Structural investigation of polydiacetylenes: A variable temperature solid state ^{13}C CP/MAS NMR study

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Abstract. The spectral features in the solid state ^{13}C CP/MAS NMR of poly (1,1,6,6-tetraphenylhexadiyn diamine) (poly(THD)) are compared with X-ray diffraction. The NMR data suggests that acetylenic carbons are nonequivalent in the unit cell resulting in two resonances. On the other hand, a single acetylenic carbon resonance was observed for poly (1,6-di-N-carbazoyl-2,4-hexadiyne) (poly(DCH)). The orientation of side groups in the crystal structures of poly(DCH) and poly(THD) are responsible for equivalence and non-equivalence of acetylenic carbons. The structural changes due to thermochromic transitions are monitored by variable temperature solid state NMR. The solid state VT NMR data suggest that the backbone and side chain conformations of blue phase and red phases of poly(bis-*n*-propyl urethane of 5,7-dodecadin-1,12-diol) (poly(PUDO)) are distinctly different. For the first time, we present a solid state NMR spectrum showing the presence of both the blue and red phases of this polymer at the thermochromic transition temperature (ca. 115–125°C).

Keywords. Nonequivalence of acetylenic carbons; thermochromic phase transitions; polydiacetylenes; solid state ^{13}C CP/MAS NMR; polymer chain conformation.

1. Introduction

The polydiacetylenes (PDA) are often obtained as single crystals that can be produced by the topochemical solid state polymerization of conjugated diacetylene crystalline monomers. The polydiacetylenes thus formed possess interesting optical and electronic properties as a consequence of fully conjugated backbone structures (Sandman *et al* 1987; Tanaka *et al* 1989). Many of the highly crystalline, topochemically polymerized PDA have large nonlinear optical coefficients that suggest applications in electronic devices. In this paper we report the applications of solid state NMR to investigate structural features of these polymers and compare the solid state NMR data with X-ray diffraction. We also report the unique application of variable temperature solid state NMR to investigate the structural changes below and above the thermochromic phase transitions in one of the PDAs. The PDAs exist in the blue phase below the thermochromic transitions and in the red phase above the transition. The changes in the solid state NMR spectral features as a result of thermochromic phase transitions are related to the backbone and side chain conformational changes of the polymer chain.

2. Experimental

2.1 Materials

PDAs were synthesized and polymerized under conditions reported previously (Morrow *et al* 1987).

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2.2 Instrumentation

The solid state ^{13}C CP/MAS spectral data were obtained on a Bruker 300 MHz spectrometer operating at a ^{13}C frequency of 75.45 MHz. All the solid state NMR experiments were performed using a CP/MAS probe with 7 mm sapphire rotors. The rotor spinning speed was 5.5 KHz. The contact time of 3 ms and the proton $\pi/2$ pulse width of 4 μs were used. A total of 128 scans were co-added with an inter pulse delay of 240 s for polymer **1a** and 1168 scans with an inter pulse delay of 15 s for polymer **1b**. The free induction decays (FIDs) were multiplied by an exponential function of 10 Hz, and were zero-filled from 2 k to 8 k data points prior to Fourier transformation.

Variable temperature solid state ^{13}C CP/MAS NMR spectral data were obtained on a Chemagnetics/Varian 300 MHz NMR instrument. The contact time of 2 ms and proton $\pi/2$ pulse width of 4 μs and 1200 data points were collected with a recycle time of 10 s at magic angle spinning of 8 kHz. A total of 128 scans were collected at each set of temperature. At higher temperatures, the probe was tuned to correct any heating effects on the receiver coil and electronic components in the probe. The temperature was allowed to equilibrate at each set of temperature.

3. Results and discussions

3.1 Equivalence and non-equivalence of acetylenic carbons in poly(DCH) and poly(THD)

The polydiacetylenes of 1,1,6,6-tetraphenylhexadiyn diamine (THD, **1a**) and 1,6-di-N-carbazoyl-2,4-hexa-

diyne (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 (Apgar and Yee *et al* 1978; Enkelmann and Schleier 1980; Enkelmann 1984). Reflection spectra polarized parallel to the chain axis reveal that **1a** has its electronic origin 2300 cm to higher energy than **1b** (Morrow *et al* 1987), presumably due to stronger interactions between side groups and backbone in **1b** compared to **1a** (Hankin and Sandman 1993; Sandman 1994).

1 a. Poly-THD

The Raman frequencies for the polymer backbone double- and triple-bond stretch modes of **1a** are higher than those of **1b** (Morrow *et al* 1987), and the features of the piezo modulated reflection spectra (Morrow and Eckhardt 1988) are consistent with those of the Raman spectra.

1 b. Poly-DCH

With respect to chemical reactivity (Eckert *et al* 1987; Sandman *et al* 1987; Yesinowski *et al* 1987), **1a** is more reactive to bromine than **1b**, presumably as a result of the lower side group redox potential of diphenylamine

vs carbazole (Sandman *et al* 1988). 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.

The ^{13}C CP-MAS spectrum of **1b** has been previously reported (Eckert *et al* 1987; Yesinowski *et al* 1987) and our new data, displayed in figure 1 is in agreement with the previous report.

Figure 2 displays the ^{13}C CP-MAS spectrum of **1a**. Of particular significance are the two resonances of comparable intensity in the triple bond region at 101 and 105 ppm. Since other reports (Wenz *et al* 1984; Sandman *et al* 1987; Tanaka *et al* 1989; Nava *et al* 1990) of ^{13}C CP-MAS spectra of PDA do not show different triple bond resonances for samples containing only one spectroscopic PDA state, this observation merits further comment. The crystal structure of **1a** has a polymer repeat unit length of 9.737 Å (Enkelmann and Schleier 1980), double the 4.9 Å repeat usually found in PDA (Enkelmann 1984). Hence, the acetylenic carbons on the inside of the 9.737 Å repeat units are crystallographically inequivalent to the acetylenic carbons on the outside of the repeat unit. This nonequivalence by symmetry is sufficient to expect a qualitative difference in the chemical shift between the nonequivalent acetylenic carbons.

In general, the ^{13}C chemical shifts of acetylenic carbons are sensitive to the length of a conjugated chain (Wenz *et al* 1984) and to mechanical strains on such carbons (Gleiter and Merger 1995), namely longer conjugated chains and more strained acetylenes are shifted downfield. For PDA in particular, it has been proposed (Tanaka *et al* 1991) that the ^{13}C chemical shift can be utilized as a diagnostic for electron delocalization along the

Figure 1. The 75.4 MHz ^{13}C CP/MAS NMR spectrum of poly(DCH) (structure **1b**).

Figure 2. The 75.4 MHz ^{13}C CP/MAS NMR spectrum of poly-THD (structure **1a**).

backbone in that 'red phase' PDA show such resonances near 103 ppm and 'blue phase' PDA show them near 107 ppm. Note that blue phase (Morrow *et al* 1987) **1b** has its acetylene shift at 104.3 ppm in the previous report (Eckert *et al* 1987; Yesinowski *et al* 1987) and at 103.8 ppm in the present work. With respect to PDA with 4- 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 (Chance 1980; Sandman 1994). While **1a** is definitively a red phase (Morrow *et al* 1987) and its acetylenic chemical shifts average to 103 ppm, other effects are likely operative in our materials. It is of interest to assign the shifts at 101 and 105 ppm to specific carbons. The crystal structure (Enkelmann and Schleier 1980) reveals that the acetylenic carbons (C2) lie in the shielding region of one of the aromatic rings of the side group and these carbons would be assigned to the resonance at 101 ppm. For example, the ortho carbons of the shielding ring (C7 and C12) 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 carbon. The shielding of carbon atoms in the shielding region of a benzene ring has been reported (Levin and Roberts 1973) for the case of 12-paracyclophane.

The observation of two signals for nonequivalent carbons has been previously noted (Fyfe 1983) for the CH_2 groups of syndiotactic and isotactic polypropylene.

3.2 Thermochromic transitions in poly(PUDO)

Some PDAs exhibit thermochromic transitions, which are well below their melting temperature. For example,

poly(bis-*n*-propyl urethane of 5,7-dodecadin-1,12-diol) poly(PUDO) exhibits such a phase transition ca. 115–125°C.

2. Poly (PUDO)

The polymer sample is in the blue phase at temperatures below the thermochromic phase transition and it is in the red phase at above this phase transition. Figure 3 displays the solid state ^{13}C CP/MAS NMR spectra of poly(PUDO) that were recorded at room temperature, 115, 130, and 140°C. As the sample passes through a thermochromic phase transition temperature, significant changes are observed in the solid state ^{13}C CP/MAS spectrum of poly(PUDO). The chemical shift of the backbone carbons $-\text{C}\equiv$ shifted upfield. A closer examination of resonances for alkyl chain carbons shows both the upfield and downfield shifts as a result of thermochromic phase transitions. The oxymethylene carbon resonances that appear at 65.9 ppm show an upfield shift of ca. 1 ppm as the sample changes from blue phase to the red phase. In the case of central methylene units of the side chain, the chemical shifts move to downfield, resulting in a new peak at 25.6 ppm in the spectrum for the red phase (shown by a solid arrow in figure 3). The chemical shift of carbonyl carbon $-\text{C}=\text{O}$ (158 ppm) is unchanged indicating that the intramolecular hydrogen bondings between the side chains are retained in the red phase.

The solid state NMR observations are sensitive to the backbone and side chain conformations in both the blue and red phases. The downfield shift of the central methylene carbon (appearing as a new peak in figure 3 and marked by a solid arrow in the figure) of the side chain in the red phase suggest that these carbons have extended their conformations to a trans state above the thermochromic phase transitions. The down-field shift of methylene carbons suggests that there is no γ -gauche effect on these carbons in the red phase. This observation is consistent with earlier work of Cholli and co workers (Cholli *et al* 1987; Cholli 1992) on high density polyethylene and Tanaka and coworkers on poly(ETCD) (Tanaka *et al* 1989). In a similar way the γ -gauche effect on oxymethylene carbons is also removed in the red phase. This results in an upfield shift of oxymethylene carbon resonances (Cholli *et al* 1991).

An extended chain conformation for methylene and oxymethylene units in the side groups and retention of

Figure 3. The 75.4 MHz variable temperature ^{13}C CP/MAS spectra of poly(PUDO).

hydrogen bonding between the side groups has a direct effect on the backbone conformation in the red phase. To accommodate the changes in the side chains while retaining the intramolecular hydrogen bonding among the side chains, it is essential to have changes in the backbone conformation. One possible change that can occur to accommodate side chain conformations in the red phase is the nonplanar conformation by small rotations about single bonds with opposite rotations in the repeating unit. The chemical shift of the resonance $-\text{C}\equiv$ is moved from downfield (106.9 ppm) to upfield (102.8 ppm) by ca. 4.1 ppm as the sample changed from a blue phase to the red phase. The upfield shift of acetylenic carbon represents contributions from various factors that may affect on the backbone in the red phase. The upfield shift may arise from many influencing factors such as relieving the mechanical strain on the backbone, nonplanarity of the backbone, change of bond angles and bond strengths in the red phase. A careful analysis is required to assess the extent of such factors for an upfield acetylenic carbon chemical shift. Recently, the upfield shift of backbone acetylenic carbons was interpreted to represent the decrease of length of conjugation along the backbone (Tanaka *et al* 1989). X-ray diffraction studies previously summarized (Sandman 1994) indicate side chain elongation and an increase in the interlayer distances as these PDAs are heated from blue phase to red phase.

4. Conclusion

In this paper we have demonstrated the sensitivity of solid state ^{13}C CP/MAS NMR to study the structural aspects of PDAs. Solid state NMR data of poly(THD) reveals that acetylenic carbons are non-equivalent due to side group orientations in the unit cell. The backbone and side chain conformation of poly(PUDO) is dependent on the phase of the material. In the blue phase, the conformation of the conjugated repeating unit is planar likely with a mechanical strain, whereas it may be nonplanar in the red phase. The side chains have an extended conformation in the red phase.

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