Identification of the High-Melting Crystalline Phase in High-Temperature Xtalline by Solid-State NMR Spectroscopy

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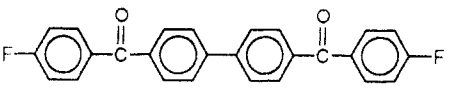
Introduction

Interest in the development of melt-processable semicrystalline thermoplastics with high melting points for application in the aerospace industry has led to the synthesis of HTX (high-temperature xtalline) polymer.[1,2] HTX is prepared to be a terpolymer of 4,4′-dihydroxydiphenyl (DHDP), 4,4′-dihydroxydiphenyl sulfone (bis-S), and a long-chain ketone (LKF, I).[3] The presence of keto



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and ether aromatic segments will lead to crystalline phases while the sulfone-containing blocks will have an amorphous character. DSC evidence suggests that there is a crystalline phase with a high melting point, in excess of 400 °C which could be either a homopolymer of the long-chain ketone, the so-called poly(LKF), or a copolymer of DHDP and LKF. Polymer quenched from above 450 °C is fully amorphous; consequently, a comparison of the crystalline phases in an HTX sample quenched at 390 and 450 °C will allow the composition of the high melting point phase to be determined.

Distinction between amorphous and crystalline phases of aromatic polymers can be readily made on the basis of their respective proton spin–lattice relaxation times in the rotating frame, $T^{H}_{1\rho}$.[4,5] Owing to the U-shaped dependence of $T^{H}_{1\rho}$ on the correlation time for the molecular motion giving rise to the relaxation in the nuclear spin magnetization, it is not possible, in principle, to say beforehand whether an amorphous or crystalline phase should have the longer $T^{H}_{1\rho}$. However, in practice, for the range of aromatic polymers with keto, ether, and sulfone linkages studied, using spin-locking fields in excess of 50 kHz, the crystalline phase has always been found to have the longer $T^{H}_{1\rho}$.[6,7] Similar behavior is seen for polymers in general,[4] such as poly(ethylene terephthalate) (PET)[8], poly(ether ketone) (PEK)[7], and poly(phenylene sulfide).[7,9] Indeed, the only common exception to this general phenomenon is poly(ethylene oxide).[10] The longer $T^{H}_{1\rho}$ for the crystalline phases can be readily understood in terms of the constraints imposed on molecular motion by the density of the polymer chain packing. Crystalline phases for the class of aromatic polymers noted here are denser than the amorphous phases and thus have less free volume, greatly restricting the polymer dynamics. Generally speaking, the predominant motion in either phase will be a torsional oscillation of the aromatic ring which may be accompanied by a complete ring flip in the amorphous phase. Certainly, in the case of poly(ether ether ketone) (PEEK) ^{1}H NMR SEDRE[11] and ^{2}H NMR line shapes[12] indicate only a fraction of the rings in the amorphous phase are flipping at room temperature. Identification of the crystalline phase necessitates that the differences in the ^{1}H relaxation times be transferred into the ^{13}C spin system where the greater resolution allows

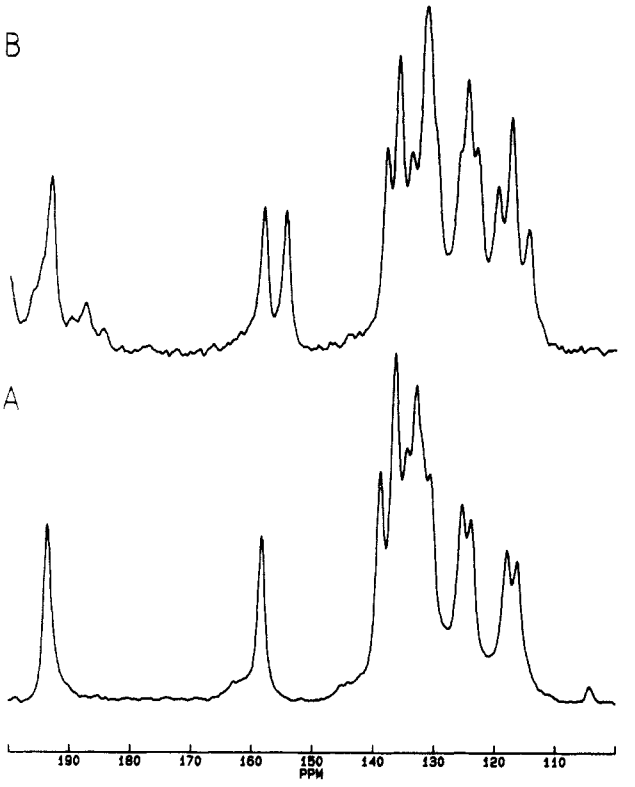

Figure 1. 50.32-MHz ^{13}C CPMAS NMR spectra of (A) poly(LKF) and (B) DHDP/LKF copolymer.

the characteristic chemical shifts for the various polymer entities to be seen. In fact this can be achieved very easily by using the standard cross-polarization technique.[13] We can therefore obtain the ^{13}C NMR spectrum of the crystalline phases in HTX quenched at various temperatures by selecting the phase with the longest $T^{H}_{1\rho}$ using a long spin-lock on the ^{1}H spins prior to cross-polarization, the so-called delayed contact cross-polarization NMR experiment.

Some complications do arise because of spin diffusion owing to the small crystalline domains commonly seen in these polymers.[14] The effect of spin diffusion is to cause the intrinsic relaxation times to be averaged by the transport of magnetization associated with the slower relaxing region to the more rapidly relaxing ones. Numerical simulations of the spin diffusion process, based on the procedure of Kenwright et al.,[15] clearly show that magnetization corresponding to a long $T^{H}_{1\rho}$ will arise predominantly from the phase with the long intrinsic relaxation time, providing of course that complete averaging has not taken place. Consequently, if we choose experimental conditions such as to observe a phase with a long $T^{H}_{1\rho}$, we can, with confidence, acquire NMR data if not selectively for this phase then at least strongly biased toward the crystalline material.

In this paper we describe the use of the delayed contact ^{13}C CPMAS NMR experiment to identify the high-melting crystalline phase in an HTX polymer.

Results and Discussion

As a comparison ^{13}C CP MAS NMR spectra of the LKF homopolymer and DHDP/LKF copolymer were acquired. These are shown in Figure 1. Differences can be seen in the region 115–140 ppm, but the most characteristic feature is that poly(LKF) only has a single resonance corresponding to a carbon ipso to oxygen, at 160 ppm, whereas for DHDP/LKF two are seen. One of these is analogous to

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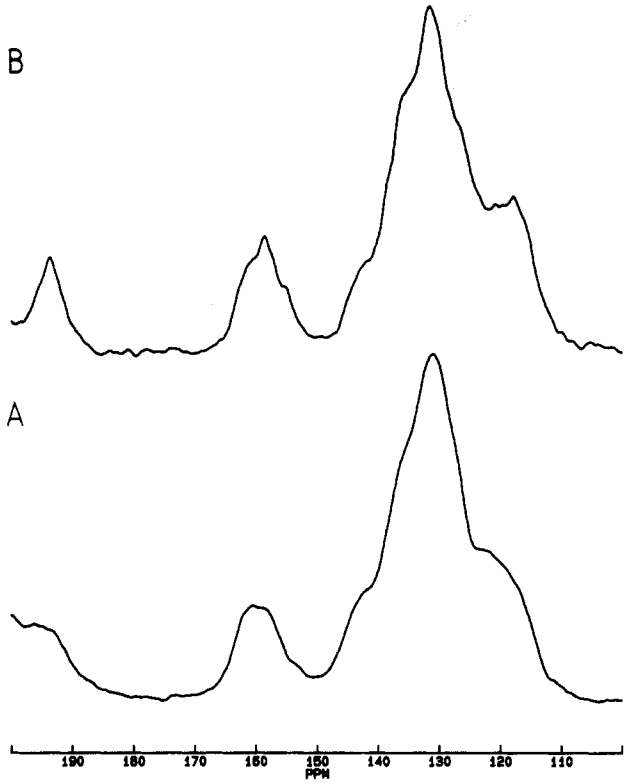

Figure 2. 50.32-MHz ^{13}C CPMAS NMR spectra of HTX quenched at (A) 450 and (B) 390 °C.

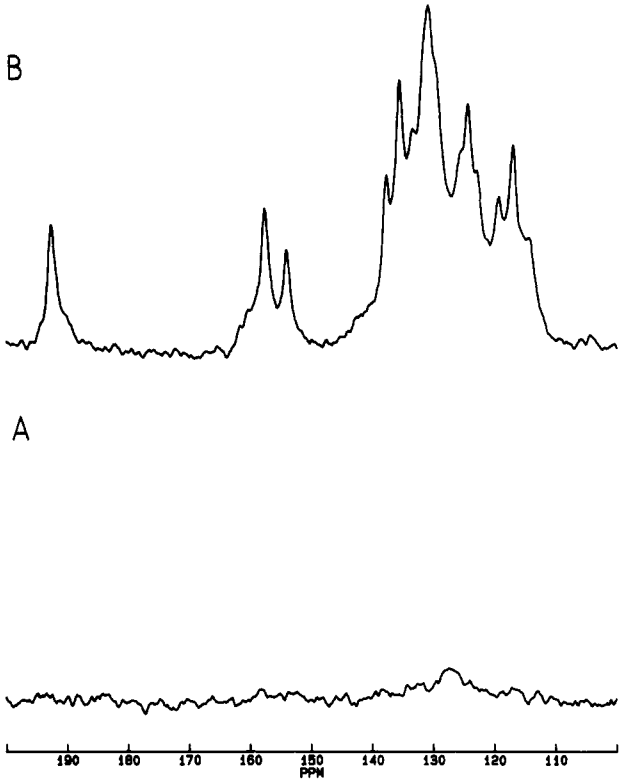

Figure 3. 50.32-MHz ^{13}C delayed contact CPMAS NMR spectra of HTX quenched at (A) 450 and (B) 390 °C.

that seen for poly(LKF) while the other at 156 ppm arises from the DHDP moiety. These spectra clearly demonstrate that ^{13}C NMR can be used to differentiate between the two possibilities for the high-melting species. Normal ^{13}C CPMAS NMR spectra of HTX quenched from 450 and 390 °C are shown in Figure 2. In contrast to the reference spectra the region around 160 ppm is very broad with little resolution as a consequence of the amorphous sulfone component. Appropriate conditions for the delayed contact experiment were found from a preliminary measurement of the $T^{H}_{1\rho}$ using a standard sample of HTX in the MAS probe and a spin-locking field fo 69 kHz. Two components were required to fit to the relaxation decay curve, the parameters of which were $f_A = 0.72$, 3.5 ms and $f_C = 0.28$, 15.9 ms, with errors of less than 0.4%. The choice of the best delay in the delayed contact experiment is a balance between eliminating the amorphous component (time constant, 3.5 ms) and maintaining a satisfactory signal-to-noise ratio for the crystalline component (time constant, 15.9 ms). In practice, the selection of crystalline phases was examined using a variable delayed contact time. Increasing the delay was found to remove the broad component from the ^{13}C NMR spectrum, supporting the identification of the short time constant with the amorphous material, but did not change the relative intensity of the two resonances in the region around 160 ppm. Overall a 10-ms delay gave the best compromise between the suppression of the amorphous component while maintaining the signal-to-noise ratio. The 10-ms delayed contact ^{13}C CPMAS NMR spectra for the two quenched HTX samples are shown in Figure 3. Notably, as expected no intensity was seen for the HTX sample quenched from 450 °C since this material is known to be fully amorphous, confirming that the conditions used to acquire the ^{13}C NMR spectra were indeed selective for crystalline phases. The polymer quenched from 390 °C, on the other hand, gives a well-resolved ^{13}C NMR spectrum, and in particular two resonances are seen in the carbon ipso to oxygen region around 160 ppm. At first sight this suggests that the high-melting species is the DHDP/LKF copolymer; however, the relative intensity of the two resonances is not equal, indicating a greater LKF content. Two interpretations are plausible; first, two distinct crystalline phases are still present corresponding to poly(LKF) and DHDP/LKF copolymer and, second, the high-melting species is an LKF-rich copolymer. In the latter case, rather than DHDP and LKF being present in the copolymer in a 1:1 ratio, the actual ratio would be nearer to 2:3.

On the basis of the NMR data, we cannot distinguish between these possibilities, for, on the one hand, the resolution is too poor to see the effects of DHDP/LKF sequencing which would clearly show whether we had a single copolymer species while, on the other hand, varying the delayed contact time gave no evidence to suggest two crystalline phases are present.

Experimental Section

HTX, poly(LKF), and DHDP/LKF copolymer were synthesized using methods analogous to that used for PEEK,[3] based on the high-temperature reaction of 4,4′-difluoro- and 4,4′-dihydroxyaryl ketones and sulfones dissolved in diphenyl sulfone together with dispersed sodium or potassium carbonates. Quenched HTX samples were prepared by heating HTX under an inert gas to either 450 or 390 °C and then rapidly cooling by quenched in iced water.

Solid-state ^{13}C NMR spectra were acquired on a Bruker MSL200 NMR spectrometer operating at 50.32 MHz. Magic angle spinning was employed to average the anisotropic nuclear spin interactions; typical spinning speeds were 5 kHz.[16] Cross-polarization was used to allow selection of the crystalline phases on the basis of differences in the $T^{H}_{1\rho}$. A contact time of 1 ms was employed in a single contact spin-lock pulse sequence. In the delayed contact experiment the delay before the contact pulse was 10 ms. For the normal CP MAS NMR spectra ca. 5000 transients were acquired, while for the delayed contact spectra 20 000 or so transients were necessary. In all cases the recycle time was set to be 3 s.

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