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Notes

Solid-State ^{13}C NMR Chemical Shift Nonequivalences in a Polydiacetylene Crystal

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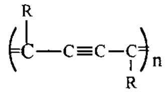
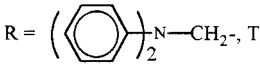
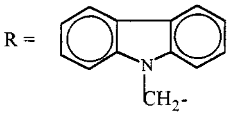
The polydiacetylenes (PDA, **1**) of 1,1,6,6-tetraphenylhexadiyndiamine (THD, **1a**) and 1,6-di-*N*-carbazolyl-2,4-hexadiyne (DCH, **1b**) are a particularly interesting pair of fully crystalline macromolecules for comparative study. Both of these PDA are completely polymerized, and their side groups are chemically similar aromatic amines. Complete crystal structures are available for these, and their conjugated backbones are reported to be planar.[1−3] Reflection spectra polarized parallel to the chain axis reveal that **1a** has its electronic origin 2300 cm^{-1} to higher energy than **1b**,[4] presumably due to stronger interactions between side groups and the backbone in **1b** compared to **1a**.[5] The Raman frequencies for **1a** for the polymer backbone double- and triple-bond stretch modes are higher than those of **1b**,[4] and the features of the piezomodulated reflection spectra[6] are consistent with those of the Raman spectra. With respect to chemical reactivity,[7] **1a** is more reactive with bromine than **1b**, presumably as a result of the lower side group redox potential of diphenylamine vs carbazole.[8] We now describe a comparative solid-state ^{13}C NMR spectral study of **1a** and **1b** using cross-polarization and magic-angle-spinning (CP−MAS) techniques.



1, PDA



, THD, **1a**



, DCH, **1b**

R = $(CH_2)_4$-O(CO)NH-R'
R' = C_2H_5, ETCD
R' = -CH_2(CO)-O-*n* C_4H_9, 4-BCMU
R' = C_6H_5, TCDU

The ^{13}C CP−MAS spectrum of **1b** has been previously reported,[7] and our new data, displayed in Figure 1, are in agreement with the previous report. Figure 2 displays the ^{13}C CP−MAS spectrum of **1a**. Our further discussion of this spectrum follows from the reported[1,2] crystal structure of **1a** (Figure 3). The crystal structure of **1a**has a polymer repeat unit length of 9.737(9) Å[2], double the 4.9 Å repeat usually found in PDA.[1] A consequence of this doubling of the unit cell is that the unit cell contains 24 nonequivalent aromatic carbons and two each nonequivalent double bond, triple bond, and methylene carbons by symmetry. This nonequivalence by symmetry is sufficient to expect a qualitative difference in the chemical shift between all nonequivalent carbons in the unit cell, although clearly not all shift differences are observable. The resonances near 150 ppm are assigned to aromatic carbons bonded to nitrogen. Of particular significance are the readily noticeable two resonances of comparable intensity in the triple bond region at 101 and 105 ppm and the two resonances for the methylene groups at 57.9 and 54.1 ppm. Since other reports[9−12] of ^{13}C CP−MAS spectra of PDA do not show different triple bond resonances for samples containing only one spectroscopic PDA state,[14] this observation merits further comment. We first discuss the acetylene ^{13}C chemical shifts of **1a** and **1b**.

In general, the ^{13}C chemical shifts of acetylenic carbons are sensitive to the length of a conjugated chain[9] and to mechanical strains on such carbons;[15] namely, longer conjugated chains and more strained acetylenes are shifted downfield. For PDA in particular, it has been proposed[13] that the ^{13}C chemical shift can be utilized as a diagnostic for electron delocalization along the backbone in that "red phase" PDA show such resonances near 103 ppm and "blue phase" PDA show them near 107 ppm. The chemical shift of acetylene carbons in the blue-phased **1b**, 103.8 ppm, is in close agreement with previously published data.[7] With respect to PDA with four $-CH_2$ units in the side group, such as PDA−ETCD and PDA−4-BCMU, both of which have their acetylene shift near 107 ppm at room temperature, backbone mechanical strains influenced by side chain packing have been proposed.[5a,16] It would seem that the proposed[13] relationship between the ^{13}C chemical shift and "electron delocalization" is an oversimplified correlation at best.

While **1a** is definitively a red phase[4] and its acetylenic chemical shifts average to about 103 ppm, other effects are likely to be significant in our materials. It is of interest to assign the shifts at 101 and 105 ppm to specific carbons. The crystal structure[2] reveals that the acetylenic carbons (C2,[2] using the numbering scheme of ref 2) lie in the shielding region of one of the aromatic rings of the side group. For example, the ortho carbons of the shielding ring (C7 and C11[2]) are 3.92 and 4.05 Å, respectively, from C2, while these same atoms are 4.77 and 4.37 Å, respectively, from C3, the other acetylenic

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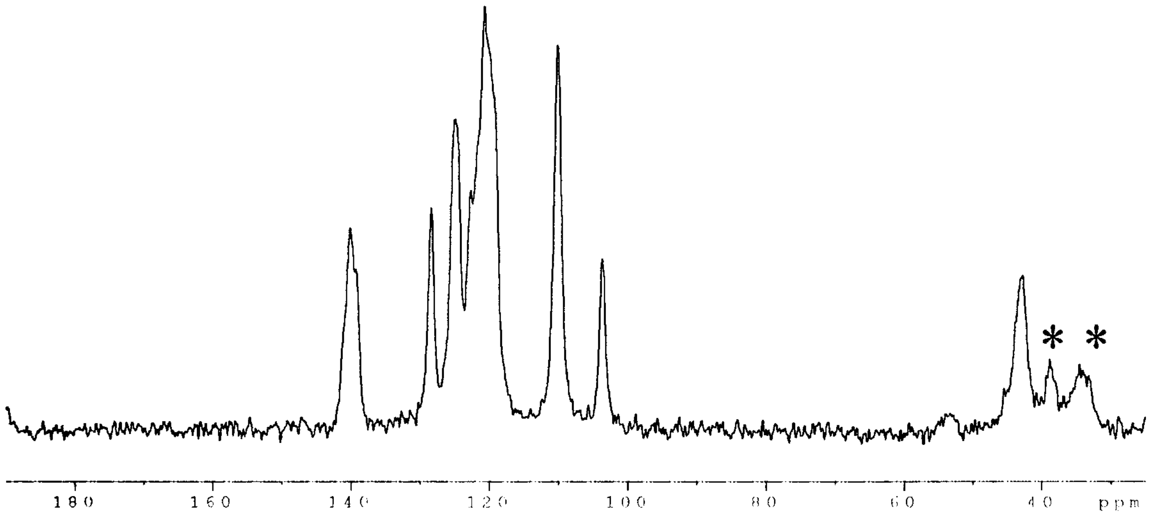

Figure 1. 75.4 MHz 13C CP/MAS NMR spectrum of poly-DCH. The experimental conditions were as follows: contact time of 3 ms, proton $\pi/2$ pulse width of 4 μs, a total of 1168 scans, and an interpulse delay of 15 s, and the rotor speed was 5.5 kHz at MAS. Asterisks indicate spinning side bands.

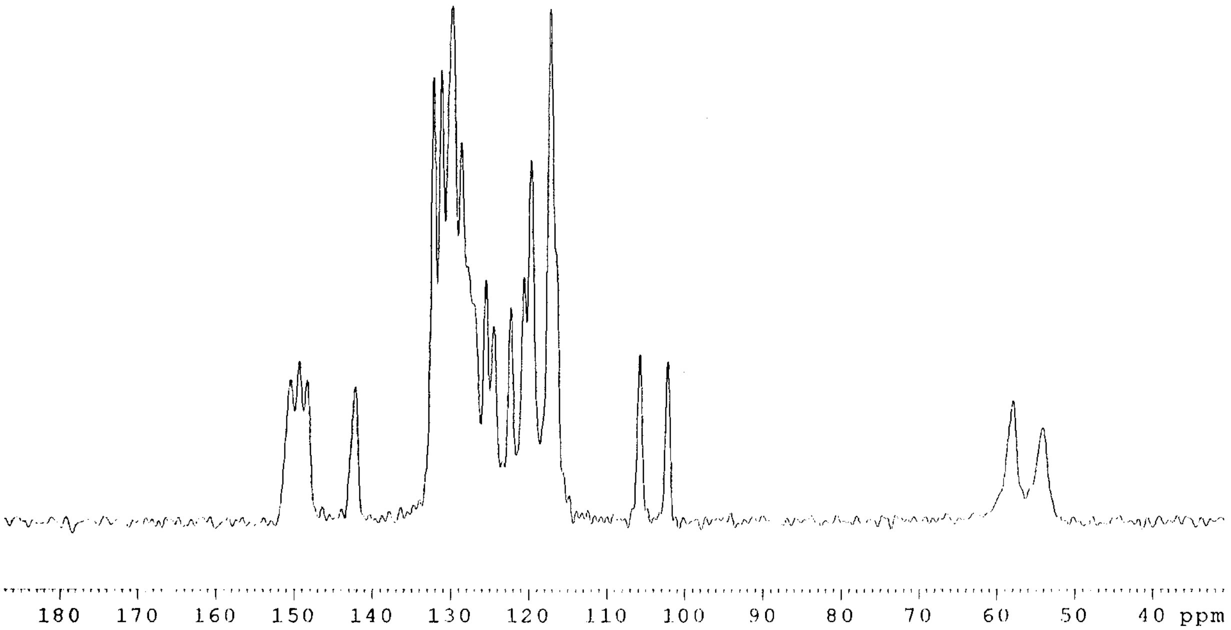

Figure 2. 75.4 MHz 13C CP/MAS NMR spectrum of poly-THD. The experimental conditions were the same as in Figure 1 except that the total number of scans was 128, and a rotor speed of 12 kHz at MAS and an interpulse delay of 240 s were used.

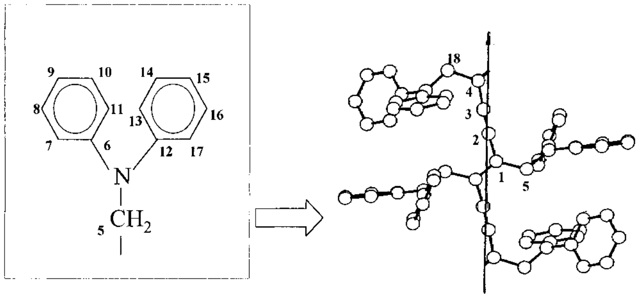

Figure 3. Crystal structure of poly-THD, modified from ref 2.

carbon. While the distances we are citing are calculated[17] crystallographic interatomic distances, it is important to appreciate that the maximum density of the π-electron cloud in an aromatic ring is estimated to have its maximum density about 1.3 Å on either side of the plane of the aromatic ring.[18] The shielding of carbon atoms in the shielding region of a benzene ring has been reported[19] for the case of 12-paracyclophane in solution**.** While the shielding effect of an aromatic ring can contribute to the chemical shift difference between the two acetylenic carbons, this effect may not be large enough[19] to account for the 4 ppm shift difference. Our tentative interpretation of a π-electron shielding effect of 4 ppm is in the solid-state crystalline environment. This is probably the first observation of such an effect in the solid state. Additional study is required to more fully understand our experimental observations.

We now discuss the possible assignment of the nonequivalent methylene groups of **1a** that are separated by about 4 ppm. The observation of two signals, separated by 8 ppm, for nonequivalent carbons in a ^{13}C CP–MAS study has been previously noted[20] for the CH_2 groups of syndiotactic and isotactic polypropylene. We have considered effects such as shielding by aromatic rings and acetylene groups and also the possibility that a γ-gauche effect[20] might be operative. None of these considerations were found to be compelling bases for

Table 1. Selected Carbon−Carbon Distances

carbon−carbon	calcd dist, Å	carbon−carbon	calcd dist, Å
C(2)−C(7)	3.92	C(5)−C(2)	2.50
C(2)−C(11)	4.05	C(5)−C(3)	3.56
C(3)−C(7)	4.77	C(18)−C(2)	3.65
C(3)−C11	4.37	C(18)−C(3)	2.54

making an assignment. Some relevant distances are given in Table 1.

To summarize, ^{13}C CP−MAS NMR spectra were recorded for the PDA crystals **1a** and **1b**. The data for **1b** confirm those of an earlier[7] report. For **1a**, a site-splitting of the crystallographically nonequivalent acetylenic and methylene carbons has been observed.

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