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On the Origin of Thermochromism in Cross-Polymerized Diacetylene-Functionalized Polyamides

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ABSTRACT: The thermochromic behavior of a cross-polymerized diacetylene-functionalized polyamide, poly(hexamethylene-10,12-docosadiyne-1,22-diamide) (PADA 6,22), has been investigated with infrared and ^{13}C solid-state NMR spectroscopy. The polymer was rendered thermochromically active by exposure to UV or electron beam radiation which creates polydiacetylene cross-links across the host polyamide chains. The NMR data indicate that the thermochromic transition of this material is associated with a temperature-induced gauche to trans conformational transition of the methylene groups pendant to the polydiacetylene cross-links. FTIR results showed that the hydrogen bonds of the host polymer remain intact during the transition, thereby ensuring its reversibility. Retention of the hydrogen-bonded network was also found to be strongly linked to the conformational transition triggered in the methylene groups nearest to the polydiacetylene backbone.

Introduction

The existence of a wide variety of chromic transitions in polydiacetylenes has been well documented and molecular level interpretations have been provided to explain the color changes observed when these polymers are exposed to changes in temperature,[1] solvent quality,[2] or mechanical stress.[3] These external stimuli are believed to induce chromic transitions by altering the effective conjugation length of the polydiacetylene backbone, thereby causing shifts in the optical absorption spectrum of the material. In general, exposing a polydiacetylene to increasing temperature or mechanical stress or placing it into a thermodynamically "good" solvent will give rise to shorter effective conjugation lengths, thereby producing a shift in its primary excitonic band to higher energies. This is typically accompanied by a dramatic color change from blue to red or yellow. Although the origin of these interesting color changes is fairly well understood, there nevertheless exists some disagreement concerning certain characteristics of these chromic transitions.

For example, although solvatochromism in the poly(*n*BCMU)'s has been extensively studied, the underlying driving force of the backbone conversion responsible for the chromic transitions in solution is still debated.[4] Notwithstanding the ambiguities, significant progress has been made in elucidating the molecular structural rearrangements accompanying the thermochromic transitions in polydiacetylenes with hydrogen-bonding side groups such as the poly(*n*BCMU)'s. Of particular note is the recent work performed by Tanaka and co-workers who employed ^{13}C nuclear magnetic resonance to study the thermochromic transitions of poly(ETCD),[5] poly(TCDU),[6] and poly(4BCMU).[7] These three polydiacetylenes have very similar structures, as indicated by the generalized molecular structure shown in Figure 1. Specifically, the side chains of these materials consist of a four-methylene alkyl sequence connecting the PDA backbone with hydrogen-bonded urethane groups. The only structural variations between these materials lie in the terminal portions of their side chains. NMR investigations have led to a general description of the chromic transitions in hydrogen-bonded PDA's, at least those thermally induced and solvent induced. Briefly summarized, it was found that the blue to red transitions of the above materials were accompanied by increasing nonplanarity in the polymer backbone. This increased electron localization in the PDA backbone was observed spectroscopically as a relatively large (∼5 ppm) upfield shift of the alkyne carbon resonance due to the additional nuclear shielding provided in the less delocalized state. In addition, the side chain methylene groups between the PDA backbone and the hydrogen-bonded urethane groups were found to undergo a gauche to trans conformational transition. Since the hydrogen bonds are maintained through the thermochromic transition, the conformational changes exert a torque on the PDA backbone that presumably causes small rotations about the backbone single bonds and therefore less delocalized electronic states.

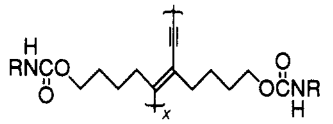

Figure 1. Generalized structure of polydiacetylenes with hydrogen-bonding side groups: poly(ETCD), R = CH_2CH_3; poly(TCDU), R = C_6H_5; poly(4BCMU), R = $CH_2COO(CH_2)_3CH_3$.

Although these conclusions appear to be generally applicable to the thermochromic transitions of PDA's formed from disubstituted diacetylenes with hydrogen-bonding side groups, they have yet to be extended to the more structurally complicated cross-polymerized diacetylene-containing polymers. These materials are created by introducing diacetylene groups along the backbone of a host polymer. Such groups may be activated by exposure of the solid material to radiation (UV, e^-, γ) to produce polydiacetylene chains across the host chains. The resultant conjugated cross-links give rise to novel optical properties[8,1b] as well as overall improvements in mechanical strength.[9,10] For example, the synthesis and optical, thermal, and mechanical properties of two diacetylene-functionalized polyamides referred to as PADA 6,22 and PADA PPD,22 have been reported. The structures of these polymers are shown in Figure 2 in their cross-polymerized forms. Optical studies have revealed that the thermochromic transitions of PADA 6,22 and PADA PPD,22 are completely reversible below characteristic upper temperature limits: 130 °C for PADA 6,22 and 160 °C for PADA PPD,22. Thus, because of their potential use as solid-state temperature sensors, it is of interest to study the molecular mechanisms responsible for the

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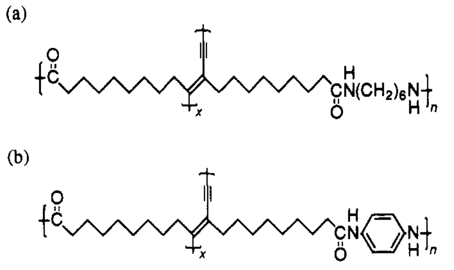

Figure 2. Cross-polymerized diacetylene-functionalized polyamides: (a) PADA 6,22; (b) PADA PPD,22.

thermochromic behavior and its reversibility. In addition, due to the structural similarities between these polymers and more conventional hydrogen-bonded polydiacetylenes, it appeared possible to check the generality of the origin of the PDA thermochromism proposed by Tanaka and co-workers. Previous investigations of the thermochromic behavior of diacetylene-functionalized polymers have focused on diacetylene-containing polyolefins[11] and segmented polyurethanes.[1b] In this paper, ^{13}C solid-state NMR and infrared spectroscopy are utilized to probe the origins of the reversible thermochromic behavior of PADA 6,22.

Experimental Section

The synthesis and optical properties of PADA 6,22 and PADA PPD,22 have been reported previously.[8] To obtain the diacetylene diacid monomer for both of these polymers, the sodium salt of 10-undecynoic acid (Farchan) was oxidatively coupled in a tetrahydrofuran/water solvent mixture with a catalyst composed of copper(I) chloride and *N,N,N′,N′*-tetramethylethylenediamine (TMED) activated by continuous oxygen bubbling. Polymers were prepared from the diacid chloride of the diacetylene diacid monomer and either 1,6-hexanediamine or *p*-phenylenediamine by an interfacial polycondensation in a high-speed blender.

Infrared spectra were recorded on a Nicolet 510P Fourier transform infrared spectrometer (FTIR). Temperature studies were conducted by using a heated precision cell equipped with a Fenwal Model 550 temperature controller (temperature range, 25–200 °C). Spectra and peak areas were recorded at each temperature after a 10-min equilibration period. For the FTIR temperature studies, solution-cast thin films were cross-polymerized by exposure to UV light at 254 nm with an intensity of 5 mW/cm^2 for 30 min.

^{13}C NMR spectra were recorded on an IBM NR/200 AF (4.7-T) spectrometer operating at 50.3 MHz and fitted with an IBM solids accessory rack for measuring solid-state spectra. A Doty Scientific probe was employed for magic angle spinning, and spectra were obtained with a cross-polarization pulse sequence (500-μs CP time) along with dipolar decoupling. The rigid (crystalline) component of the polymer was selectively observed by insertion of a 5-s T_1 delay for destruction or relaxation of the amorphous magnetization before acquisition. The NMR temperature studies were conducted with a Bruker variable temperature unit and a Doty Scientific probe which was tuned and matched at each temperature. Samples were equilibrated at each temperature for a period of 30 min prior to data collection. High-temperature Vespel end caps were used to plug the aluminum oxide rotor. The powdered polymers were cross-polymerized by exposure in air to 40 Mrad of high energy electrons generated with a Van de Graff accelerator operated at 2.6 MeV.

Results and Discussion

The cross-polymerized diacetylene-containing polyamides examined in this study are shown in Figure 2 in which the structures are presented in such a manner as to emphasize the segments connecting the PDA backbone with the hydrogen-bonding portion of the "side chains". Comparison with the structure shown in Figure 1 for the more conventional hydrogen-bonded polydiacetylenes reveals the basic structural similarities shared by these materials (methylene segments bridging a polydiacetylene chain and a hydrogen-bonded functional group).

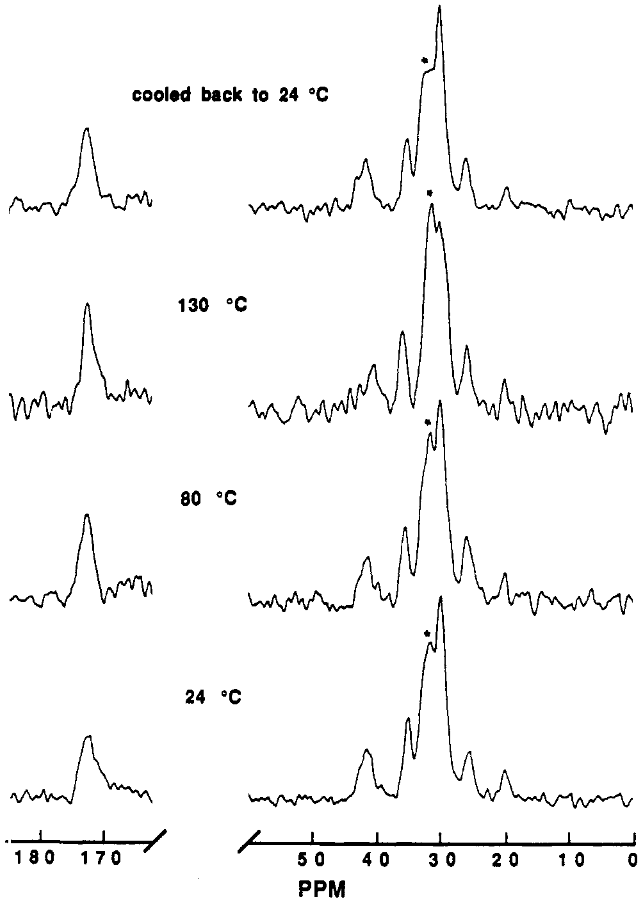

Figure 3. ^{13}C NMR spectra of the rigid component of cross-polymerized PADA 6,22 recorded as a function of temperature. Spectra are scaled to the most intense peak of each respective spectrum. The interior methylene carbons connecting the hydrogen-bonded amide groups with the polydiacetylene cross-links are represented by the peak at 32 ppm (*).

The thermochromic behavior of cross-polymerized PADA 6,22 has been previously described.[8,12] Upon thermal ramping, the color of the material slowly and progressively turns from purple to red. This process is completely reversible as long as an upper temperature of about 130 °C is not exceeded. For the nonirradiated material, the sequence of eight methylene units connecting the diacetylene group to the amide linkage initially adopts an all-trans conformation which is subsequently converted into one containing a significant population of gauche conformations after cross-polymerization.[13] Evidence for this conclusion was provided by solid-state NMR investigations of the rigid or crystalline component of the polymer. It is within these regions of the polymer that the diacetylene cross-polymerization reaction is primarily restricted and therefore where the chromic behavior originates. Since it has been demonstrated that NMR is sensitive to the conformational state of the side group methylenes of this material, this technique may be used to investigate the temperature-induced structural changes of these units during the thermochromic transition.

Figure 3 shows the ^{13}C NMR spectra of the rigid component of cross-polymerized PADA 6,22 as a function of temperature. Spectra are presented for the material at 24, 80 and 130 °C and after cooling back to 24 °C. Each spectrum is scaled to the height of the most intense peak in that spectrum so that absolute intensity comparisons between spectra are not valid. The emphasis in the following discussion is placed on the relative peak heights within each respective spectrum, in particular regarding the two peaks at 30 and 32 ppm. The primary temperature-induced structural modifications as manifested in the NMR spectra involve the methylene carbons represented by the 32 ppm peak (signified in each spectrum by an asterisk). This peak has been assigned to interior methylene groups of the diacid moiety. In the nonirradiated polymer, these are methylene groups whose chemical shifts are determined by the presence of trans-bonded methylene groups in the γ-positions relative to each carbon.[14] It has been shown that, upon radiation-induced cross-polymerization of PADA 6,22, the 32 ppm peak is reduced in intensity and broadened, as compared to the same peak in the spectrum of the nonirradiated material.[13] Shown as the room temperature spectrum in Figure 3, this indicates the presence of some gauche methylene conformations for the cross-polymerized polymer. At 80 °C it can be seen that the intensity of the methylene peak at 32 ppm is increased relative to the other peaks in the spectrum (e.g., the 30 ppm peak), indicating an increase in the population of the trans conformers. By 130 °C, this trend has been followed to the point that a significant fraction of the methylene groups are ordered in trans conformations. Indeed, the NMR spectrum at this temperature appears very similar to that of the pristine host polymer in which all methylene groups were presumably ordered in fully extended trans conformations.[13] Upon cooling back to room temperature, the relative peak intensities revert back to their starting state; that is, the 32 ppm peak is reduced in intensity relative to the other peaks. This observation is consistent with the reversible nature of this thermochromic transition. The observed decrease in the relative height of the 32 ppm peak intensity for the spectrum recorded after cooling to room temperature compared to the original spectrum at room temperature is most likely due to additional thermal polymerization of unreacted diacetylene groups since the sample was kept at prolonged elevated temperatures during the experiment. Upon further temperature cycling, the same relative intensity increase of the 32 ppm peak is observed. Nevertheless, the temperature-induced conformational transition is seen to be essentially reversible upon cooling back to room temperature. In fact, the NMR experiment was repeated many times after the first cycle with complete reversibility of the peak intensities observed upon subsequent temperature cycling.

A detailed analysis of these results is complicated by the presence of a large number of methylene groups which are not expected to take part in the thermally induced structural rearrangements directly related to thermochromism (for example, the methylene groups that are part of the diamine residue). Because of the abundance of methylene groups in this polymer with different chemical shifts, it is difficult to say precisely which carbons take on which conformations. However, the nature of the behavior shown in Figure 3 suggests that only a conformational transition of gauche-rich side group methylenes can account for the reestablishment of an extended trans bonding scheme. As indicated previously, the methylene groups nearest to the polydiacetylene backbone are forced to adopt a gauche-rich conformational state after diacetylene cross-polymerization.[13] It should also be noted that the complex structure of the cross-polymerized PADA 6,22 and the NMR technique employed here prevented the observation of the alkyne carbon resonance associated with the polydiacetylene backbone (the alkyne resonance was simply diluted by the methylene carbon signals). However, the transition observed for the methylene resonances and the reversibility of this transition after cooling back to room temperature provide strong evidence that the thermochromic behavior is indeed related to a thermal population of trans conformational states and that no permanent chemical changes are taking place.

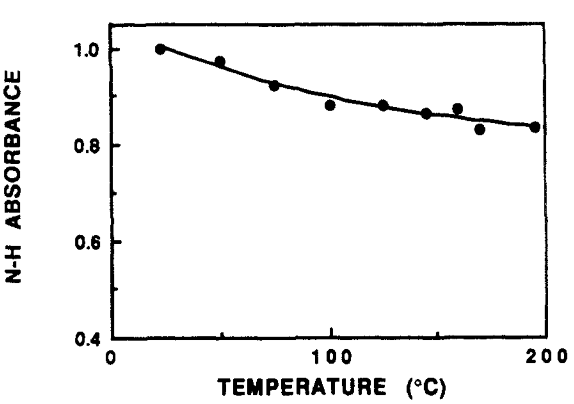

Figure 4. Integrated infrared absorbance of the N–H stretch of cross-polymerized PADA 6,22 as a function of temperature. Data normalized to room temperature.

A thermally induced transition to a trans-rich conformational state may seem counterintuitive but not when one considers the constraints placed on this molecular system by the PDA backbone and the hydrogen bonds. It has been verified by infrared spectroscopy that the hydrogen bonds are completely retained during the thermochromic transition of this material. These data are presented in Figure 4 for PADA 6,22 in which the integrated N–H intensities normalized to room temperature are plotted as a function of temperature. The smooth decrease in intensity with increasing temperature that is observed in this figure is simply due to the change in hydrogen bond strength that occurs with thermal expansion of the polymer.[8,15] There appears to be no first-order transition representative of hydrogen bond disruption and no production of nonbonded N–H groups (as indicated directly in the FTIR spectra). Retention of hydrogen bonds through the thermochromic transition is also indicated by the unchanged chemical shift (i.e., frequency) of the carbonyl resonance observed in the NMR spectra of Figure 3 (at 173 ppm). Complete retainment of hydrogen bonds through the thermochromic transition of disubstituted PDA's with hydrogen-bonding side groups was first reported by Rubner[16] and later confirmed by Tanaka and co-workers.[5] This is an important finding because it rules out the possibility that the thermochromic behavior of these materials is caused by a thermal disruption of the hydrogen-bonded network.

On the basis of the above results, we conclude that the energetically favored organization at room temperature consists of a hydrogen-bonded network, a planar polydiacetylene backbone, and methylene segments which must adopt an appropriate conformation to bridge these two molecular constraints. In this case, the methylene segments are forced by steric requirements to be primarily gauche in nature. This conclusion is readily verified by the construction of CPK[17] space-filling molecular models.[13] Thus, a polydiacetylene cross-link cannot be inserted into the host polymer lattice with complete retention of hydrogen bonds unless the methylene segments are forced to deviate from their all-trans conformations. At elevated temperatures, the tendency of the methylene groups to reestablish their all-trans state and the associated increased torsional mobility of the PDA backbone (it essentially becomes partially unlocked) combine to allow the conjugated backbone to relax to a less planar conformation with more localized electronic states. The fully hydrogen-bonded network of the side chains, in turn, limits and controls the kinds of molecular adjustments that can take place at elevated temperatures. The structural origin of thermochromism in semicrystalline, cross-polymerized polyamides is therefore very similar to that discovered for urethane-substituted polydiacetylenes such as poly(ETCD).

One of the more important aspects of the thermochromic behavior of these materials is the pronounced reversibility of this transition. Described in detail elsewhere,[8] the thermochromic reversibility of PADA 6,22 and PADA PPD,22 is undoubtedly due to the identical molecular structure of these polymers in the vicinity of the diacetylene groups (see Figure 2). In fact, it is interesting to note the influence of the diamine residue on their thermochromic properties. Replacing a flexible hexamethylene segment with a more rigid *p*-phenylene segment raises the ceiling temperature for complete thermochromic reversibility by only 30 deg whereas the melting temperature of the polymer is raised by 60 deg. These observations simply reinforce the notion that thermochromism is being triggered by localized molecular rearrangements of the methylene segments nearest to the conjugated backbone. The reversible nature of this transition is ensured as long as the constraint points are not permanently disrupted.

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