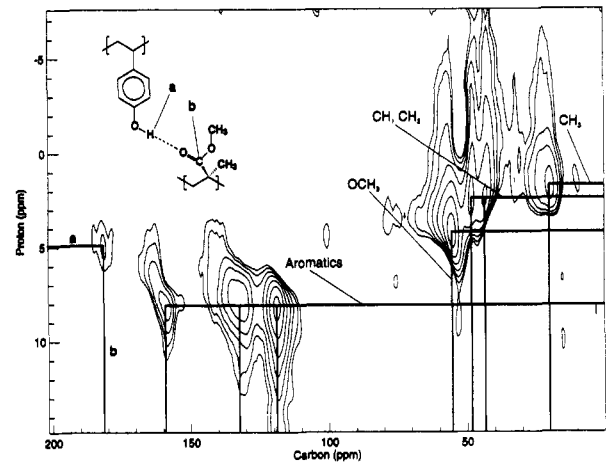

Figure 3. Absorption phase 2D HETCOR/TOSS spectrum of the 1:1 PVPh/PMMA blend cast from methyl ethyl ketone. The assignments are shown along with the intermolecular correlation between the hydroxyl protons (a) and the carbonyl carbon signal (b) of PMMA.

Since the phenolic hydrogens are directly involved in the hydrogen-bonding interaction, it might be anticipated that these protons would provide a valuable probe of hydrogen bond formation. The line widths of most polymers in the solid state are much larger (~50 kHz) than the chemical shift dispersion (~5 kHz), so low-resolution spectra are obtained. However, high-resolution spectra can be obtained with a combination of magic-angle spinning and multiple-pulse decoupling using the CRAMPS technique.[15,16] The ^{1}H CRAMPS spectra of PVPh and the 1:1 PVPh/PMA blend are shown in parts a and b of Figure 1, respectively. Two groups of signals are observed in the PVPh spectrum that can be assigned to the aromatic (7.4 ppm) and aliphatic (2.1 ppm) protons. The spectra are similar to those reported for polystyrene,[11] and the signals from the hydroxyl protons are not observed. While reports of the chemical shifts of the hydroxyl hydrogens are rare in the literature for solid polymers, it has been reported that the hydroxyl protons in crystalline tartaric acid[11] and critic acid[18] range from 4.3 to 6.5 ppm. The most likely explanation for the lack of a hydroxyl signal in Figure 1a is that the peak overlaps with the tails of the aromatic and aliphatic signals. The spectrum for the 1:1 PVPh/PMA blend differs in the appearance of a strong signal at 4.2 ppm that is assigned to the methoxyl protons and additional intensity in the aliphatic region from the main-chain protons of PMA.

The two-dimensional ^{13}C–^{1}H HETCOR/TOSS spectrum for the same 1:1 PVPh/PMA sample of Figure 1b is shown in Figure 2. The most intense correlations in Figure 2 arise from the dipolar coupling between carbons and their directly bonded protons, and the signals for the main-chain, methoxyl, and aromatic C_2 and C_3 resonances are noted. Weaker correlation peaks are observed for the PVPh C_1 and C_4 carbons that do not have directly bonded protons.

The most interesting feature of Figure 2 is the correlation that arises from intermolecular dipolar interactions rather than the intramolecular ones described above. Figure 2 shows that the PMA carbonyl resonance at 176 ppm is weakly correlated with a proton resonating at 5.0 ppm. The low peak intensity suggests that this peak arises from a dipolar interaction that is slightly weaker than the intramolecular correlation between the C_4 carbon and the C_3 proton, and we note that the proton frequency for this peak differs from any of the other assigned peaks in the spectrum. A 5.0 ppm proton shift is consistent with that expected for a hydroxyl hydrogen in the solid state, and we assign this correlation to the intermolecular carbon–

proton dipolar interaction resulting from hydrogen bonding between the carbonyl carbon of PMA and the hydroxyl hydrogen of PVPh. This assignment is confirmed by the absence of this correlation in an identical experiment performed on a blend in which the hydroxyl proton was exchanged for a deuteron by dissolution in deuterated ethanol prior to blend formation (not shown). These data are a direct measure of the intermolecular hydrogen bonding that contributes to miscibility of the solid polymer blends. Experiments run with three WIM cycles to enhance signals arising from weaker couplings[9,11] did not lead to an increase in the relative intensities of the carbonyl or nonprotonated carbon signals, as might be expected from studies on rigid polymers or crystalline organic samples. We have observed in several blend systems that all signals decay quickly with longer mixing times, presumably due to motions which cause relaxation under the multiple-pulse spin-locking WIM period, or cumulative pulse errors.

Solid-state HETCOR 2D NMR was also used to investigate hydrogen bonding in PVPh/PMMA blends under the same experimental conditions. As shown in Figure 3, a weak correlation is observed connecting the hydroxyl protons and the carbonyl signal from PMMA, indicating the formation of intermolecular hydrogen bonds. In the absorption phase spectrum with quadrature detection in the t_1 dimension, the hydroxyl peak at 4.9 ppm can be resolved from the methoxy signal at 4.3 ppm in the proton dimension. We note that the observation of molecular level miscibility in the PVPh/PMMA blends differs from that reported by Zhang et al.[4] where the blends were cast from tetrahydrofuran rather than from methyl ethyl ketone.

The results reported here show that solid-state HETCOR is a valuable tool for the investigation of intermolecular interactions in polymer blends. We anticipate that these experiments will be important for the investigations of hydrogen bonding in complex materials containing many types of hydrogen bond donors and acceptors.

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