

Application of a Two-Dimensional ^1H - ^{13}C Heteronuclear Correlation Experiment in Solids to Polymer Blends

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ABSTRACT: Miscibility and inter-polymer hydrogen bonding of poly(methyl acrylate)/poly(vinyl phenol)(PMA/PVPh) blend are studied by a two-dimensional ^1H - ^{13}C heteronuclear correlation experiment in solids. For a short spin-diffusion time of 0.2ms, there are no apparent correlation peaks between the different polymers. After a long spin-diffusion time of 1ms, there appears a correlation peak between the aromatic protons of PVPh and the carbonyl carbon of PMA. The inter-polymer correlation peak is a clear evidence of miscibility on a molecular level and is consistent with the existence of an inter-polymer hydrogen bonding.

KEY WORDS Polymer Blend / Solid-State NMR / Miscibility / Two-Dimensional NMR / Hydrogen Bonding /

Macroscopic properties of a blend are influenced largely by its microscopic degree of mixing. In NMR, microheterogeneity manifests itself in the magnetic relaxation phenomena such as spin diffusion and spin-lattice relaxation. These phenomena are mostly governed by a dipole-dipole interaction, which is a function of distances between spins concerned. In fact, the ^1H spin diffusion measurements *via* the T_1 and $T_{1\rho}$ relaxation times have been used to establish the length scale over which the blend is homogeneously mixed.¹ This approach, however, does not yield information of polymer-polymer interactions.

Caravatti *et al.* observed two-dimensional (2D) ^1H exchange spectra of a polystyrene/poly(vinyl methyl ether) blend.² High-resolution ^1H NMR was achieved by applying a multiple pulse technique and magic angle spinning (MAS). The cross peaks between different ^1H species show that they are close

enough to realize spin diffusion among them. For many blends, however, the resolution of ^1H spectra is not enough to discriminate component polymers. To improve this, Spiess *et al.* combined high-resolution ^{13}C NMR technique to the spin-diffusion experiment.³ They select ^1H magnetization of one component polymer based on ^1H chemical shift or mobility. The resulting ^1H magnetization after variable spin diffusion times is transferred to ^{13}C spins by cross polarization (CP) and observed. Alternatively, a two-dimensional ^1H - ^{13}C heteronuclear correlation (2D-HETCOR) experiment⁴ can be used to study miscibility and polymer-polymer interactions in a blend. So far, a HETCOR approach has been applied to a blend of polycarbonate and an aromatic dianine^{5a} and a phenylene ring-deuterated polystyrene/poly(2,6-dimethyl-*p*-phenylene oxide) blend.^{5b} In this work, we have applied 2D-HETCOR to a blend of

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poly(methyl acrylate) and poly(vinyl phenol) (PMA/PVPh) blend. PMA/PVPh is a miscible blend and it has been shown that inter-polymer hydrogen bonding is formed between the carbonyl carbon of PMA and the hydroxyl group of PVPh.⁶

EXPERIMENTAL

A PMA/PVPh blend mixed at a monomer-unit ratio of 1.5:1.0 was prepared as described previously.⁶ The ^1H $T_{1\rho}$ values for PMA and PVPh were agreed with each other, indicating intimate mixing on a scale of 20–30 Å.

^{13}C NMR measurements were made using a modified JEOL GX-270 spectrometer operating at frequencies of 67 MHz for ^{13}C and 270 MHz for ^1H . The following modifications have been done to realize 2D-HETCOR: (1) The original pulse programmer was replaced by one developed at the Physics Department of University of British Columbia,⁷ and a software was developed on a microcomputer (NEC9801) to perform multi-dimensional NMR. (2) A quick four-phase shifter (JEOL JNM-4PH) for a radio-frequency (rf) pulse was installed for both ^1H and ^{13}C channels. (3) A rf-amplifier (THAMWAY PA-40 2801m) which accepts a blanking pulse was inserted between the ^1H oscillator and the high-power amplifier to improve the shape of a rf pulse.

The rf field strength for both ^1H and ^{13}C was about 55.6 kHz. A double-bearing aluminum oxide rotor was used at a spinning frequency of 3 kHz. The setting of the magic angle was monitored by the ^{79}Br NMR spectrum of KBr incorporated in the rotor.

THE 2D-HETCOR EXPERIMENT

A 2D-HETCOR experiment may consist of three periods: (i) the evolution period (t_1), where a high-resolution ^1H spectrum is achieved, (ii) the mixing period, where the ^1H magnetization is transferred to the ^{13}C spins nearby, and (iii) the detection period, where a

high-resolution ^{13}C spectrum is observed. A number of pulse sequence have been proposed to suppress homonuclear and heteronuclear dipole-dipole interactions during the evolution period. We have adopted BLEW-48 and BB-48.^{4c} For a mixing period, WIM-24 is frequently used, which suppresses spin-diffusion among ^1H spins, but allows a mixing of ^1H and ^{13}C spins.^{4b,c} Therefore, if inter-polymer magnetization transfer occurs from ^1H spins of one component polymer to ^{13}C spins of the other occurs, it would bring inter-polymer correlation peaks. However, such a long-range dipole interaction may not cause efficient polarization transfer under WIM-24/MAS. In order to investigate a long-range inter-polymer interaction, one should add a spin-diffusion period ahead of the mixing period,⁵ where no rf-pulses are applied to ^1H . Or the conventional CP sequence by spin-locking may be used. We have not added the spin-diffusion period, and the conventional CP sequence was used as for a mixing sequence (ii). This is because extensive spin diffusion among ^1H spins may blur the specifically interacting regions. Further, the spin-locking rf-field on ^1H during CP does scale the homonuclear dipole interaction by $-1/2$. This reduction of the dipole interaction would retard the spin-diffusion rate,⁸ thus enabling us to observe closely the fast spin-diffusion process. The pulse sequence used in this work is schematically shown in Figure 1. The phase of the CP spin-locking field of ^1H is altered by 90

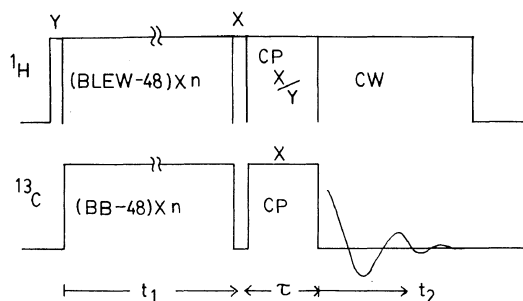


Figure 1. Pulse sequence used to obtain a 2D-HETCOR spectrum in solids.

degrees for a quadrature detection in t_1 . The 2D experiments were taken with 1024 data points along t_2 and with 300–400 t_1 increments.

RESULTS AND DISCUSSION

Figure 2a shows the 2D-HETCOR spectrum of PMA/PVPh taken with a contact time (τ) of 0.2 ms. Assignments of the carbon signals were made by the reference to ref 6. In the spectrum, the carbonyl carbon of PMA correlates to the aliphatic protons (~ 1 ppm) and the methyl protons (~ 4 ppm) of PMA. And the aromatic carbons of PVPh correlate

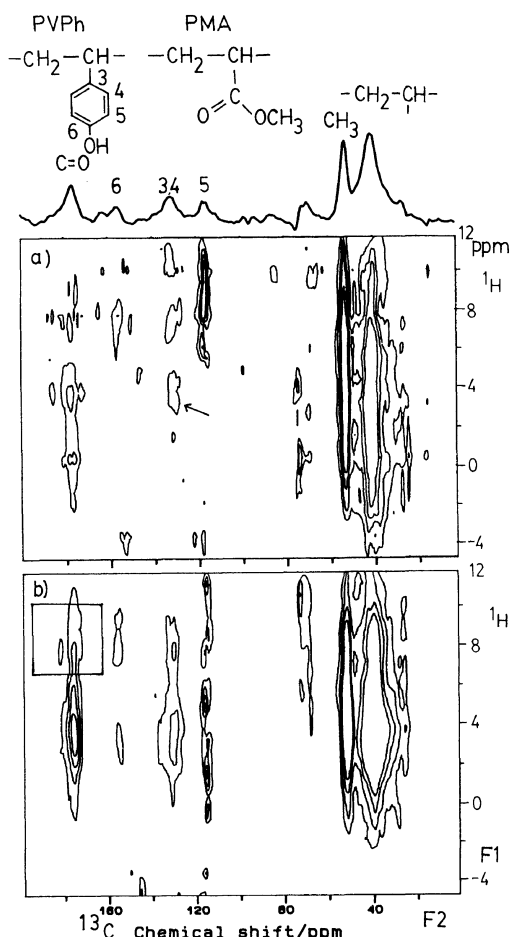


Figure 2. The 2D-HETCOR spectra of PMA/PVPh = 1.5/1 with a contact time of (a) 0.2 ms and (b) 1 ms.

to the aromatic protons (~ 8 ppm) of PVPh. The weak peak marked by an arrow may be one of the spinning side bands of the carbonyl carbon of PVPh. The resolution for the aliphatic carbons is not enough to analyze correlations. All correlation peaks in the spectrum originate from intra-polymer CP, and no appreciable inter-polymer correlation peaks are observed. This shows that during the short contact time of 0.2 ms only the intra-polymer CP takes place.

Figure 2b shows the 2D-HETCOR spectrum taken with a contact time of 1 ms. Apart from the intra-polymer correlation peaks, there is a peak between the carbon at ~ 175 ppm and the proton at ~ 8 ppm (marked by the box in Figure 2b). This peak is not a spinning sideband of the aromatic carbon-3, 4 of PVPh, because the intensity is greater than that of the main peaks of C-3, 4 appeared at ~ 130 ppm. Therefore, this peak in the box is attributed to the correlation peak between the carbonyl carbon of PMA (C_{PMA}) and the aromatic protons of PVPh (H_{PVPh}). This inter-polymer correlation peak indicates that an inter-polymer CP takes place between the C_{PMA} and H_{PVPh} . There are two possibilities of the pathway of the observed inter-polymer CP: one is that a direct transfer from H_{PVPh} to C_{PMA} and the other is that the magnetization of H_{PVPh} once spin-diffuses (homonuclear Hartman-Hahn transfer) to the protons of PMA and cross-polarizes C_{PMA} . Our experiments do not enable us to decide which pathway is dominant. We believe that the former is more efficient than the latter, because the latter involve two magnetization transfer processes while only one process is concerned for the former. In either case, we can conclude that PMA and PVPh is miscible on a molecular level and the carbonyl carbon of PMA and the aromatic protons of PVPh are in close proximity. The latter observation is in agree with the formation of the inter-polymer hydrogen bonding suggested previously.^{6a}

The inter-polymer CP experiment from

protons in one component to carbons of another deuterated component has been frequently used to study miscibility.⁹ Without such inter-polymer CP, the ¹³C signal intensity of a deuterated polymer should be much smaller than those of the protonated ones. Therefore, an appreciable signal enhancement for the deuterated component is taken as evidence of miscibility. Since effective ¹H-¹³C CP transfer is limited to about 10 Å, the signal enhancement of the latter carbons by CP shows that at least parts of the deuterated molecules are miscible. The present HETCOR experiment makes it possible to perform such examination without deuterating one of the component polymers. This is important because the miscibility of a blend may be altered by deuteration. Further, the present experimental result gives us a criterion for the contact time to be used in many spin-diffusion experiments involving CP. For example, the Goldmann-Shen experiment modified to incorporate ¹³C observation,¹⁰ the CP contact time should be short enough to neglect the spin-diffusion during the CP contact time. On the other hand, for an extremely short CP time, one may expect very low signal-to-noise ratios. As for a compromise value, we recommend to use 200 μs for a rigid polymer blend. For a very mobile blend, a longer CP time may be preferable.

The miscibility on the scale of 20–30 Å has been shown for PMA/PVPh by the ¹H T_{1ρ} experiments.^{6a} The miscibility on the scale of 10 Å suggested by the present HETCOR study is in consistent with the former results because the value of 20–30 Å is an upper-limit of the size of the domains involved. The “10 Å” is also an upper-limit, and a more reliable value would be obtained from several experiments with various CP times. However, since a 2D experiment is time-consuming, a 1D experiment such as the modified Goldmann-Shen experiment may be the one to choose for the

purpose. Therefore, a 2D-HETCOR approach is not very appealing if one is not interested in polymer-polymer interactions.

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