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Polymer Conformation Effects in Solid-State High-Resolution Proton NMR Spectra Obtained by CRAMPS

Nicholas Zumbulyadis,* James M. O'Reilly, and David M. Teegarden

Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2110

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The technique of combined rotation and multiple-pulse spectroscopy (CRAMPS)[1-3] was developed to obtain high-resolution solid-state NMR spectra of abundant nuclei such as protons[1,2] or fluorine[3] by simultaneously suppressing the line-broadening effects of homonuclear dipolar couplings and chemical shift anisotropy. While CRAMPS has found applications in the study of conformation and hydrogen bonding in small molecules,[4] relatively few CRAMPS spectra of polymers have been published;[5-7] most of them survey spectra that did not address specific problems in polymer science. One exception is the use of two-dimensional proton spin-diffusion spectroscopy based on CRAMPS to characterize the miscibility of polymer blends.[8-10]

In this paper we present preliminary data that extend the scope of CRAMPS applications in polymer science to the determination of conformations, conformational transitions, and specific interactions in polymer blends. The motivation for such studies stems primarily from the much higher sensitivity of proton NMR compared to other nuclides. That makes ^{1}H an attractive nucleus for our studies of polymers at surfaces and interfaces. However, as we shall see below, proton CRAMPS spectra can sometimes also provide structural information not immediately evident in the corresponding ^{13}C CP/MAS spectra and are thus complementary to them.

The crystal structure of poly(*p*-phenylene sulfide) (PPS) has been determined by X-ray[11] and electron diffraction methods.[12] It was shown that the C–S bonds lie in a zigzag pattern in a plane, and the phenyl rings make an angle of ±45° with respect to that plane. This conformation produces from the NMR chemical shift point of view two nonequivalent environments for the protonated carbons and the protons in the molecule. In fact Schaefer et al. have reported two ^{13}C resonances for the protonated carbons of the structurally analogous poly(2,6-dimethyl-1,4-phenylene oxide)[13,14] (PPO). On the other hand, Gomez and Tonelli in their search for a corresponding chemical shift inequivalence in crystalline PPS observed a single resonance.[15] On the basis of indirect evidence based on model compounds, the authors postulated accidental chemical equivalence and not fast ring flips to explain this observation.

The ^{1}H CRAMPS spectrum of partially crystalline PPS (Ryton P4 from Phillips) is shown in Figure 1. Two well-resolved lines separated by 1.4 ppm are observed together with a broad shoulder on the low-field line. We interpret these two lines as reflecting the chemical shift inequivalence of the protons expected in the crystalline phase. Specifically, the two protons differ in their distance and orientation with respect to the magnetically anisotropic phenyl rings.

Our findings confirm the suggestion of Gomez and Tonelli that no ring flips occur in the crystal. The broader shoulder and broad, featureless spectra obtained from completely amorphous PPS samples (spectra not shown) are consistent with ring flips as reported by Henrichs et al. from ^{2}H and ^{13}C NMR measurements[16] in the amorphous phase, but also with static disorder.

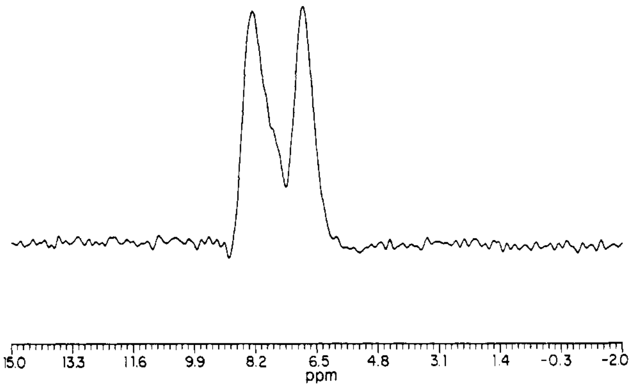

Figure 1. 300-MHz CRAMPS spectrum of PPS obtained using the BR-24 pulse sequence; 64 transients; relaxation delay 8 s.

The conformation of ethylene glycol polyesters with aliphatic and aromatic diacids has been the subject of numerous spectroscopic and crystallographic studies. We have recorded the proton CRAMPS spectra of PEA (Aldrich; M_w = 3800) and PET (Eastman Kodak). The crystal structures of both poly(ethylene terephthalate) (PET)[17] and poly(ethylene adipate) (PEA)[18] show a nonplanar configuration. The main source of nonplanarity is the rotation of the ethylene group around the O–CH$_2$ bond by 20° in the case of PET and by as much as 80° in the case of PEA. This twist renders the two protons of the O–CH$_2$ group chemically inequivalent, particularly in their disposition toward the neighboring carbonyl group. The glycol region (4–6 ppm) of the PEA proton CRAMPS spectra shown in Figure 2a displays a doublet that reflects this inequivalence. The doublet separation is ~0.4 ppm. The glycol region of PET (cf. Figure 2b) also displays a doublet separated by ~0.7 ppm. The poorer resolution is probably attributable to an underlying broad amorphous peak comparable to that of amorphous PET film (Toray) shown in Figure 2c.

The different extents to which PEA and PET deviate from a planar structure have led Daubeny et al.[17] to conclude that the rotation around the O–CH$_2$ bond requires very little energy. Thus, the departure from planarity is determined primarily through intermolecular packing forces in the crystal. Recent calculations by Tonelli[19] have shown that polyesters confined in the channels of urea inclusion compounds assume mostly an all-trans, planar zigzag conformation. We have synthesized the PEA/urea clathrate, already described in the literature,[20] but using a modified procedure.[21] The CRAMPS spectrum of this material is shown in Figure 2d and consists primarily of three lines of comparable intensity. This is consistent with a planar structure in which only three chemically inequivalent methylene groups are distinguishable, one on the glycol moiety and two on the acid. The presence of only three proton environments agrees with the all-trans structure predicted by Tonelli. However, we cannot exclude an averaging of chemical shifts by rapid conformational interconversions on the basis of CRAMPS data. The theoretical calculations of ref 19 suggest that the urea channels are not large enough for such motions to take place. These calculations do predict, however, a minor, noninterconverting population of kinked conformers. The smaller peak on the lower field side of the glycol proton signal may arise from such a population. Further experiments involving variable-temperature CRAMPS and

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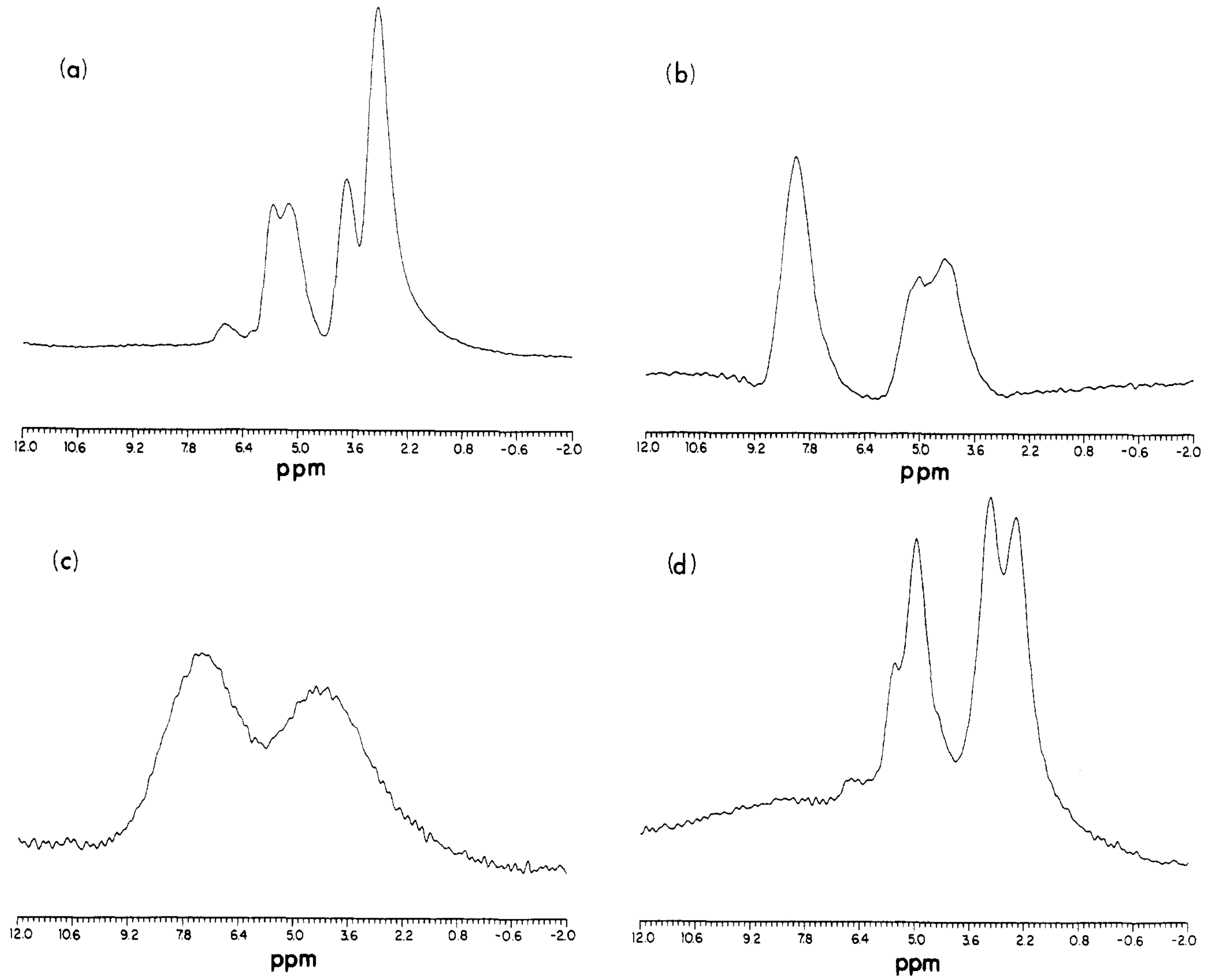

Figure 2. 300-MHz spectra of various polyesters: (a) Poly(ethylene adipate); 64 transients; relaxation delay 10 s. (b) Partially crystalline poly(ethylene terephthalate) from Kodak; 1000 transients; relaxation delay 5 s. (c) Amorphous poly(ethylene terephthalate) from Toray; 64 transients; relaxation delay 5 s. (d) Urea inclusion compound of poly(ethylene adipate); 212 transients; relaxation delay 4 s.

deuterium NMR would be required to determine the dynamics of PEA in a urea clathrate.

The signal from the urea protons is broadened and appears as a broad hump on the base line centered around 8 ppm. This broadening originates from the well-known effect that coupling between spin $^1/_2$ nuclei and quadrupolar nuclei is not completely averaged by magic angle spinning.[22-24]

The crystal structure of PEA further shows that the carbonyl group is 6° out of the plane spanned by the $-CH_2C(O)O-$ groups. That makes the two protons of the methylene group on the diacid α to the carboxyl chemically inequivalent and may explain the peak around 3.8 ppm integrating to two protons. In the clathrate the two α-protons are equivalent and give rise to the peak at 3.25 ppm. Crystallographic studies[17] as well as calculations by Tonelli[25] indicate an analogous twist in PET. The carbonyl group is about 12° out of the plane of the benzene ring. This may explain the observation of a single, relative narrow peak for the aromatic protons. In the spectrum of the fully planar model compound dimethyl terephthalate (not shown) two inequivalent sets of aromatic protons, separated by 1.6 ppm, are observed. A more complete discussion of polyester configuration studies by CRAMPS is in preparation.

The conformationally-induced chemical shift differences reported above appear to depend on the mutual configuration of the observed proton and magnetically highly anisotropic functional groups such as phenyl rings and carbonyl bonds. One might expect that specific intermolecular interactions that drive polymer miscibility may lead to similar effects. We have explored this possibility by studying tetramethylbisphenol A polycarbonate (TMPC) and a blend of TMPC and perdeuterated polystyrene (PS-d_8) (to eliminate background protons) containing 10% TMPC. The TMPC/PS-d_8 (to eliminate background protons) containing 10% TMPC. The TMPC/PS-d_8 pair forms a miscible blend as characterized by T_g and χ parameters measured by SANS. Blends of TMPC and PS-d_8 were cast from toluene solution and then dried in vacuum near T_g ($\sim$110°).[26] The CRAMPS data from the blend are shown in Figure 3. The six methyl groups of TMPC (Figure 3a) have overlapping chemical shifts. In the blend, however, the methyl groups split into two inequivalent sets, separated by $\sim$0.61 ppm, while the aromatic region remains unchanged.

There are several possible reasons for such a shift. The blend system has a negative excess volume of mixing.[27] It is conceivable that the decrease in volume upon blending freezes an internal motion such as ring flips, leading to a chemical shift difference among the methyl groups that might otherwise be motionally averaged out. It has been reported, for example, that the β peak of bisphenol A polycarbonate is suppressed by the addition of poly(methyl

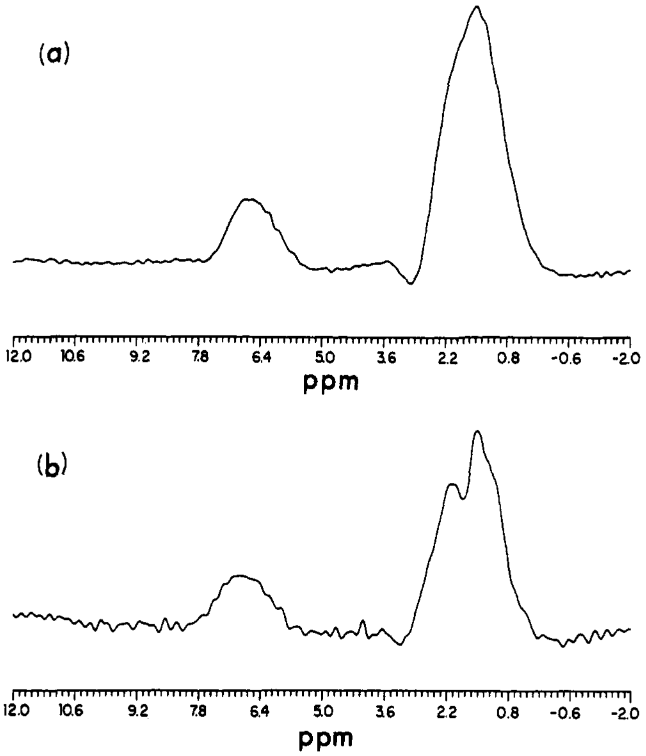

Figure 3. 300-MHz spectra of (a) tetramethylbisphenol A polycarbonate (1000 transients; relaxation delay 5 s) and (b) a tetramethylbisphenol A polycarbonate blend with perdeuterated polystyrene (10/90) (4000 transients; relaxation delay 5 s).

methacrylate) and that this loss of mobility is reflected in the deuterium NMR spectra.[28] We think this possibility is not very likely in the case of TMPC/PS blends, since dynamic-mechanical measurements by Yee and Maxwell[27] indicate no changes in the chain mobility of TMPC upon blending as reported by β relaxation. Another possibility is that the loss of free volume is associated with a change in the equilibrium conformation on TMPC and that the change in the methyl chemical shifts is related to this new conformation. We cannot exclude this possibility. However, one can also postulate a specific interaction between some of the methyl groups of TMPC and the phenyl ring of PS. Evidence for such a specific interaction in the miscible system PPO/PS has been reported from solution[29] and solid-state[30] NMR studies.

We also need to consider the possibility that we may not be observing a change in the chemical shifts but a better resolution of the methyl region. The dilution of TMPC chains by perdeuterated polystyrene reduces the interchain dipolar coupling and may result in improved resolution. On the other hand, interchain dipolar coupling is weaker and is averaged out more effectively by CRAMPS than intrachain coupling. Unpublished results from our laboratory on blends of deuterated and protonated PMMA of different tacticities do not yield any evidence in support of this possibility.

All spectra shown in this work were obtained on a Chemagnetics CMX-300 solid-state NMR spectrometer using the BR-24 pulse sequence.[31,32] A Chemagnetics probe, specially designed for proton CRAMPS experiments with a 1.21-μs 90° pulse width, was used. The optimal spinning rate for maximum resolution, compatible with a multiple-pulse cycle time of 108 μs (pulse sequencing of 3 μs), was found to be around 1100 Hz and was electronically controlled to within ±2 Hz. Spectra were run at various spinning speeds around the optimal value to identify and eliminate possible artifacts from "rotor lines".[33]

Our preliminary results show that CRAMPS can be used to characterize conformation in crystalline polymers and conformational changes and/or specific interactions in miscible polymer blends. Because of the higher sensitivity of proton NMR compared to other nuclides, CRAMPS may prove particularly useful in studying interfacial effects such as surface crystallization, epitaxial phenomena in polymer films, or the fate of compatibilizers at the phase boundaries of immiscible polymer blends.

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