(17) Risen, W. M., presented in part at the 193rd meeting of the American Chemical Society, Denver, April, 1987.

* Author to whom correspondence should be sent.

A. F. Galambos, W. B. Stockton, J. T. Koberstein, A. Sen, and R. A. Weiss*
Institute of Materials Science and Department of Chemical Engineering, University of Connecticut
Storrs, Connecticut 06268

T. P. Russell
IMB Almaden Research Center, 650 Harry Road
San Jose, California 95720

Received June 23, 1987

Study of the Thermochromic Phase Transition of Polydiacetylene by Solid-State ^{13}C NMR

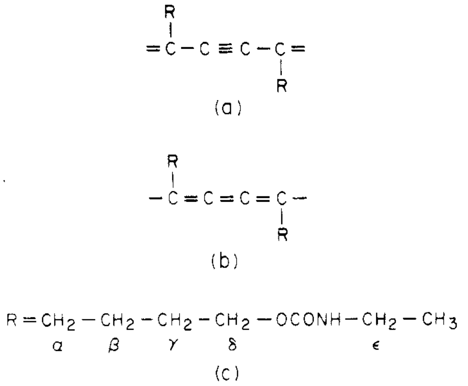
Poly(diacetylenes) (PDA) have been studied extensively by many researchers,[1,2] because they have unusual optical properties. They are also unique among synthetic organic polymers in that they can be obtained as single crystals by solid-state polymerization of suitably substituted diacetylenes. PDA has a backbone consisting of conjugated double and triple bonds as shown in Figure 1a. This is the so-called acetylenic structure. The substituents R are in the trans position with regard to the double bond. The optical properties are closely related to the electronic state of the conjugated backbone. The carbon atoms of the backbone are in a plane within the lattice and chains are extended along the *c* axis of the crystal. Another structure called the butatrienic structure (see Figure 1b) has also been proposed for the PDA backbone; however, its existence has not been firmly established.[2]

Some PDA show the thermochromic solid-state transition accompanying the changes in optical absorption and color, which is ascribed to a change in the electronic state of the backbone. Some models have been proposed for the thermochromic transition,[1,2] however, the mechanism is still not experimentally established.

The side-chain organization should strongly influence the electronic properties of the backbone through the strain it places on the backbone. The thermally induced change in molecular conformation of the side chain and its influence on the electron density distribution of the backbone will be studied in this paper.

Solid-state ^{13}C nuclear magnetic resonance (NMR) is a powerful tool for studying the conformation and the dynamics of motion in macromolecules. The chemical shift position reflects the shielding of the magnetic field due to the electronic environment of carbons; therefore, it should be sensitive to the electronic structure of the backbone, such as the conjugation length or the delocalization of electrons. There are several ^{13}C NMR studies of PDA in solutions[3-5] and in the solid state;[6] however, to our knowledge, there has been no study of the thermochromic phase transition of PDA in the solid state by NMR. Compared to other methods, such as optical,[7,8] IR,[9,10] and Raman[7,8] spectroscopic measurement, ^{13}C NMR should give much more direct information on the conformation of the backbone. Since the quality of some PDA crystals is less than optimal for a precise X-ray crystal structure determination, solid-state ^{13}C NMR provides an alternative approach for obtaining detailed structural information about the backbone. Furthermore, the motional state of both the side chain and the backbone can be studied by NMR.

Here we report the preliminary results of a ^{13}C NMR study of the thermochromic phase transition of poly(ETCD) whose substituent R is $(CH_2)_4OCONHCH_2CH_3$. Poly(ETCD) is one of the typical polydiacetylenes with a thermochromic phase transition.



$$=\overset{R}{\underset{}{C}}-C\equiv C-\underset{R}{C}=$$

(a)

$$-\overset{R}{C}=C=C=\underset{R}{C}-$$

(b)

$$R=\underset{\alpha}{CH_2}-\underset{\beta}{CH_2}-\underset{\gamma}{CH_2}-\underset{\delta}{CH_2}-OCONH-\underset{\epsilon}{CH_2}-CH_3$$

(c)

Figure 1. (a) Acetylenic structure, (b) butatrienic structure, and (c) the substituent R of poly(ETCD).

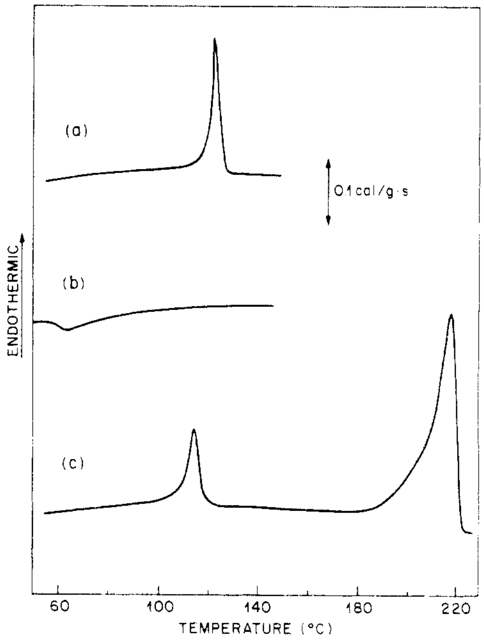


Figure 2. DSC scans at 10 °C/min for (a) the first heating process, (b) the following cooling process, and (c) the second heating process to above the melting point.

Poly(ETCD) was obtained by the solid-state polymerization of ETCD (5,7-dodecadiyne-1,12-diol bis(ethylurethane)). The synthesis of ETCD was performed by the procedure reported in the literature.[11] The polymerization was accomplished by irradiation with 50 Mrd of ^{60}Co γ-rays at room temperature. Unreacted monomer was removed by extraction with acetone.

^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer at a static magnetic field of 4.7 T. Magic angle sample spinning (MAS) at a speed of ca. 3 kHz was achieved with a Doty Scientific variable-temperature probe, which utilizes a double air bearing design. The temperature was varied from 20 to 135 °C by use of heated flow. Temperature was controlled within ±1 °C. Poly(ETCD) in powder form was packed in an aluminum oxide rotor with Kel-F [poly(chlorotrifluoroethylene)] caps. A 45-KHz rf field strength was used for dipolar decoupling (DD), with a decoupling period of 200 ms. The optimum cross polarization (CP) time was found to be 2 ms at room temperature and we used this value at all temperatures. The spectra were referenced to the resonance of POM (89.1 ppm from TMS) added to the rotor.

The thermochromic transition was also studied by dif-

0024-9297/87/2220-3094$01.50/0

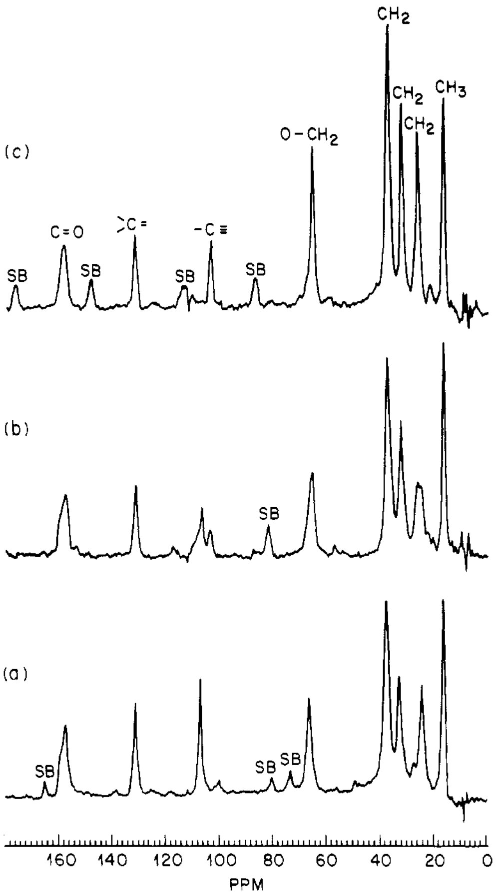


Figure 3. CP MAS/DD spectra of poly(ETCD) at 23 (a), 115 (b), and at 127 °C (c). Spectra were referenced to the resonance of POM (89.1 ppm from TMS). The peaks labeled as SB corresond to the spinning sidebands.

ferential scanning calorimetry (Perkin-Elmer DSC-4). The peak position of the transition is at 125 °C in the heating process and at 65 °C in the cooling process as shown in Figure 2. The second endotherm in the heating process corresponds to the melting and it has a much larger heat of fusion than the thermochromic transition. This suggests that much of the crystalline order is preserved above the thermochromic transition and indirectly indicates that there is no disruption of hydrogen bonding between side chains during the transition.

Figure 3 shows the temperature dependence of ^{13}C NMR spectra in the heating process. The cooling process was also studied. Here the changes in the spectra are essentially the same as during the heating process except for the lower transition temperature. According to dipolar dephasing experiments, the three most downfield resonances belong to carbons having no protons directly bonded. From downfield to upfield, these peaks are assigned to C=O, >C=, and —C≡, respectively. The most upfield peak is assigned to the methyl group. The other four peaks are assigned to the CH_2 carbons of the side chains. The assignment of CH_2 carbons was done by comparison with model compounds. Relative chemical shifts for each carbon are listed in Table I. The results are consistent with those obtained for poly(nBCMU) in solution.[3] One CH_2 resonance is not observed in the spectra probably due to overlap. (The resonance assigned to β,γ-CH_2 is resolved into individual peaks during spin-lattice relaxation measurements).

We can clearly see the coexistence of both phases at 115 °C in the heating process (see Figure 3) and at 60 °C in the cooling process. There is a large thermal hysteresis of over 50 °C. These facts indicate the transition to be of the first order, as established in earlier studies.[7,8,10]

Table I
^{13}C NMR Chemical Shifts (ppm) for Poly(ETCD) in the Solid State

	δ ^{13}C, ppm vs TMS[a]	
carbon[b]	blue phase[c]	red phase[d]
C=O	157.5	158.3
>C=	131.6	132.0
—C≡	107.4	103.6
δ-CH_2	66.6	65.5
α-CH_2	37.3	37.8
ϵ-CH_2	32.9	32.6
β,γ-CH_2	24.5	26.4
CH_3	16.2	16.7

[a] Referenced to the POM resonance at 89.1 ppm from TMS. [b] See Figure 1 for the structure of poly(ETCD). [c] Low *T*. [d] High *T*.

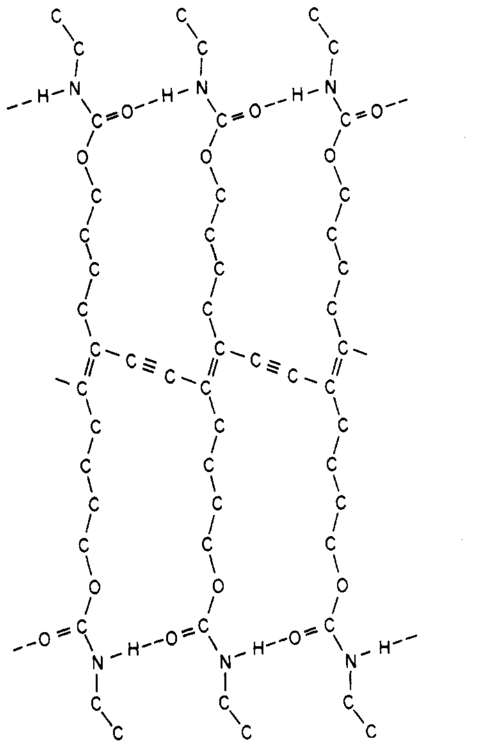


Figure 4. Schematic diagram for the intramolecular structure of poly(ETCD) with hydrogen bonding. Protons are not drawing in this figure and --- represents the hydrogen bond. This diagram is an approximation of the crystal structure reported[12] for poly(TCDU), which differs in molecular structure from poly(ETCD) only by the substitution of a phenyl ring for the ethyl group in the side chains.

Here we discuss the chemical shift difference between the low-temperature (blue) phase and the high-temperature (red) phase (see Table I). The resonance of —C≡ in the red phase is shifted upfield by 4 ppm compared to that of the blue phase. The most upfield CH_2 peak of the red phase is shifted 2 ppm downfield compared to that of the blue phase. These two resonances show the largest chemical shift change. The chemical shift changes of the other carbon resonances are rather small, but not negligible.

The hydrogen bonding between substituents has a strong effect on the whole structure of PDA. The intramolecular hydrogen bonding (see Figure 4) is probably dominant in poly(ETCD). The hydrogen bonds between C=O and N—H may affect the chemical shift of C=O. Recently, however, it has been suggested from FTIR studies that there is no significant change of N—H vi-

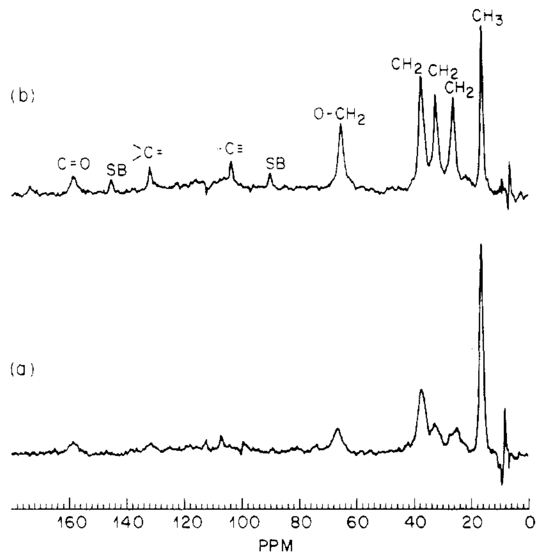


Figure 5. MAS/DD spectra of poly(ETCD) at 80 (a) and 135 °C (b). Spectra were referenced to the resonance of POM (89.1 ppm from TMS). The peaks labeled as SB correspond to the spinning sidebands.

bration in poly(ETCD) during the transition.[10] Consistent with this suggestion is the observation that the chemical shift of C═O is nearly insensitive to the thermochromic transition (see Table I and Figure 3). Thus, the transition of poly(ETCD) is not caused by the thermal disruption of hydrogen bonding and it is different in this respect from that of poly(nBCMU), which is caused by the breakdown of the hydrogen-bonded network of side groups.

Parts a and b of Figure 5 show the MAS/DD spectra of the blue phase and the red phase, respectively. All CH_2 and CH_3 carbons become mobile in the red phase, while in the blue phase only the terminal CH_2 and CH_3 carbons are mobile. However, the motional state of C═O is not affected much by the transition. This suggests that the hydrogen bonds between C═O and N—H are maintained, while the methylene segments between the backbone and the urethane groups become mobile and their conformation becomes disordered in the red phase.

Here we consider the electron density distribution and the conformation of the backbone. According to recent theoretical calculations, a significant decrease of the electron density about >C═ occurs as the degree of delocalization increases.[13] As the backbone transforms from the acetylenic to the butatrienic form, the shift in the electron densities between atoms >C═, and —C≡ flows from >C═ to —C≡.[13] This should cause a decrease in the magnetic shielding at >C═ and an increase at —C≡. Therefore, chemical shifts of both backbone carbon resonances should accompany the transition. This expectation is inconsistent with our NMR results, in which only the chemical shift of —C≡ changes significantly. The chemical shift of ═C═ in a butatrienic structure is estimated to be about 200 ppm from TMS.[3] Comparison with the chemical shifts observed for the unsaturated backbone eliminates the possibility of the butatrienic structure (see Table I).

Because of the small observed change in chemical shift (0.5 ppm) for the α-CH_2 resonance, trans–cis isomerization about the —C═C— backbone bonds does not accompany the thermochromic transition in poly(ETCD). Such an isomerization has been suggested[14] to accompany the rod-to-coil transition observed in solution for soluble PDA's such as poly(4BCMU).

The transition is ascribed to the transformation from a planar to a slightly nonplanar conformation of the backbone. The more disordered conformation should produce a less delocalized electronic state. Rotation about the single bond of the acetylenic structure is not difficult. Our data reveal that only the chemical shift of —C≡ changes, about 4 ppm upfield. This shows that the degree of delocalization of electrons decreases and —C≡ becomes more shielded. According to the motional state study, via measurement of carbon spin–lattice relaxation times, the motion of the main chain is much less in the blue phase than in the red phase, which also suggests that the conformation of the backbone in the blue phase is the rigid, planar one.

This change in backbone conformation is accompanied by a change of side-chain conformation. Relative to the chemical shift change for —C≡, the smaller change in the chemical shift of >C═ is probably a result of cancellation of the effects of electron delocalization and the conformational change in the side chains. The flexibility of side chains may allow the backbone to relax to a lower free energy, higher entropy state. Extension of conformational energy calculations[13] to include side-chain flexibility might shed light on this question.

The difference in side-chain conformations is apparent because of the chemical shift change of the β,γ-CH_2 carbon resonances. The backbone conformation seems to be more stable than that of the side chain. The melting point of an alkyl chain is usually low. In this PDA, both ends of the alkyl sequence are anchored by the backbone and hydrogen bonds and the sequence motion is restricted. The high transition temperature is caused by these motional constraints. The lowest energy conformation for the side chain is an all-planar zigzag. NMR results suggest that the conformation of the side chain is changed during the thermochromic transition (see Figure 3). Generally, the conformation and crystalline structure of a polymer are very strongly affected by side-chain conformations and their motional state. Some solid-state transitions in polymer crystals are thought to be induced by the transition of side chains, as in the case of the polysilanes.[15]

The importance of the conformation of the alkyl side chains to the transition is clear from other evidence; no thermochromic transition is obtained for the analogous PDA with substituent groups $(CH_2)_nOCONHC_2H_5$, where $n = 2$ or 3. This is probably because the alkyl groups are too short and the conformational restriction from both backbone and hydrogen bonding is too strong. The motion of the alkyl chains in poly(butylene terephtalate) (PBT), both ends of which are restricted, has been studied by Jelinski et al.[16] The conformations and motions of the alkyl side chains in the red phase may be similar to that of PBT.

It has been suggested from optical and Raman spectra that above the transition point only one π-electron delocalization domain dominates, while below the transition point three dominant delocalization lengths exist.[7] Furthermore, the existence of three different chain types with different conformations was suggested. However, these suggestions are inconsistent with our NMR results. Our results show that, on the NMR time scale, there is no coexistence of two different kinds of backbone conformations in the temperature region far from the transition.

In conclusion, the thermochromic transition in poly(ETCD) is found to be due to a planar–nonplanar conformational change of the backbone. This conformational change is assisted by the thermal motion and consequent change in the conformation and crystal packing of the side chains. Hydrogen bonding does not play a direct role in the transition. Contribution of the butatrienic form is negligible in both phases, and the thermochromic transition is not accompanied by trans–cis isomerization of C=C bonds. While the planar to nonplanar conformational transition had previously been suspected to cause the thermochromic transitions observed in some PDA's, this work provides unambiguous experimental support for this suggestion.

References and Notes

(1) For a review, see: Bloor, D.; Chance, R. R. *Polydiacetylenes*; NATO ASI Series E. Applied Science, Martinus Nijhoff Publishers: 1985.
(2) Chance, R. R. *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1986; Vol. 4, p 767.
(3) Babbitt, G. E.; Patel, G. N. *Macromolecules* **1981**, *14*, 554.
(4) Plachetta, C.; Schulz, R. C. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 815.
(5) Wenz, G.; Muller, M. A.; Schmidt, M.; Wegner, G. *Macromolecules* **1984**, *17*, 837.
(6) Havens, J. R.; Thakur, M.; Lando, J. B.; Koenig, J. L. *Macromolecules* **1984**, *17*, 1071.
(7) Exarhos, G. J.; Risen, W. M., Jr.; Baughman, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 481.
(8) Chance, R. R.; Baughman, R. H.; Muller, H.; Eckhardt, C. J. *J. Chem. Phys.* **1977**, *67*, 3616.
(9) Walters, G.; Painter, P.; Ika, P.; Frisch, H. *Macromolecules* **1986**, *19*, 888.
(10) Rubner, M. F.; Sandman, D. J.; Velazquez, C. S. *Macromolecules* **1987**, *20*, 1296.
(11) Sandman, D. J.; Samuelson, L. M.; Velazquez, C. S. *Polym. Commun.* **1986**, *27*, 242.
(12) Enkelmann, V.; Lando, J. B. *Acta Crystallogr., Sect. B* **1978**, *B34*, 2352.
(13) Orchard, B. J.; Tripathy, S. K. *Macromolecules* **1986**, *19*, 1844.
(14) Berlinsky, A. J.; Wudl, F.; Lim, K. C.; Fincher, C. R.; Heeger, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *22*, 847.
(15) Schilling, F. C.; Bovey, F. A.; Lovinger, A. J.; Ziegler, J. H. *Macromolecules* **1986**, *19*, 2660.
(16) Bovey, F. A.; Jelinski, L. W. *J. Phys. Chem.* **1985**, *89*, 571.

[†] Permanent address: Department of Applied Physics, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan.

[‡] Permanent address: Instituto de Plasticos y Caucho, C.S.I.C., Juan de la Cierva 3, 28006 Madrid, Spain.

Hajime Tanaka,[†] M. Thakur, M. A. Gomez,[‡] and A. E. Tonelli*

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Received August 31, 1987