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Structural Aspects of the Thermochromic Transition in Urethane-Substituted Polydiacetylenes

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ABSTRACT: Thermochromic transitions of the polydiacetylenes (PDAs) of the bis(ethyl)- and bis(isopropyl)urethanes of 5,7-dodecadiyne-1,12-diol (poly(ETCD) and poly(IPUDO)) were investigated by solid-state ^{13}C cross-polarization and magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectroscopy and differential scanning calorimetry (DSC). Side group conformational changes resulting from the polymerization and thermochromic transition were monitored by solid-state ^{13}C CP/MAS NMR. Consecutive heating/cooling cycles in DSC experiments in the temperature range that includes the thermochromic transition reveal that poly(IPUDO) displays better reversibility than poly(ETCD). In solid-state ^{13}C CP/MAS NMR spectra, poly(IPUDO) showed more restricted side group movement during the transition than poly(ETCD), which may be the major factor for better reversibility. A nonthermochromic form of poly(ETCD) was prepared and compared to its thermochromic counterpart by means of X-ray powder diffraction, DSC, Fourier transform infrared spectroscopy (FT-IR), and solid-state ^{13}C CP/MAS NMR spectroscopy. Nonthermochromic poly(ETCD) maintains intramolecular hydrogen bonding between neighboring urethane functions as in thermochromic poly(ETCD). The ^{13}C NMR chemical shifts, sensitive to mechanical strain, of nonthermochromic poly(ETCD) showed an upfield shift of 2 ppm from the red phase alkyne carbon resonance of thermochromic poly(ETCD), which may be an indicator of the removal of thermochromic interactions.

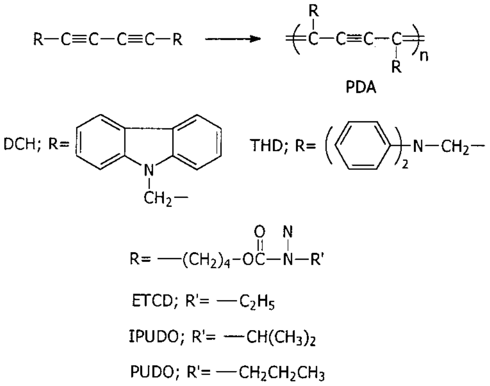
Introduction

Polydiacetylenes (PDAs) are a class of conjugated polymers that have better definition than other conjugated polymers in terms of polymerization mechanisms and solid-state electronic properties since defect-free macroscopic single crystals of PDAs are prepared by solid-state topochemical and topotactic polymerization.[1] The electronic spectra of PDAs are often described by

$$E(\mathbf{k}) = E_0 + D + I(\mathbf{k})$$

where E_0 is the transition energy of an isolated molecule in the gaseous state, D summarizes the energetics of the gas-to-crystal shift, and I is the matrix of the exciton transfer interaction between translationally equivalent and nonequivalent molecules.[2] Local environmental effects on the electronic properties of the PDA backbone are included in the term D. The importance of such an effect is well exemplified by the electronic spectra of single crystals of poly(DCH) and poly(THD).[3] While side groups of these two PDAs are structurally analogous, the carbazole group is more polarizable than diphenylamine, and this results in a stronger interaction with the backbone leading to lower energy absorption.

Thermochromic PDAs such as the PDA of bis(ethylurethane) of 5,7-dodecadiyne-1,12-diol (ETCD),[4,5] the bis(isopropylurethane) of 5,7-dodecadiyne-1,12-diol (IPUDO),[6] and the bis(*n*-propylurethane)-5,7-dodecadiyne-1,12-diol (PUDO)[7] are of particular interest because they exhibit spectral maxima comparable to that of poly(DCH) without suitable polarizable side groups. In addition, these PDAs exhibit a first-order thermochromic phase transition at elevated temperature from a blue to a red phase manifested by optical spectral changes. Thermochromic transition temperatures and $\lambda_{\max}$ below (blue phase) and above (red phase) the transition temperature of these materials are listed in Table 1.



Several proposals have been advanced to understand the molecular and structural basis for this first-order phase transition. An early proposal[4] suggested that the spectral shift was related to a change in the number of “delocalization lengths”. Another suggestion[5,6] involved a change from the acetylenic en-yne structure at room temperature to a butatrienic structure above the temperature of the phase transition. This was ruled out by crystallographic data and quantum chemistry calculations.[1] In addition, a ^{13}C CP/MAS NMR study[8] of PDA−TCDU showed its backbone to be acetylenic and not butatrienic. Another proposal[9] involved the formation of an “orbital-flip defect” or backbone planar−nonplanar transition. This process requires a change in the backbone repeat distance and was ruled out by variable temperature X-ray powder diffraction studies.[10] Local dielectric effects were proposed[11] to be involved in the transition. While this proposal is not quantitated and

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Table 1. Thermochromic Transition Temperatures and λ_{max} at below and above Transition Temperature of Thermochromic PDAs

polymers	T_t (°C)[a]	λ_{max} (nm) ($T < T_t$)	λ_{max} (nm) ($T > T_t$)
poly(ETCD)	120[b]	635[b]	540[b]
poly(IPUDO)	143[c]	649[d]	536[d]
poly(PUDO)	127[e]	640[e]	539[e]

[a] Thermochromic transition temperature. [b] Reference 5. [c] Reference 16. [d] Reference 6. [e] Reference 7.

mechanical strains were not ruled out, it has been criticized.[12] Another proposal was a possible mechanical strain[13] involving side group and backbone during polymerization to maintain intramolecular hydrogen bonding between neighboring urethane functions. To maintain the urethane hydrogen bonds, the methylene groups will be distorted, resulting in a mechanical strain on the backbone.[14] Theoretical calculations revealed that such a side group strain could induce a change in the electronic structure of PDAs.[15] Apparently, during the transition, thermal stimulus gives the side group enough energy to release the mechanical strain by rotation around the single bonds between methylene units although such movement of the side group seems somewhat restricted to maintain the necessary crystal unit cell parameter for reversibility. The side group movement decreases strain on the backbone concomitantly. This proposal was manifested by crystal unit cell volume expansion[10,16] during the transition as a consequence of release of strain. The expansion of the crystal unit cell during transition was found to be largely in the side group direction and between layers while maintaining the backbone repeat distance. The four methylene units between backbone and urethane function in the side group are found to exhibit a change in the conformer population in the course of the transition as evidenced by infrared[17] and solid-state ^{13}C NMR spectroscopy.[18,19] The ambiguity that residual monomer contributes to the phase transition was ruled out by study on poly(IPUDO),[16] which has a conversion from monomer to polymer greater than 99%.[20] In an attempt to find the nature of the thermochromic phase transition, a crystalline nonthermochromic form of poly(ETCD) was prepared from its thermochromic form.[21,22] Interestingly, the nonthermochromic form of poly(ETCD) does not lose crystallinity and maintains vibronic structure in the reflection spectra polarized parallel to the chain axis.[22] Nonetheless, no attempt has been made to establish a correlation between thermochromic and nonthermochromic poly(ETCD) in conjunction with their structures. Therefore, it is worthwhile to investigate the spectral changes of thermochromic vs nonthermochromic poly(ETCD) by solid-state ^{13}C CP/MAS NMR techniques.

Poly(IPUDO) also shows[6] a thermochromic transition below its melting temperature in a similar manner as poly(ETCD). The DSC experiments on poly(IPUDO) revealed that the manifestation of the phase transition during cooling process is much sharper than that of poly(ETCD). Additional information from a calorimetric study on poly(IPUDO) is that changes in the transition temperature and heat of transition during consecutive heating and cooling[16,23] are less prominent than those of poly(ETCD). It is reasonable to assume that the above thermal behavior of poly(ETCD) and poly(IPUDO) at the thermochromic transition under consecutive heating/cooling experiments is closely related to the allowed molecular motions set by each initial crystal packing; thus, the reversibility of the transition may be studied by variable temperature solid-state ^{13}C CP/MAS NMR. However, no solid-state ^{13}C CP/MAS NMR experiments on the thermochromic transition of poly(IPUDO) have been reported to date. Thus, it is of interest to investigate the NMR spectral changes during the transition of poly(IPUDO) in comparison with those of poly(ETCD) and poly(PUDO).

The combined ^{13}C cross-polarization (CP), magic angle spinning (MAS), and high-power dipolar decoupling (DD) CP/MAS/DD NMR technique is very powerful, especially for resolving different conformations present in polymeric materials in the solid state[24−27] that are averaged out by fast molecular motion in solution. PDA crystals have been subjects for solid-state ^{13}C NMR study for establishing the en-yne repeat structure of poly(TCDU),[8] monitoring solid-state modification of poly(DCH),[28] and detecting chemical shift nonequivalence in poly(THD) crystal.[29] Thermochromic transitions in some PDAs are of particular importance due to their particular behavior of conformation change as well as a change in the electronic state of the conjugated backbone, and this is an active research topic for solid-state ^{13}C CP/MAS NMR spectroscopy. Changes in the side group conformer population during the thermochromic transition of poly(PUDO) were successfully characterized by this technique with the highest spectral resolution reported to date.[18] This report also shows solid-state ^{13}C NMR spectra that contain both blue and red phases at the transition temperature, in accord with earlier[19] observation. Other reports include studies on thermochromic poly(ETCD)[19,30,31] that reveal similar results as in the case of poly(PUDO), namely, side group conformer change during the transition. With the recent advancements in solid-state NMR instrumentation, efforts have been made to understand the detailed molecular basis for thermochromic behavior in some PDAs. However, it is still not possible to disclose fully the detailed molecular basis for thermochromic behavior. To understand the molecular basis of thermochromism, one approach may be that an appropriate system could be chosen for more intensive study by different solid-state characterization techniques that are suitable for PDAs.

In this work, we chose thermochromic and nonthermochromic poly(ETCD) for a systematic study by X-ray powder diffraction, Fourier transform infrared spectroscopy, differential scanning calorimetry, and solid-state ^{13}C CP/MAS NMR spectroscopy to understand the molecular basis for the thermochromic phase transition. Also, the thermal behavior of poly(IPUDO) and poly(ETCD) was studied by consecutive heating/cooling by DSC and also by solid-state ^{13}C CP/MAS NMR techniques to understand the nature of the difference in the reversibility of these thermochromic PDAs.

Experimental Section

Preparation of Thermochromic PDAs (Poly(ETCD)-P, Poly(ETCD)-ME, and Poly(IPUDO)) and Nonthermochromic PDA (Poly(ETCD)-CE). ETCD and IPUDO monomers were synthesized according to the method previously reported.[32] Polymerization was performed in an evacuated ampule with ETCD or IPUDO monomer by exposure to ^{60}Co γ-radiation (50 Mrad). The pristine PDA of ETCD and IPUDO are designated poly(ETCD)-P and poly(IPUDO), respectively. Poly(ETCD)-ME was prepared by exposing poly(ETCD)-P to boiling methanol for 12 h (weight loss = 7.4%).

A nonthermochromic form of PDA−ETCD was prepared[22] by exposing poly(ETCD)-P to boiling chlorobenzene for 48 h and is designated as poly(ETCD)-CE (weight loss = 16.0%).

Characterization. FT-IR spectra were recorded on a Perkin-Elmer 1720 FT-IR spectrometer from samples dispersed in KBr pellets with a resolution of 2 cm^{-1} using 64 scans. Thermal properties were recorded with a TA Instrument differential scanning calorimeter model DSC 2910 at a heating and cooling rate of 5 °C/min. The sample weight for a differential scanning calorimetry (DSC) experiment was typically 5 mg. ^{1}H and ^{13}C NMR of ETCD and IPUDO monomers were collected on a Bruker ARX 250 MHz NMR spectrometer using samples in $CDCl_3$ solutions. All X-ray powder diffraction patterns were obtained on a Phillips vertical diffractometer using the Bragg Brentano geometry with a 3.0 kVA constant potential X-ray generator and Cu Kα radiation. The diffractometer is equipped with a diffracted beam monochromator of highly ordered pyrolitic graphite (HOPG) and a scintillation detector. The slit arrangement has a $^1/_4$ degree receiving slit with a preslit of 4 degrees. The samples were prepared in the conventional manner, but because of the limited quantity of materials, a modified holder was employed. The modified holder is front-loaded and approximately half the depth of a standard mount. Several samples were prepared in a few substrates to eliminate the nonsample amorphous background.

^{13}C CP/MAS NMR Spectroscopy. The solid-state ^{13}C NMR spectra of the diacetylene monomer (ETCD and IPUDO) and corresponding polymers were recorded using a Bruker DMX 300 NMR wide bore spectrometer operating at a frequency of 75.47 MHz for ^{13}C nuclei. A ZrO_2 4 mm o.d. rotor was used with Kel-F and a ZrO_2 cap for room temperature and variable temperature measurements, respectively. Cross-polarization (CP) with magic angle spinning (CP/MAS) and dipolar decoupling (DD) techniques were used to obtain ^{13}C NMR spectra of these highly crystalline monomer and polymeric materials. A one time magic angle adjustment was accomplished by maximizing the spinning sideband intensities of the KBr sample in the ^{79}Br NMR spectrum. All spectra were recorded using a rotor spinning speed of 10 kHz to minimize chemical shift anisotropy, and the resulting spectra are free of spinning sidebands in the 0−200 ppm spectral range. A total of 128 free induction decays (FID) were co-added using a pulse width of 3.6 μs, a repetition delay of 10 s, a contact time of 2 ms, a sweep width of 31 kHz, and a decoupling field of 70 kHz. All the FIDs were processed by exponential apodization using a line broadening of 10 Hz. All the ^{13}C CP/MAS NMR spectra were externally referenced to glycine by assigning the carbonyl signal at 176.3 ppm with respect to tetramethylsilane (TMS).

Variable temperature (VT) NMR measurements were performed on the thermochromic PDAs from room temperature up to 160 °C depending on the phase transition temperature of the sample under study. The actual sample temperature was determined by using a calibration curve for ^{207}Pb NMR signal of lead nitrate.[33] For each sample two successive heating and cooling cycles were recorded. The sample was heated at the rate of 5 °C/min and kept at the desired temperature for 10−15 min for temperature equilibration prior to data acquisition. During the VT-NMR measurement, the probe frequently became detuned, resulting in a radio-frequency mismatch leading to increased reflected radio-frequency power. To avoid this, the probe was tuned at each 5 °C increment stage, and the tuning was checked again prior to data acquisition. All spectral parameters remained the same as in the case of the room temperature measurement.

Results and Discussion

Polymerization of ETCD and IPUDO Monomers and ^{13}C NMR Assignments. Thermochromism in some PDAs with tetramethylene−urethane functions is proposed to be due to the relief from mechanical strain initially imposed on the backbone and tetramethylene side groups during polymerization to maintain intramolecular hydrogen bonding between neighboring urethane moieties. To study the molecular basis for the strain imposed on both side groups and backbone by solid-state ^{13}C CP/MAS NMR, the first step requires assignment of all carbon resonances. To assist in the assignments of all carbon resonances in poly(ETCD), ETCD monomer was studied not only by solid-state NMR but also by $^{1}H-^{1}H$ homonuclear correlation (COSY) and $^{1}H-^{13}C$ heteronuclear correlation (HETCOR) NMR experiments in solution (Supporting Information). Table 2 summarizes the assignment of carbon resonances in ETCD monomer and poly(ETCD)-P (see also Figure 1).

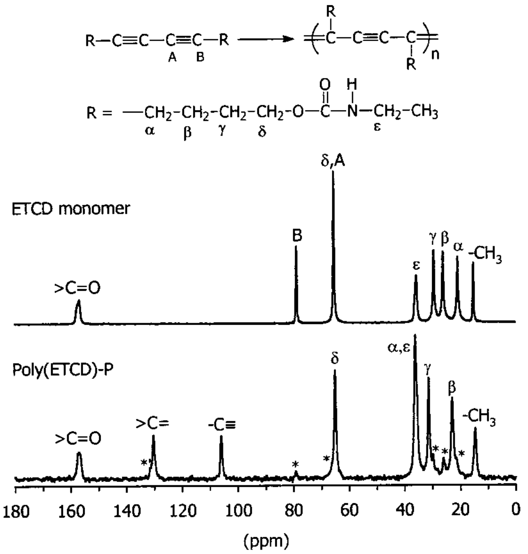

Figure 1. Solid-state ^{13}C CP/MAS NMR spectra of ETCD and poly(ETCD)-P. The peak labeled as * and *′ correspond to residual monomer and oligomer, respectively.

Table 2. Chemical Shift Assignments of ETCD and IPUDO Monomers and Poly(ETCD)-P and Poly(IPUDO) in Solid-State ^{13}C CP/MAS NMR Spectra

	ETCD monomer	poly(ETCD)-P	IPUDO monomer	poly(IPUDO)
>C=O	156.9	157.1	155.4	155.2
>C=		130.4		129.6
−C≡	78.8, 65.4	106.1	77.8, 64.8	105.6
δ	65.4	65.1	65.8	64.7
α	20.8	36.2	19.4	34.9
ϵ	35.7	36.2	42.3	41.4
γ	29.4	31.4	28.4	30.4
β	26.1	23.0	25.2	23.0
CH_3	15.1	14.7	23.9	23.7, 21.4

Although discrepancies in assigning the carbon resonances of the tetramethylene units from an earlier report are noted,[19,31] to the best of our knowledge these assignments in Table 2 fit well for the carbon resonances of poly(ETCD) in the solid-state NMR spectra, taking into consideration the chemical shifts for the crystalline monomers. From the crystal structure of ETCD monomer, the tetramethylene moiety in the side group adopts an all-trans conformation,[34] and all urethane moieties are involved in hydrogen bonding such that the resulting polymer maintains intramolecular hydrogen bonding between the neighboring urethane groups. The chemical shifts of the tetramethylene carbons in the monomer reflect the carbon resonances of a trans conformer. Note a downfield shoulder for the C=O carbon resonance. It implies that there may be more than one species with respect to the geometry of the hydrogen bonds. The possibility of the existence of free C=O is rather unrealistic since the ^{13}C chemical shift of free C═O appears at about 3 ppm upfield from that of hydrogen-bonded C═O.[35] The crystallographic study[34] of ETCD monomer conducted at the temperature of −173 °C reveals only one molecular structure. The downfield shoulder of the C═O carbon resonance in the solid-state ^{13}C CP/MAS NMR spectrum at room temperature may be associated with the defects in the crystalline order, reflecting minute variations in the strength of hydrogen bonding.

The changes in the ^{13}C chemical shift upon polymerization were monitored by solid-state NMR spectroscopy. It is reasonable to assume that the methylene carbon resonances in the side group would have a downfield shift after polymerization as the result of a deshielding effect by the double bond in the backbone. The largest change in the chemical shift of ^{13}C resonances of these methylene groups after polymerization was at the α carbon. The 15.4 ppm downfield shift results because that atom is no longer in the shielding zone of the acetylene. Another noteworthy change is the shift of the β carbon. This carbon experiences a 3.1 ppm upfield shift upon polymerization. It is most likely that this upfield shift is due to a γ-gauche effect. The maximum effect of a gauche conformation on the chemical shift is known to be approximately a 5 ppm downfield shift from that of trans conformer in a linear chain.[36] The discrepancy between these two numbers may come from counteracting effects involving shielding by a γ-gauche effect and deshielding by the backbone double bond. Clearly, a mechanical strain in the side group may arise from having an energetically less stable conformation than that of the all-trans form to maintain stable intramolecular hydrogen bonding between urethanes. Unlike the β carbon, the "γ" carbon shows a downfield shift of 2 ppm, indicative of a double bond deshielding effect on the γ carbon. The alkyne carbon in poly(ETCD)-P has a chemical shift comparable to that in reported data.[19,31] One important observation that merits a comment is the C═O carbon resonance for the monomer and polymer. The chemical shift of the C═O carbon is not affected by polymerization, implying that intermolecular hydrogen bonding between neighboring urethanes of the monomer is maintained in the polymer. Weak carbon resonances arising from residual monomer and oligomer were also observed, as noted in Figure 1.

Chemical shift assignments of IPUDO monomer and poly(IPUDO) are listed in Table 2 (see also Figure 2).

Side group conformational changes in the course of polymerization of IPUDO monomer have a similar tendency as in the case of ETCD (see Table 1). However, the β carbon has an upfield shift in the case of poly(IPUDO) of about 1 ppm less than in the case of poly(ETCD). A possible consequence of this information may be less strain on the side group and the conjugated backbone. Nevertheless, the fact that the chemical shift change in the alkyne carbon of poly(IPUDO) during the phase transition showed similar behavior to poly(ETCD) rules out this prediction and will be further discussed. It is interesting that the isopropyl group showed two resonances for methyls after polymerization. To ensure a correct assignment, a dipolar dephasing experiment was performed, resulting in a spectrum showing the resonances only for methyl carbons (Supporting Information). The presence of two methyl carbon resonances suggests that the methyl groups have different environments after polymerization in the unit cell. However, these two methyls are equivalent in the monomer, showing a single peak in the spectrum in Figure 2a. Note that resonances from monomer are absent in the solid-state ^{13}C CP/MAS NMR spectrum of poly(IPUDO).

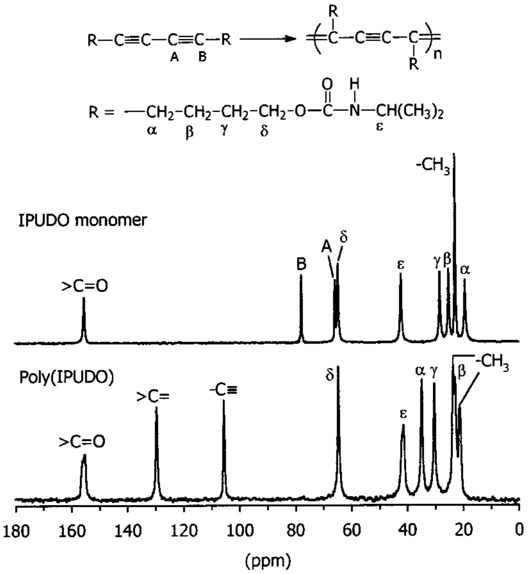

Figure 2. Solid-state ^{13}C CP/MAS NMR spectra of IPUDO and poly(IPUDO).

Table 3. Lattice Spacing of Thermochromic and Nonthermochromic Poly(ETCD) from X-ray Powder Diffraction

	thermo-chromism	*d*-spacings (Å)				
poly(ETCD)-P	yes	17.8	9.0	6.0	5.3	3.8
poly(ETCD)-ME	yes	18.0	9.0	6.1	NA[a]	3.8
poly(ETCD)-CE	no	19.8	10.1	6.8	NA	3.9
poly(IPUDO)	yes	20.3	9.9	6.6		

[a] NA = not available.

Table 4. Transition Temperature and Heat of Transition of Thermochromic and Nonthermochromic Poly(ETCD)[a]

	T_t (°C)	ΔH_t (J/g)	T_m (°C)	ΔH_m (J/g)
ETCD monomer			126.5	166.1
poly(ETCD)-P	123.3	20.8	213.1	107.6
poly(ETCD)-ME	123.3	15.6	214.1	107.2
poly(ETCD)-CE	NO	NO	223.2	113.0
poly(IPUDO)	147.4	34.9	224.6	166.1

[a] T_t and T_m are the thermochromic and melting transition temperature, respectively. ΔH_t and ΔH_m are the heat of thermochromic and melting transition, respectively. NO = not observed.

Thermochromic Phase Transition of Poly(ETCD) and Poly(IPUDO). Poly(ETCD)-P was subjected to solvent extraction with boiling methanol (poly(ETCD)-ME) to remove unreacted monomer. Colorless extracts were produced that contain only unpolymerized monomer, and the color of the crystal remained the same (7.4% weight loss). No significant change in *d* spacings was observed from X-ray powder diffraction in comparison to those of a pristine sample (Table 3).

DSC data revealed that the heat of the thermochromic transition decreased by 25% as compared to poly(ETCD)-P due to the removal of residual monomer while the transition temperature remained same, 123 °C (Figure 3 and Table 4).

The content of residual monomer in poly(ETCD)-P was determined by both gravimetric and calorimetric measurements, knowing the heat of fusion for pure monomer. Calorimetric measurements suggest that poly(ETCD)-P contains 3.5% unreacted monomer, a discrep-

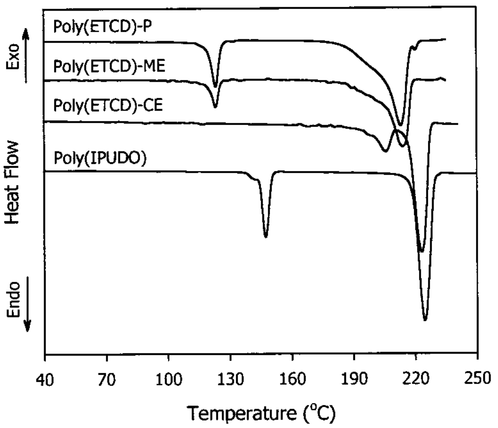

Figure 3. DSC thermograms of thermochromic, nonthermochromic poly(ETCD), and poly(IPUDO).

ancy compared to the gravimetric measurement, 7.4%. It is most likely that the residual monomer in the polymer lattice no longer maintains the same crystal packing as in the bulk monomer crystal. Further, complete removal of residual monomer was not achieved; this is confirmed by the existence of resonances from residual monomer in solid-state ^{13}C CP/MAS spectra, to be discussed later. Thus, applying the heat of fusion of pure monomer to determine the content of unreacted monomer in poly(ETCD)-P is rather unsatisfactory. Poly(ETCD) samples were also studied by FT-IR spectroscopy, and data are presented in the Supporting Information.

The FTIR spectra show that monomer extraction by boiling methanol did not change spectral features of the pristine sample. The FT-IR spectra of poly(ETCD)-P and poly(ETCD)-ME are indistinguishable. The most important observations from the FT-IR spectroscopic study for poly(ETCD)-P and -ME samples are that these samples maintain intramolecular hydrogen bonding[17] between urethane groups by showing a strong C=O stretching at ca. 1690 cm^{-1}.[37] In addition, hydrogen-bonded N−H stretching (3320 cm^{-1})[38,39] in poly(ETCD)-P remained unchanged after methanol extraction (poly(ETCD)-ME). These data also suggest that there are no free C=O moieties that are not participating in hydrogen bonding.

In an analogous manner to poly(ETCD), poly(IPUDO) was also studied by infrared spectroscopy, X-ray powder diffraction, and DSC. Poly(IPUDO) also maintains intramolecular hydrogen bonding between neighboring urethane groups confirmed by C=O stretching at 1687 cm^{-1} [37] and N−H stretching at 3320 cm^{-1}.[38,39] Major diffraction from 0 to 16° in the XRD experiment gave *d* spacings (Table 3) in close agreement to reported data.[16] Thermal properties of poly(IPUDO) are summarized in Table 4. Poly(IPUDO) has a heat of transition twice that of poly(ETCD)-ME as well as a higher transition temperature. Nonetheless, it does not necessarily imply a higher degree of side group movement. Presumably, the initial crystal packing is primarily responsible for the observed difference in the heat of the thermochromic transition. In addition, isopropyl side groups are found to rearrange during the thermochromic transition, which would contribute to the heat of transition. This will be discussed further in the solid-state ^{13}C CP/MAS NMR study.

Two consecutive heating/cooling experiments for the solid-state ^{13}C CP/MAS NMR study of thermochromic poly(ETCD) and poly(IPUDO) in the temperature range that includes the thermochromic transition were performed. The change in the chemical shifts during the thermochromic transition at the first and second heating/cooling cycle was almost exactly the same except for the lowering of the transition temperature during the second cycle with good correlation with the calorimetric experiment. Since chemical shift changes as the samples undergo the thermochromic transition are better presented in the second heating/cooling scan, solid-state ^{13}C CP/MAS NMR spectra of the second set of heating and cooling cycles will be discussed for the changes in chemical shifts during the transition. Poly(ETCD)-P exhibits similar behavior during the thermochromic transition as observed in the solid-state ^{13}C CP/MAS NMR spectra for poly(ETCD)-ME, as discussed.

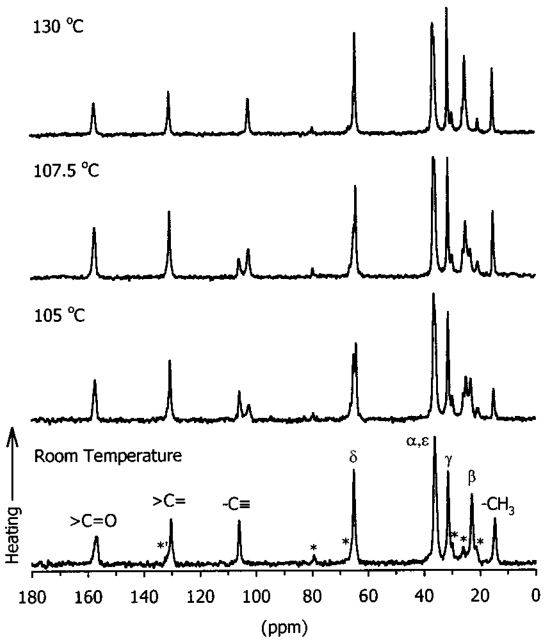

Figure 4. Solid-state ^{13}C CP/MAS NMR spectra of poly(ETCD)-ME in the second heating cycle. The peak labeled as * and *′ correspond to residual monomer and oligomer, respectively.

Significant changes in the chemical shifts of the alkyne, β, and δ carbons were observed as poly(ETCD)-ME undergoes the transition from the blue to red phase as a result of heating (Figure 4 and Table 5).

The β and δ carbons shifted by 2 ppm downfield and 0.9 ppm upfield, respectively, in the red phase to release strain imposed on the side group during polymerization by adopting an energetically more stable conformation with the help of thermal stimuli. The upfield shift of the δ carbon in the red phase is similar to an earlier report,[40] in that the upfield shift of the methylene carbon of poly(ethylene oxide) (7/2 helix) during a change in the gauche to trans conformational state is described. Overlapping carbon resonances of the α and ϵ carbons in the blue phase were resolved in the red phase by 0.6 ppm. Interestingly, no change in the shift for the γ carbon was detected. In addition, the strength of the intramolecular hydrogen bonds is not affected by the thermochromic transition. This is based on the observation that the ^{13}C NMR chemical shift of C=O is unchanged in Figure 4.[35] It is also supported by FT-IR data in which the stretching frequencies for C=O and −NH− were unchanged as the polymer goes through the thermochromic transition. The chemical shift changes

Table 5. Chemical Shift Assignments (ppm) of Thermochromic and Nonthermochromic PDAs in Solid-State ^{13}C CP/MAS NMR Spectra

	poly(ETCD)-ME		poly(IPUDO)		poly(ETCD)-CE	
	blue phase	red phase	blue phase	red phase	at RT[a]	at 135 °C
>C=O	157.0	157.4	155.2	155.9	157.3	157.6
>C=	130.3	130.7	129.6	130.2	130.6	131.0
−C≡	106.0	102.5	105.6	101.7	100.2	100.6
δ	65.1	64.2	64.7	63.6	64.8	65.4
α	36.2	36.5	34.9	35.9	35.6	35.8
ϵ	36.2	35.9	41.4	42.2	35.6	35.8
γ	31.4	31.3	30.4	30.5	27.2	27.9
β	23.0	25.0	23.0	23.0	23.2	24.1
$-CH_3$	14.7	15.2	23.7, 21.4	24.3, 23.0	15.0	15.1

[a] Room temperature.

in the tetramethylene unit lead to the conclusion that the side group adopts a conformation that lessens the strain stored in the blue phase yet maintains hydrogen bonding in the side group so that the β and δ carbons have changed their conformations. As a consequence of strain released in the red phase, the alkyne carbon resonance shifted upfield by 3.5 ppm. In general, the chemical shift of alkyne carbon is highly sensitive to the conjugation length[41] and mechanical strain[42] on such carbons. The ^{13}C chemical shift of alkyne carbons with respect to the degree of ring strain is well documented.[35] In some strained cyclic mono- and dialkyne, strain on the alkyne carbon results in the bending of the triple bond.[42] The bending of the triple bond does not affect bond lengths significantly even with an angle of 150° at the sp center. However, ^{13}C chemical shift of alkyne carbons is very sensitive to such a strain as manifested[42] by downfield shift of the alkyne carbon resonance in ^{13}C NMR spectra by about 30 ppm as bending angle of alkyne varies from 180° to 150°. This systematic study[42] of strained alkyne compounds helps to appreciate the strain exerted on the backbone by monitoring the changes in the chemical shift of the polymer backbone alkyne carbons. Another contributing factor for changes in the chemical shift of alkyne carbon could be related to the shortening of the conjugation length. The upfield shift of the alkyne carbon resonance could imply that the electron density on that carbon has been increased, meaning a decrease of the strength of π-electron delocalization. This is ruled out by the existing[10,16] crystallographic data. Clearly, solid-state ^{13}C CP/MAS NMR data show a conformer population change in the side group upon thermochromic transition. Nevertheless, it is still unclear whether the side group or backbone experiences complete relief from mechanical strain.

During the cooling cycle, all shifted resonances regained their original chemical shifts at room temperature in the blue phase (Figure 5). The transitions in the heating and cooling cycles observed by solid-state ^{13}C CP/MAS NMR had a good correlation with those detected by DSC. A comment should be made on the observation of carbon resonances assigned for residual monomer and oligomer. Boiling methanol extraction does not seem harsh enough to allow solvent molecules to penetrate the crystal to remove completely the residual monomer or oligomer that are surrounded by the crystal lattice. Contrast this with boiling chlorobenzene extraction discussed below.

In the case of poly(IPUDO), alkyne, δ, α, and γ carbons showed the same pattern in change of chemical shift upon transition as in thermochromic poly(ETCD) (Supporting Information). Unlike poly(ETCD), with no interfering resonance for the α carbon, it was possible to determine the exact chemical shift change in the α carbon (Table 5).

It is surprising that neither the β nor γ carbon changed their chemical shifts during the transition while the alkyne carbon resonance showed a 3.9 ppm upfield shift. A methyl carbon resonance at 21.4 ppm moved downfield by 1.6 ppm although separation from the other methyl was still observed. In the cooling process, all resonances regained their original chemical shifts, indicating reversibility.

Reversibility of the Thermochromic Transitions of Poly(ETCD) and Poly(IPUDO). To investigate the reversibility of the thermochromic transitions of poly(ETCD) and poly(IPUDO), four consecutive heating/cooling scans for DSC were performed. Both poly(ETCD)-P and poly(ETCD)-ME showed a decrease in the thermochromic transition temperature (T_t) and the heat of transition (ΔH_t) as well as broadening of transition on repeated temperature cycling. In the case of poly(ETCD)-P, the decrease in both T_t and ΔH_t by 12.6 °C and 14.6%, respectively, as observed at the fourth heating cycle (Table 6). Likewise, poly(ETCD)-ME also showed a decrease in T_t by 11.8 °C and ΔH_t by 18.9% at the fourth heating cycle (Figure 6 and Table 6).

These results are consistent with an earlier report.[4] Since T_t and ΔH_t are not reproducible over consecutive heating and cooling, thermochromism in poly(ETCD)

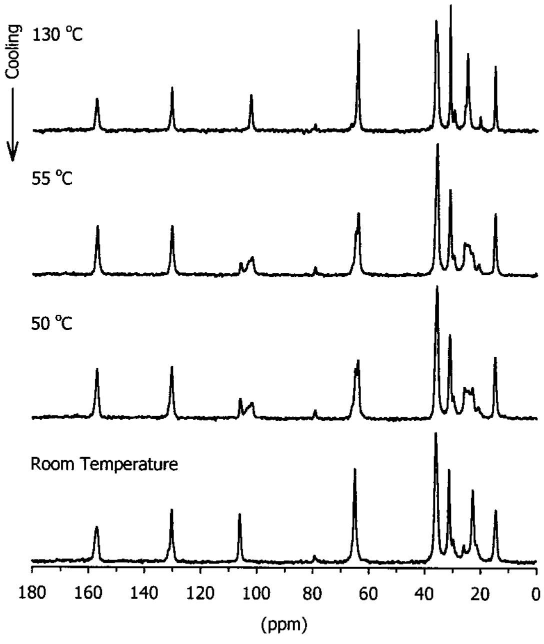

Figure 5. Solid-state ^{13}C CP/MAS NMR spectra of poly(ETCD)-ME in the second cooling cycle.

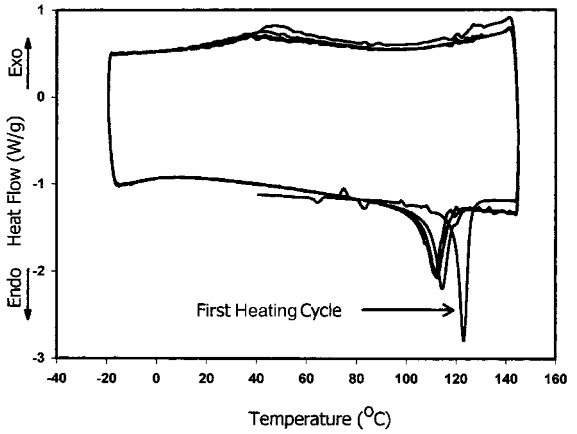

Figure 6. DSC thermograms of poly(ETCD)-ME in the consecutive heating/cooling cycles from −20 to 145 °C.

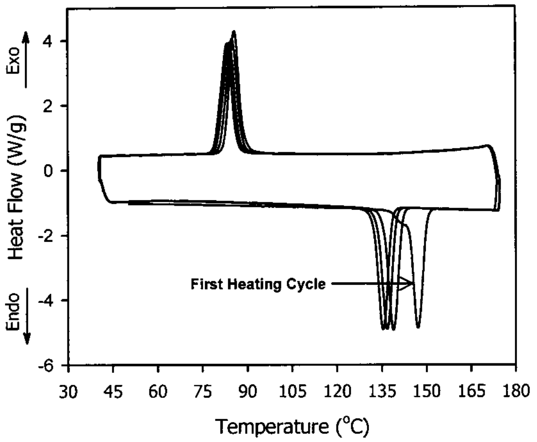

Figure 7. DSC thermograms of poly(IPUDO) in the consecutive heating/cooling cycles from 40 to 175 °C.

Table 6. Comparison of the Thermochromic Temperature and Heat of Transition in the First and Fourth Heating Cycle

	ΔT_t (°C)	$\Delta(\Delta H_t)$ (%)
poly(ETCD)-P	12.6	14.6
poly(ETCD)-ME	11.8	20.1
poly(IPUDO)	11.8	4.1

may not be fully reversible, and there may be some hysteresis as the system goes through blue−red−blue transitions. Reversibility of thermochromism of poly(IPUDO) was investigated by DSC with consecutive heating and cooling experiment between 40 and 175 °C (Figure 7).

A thermal lag in reversibility under repetitive heating and cooling was observed in the same manner reported as earlier.[16,23] Comparison to poly(ETCD) suggests that poly(IPUDO) (Table 6) is superior to poly(ETCD) in terms of reversibility. A sharp transition in the cooling process, clearly from the red to the blue phase, accounts for the better reversibility of poly(IPUDO) although a slight thermal lag is still noticeable.

There are two observations in the solid-state ^{13}C CP/MAS NMR spectra that relate to the DSC data for these polymers. First, the line width of the red phase alkyne carbon resonance of poly(ETCD)-ME upon the transition in cooling is significantly broader than that in the heating (Figure 8).

It seems that the chromic change from red to blue in the cooling cycle is slower and covers a wider temperature range than that in the heating cycle although the transition upon cooling seems complete when the temperature reaches ambient. Many intermediate electronic states may overlap. This is also evidenced by the broad exotherm in the calorimetric experiment in the cooling cycle (Figure 6). In the case of poly(IPUDO), the line width of the red phase alkyne carbon in the cooling process is narrower than that of poly(ETCD) in the cooling process (Figure 8), which implies a more confined geometry in the case of poly(IPUDO), giving a well-defined transition in the cooling process. This observation corresponds well to the calorimetric study (Figure 7). Second, side group movement of poly(IPUDO) during the transition is more restricted than that of poly(ETCD)-P (Table 7).

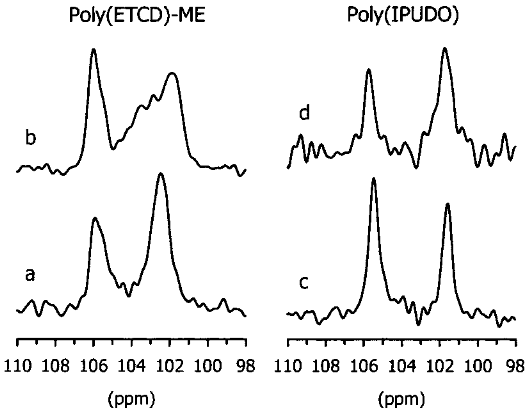

Figure 8. Blue and red phase alkyne carbon resonances of poly(ETCD)-ME (a: at 107.5 °C during second heating; b: at 50 °C during second cooling) and poly(IPUDO) (c: at 135 °C during second heating; d: at 95 °C during second cooling).

Table 7. Summary of Chemical Shift Change of Carbon Resonances in Poly(IPUDO) and Poly(ETCD) during Thermochromic Transition

	poly(ETCD)[a]		poly(IPUDO)	
	$\Delta\delta$ (ppm)	direction	$\Delta\delta$ (ppm)	direction
−C≡	3.5	upfield	3.9	upfield
α	UD[b]	downfield	1.0	downfield
β	2.0	downfield	no[c]	
γ	no		no	
δ	0.9	upfield	1.1	upfield

[a] Poly(ETCD)-ME. [b] Unable to determine. [c] No change was observed.

With all the information obtained so far, it appears that more restricted movement in the side group during the thermochromic transition produces better reversibility. This interpretation is supported by a previous report[43] on poly(4-BCMU) which contains tetramethylene urethane functions in the side group. Although poly(4-BCMU) shows a chromic change from blue to red on heating, this is an irreversible chromic change due to disruption of intramolecular hydrogen bonding. The largest chemical shift change in the tetramethylene carbons was observed by 5 ppm downfield shift at the first heating from solid-state ^{13}C CP/MAS NMR study.[43] In summary, with the results of solid-state ^{13}C CP/MAS NMR study on thermochromic poly(ETCD) and poly(IPUDO) during the transition, the degree of thermal movement of the tetramethylene side group may be a major factor that determines the reversibility of the thermochromic transition. This may be related to the initial crystal packing.

Thermochromic vs Nonthermochromic Poly(ETCD). Solvent extraction of poly(ETCD)-P with boil-

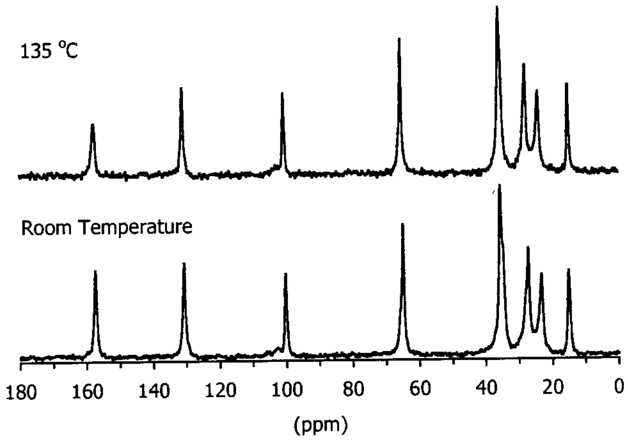

Figure 9. Solid-state ^{13}C CP/MAS NMR spectra of poly(ETCD)-CE at room temperature and 135 °C.

ing chlorobenzene[21,22] removes oligomer as well as residual monomers and produces a red nonthermochromic form of PDA, poly(ETCD)-CE, while giving orange extracts (16.0 wt % weight loss). Unit cell expansion was observed by X-ray powder diffraction (Table 3) for poly(ETCD) after chlorobenzene extraction. The data were consistent with the reported values.[22] The thermochromic transition completely disappeared whereas a slight increase in both T_m and ΔH_m was detected by DSC (Figure 3 and Table 3). It appears that residual oligomers and monomer may act as impurities to depress the melting point of poly(ETCD)-P. No change in the DSC thermogram was observed with poly(ETCD)-CE after the consecutive heating and cooling run from −20 to 145 °C (Supporting Information), implying the removal of interactions that result in thermochromism by boiling chlorobenzene extraction.

The chemical shift of the alkyne carbon in poly(ETCD)-CE) (100.2 ppm) has a value close to that of PDA in solution (99.4 ppm)[41] (Figure 9 and Table 5).

A similar alkyne chemical shift is also observed in poly(4-BCMU) cooled from the red melt in which intramolecular hydrogen bonding has been disrupted.[43] In addition to the main alkyne carbon resonance in poly(ETCD)-CE, the presence of a weak and broad downfield shoulder suggests the persistence of some other poly(ETCD) phases, as also indicated in the electronic spectra.[22] While the electronic spectra observed by reflectance probe the surface, ^{13}C NMR monitors the bulk. It is surprising to notice an upfield shift of 4 ppm for the γ-carbon of the nonthermochromic poly(ETCD)-CE from that of blue phase chemical shift of poly(ETCD)-ME (or poly(ETCD)-P). A detailed conformational analysis may be required to understand the dynamics of the methylene carbons in the side chain. No significant spectral changes were observed for the alkyne and other carbon resonances at elevated temperatures, indicating the absence of a transition in this sample. The chemical shift of the alkyne carbon, which is sensitive to strain, in the poly(ETCD)-CE spectrum may be an indicator of the removal of the thermochromic transition since poly(ETCD)-CE is thought to be largely free of strain. To ensure that the removal of the thermochromic transition is not due to a thermal annealing effect, poly(ETCD)-P was annealed at 132 °C (boiling point of chlorobenzene) for 48 h. Solid-state ^{13}C NMR spectrum of annealed poly(ETCD)-P (Supporting Information) showed identical ^{13}C chemical shifts as those of pristine poly(ETCD)-P, which rules out the possibility of a thermal annealing effect on the removal of thermochromic interactions during boiling chlorobenzene extraction.

Conclusions

Solid-state ^{13}C CP/MAS NMR spectroscopy, in correlation with calorimetric study, reveals a molecular basis for the thermochromism of poly(ETCD) and poly(IPUDO). The differences in the conformational change of the tetramethylene side group of thermochromic poly(ETCD) from poly(IPUDO) are observed by solid-state ^{13}C CP/MAS NMR spectroscopy. The results of NMR spectroscopy correspond to the observed differences in reversibility and the thermal lags of these materials found by calorimetric study. The extent of the change in the chemical shift of the β carbon during the thermochromic transition, which induces the release of mechanical strain on the backbone, in thermochromic poly(ETCD) shows a significant difference from that of poly(IPUDO). These observations yield a conclusion that the reduction of strain on the conjugated backbone does not necessarily require the side groups to be completely relieved from strain. Moreover, less freedom of movement of the side group during transition may be a requisite for better reversibility, as observed in the solid-state ^{13}C CP/MAS NMR study on poly(IPUDO).

As noted earlier, triple bond ^{13}C chemical shifts are sensitive to the conjugation length and to mechanical strain on such carbons. The ^{13}C chemical shifts observed here for blue phase of thermochromic poly(ETCD), red phase of thermochromic poly(ETCD), and nonthermochromic poly(ETCD) (poly(ETCD)-CE) are consistent with a continual decrease of mechanical strains as revealed by a gradual increase of electron density on the alkyne ^{13}C nuclei. This is reflected in the ^{13}C chemical shifts of the alkyne carbon.

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Supporting Information Available: FT-IR and ^{13}C CP/MAS NMR spectra of poly(ETCD) and poly(IPUDO), 2-D NMR spectra of ETCD and IPUDO, ^{1}H−^{13}C heteronuclear correlation NMR spectra of ETCD and IPUDO, solid-state NMR spectrum of poly(ETCD)-P, and DSC thermogram of poly(ETCD)-CE. This material is available free of charge via the Internet at http://pubs.acs.org.

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