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Solid State Nuclear Magnetic Resonance Studies of the Thermochromic Phase Transition of the Polydiacetylene from the *Bis*-*n*-Propylurethane of 5,7-Dodecadiyne-1,12-diol

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The polydiacetylene (PDA) from the *bis*-*n*-propylurethane of 5,7-dodecadiyne-1,12-diol (PUDO) undergoes a first order phase transition near 135°C that is associated with a color change from blue at temperatures below the transition to red at temperatures above the transition. We have studied PDA-PUDO by solid state ^{13}C nuclear magnetic resonance (NMR) spectra using cross polarization and magic angle spinning (CP-MAS) techniques at temperatures between 25° and 140°C. As observed previously, the acetylene carbon shift moves up field as the temperature is raised above the transition temperature. In addition, near 130°C, the oxymethylene carbon shows 3 resonances, indicating multiple side chain conformations as the PDA undergoes the phase transition.

Keywords: PDA-PUDO, thermochromic phase transition, CP-MAS NMR study, oxymethylene carbon resonances

1 Introduction

The polydiacetylenes (PDA) are a class of conjugated polymers that are available, in optimal cases, in the form of macroscopic single crystals. (1–3) Hence, their physical properties have a higher degree of definition than those of less ordered materials.(4) Among PDA, those of the *bis*-alkylurethanes of 5,7-dodecadiyne-1,12-diol are of particular interest because they exhibit a thermochromic phase transition in the 120–140°C temperature range. (5) For example, PDA-ETCD (ETCD is the *bis*-ethyl urethane of 5,7-dodecadiyn-1,12-diol) exhibits a maximum polarized in the direction of its chain axis in its ambient temperature reflectance spectrum at 635 nm that shifts to 540 nm on heating above 125°C. This is a shift of 0.34 eV. (6) Similar data were reported (7) for PDA-PUDO (PUDO is the *bis*-*n*-propyl urethane of 5,7-dodecadiyn-1,12-diol). This spectral shift is commonly referred to as a "blue"-"red" shift. Ultraviolet photoelectron spectroscopy studies (8) revealed that the change in solid state ionization energy above and below the phase transition corresponds very closely to the energy shift in the visible spectra. Hence all of the energetic changes are associated with the valence band. The details of the structural changes that take place in the course of this transition are the topic of major interest.

The crystals of the PDA of the *bis*-alkylurethanes of 5,7-dodecadiyne-1,12-diol reveal disorder such that the structural changes have not been available from single crystal X-ray diffraction (9). It is assumed that the growing polymer chain is incompatible with the existing monomer lattice. The crystal structure of ETCD monomer (10) reveals intermolecular distances that are near optimal for topochemical diacetylene polymerization. It has been proposed (11) that the "red" phase has a fairly well defined nonplanar geometry. This is in spite of the publication of two complete structural determinations (12, 13) that reported the "red" PDA-TCDU (TCDU is the *bis*-phenylurethane of 5,7-dodecadiyne-1,12-diol) has a planar backbone. The similarity of the lattice constants of a series of *bis*-alkylurethanes of 5,7-dodecadiyne-1,12-diol to those of the structurally established PDA-TCDU has been noted (9).

Since the initial report (5) of thermochromism in PDA-ETCD, numerous proposals have been advanced concerning structural changes to account for the spectral shift. These were summarized and discussed (8). The "blue"-"red" spectral shift has been observed in other PDA systems, especially Langmuir-Blodgett films. Infrared spectral studies (14) revealed conformational changes in the methylene groups of PDA-ETCD side chains, and this is widely accepted as being relevant to the observed color change. Of all PDA undergoing this color change, the PDA of the

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*Address correspondence to: Daniel J. Sandman, Center for Advanced Materials, Department of Chemistry, University of Massachusetts Lowell, Lowell, MA 01854-5046. E-mail: Daniel_Sandman@uml.edu *bis*-alkylurethanes of 5,7-dodecadiyne-1,12-diol are by far the best defined.

A purple color has been observed in the course of the study of "blue"-"red" spectral shifts (15–19). These observations have been taken (11) to imply the existence of a "purple phase." Examination of the reported data indicates that the purple color is most likely due to a mixture of "red" and "blue" phases and there is no compelling evidence for the existence of a distinct phase.

It has been suggested (20, 21) that mechanical strains on the conjugated backbone can have a significant effect on the optical properties of PDA. It is conceivable that these would arise from the presence of higher energy conformations in the methylene groups of the side group (14) that transmit a strain to the backbone.

It is likely that the species designated as "red' or "blue" phases have multiple conformations associated with the methylene groups of the side chains. It is also likely that the experimental specimens of the *bis*-alkylurethanes of 5,7-dodecadiyne-1,12-diol are not "pure" species to the complete absence of the alternative phase. For example, the Raman spectra of the PDA of *bis*-isopropyl urethane of 5,7-dodecadiyn-1,12-diol (22) taken at ambient temperature with 514.5 nm excitation (nominally in the "red" region of the spectrum under conditions where the "blue" phase would dominate) vary from crystal to crystal. More than one species is indicated for the normal modes associated with both double and triple bond stretching and the relative intensities of these lines also vary from crystal to crystal.

The thermochromic phase transition of the *bis*-alkylurethanes of 5,7-dodecadiyne-1,12-diol has been studied by ^{13}C solid state nuclear magnetic resonance (NMR) (23, 24). The acetylenic carbon resonance is the signal that experiences the largest change in the course of the thermochromic transition. It has been proposed (25) that "blue" phase PDA have the acetylenic resonance at approx. 107 ppm and "red" phase PDA have the same resonance at approximately 103 ppm. While this generalization is accurate for the *bis*-alkylurethanes of 5,7-dodecadiyne-1,12-diol, it is not true in general (26).

In this paper, we describe the results of a variable temperature study of the ^{13}C solid state NMR spectrum of PDA-PUDO and report novel observations concerning side group resonances. PDA-PUDO exhibits its thermochromic phase transition near 135°C (27), and nanoscale specimens of this PDA exhibit an absorption maximum near 660 nm, a wavelength longer than that observed for bulk specimens (27).

2 Experimental

Instrumentation. The solid-state ^{13}C CP/MAS NMR sectral data were obtained on a 300 MHz spectrometer operating at a ^{13}C frequency 75.51 MHz. 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 10s at magic angle spinning of 8 kHz. A total of 128 scans were collected at each temperature. At higher temperatures, the probe was tuned to correct any heating effects in the probe. The temperature was allowed to equilibrate at each set of temperature.

2.1 Materials

PDAs were synthesized and polymerized under conditions reported previously (27).

3 Results and Discussion

Some PDAs exhibit thermochromic transitions, which is well below the melting temperature of these materials. For example, poly (PUDO) exhibits such a phase transition ca. 130°C. The polymer sample is in the blue phase at temperatures below the thermochromic phase transition. It is in the red phase above this thermochrmoic transition temperature. Figure 1 shows the solid-state ^{13}C CP/MAS NMR spectrum of poly (PUDO) that was recorded at room temperature. The assignments of resonances for backbone and side chain carbons are also presented in Figure 1.

The solid-state ^{13}C CP/MAS NMR spectra were also recorded at elevated temperatures, and this information was previously reported (28). The earlier report shows a series of spectra recorded at 115, 130, and 140°C to observe the influence of temperature on the backbone and side chain carbon resonances. As the sample passes through the thermochromic phase transition temperature, significant changes were observed in solid state NMR spectrum of poly (PUDO) presented (28).

One of the major changes observed was for the backbone acetylene carbon resonance when the temperature was changed from room temperature to 140°C. As the sample was heated to 140°C, the chemical shift of the backbone carbon acetylenic carbons -C$\equiv$ shifted from 106.9 ppm to 102.8 ppm. The spectrum recorded at 130°C showed two resonances with unequal intensities for acetylenic carbons. As the sample goes through the thermochromic transition from blue phase to the red phase, two sets of resonances for this backbone carbon were observed in the sample recorded at 130°C. The spectrum recorded at 130°C suggests that polymer had just passed through the thermochromic transition at this temperature and the majority of the population of poly (PUDO) chains is in the red phase.

In these spectra, the most down field resonance that appears ca. 155 ppm is assigned to the carbonyl carbon peak of the side chain. The chemical shift position of this resonance is not altered as the sample temperature changed in the solid-state NMR probe. This means that the intramolecular hydrogen bonds between the side chains are not significantly disturbed in the crystalline poly (PUDO) as the polymer changed its state from blue to the red phase, and as it moved into its red phase state. The maintenance of the

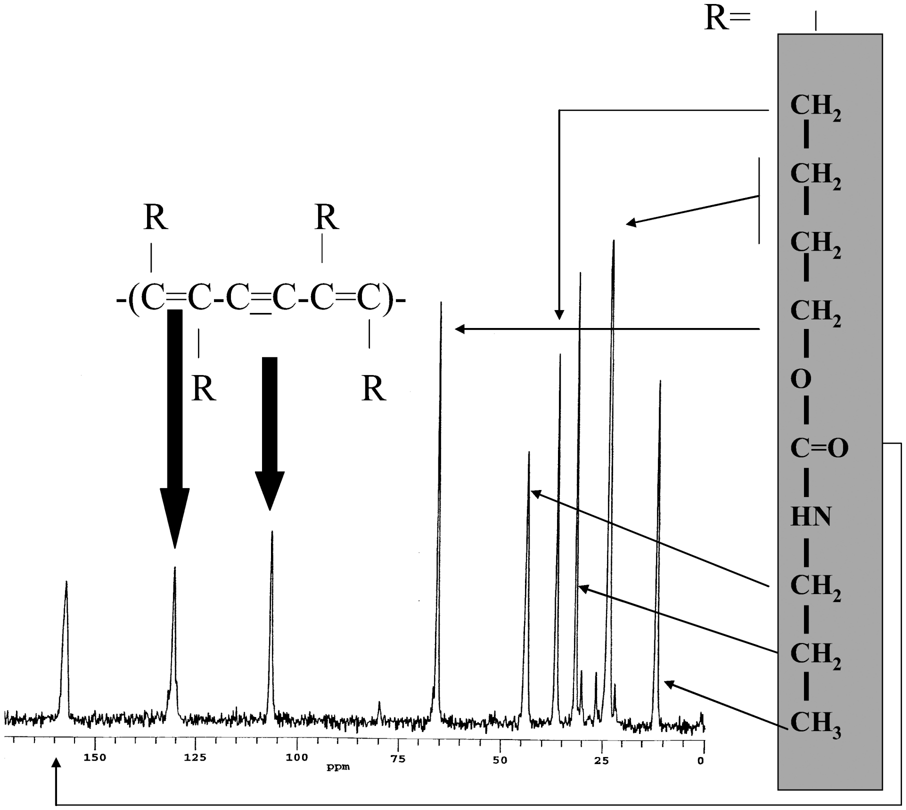

Fig. 1. Room-temperature 75.5 MHz ^{13}C CP/MAS NMR spectrum of poly (PUDO) with assignments of resonance peaks.

hydrogen bonding above the phase transition was earlier noted (14) in infrared spectral studies.

The alkyl carbon resonances for poly (PUDO) appear between 10–70 ppm in the solid state NMR spectra presented in Figure 1. A closer examination of resonances for alkyl chain carbons shows both the up-field and down-field shift as a result of phase transition. The oxymethylene carbon resonance at 65.9 ppm shows an up-field shift as the sample changes from blue phase to the red phase. Figure 2 shows an expanded spectrum showing the changes in the oxymethylene carbon resonance of the polymer chains at 130°C. It shows three distinct resonances for this carbon. It appears that oxymethylene carbon resonance is very sensitive to changes that are occurring in the polymer arising from the thermochromic phase transition. The two outer resonances in the lower spectrum of Figure 3 are due to blue phase (down-field peak) and red phase (up-field peak), respectively. The central peak may arise from a population of oxymethylene conformations present as the sample converts from blue to red phase. The additional oxymethylene carbon resonance is not associated with a distinct phase, as evidence for that is not found in differential scanning calorimetry studies (27).

In the case of central methylene units of the side chain, the chemical shift moves to down field as the sample changes to red phase. A new peak for methylene carbon appears in the red phase at 25.6 ppm is shown by a solid

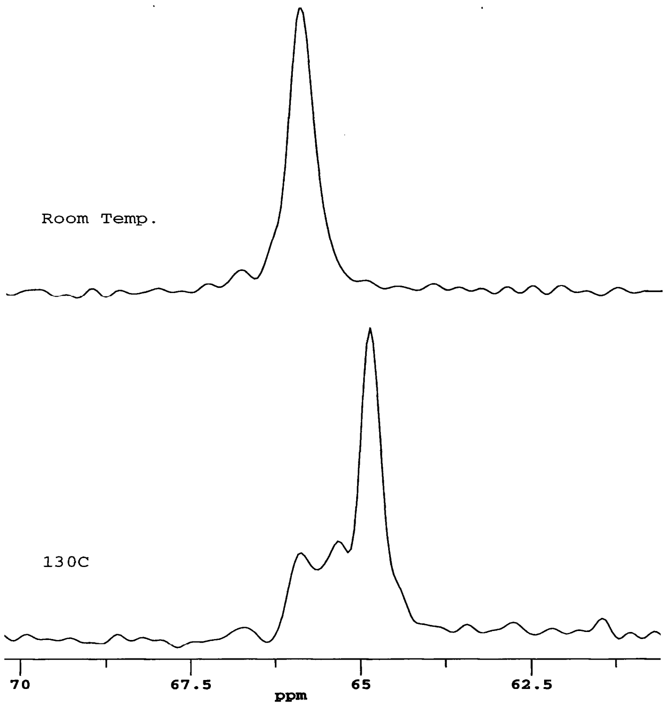

Fig. 2. Expanded spectra showing the behavior of the oxymethylene carbon resonance at the thermochromic transition.

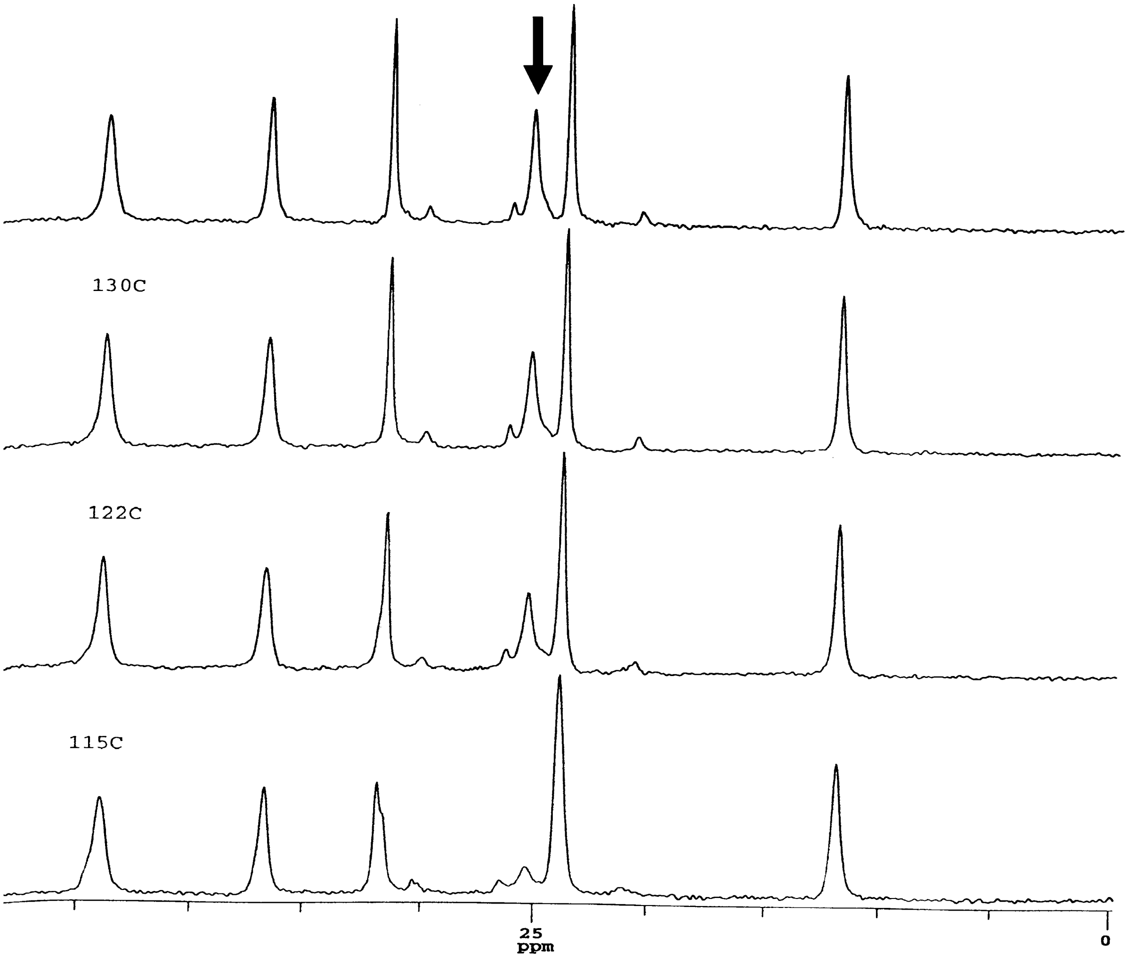

Fig. 3. Stacked plot of the expanded region of solid state 13C-NMR spectra showing the spectral changes for alkyl side chain carbons as the poly (PUDO) go through a thermochromic transition.

arrow in Figure 3. The downfield shift of the central methylene carbon of the side chain in the red phase suggests that these carbons have an increased population of trans conformations above the thermochromic transitions (30). The downfield shift of methylene carbons suggests that there are no γ-gauche effects on these carbons in the red phase. This observation is consistent with the earlier work (31–33) on high density polyethylene and Tanaka and coworkers on poly (ETCD) (23). In a similar way, the γ-gauche effect on oxymethylene carbons is also removed in the red phase. This results in the up-field shift of oxymethylene carbon resonances. This observation is again consistent with earlier work by Cholli et al. (34) on polyoxymethylene (34, 35).

An extended chain conformation for methylene and oxymethylene units in the side chain and retention of hydrogen bonding may have a direct effect on the backbone. Further studies are needed to test the proposal (11) that all red phases have nonplanar conformations.

The up-field shift of acetylenic carbon —C≡ by 4.1 ppm as the sample changed from a blue phase to the red phase represents contributions from factors that may affect the backbone in the red phase. The upfield shift may arise from influencing factors such as decreased conjugation length and decrease in mechanical strain (23). The latter would result in a change of bond angles and bond strengths in the red phase relative to the blue phase. A careful analysis is required to assess the extent of such factors for an upfield acetylenic carbon chemical shift. X-ray diffraction studies, both powder and single crystal photographs, previously summarized indicate side chain elongation and an increase in the interlayer distances as these PDAs are heated from blue phase to red phase and also have a backbone repeat distance of about 4.9Å, suggesting backbone planarity.

4 Conclusions

Variable temperature solid-state ^{13}C CP/MAS NMR is a sensitive probe of the structural changes that are responsible for a thermochromic transition in poly (PUDO). The changes in the side chain conformation of the conjugated unit have a significant influence on the phase transition. The oxymethylene resonances near 130°C reveal a more complex conformational population in the side groups than previously appreciated. The possibility of a geometry change of the conjugated backbone in the course of the phase transition remains an open issue.

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