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Solid-State Two-Dimensional ^{13}C–^{1}H Correlation (HETCOR) NMR Spectrum of Amorphous Poly(2,6-dimethyl-*p*-phenylene oxide) (PPO)

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ABSTRACT: A two-dimensional ^{13}C–^{1}H correlation NMR spectrum is presented for the glassy amorphous polymer poly(2,6-dimethyl-*p*-phenylene oxide) (PPO). Correlation was obtained through a multiple-pulse selective cross-polarization using the sequence WIM-24 along with an improved ^{13}C–^{1}H multiple-pulse decoupling sequence during the evolution period. With the improved method, high-quality, two-dimensional correlation data can be obtained for polymers in the solid state. The two-dimensional data presented here provide evidence supporting the solid-state ^{13}C and ^{1}H assignments for PPO. Correlation intensities provide conformational information about the dihedral angles associated with the conformation of amorphous PPO.

Two-dimensional heteronuclear ^{13}C–^{1}H NMR methods (HETCOR) have been used successfully to assign spectra and characterize the structure of macromolecules in solution.[1] It is desirable to extend these methods to the study of polymers in the solid state.[2,3] Such methods can potentially aid the assignment of ^{13}C cross-polarization/magic angle spinning (CP/MAS) spectra and provide molecular distance information through the ^{13}C–^{1}H and ^{1}H–^{1}H dipolar interactions. An improved method is described to obtain heteronuclear correlation spectra of polymers in the solid state, and a two-dimensional ^{13}C–^{1}H HETCOR spectrum is presented here for the glassy amorphous polymer poly(2,6-dimethyl-*p*-phenylene oxide) (PPO). Two-dimensional correlation was obtained through a multiple-pulse selective cross-polarization using the sequence WIM-24[3] along with an improved ^{13}C–^{1}H multiple-pulse decoupling sequence during the evolution period.[4] It is shown here that high-quality, two-dimensional correlation data can be obtained for a polymer in the glassy amorphous state. These data provide evidence supporting the solid-state ^{13}C and ^{1}H assignments for PPO.[5] An analysis of correlation intensities provides conformational information that can place limits upon the dihedral angles associated with the conformation of amorphous PPO.[6,7]

Figure 1 shows a two-dimensional ^{13}C–^{1}H heteronuclear correlation spectrum of PPO.[8] The horizontal axis (F2) of Figure 1 corresponds to the ^{13}C chemical shift range (−5 to +165 ppm), and the vertical axis (F1) corresponds to the proton shift range (−2.5 to +11 ppm). Contour spots in the spectrum result from individual ^{13}C–^{1}H pairs, correlated by the through-space ^{13}C–^{1}H dipolar interaction. The chemical shift of the ^{1}H and the ^{13}C for each pair can be obtained from the F1 and F2 axes, respectively. Horizontal (^{13}C) and vertical (^{1}H) projections of the two-dimensional spectrum are shown above and to the left.

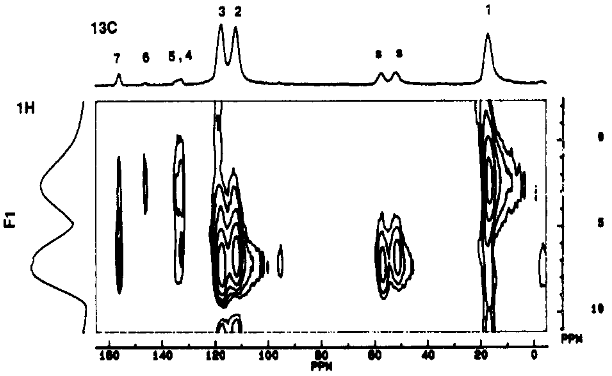

Figure 1. Two-dimensional ^{13}C–^{1}H HETCOR spectrum of amorphous PPO. ^{13}C and ^{1}H projections are shown above and to the left of the plot. Labels of ^{13}C peaks are those of Table I.

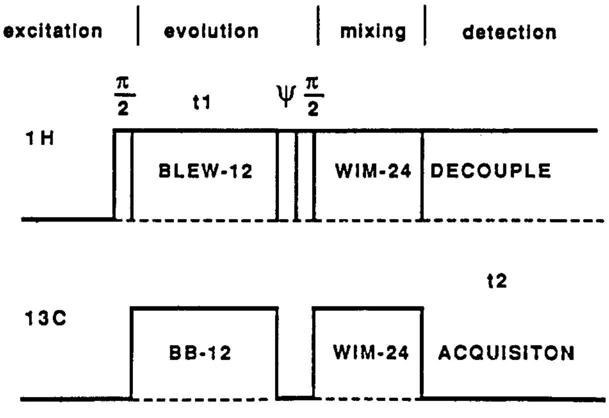

Figure 2. Pulse sequence used to obtain the two-dimensional data of Figure 1. $\psi \approx 63°$.

The spectrum of Figure 1 was obtained with the pulse sequence shown in Figure 2.[8] The ^{1}H frequency selection in the F1 dimension was effected by the usual polarization and selection pulses, separated by an F1 evolution period.[9] Multiple-pulse ^{1}H decoupling (BLEW-12)[4] was applied during evolution to suppress ^{1}H–^{1}H dipolar interactions. Additional multiple-pulse ^{13}C irradiation (designated BB-12) was applied synchronously with BLEW-12 to suppress ^{13}C–^{1}H dipolar interactions.[4] The ^{1}H chemical shift scale factor during evolution was determined experimentally (0.41) from the ^{1}H offset dependence of the two-dimensional spectrum. Chemical shifts are adjusted by this value. The experimental scale factor is reproducibly lower than the theoretical value of (0.475).[4] The cause of the deviation is probably radio-frequency inhomogeneity and is under study. At present the chemical shifts given in Table I should be considered approximate. Following the evolution period, ^{1}H intensity was selectively transferred to carbon with a single cycle of the multiple-pulse sequence WIM-24,[3] which causes cross-polarization while

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Table I
^{13}C and ^{1}H Correlations of PPO[a]

		chemical shift (ppm)	
	^{13}C peak	^{1}H(direct)	^{1}H(indirect)
1.	17.0 (C7, C8)	2.2 (H7, H8)	
2.	113.0 (C3′)[b]	6.6 (H3′)	
3.	118.0 (C5′)	7.2 (H5′)	
4.	135.0 (C2)		2.2 (H7), 6.6 (H3), 7.2 (H5), 6.6 (H3′)
5.	137.0 (C6)		2.2 (H8), 6.6 (H3), 7.2 (H5)
6.	147.0 (C1)		2.2 (H7, H8)
7.	157.0 (C4′)		6.6 (H3′), 7.2 (H5′)

[a] Peak numbers refer to Figure 1; C*n* and H*m* refer to Figure 3, ring I; C*n*′ and H*m*′ refer to Figure 3, ring II. [b] The additional intersegmental correlation is suggested by the data of Figure 4.

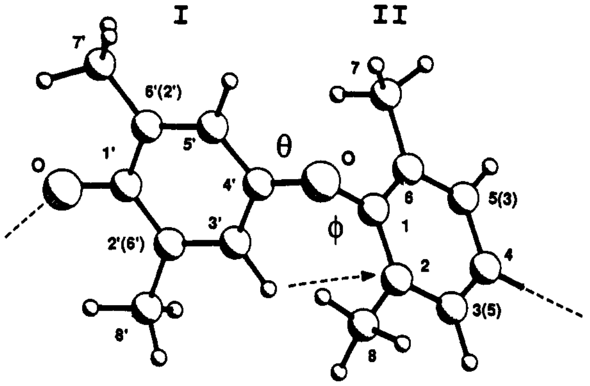

Figure 3. Two segments of PPO in a conformation with $\theta = 40°$ and $\phi = 83°$ showing the carbon and proton numbering scheme for Table I. A conformation with $\theta < 40°$ is suggested by a correlation between C2 and H3′.

effectively suppressing $^{1}H-^{1}H$ dipolar interactions. For methyl and methine carbons, magic angle spinning (MAS) modulates the dipolar $^{13}C-^{1}H$ evolution into a set of rotational spin echos[10,11] (a cross-polarization null occurs at one full cycle). It was necessary to set the magic angle spinning rate such that the length of the WIM-24 cycle was equal to or less than half a rotor cycle. Selective cross-polarization was followed by ^{13}C detection with continuous-wave ^{1}H decoupling. A pure-phase spectrum was obtained through the use of time-proportional phase incrementation (TPPI)[12] in the F1 dimension. Cross-peak intensities in the two-dimensional HETCOR experiment depend upon the strength of the scaled $^{13}C-^{1}H$ dipolar coupling and upon the sample rotation rate. Protonated sites (bond length ~0.108 nm) are nearly fully polarized at half a rotor cycle. Nonprotonated sites with nearest neighbor protons (0.2–0.3 nm) show lesser intensities. With the typical sensitivity of the two-dimensional experiment, protons at a distance greater than about 0.3 nm are not detected.

Data from Figure 1 allow for the ^{13}C and ^{1}H NMR assignment of PPO. The individual ^{13}C and ^{1}H chemical shifts of PPO are shown in Table I, along with the assignment. Peak numbers are labeled in the ^{13}C projection of Figure 1, and the carbon and hydrogen numbering scheme (C*n* and H*m*) is that shown in Figure 3. The most intense contour spots of Figure 1 result from the protonated aromatic carbons (C3 and C5 at 113 and 118 ppm) as well as the methyl carbons (C7 and C8 at 17 ppm). The ring carbon pairs (C3,C5) and their associated protons (H3,H5) are clearly distinguishable. The upfield protonated aromatic carbon (arbitrarily designated C3, at 113 ppm) is correlated with the proton with the upfield chemical shift at 6.6 ppm (H3). The downfield carbon (C5, at 118 ppm) is correlated with a proton chemical shift at 7.2 ppm (H5). Chemical shift separation in the ^{13}C dimension resolves the two proton resonances, which would otherwise overlap due to broad proton line widths. These two proton resonances are not resolved in the corresponding one-dimensional high-resolution solid-state proton spectrum obtained with combined rotation and multiple-pulse (CRAMPS) methods,[13] and the HETCOR method provides a new method to resolve solid-state ^{1}H chemical shifts.

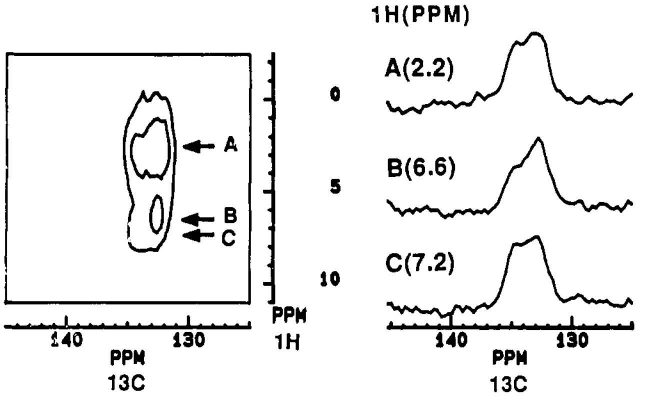

Figure 4. Expansion of Figure 1 in the region 125–145 ppm and individual slices in the ^{13}C dimension at the particular, designated ^{1}H chemical shifts (A–C). The triangular shape of Figure 4C has been attributed to an extra correlation between C2 and the upfield edge of H3′ (Figure 3).

An assignment of the nonprotonated sites of PPO can be obtained from the pattern of proton correlations due to nearest-neighbor interactions. These interactions occur through space but occur principally with those protons at adjacent carbon sites and so provide assignment information. The peak at about 135–137 ppm has been attributed to the two nonprotonated aromatic carbons (C2 and C6) attached to the methyl groups (C7 and C8). It can be seen in Figure 1 that the resonance at 135–137 ppm has two approximately equal correlations, with aromatic protons (H3 and H5) and with methyl protons (H7 and H8). A small (2 ppm) chemical shift separation can be detected between C2 and C6 (the upfield peak is designated C2 in Figure 3). The separation is particularly evident in the methyl proton correlation spots. Figure 1 provides evidence for the individual assignment of the two ether oxygen bound carbons (147 and 157 ppm). The resonance at 147 ppm has only a very weak methyl correlation and is therefore assigned to C1 (with no next-nearest-neighbor protons). The resonance at 157 ppm is most strongly correlated with aromatic protons and is assigned to C4. Solution-state spectroscopy and an understanding of ^{13}C chemical shifts[5,14] would indirectly suggest this assignment of C1 and C4, but two-dimensional spectroscopy provides direct evidence for the solid, based only upon the $^{13}C-^{1}H$ dipolar interaction.

The chemical shift inequivalence of carbons C3 and C5 and their attached protons (as well as that of C2 and C6) should be determined by the dihedral angles θ and ϕ (Figure 3) associated with the ether linkage between segments. The observation of distinct chemical shifts in both dimensions suggests a set of well-fixed dihedral angles for this polymer.[5,6] Schaefer and co-workers[7] have used ^{13}C data to suggest that phenylene rings of PPO are approximately perpendicular ($\theta = 0°$ and $\phi = 90°$). Calculations of conformational energy indicate that the dihedral angle ϕ is well determined (83°)[5] but that θ could show greater uncertainty. For $\phi = 83°$ and $\theta < 40°$ one should expect a close contact (and extra NMR correlation) between C2 of ring II and H3′ of ring I. Figure 4 shows an expansion of Figure 1 in the region of the nonprotonated aromatic carbons (135–137 ppm), and the one-dimensional spectra to the right are slices at the chemical shifts of the methyl and two aromatic protons. The strongest correlation intensity occurs at a ^{1}H chemical shift of 6.6 ppm, and this intensity is found in a peak at the upfield edge of the carbon resonance (135 ppm). The effect is reproducible for a variety of ^{1}H frequency offsets and is also found in PPO and polystyrene/PPO blends cast from $CHCl_3$.[15] The effect is independent of PPO crystallinity.[8] Carbon C3 can be assigned to the carbon near the phenylene ring of the adjacent segment, based upon this close contact, and C6 must be near the lone-pair electrons of the ether oxygen. Carbon C2 must be the site tilted toward H3′ and away from the lone-pair electrons of oxygen. These results are preliminary and other explanations for the pattern of intensities in Figure 4 are under study (including the possibility of correlation between the dihedral angles of adjacent segments of variation in the effective bond lengths at the sites C3 and C5). This particular assignment might be verified through the examination of the two-dimensional spectra of other, crystalline phenylene ether model compounds with known chemical shift data.[16] In studies of this kind, HETCOR can provide a new, practical adjunct to the analysis of solid-state ^{13}C tensor components.[17]

The two-dimensional HETCOR experiment is readily performed and relatively insensitive to pulse-amplitude and phase errors in comparison with multiple-phase ^{1}H CRAMPS experiments.[13] The heteronuclear detection removes the need for ^{1}H detection with simultaneous multiple-pulse ^{1}H decoupling. We believe that the improvement of this procedure over previous uses of the WIM-24 method[2,3] results from a more effective ^{13}C decoupling during the evolution period. ^{13}C–^{1}H dipolar interactions interfere with ^{1}H decoupling of protons attached to ^{13}C, and it is precisely these protons that are detected in the two-dimensional experiment. The sensitivity of the HETCOR experiment is necessarily lower than that of the related two-dimensional ^{1}H CRAMPS experiment,[18] due to the low natural abundance of ^{13}C. Figure 1 required a data collection time of 18 h. As with most two-dimensional methods, considerable data are obtained from a single experiment, making the long data collection times worthwhile. We believe that HETCOR can be a routine part of the ^{13}C CP/MAS investigation of a new material.

The HETCOR experiment can be modified to obtain additional data and can serve as a component of other two- and three-dimensional experiments. Insertion of a mixing period for ^{1}H spin diffusion will produce additional correlations due to longer range ^{1}H–^{1}H dipolar interactions.[18] ^{1}H–^{1}H spin diffusion measurements can be obtained with ^{13}C detection and consequently can be applied to a wider variety of materials.[19] This approach is now being used for the study of domain structure in polymer blends and composites. The pulse sequence of Figure 2 can also be used as a "chemical shift selection pulse" in a one-dimensional heteronuclear experiment involving spin diffusion.[20] This experiment has been previously performed with a nonselective, short-contact cross-polarization. WIM-24 adds complete selectivity during the cross-polarization, and the new sequence of ^{13}C irradiation during the evolution period provides the improved ^{13}C decoupling during evolution that is required for good sensitivity. The pulse sequence of Figure 2 is the method of choice for the study of short-range interactions (for example, in a miscible polymer blend), where it is necessary to resolve the proton resonances of an individual segment or of those in the first coordination shell. For larger domains the short-contact method is adequate and may be preferable due to increased sensitivity.[20] The HETCOR experiment might also be used to an advantage in conjunction with the "dipolar resolved", laboratory-frame separate-local-field (SLF) experiment[11,12] in either a two- or three-dimensional experiment. The HETCOR experiment provides a one-point measurement of the ^{13}C–^{1}H dipole interaction, along with chemical shift identification of those protons that contribute to the local field. The SLF experiment provides multiple-point determination of the same interaction without chemical shift identification. The solid-state HETCOR experiment, along with this previous SLF experiment, can provide new opportunities for use of the heteronuclear dipolar interaction for the study of polymer conformation and for the study of surface interactions involving polymer blends or composites or of biomolecular materials.

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(8) PPO (General Electric) was used as received (crystallinity ~30%) or cast as film from $CHCl_3$ (crystallinity 0%) followed by cryogenic grinding (SPEX Cryo-Mill). The crystallinity was determined by DSC: Wenig, W.; Hammel, R.; MacKnight, W. J.; Karasz, F. E. *Macromolecules* **1976**, *9*, 253. Two-dimensional spectra were obtained at 75 MHz with a Bruker MSL-300 in the 7-mm high-range CP-MAS probe, with a spinning rate of 4500 Hz, ^{1}H and ^{13}C $\pi/2 = 4.0\ \mu s$, 1024 scans. The F1 evolution consisted of (0–63 cycles) of BLEW-12 (012232010032) with $+X = 0$, $+Y = 1$, $-X = 2$, and $-Y = 3$ (F1 dwell = $4.0 \times 12 = 48\ \mu s$). BB-12 ^{13}C decoupling (212012210212) was applied synchronously with BLEW-12. A 3.0-μs ^{1}H tilt pulse rotated the plane of ^{1}H evolution to the $X-Y$ plane. WIM-24 cross-polarization was employed with the sequence (303303101110132332312121) for both ^{1}H and ^{13}C. TPPI was implemented with a $\pi/2$ phase advancement of the selection pulse, ^{1}H phases of WIM-24, and the reciever.

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