Thermochromic Phase Transition of a Polydiacetylene, Poly(ETCD), Studied by High-Resolution Solid-State ^{13}C NMR

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ABSTRACT: The thermochromic phase transition of a polydiacetylene, poly(ETCD), whose substituent is $(CH_2)_4OCONHC_2H_5$, has been studied by use of high-resolution, solid-state ^{13}C NMR. The change in the electronic state of the conjugated backbone, which is responsible for the color change, is directly monitored through the change in the chemical shift observed for the —C≡ backbone carbon, which reflects the change in the delocalization of backbone π-electrons. We demonstrate the absence of a stable butatrienic structure. The side-chain conformations have been delineated by the comparison of their chemical shifts with those observed for several model compounds and polymers whose conformations are known. The side chains have more gauche character in the low-temperature blue phase than in the high-temperature red phase. The transition of the backbone electronic structure has been found to be related to the conformational transition of the side-chain alkyl group, which permits a retention of inter-side-chain hydrogen bonding through the transition. The thermochromic phase transition may be caused by the strain placed on the backbone by the hydrogen-bonded side chains. The difference in the motional states of both backbone and side chains in each phase is also discussed.

Introduction

Poly(diacetylene)s (PDA's) are unusual among synthetic organic polymers in that they can be obtained as single crystals by the solid-state topochemical polymerization[1] of substituted diacetylene. PDA's also have interesting optical properties, such as large nonlinear optical responses and thermochromic phase transitions. These properties have been studied by many researchers.[2,3] Their optical properties originate from their backbone structures consisting of conjugated double and triple bonds as illustrated in Figure 1. Two structures have been proposed for the conjugated backbone in PDA, the acetylenic (a) and the butatrienic (b) structures. Since the optical properties of PDA's directly reflect the electronic state of their backbones, it is very important to understand their backbone conformations.

Recently[4] we have demonstrated that solid-state ^{13}C NMR is a very powerful method for studying the backbone and side-chain conformations of PDA's. The electronic state of each backbone carbon determines the extent to which its nucleus is shielded from the applied magnetic field, as manifested by the observed chemical shift positions. Like other commonly used methods, such as X-ray diffraction,[5-7] optical,[8,9] IR,[10,11] and Raman[8,9] spectroscopic measurements, high-resolution, solid-state ^{13}C NMR can provide conformational information.

The conformation of the side chains in PDA's, which may have an important effect on the backbone organization, can be especially clearly studied by solid-state NMR. Another advantage of NMR is that it provides information concerning the motional state of backbone and side-chain carbons through measurement of the spin–lattice relaxation time, T_1, the spin–lattice relaxation time in the rotating frame, $T_{1\rho}$, and the resonance line width.

Here we report the ^{13}C NMR study of the thermochromic phase transition in poly(ETCD), whose substituent R is $(CH_2)_4OCONHCH_2CH_3$ (see Figure 1c). Poly(ETCD) is typical of the PDA's which exhibit a thermochromic transition, as evidenced by a change in color from blue to red at ca. 115 °C in the heading process. The molecular mechanism of the thermochromic transition has not been established, and in particular the backbone structure in the high-temperature red phase has not been fully understood. A physical understanding of the mechanism of the thermochromic transition at the molecular level is very important. In a previous paper,[4] we demonstrated that the butatrienic structure does not exist in either the blue or red phases, and the conjugation length of the blue phase is much longer than that of the red phase, as suggested by other techniques.[1-3,8,9] Among the various PDA's, poly(ETCD) is one of the most suitable for checking the backbone conjugation, or valence structure, because this PDA does not have any double or triple carbon–carbon bonds in its side chains. This permits a clear, unambiguous check for the existence of a stable butatrienic structure.

In addition to a more complete discussion of the previous results,[4] the present paper will discuss the relation between side chain and backbone conformations and also the motional differences between both in the blue and red phases. Possible mechanisms for the thermochromic phase transition will also be discussed.

Experimental Section

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.[12] Polymerization was accomplished by irradiation with 50 Mrad of ^{60}Co γ-rays at room temperature. Unreacted monomer was extracted 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 utilized a double air bearing design. The temperature was varied from 20 to 135 °C by use of a heated N_2 flow, and the temperature was controlled within ±1 °C with the standard Varian temperature-control unit. Poly(ETCD) in powder form was packed in an aluminum oxide rotor with Kel-F [poly(chlorotrifluoroethylene)] end caps. A 45-kHz radiofrequency 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 poly(oxymethylene) (POM) (89.1 ppm from TMS)[13] added to the rotor.

Spin–lattice relaxation times, T_1, were measured for each carbon under the CP condition by application of the pulse sequence developed by Torchia.[14] Spin–lattice relaxation times of protons

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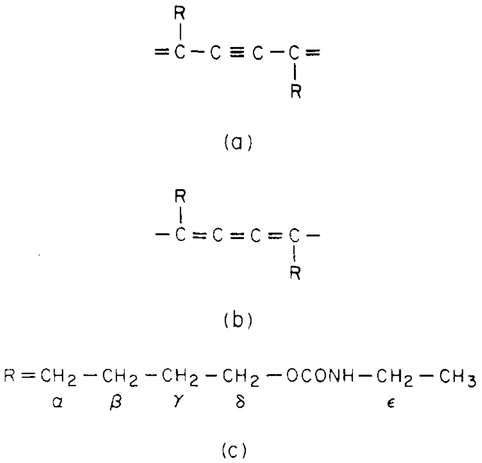

Figure 1. Acetylenic (a) and butatrienic (b) backbone structures and the side chain R (c) of poly(ETCD).

Table I
Thermal Data[a] for Poly(ETCD)

transition	temp of transition, °C	heat of transition, J/g
thermochromic	123	0.82
melt	216	3.7

[a] Obtained at a heating rate of 10 °C/min.

in the rotating frame, $T_{1\rho}$, were determined[15] by changing the contact time between ^{13}C and ^1H spins in the CP experiment. The data were analyzed by the nonlinear least-squares method.

Differential scanning colorimetry (Perkin-Elmer DSC-4) was also used to study the thermochromic phase transition in poly(ETCD).

Results

DSC scans of poly(ETCD) in the heating and cooling processes were presented in a previous paper. The transition temperatures and the associated heats of transition observed there are listed in Table I.

Figure 2 presents the temperature-dependent CP MAS/DD ^{13}C NMR spectra in the heating and cooling processes. According to dipolar dephasing experiments,[16] the three most downfield resonances belong to carbons having no directly bonded protons. With increasing field, these peaks are assigned to C=O, >C=, and —C≡, respectively. The most upfield peak is assigned to the methyl carbon, with the remaining four resonances belonging to the side-chain methylene carbons. The assignment of CH_2 resonances was achieved by comparison with model compound spectra. Relative chemcal shifts for each carbon were listed previously.[4] The results are consistent with those obtained[17] for poly(nBCMU) in solution. One CH_2 resonance is not observed in the spectra, because of the overlapping of the β,γ-CH_2 peaks. The ^{13}C chemical shifts for poly(ETCD) are listed in Table II.

We can clearly see the coexistence of both phases at 115 °C in the heating process and at 60 °C in the cooling process (see Figure 2). There is a large hysteresis of over 50 °C, which indicates the thermochromic phase transition to be of the first order.[8,9,11]

There are some interesting points to be mentioned in the spectra of poly(ETCD). First, the C=O resonance is split in the blue phase but not in the red phase. Second, in the red phase a new small resonance appears at 22 ppm. These observations are critically dependent on whether the temperature is higher or lower than the transition point, and they are reversible.

The temperature-dependent MAS/DD ^{13}C NMR spectra of poly(ETCD) observed in the heating process are

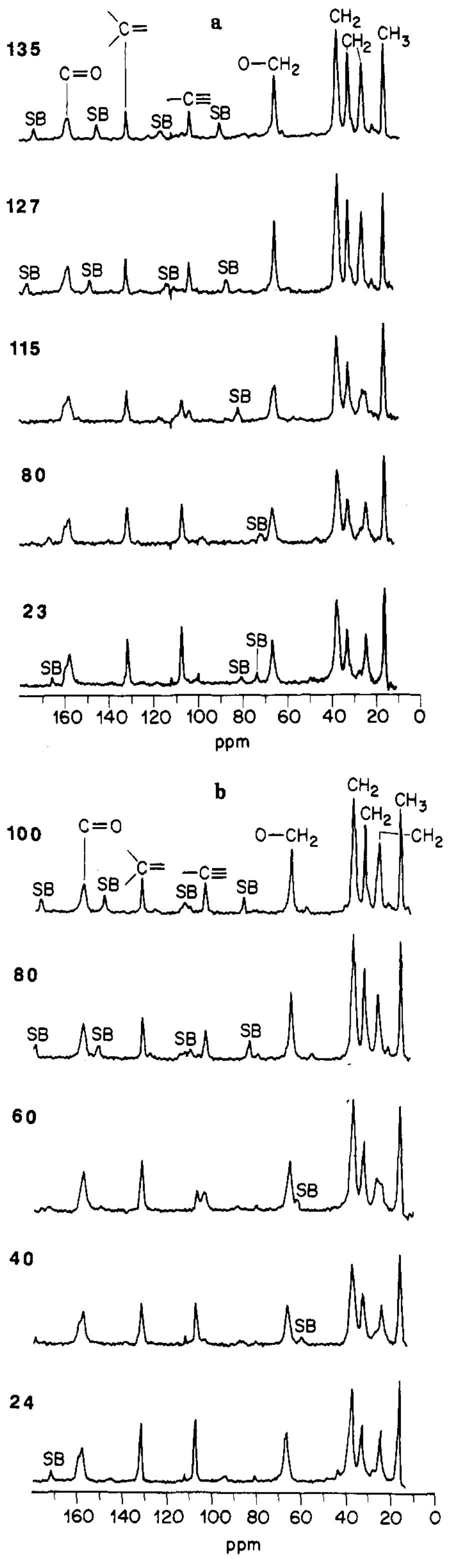

Figure 2. CP/MAS/DD ^{13}C NMR spectra of poly(ETCD) in the heating (a) and cooling (b) processes.

Table II
^{13}C Chemical Shifts of Poly(ETCD) (ppm versus TMS)

carbon	blue phase (low T)	red phase (high T)
C=O	159.3, 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_2		22.6
CH_3	16.2	16.7

Table III
$T_1(^{13}C)$ in Seconds for Poly(ETCD)

carbon	blue: 23 °C ↑[a]	blue: 80 °C ↑	blue and red: 59 °C ↓	blue and red: 80 °C ↓	red: 110 °C ↓
C═O	137	135			
C═O	116	112	65	53	47
>C═	153	107	79	34	25
—C≡(B)	172	126	118	110	
—C≡(R)			53	42	30
δ-CH_2	11 (22%), 110 (78%)	15 (34%), 80 (66%)	8 (61%), 139 (39%)	3 (75%), 26 (25%)	6
α-CH_2	9 (34%), 103 (66%)	7 (32%), 56 (68%)	5 (46%), 43 (54%)	2 (50%), 20 (50%)	8
ϵ-CH_2	9 (15%), 108 (85%)	3 (15%), 56 (85%)	5 (55%), 78 (45%)	3 (70%), 22 (30%)	6
β,γ-CH_2 (B)	2 (9%), 97 (91%)	3 (12%), 50 (88%)	9 (45%), 66 (55%)	35	
β,γ-CH_2 (R)			4	1 (67%), 10 (33%)	4
CH_3	2 (81%), 14 (19%)	4 (70%), 18 (30%)	5	6	6

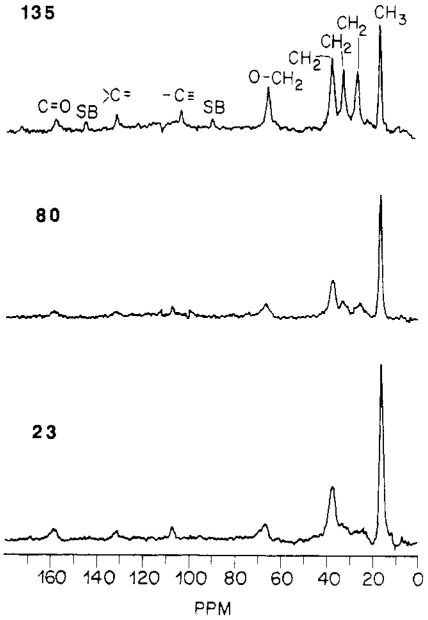

Figure 3. MAS/DD ^{13}C NMR spectra of poly(ETCD) in the heating process.

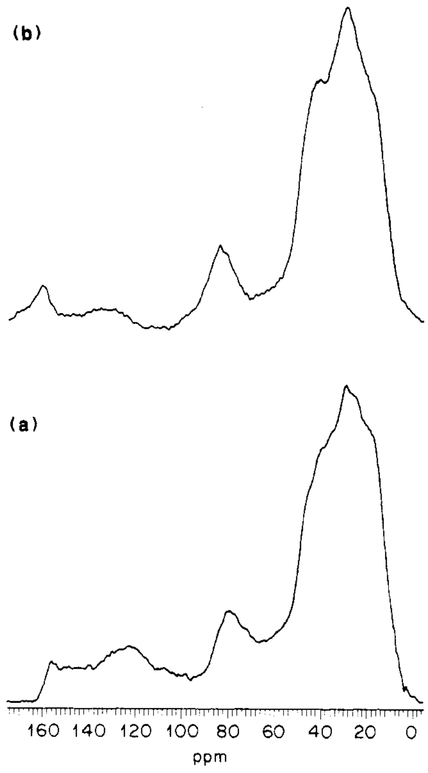

Figure 4. Nonspinning CP/DD ^{13}C NMR spectra of poly(ETCD) in the blue (a) and red (b) phases.

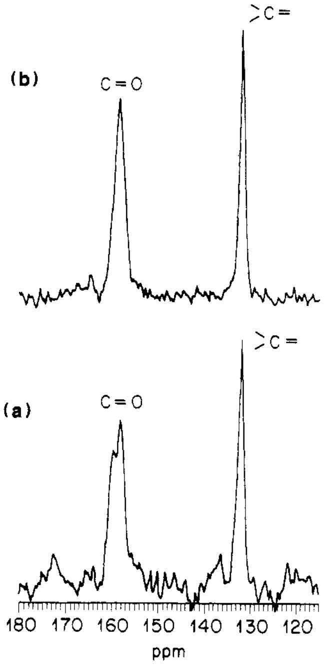

Figure 5. (a) C═O resonances observed in the blue phase at 80 °C in the CP T_1 decay process (τ = 30 s). (b) Single C═O resonance observed in the red phase at 80 °C in the CP T_1 decay process (τ = 4 s).

presented in Figure 3. The repetition time was set at 5 s, and the signal intensity is related[18] to the T_1 value of each carbon.

The powder pattern spectra obtained with CP and DD, but without MAS, are presented in Figure 4.

We performed the CP T_1 measurements at 23 and 80 °C in the heating process and at 110, 80, and 59 °C in the cooling process. T_1 values obtained from these measurements are listed in Table III. Two distinct C═O resonances are clearly observed in the CP T_1 decay process at 80 °C as shown in Figure 5a. On the other hand, the single C═O resonance in the red phase is completely symmetric (see Figure 5b). At 59 and 80 °C, there are two resonances each for the —C≡ and β,γ-CH_2 carbons, which indicates the coexistence of the blue and red phases. Figure 6 shows the distinct resonances from the coexisting phases, which are observed in the CP T_1 measurement at 80 °C in the cooling process. Because of the difference in the T_1's between the two phases, the two peaks can be more clearly observed during the T_1 decay process. The β,γ-CH_2 resonances are completely overlapped in all the blue- and red-phase spectra. In the blue phase there are two components for the T_1 decay processes of the CH_2 and CH_3 carbons. The relative amounts of the two distinctly relaxing, blue-phase CH_2 and CH_3 carbons are given in parentheses.

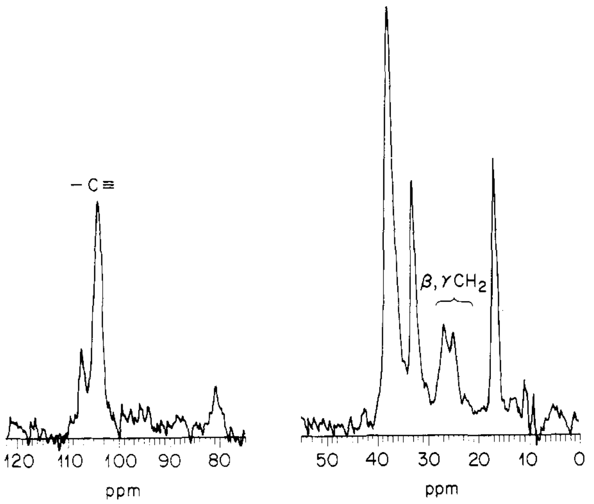

Figure 6. CP/MAS/DD ^{13}C NMR spectrum at 80 °C in the cooling process. In the CP T_1 measurement there are two resonances for —C≡ and β,γ-CH_2 corresponding to the coexistence of the red and blue phases.

Table IV
$T_{1\rho}(^1H)$ for Poly(ETCD)

	80 °C ↑	80 °C ↓	59 °C ↓
$T_{1\rho}$, ms	29	41	15

We also measured the $T_{1\rho}(^1H)$ decay process observed in both the blue and red phases, which were measured at 80 °C during the heating and cooling processes, respectively. The $T_{1\rho}$ at 59 °C, where both the red and blue phases coexist, was also obtained. The $T_{1\rho}$ values obtained from these measurements are listed in Table IV. Later we will discuss the domain size of the two coexisting phases in terms of the spin diffusion concept.[19]

The solid-state ^{13}C NMR spectra of poly(ϵ-caprolactone) (PCL), poly(butylene terephthalate) (PBT), and several PBT model compounds,[20] which have CH_2 sequences similar to that of poly(ETCD), were also measured. The structures of these polymers and model compounds and the chemical shifts observed at each of their β- and γ-carbons are presented in Figure 7.

Discussion

Thermal Behavior. There is a large thermal hysteresis of the thermochromic phase transition (see Figure 2 in ref 4). At a cooling rate of 10 °C/min, there seems to be a time lag, and the transformation from the red to the blue phase may be slow. The NMR results also support the coexistence of both phases over a wide range of temperatures in the cooling process, as shown in Figures 2 and 6. On the other hand, the coexistence of both phases is limited to a rather narrow temperature range in the heating process. These behaviors are schematically illustrated in Figure 8 and are similar to the first-order ferroelectric transition. The thermal hysteresis observed in the poly(ETCD) system indicates the first-order nature of the thermochromic phase transition.

The $T_{1\rho}$ decays for the —C≡ resonances in the coexisting blue and red phases are well described by a single exponential function with the same relaxation time. This might indicate that the spatial size of the heterogeneity, or the domain size, is smaller than the effective path length of the spin diffusion. The domain size may be on the order of 10 Å. However, it should be mentioned that if the difference in $T_{1\rho}$ between the two phases is small, then a single $T_{1\rho}$ decay would also be expected.

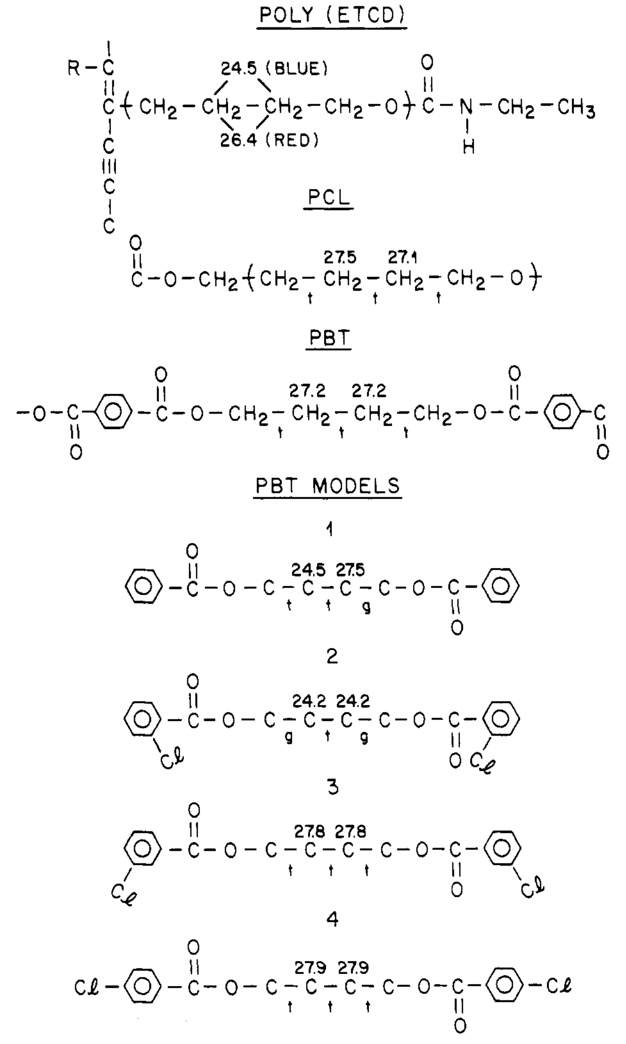

Figure 7. ^{13}C chemical shifts for the β- and γ-CH_2 carbons observed in the solid state for poly(ETCD), PCL, PBT, and PBT model compounds. Conformations (t = trans, g = gauche), as determined by X-ray diffraction,[20] are indicated below each of the central C–C bonds.

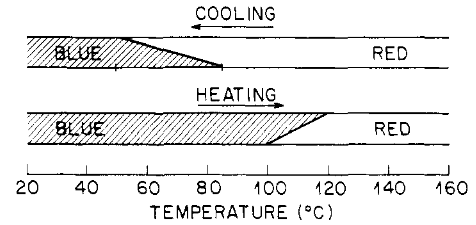

Figure 8. Schematic diagram for the phase behavior of poly(ETCD).

Backbone Structure. The absence of >C= and —C≡ carbons in the side-chain substituents of poly(ETCD) makes possible the clear determination of the backbone chemical structures. The chemical shift of the backbone —C≡ carbon is especially sensitive to the transition, changing from 107 to 103 ppm on transition from the blue to the red phase. In contrast to —C≡, the chemical shift of >C= does not change very much. These chemical shift changes suggest that the valence structure, or chemical bonding, is not altered by the thermochromic transition. There is no appearance of a peak corresponding to the butatrienic structure in any of our spectra. This suggests the absence of a stable butatrienic structure[17,21] in either the blue or red phase. The butatrienic structure, according to theoretical calculations, is a higher energy isomer (10–20 kcal)[22] compared to the acetylenic form, making it difficult

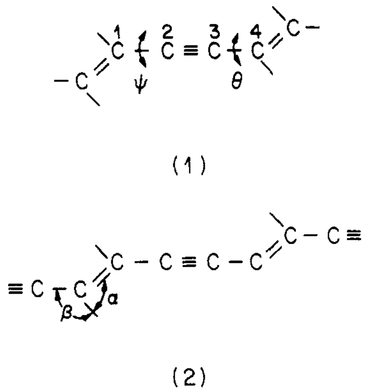

Figure 9. Possible models for distortions of the backbone structure in polydiacetylenes.

to activate thermally. The absence of a stable butatrienic structure is also consistent with the observation[23] that the butatrienic structure does not stably exist in PDA's with a degree of polymerization >6. Very recent calculations[24] also support the above facts.

From the results above, the chemical shift change observed for the backbone $-\mathrm{C}\equiv$ carbon is attributed[11] to the distortion of the acetylenic structure resulting from the change in side-chain conformation, which will be described in the next section. The chemical shift change is thought to originate both from changes in the conjugated π-electrons and distortion of the σ-electrons. The relation between the chemical shift and the conjugation length in PDA's has been studied by Wegner et al.[25] who used model compounds. They found a strong correlation between the conjugation length and the chemical shift. It is apparent that the observed chemical shift change of the $-\mathrm{C}\equiv$ resonance cannot be explained by defects in the backbone structure, which would also decrease the conjugation length, because only a single resonance is observed for $-\mathrm{C}\equiv$ in both phases. The backbone must be uniformly distorted. Possible distortions of the acetylenic backbone structure, which may be caused by strains from the side chains, are (1) the *rotation about the single bonds in the backbone* (change in the planarity of the backbone) and (2) the change in the valence bond angles of the backbone, but with retention of a planar backbone conformation (see Figure 9).

The rotation θ around the single bond may be energetically less costly than a change in the valence angles α and β. Thermochromic phase transitions observed in soluble polydiacetylenes are readily explained by the first mechanism (1), and the solid-state transition may be governed by the same mechanism. Furthermore, we have found the two kinds of backbone structures (planar and nonplanar) consistent with mechanism 1 to be generally observed in a variety of polydiacetylenes. It is difficult to explain the generality of these observations with mechanism 2, because the potential barrier for the change in valence angles is likely a smooth function of α and β. It is unlikely that two stable backbone structures would result from model 2. Large side chains may cause potential minima for rotations about the single bonds in mechanism 1. Without the effect of the side chains the potential energy monotonically increases with an increase in the rotation angle θ, as demonstrated by the simple overlap integral of π-electron clouds.[26]

Alternate rotations θ around the single bond between carbons 3 and 4 (see Figure 9) have been proposed by Orchard and Tripathy.[22] Recent X-ray studies[27,28] show little change in the unit cell dimension along the chain direction when transforming from the blue to the red phase. It may be possible for small rotations (ψ, θ) of the opposite sign to occur about both single bonds in each repeat unit. Considerations of side-chain packing and hydrogen bonding place limits on these kinds of backbone rotations, and these details will be discussed elsewhere.

The chemical shift change of the $>\mathrm{C}=$ carbon is not very large, which may be due to the cancellation of competing effects. The decrease in the delocalization between the π-electrons of $>\mathrm{C}=$ and $-\mathrm{C}\equiv$ should move the chemical shift of $>\mathrm{C}=$ upfield. The electron cloud between adjacent $>\mathrm{C}=$ carbons may become more delocalized, which would move the chemical shift the opposite way or downfield. Another important factor is the distortion[29] of the bond between $>\mathrm{C}=$ and the α-$\mathrm{CH_2}$ carbon, which would also cause the redistribution of the electron cloud. Any conformational change about the bond between the α- and β-carbons also affects the chemical shift of $>\mathrm{C}=$. These possibilities will be discussed in the next section.

The chemical shifts of the backbone carbons suggest a change in the conjugation length, but the absence of a change in chemical structure. The change in the conjugation length is responsible for the blue to red color change, as suggested by many researchers[8,9,24] based on various techniques. We believe, as suggested by Rubner et al.,[11] the origin of the change lies in the conformational alteration of the side chain.

Side-Chain Conformation. As observed previously,[4] *the only large changes in the side chain chemical shifts are* observed for the β,γ-carbons. The chemical shifts of the β,γ-carbons move 2 ppm downfield when poly(ETCD) transforms from the blue to the red phase.

The absence of a significant chemical shift change for the side-chain C=O carbon suggests retention of interurethane hydrogen bonding,[30] a finding consistent with a recent FTIR[11] study of the N–H vibration in poly(ETCD). However, it should be mentioned that the C=O resonance has a shoulder on the downfield side only in the blue phase. This implies the existence of different kinds of hydrogen bonding, such as interchain hydrogen bonding, or different CONH geometries, which may produce a quadrupolar splitting of the C=O resonance by the adjacent $^{14}\mathrm{N}$ nucleus. We should also mention that a small resonance in the $\mathrm{CH_2}$ region at 22 ppm appears only in the red phase.

At the present stage, it is difficult to understand clearly the phenomena mentioned above. However, we can suggest the existence of different side-chain conformations and/or packings. The conformation of the alkyl portion of the side chain should have a close relationship with the configuration (geometry, conformation) of the neighboring CONH group. This suggestion will be discussed further when we consider the packing of side chains.

The absence of a chemical shift change in the terminal ethyl group suggests the same conformation and packing in both phases for the terminal portion of the side chains.

Next we will discuss the conformation and packing of the alkyl portions of the side chains. As described before, the chemical shifts of the β,γ-$\mathrm{CH_2}$ carbons are 2 ppm downfield in the red phase compared to their position in the blue phase. This strongly suggests that the alkyl side-chain bonds have more trans or planar character in the red phase. No significant changes in the chemical shifts of the α, δ, C=O, and methyl carbons suggests that the conformations of the side-chain bonds 1, 4, 6, 7, 8, and 9 illustrated in Figure 10 do not change very much as a consequence of the thermochromic phase transition in poly(ETCD). Significant rotations around bonds 2, 3, and 5 may accompany the phase transition. Rotation around bond 2 would be expected to affect the chemical shift of

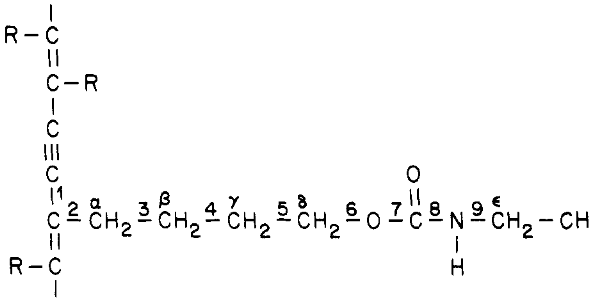

Figure 10. Schematic drawing of poly(ETCD) structure.

the backbone >C═ carbon. No significant change in the chemical shift of the α-CH_2 carbon suggests that the conformational change around bond 1 is reasonably small. It should be noted that small rotations (ca. 5°) around bond 1 may cause significant changes in the π-electron conjugation length according to recent theoretical calculations.[22]

In order to discuss the conformational changes which accompany the thermochromic phase transition more quantitatively, we compare the chemical shifts of the β,-γ-carbons in poly(ETCD) with those of model systems whose solid-state conformations are known.[31] These systems are poly(butylene terephthalate) (PBT), several of its model compounds,[32] and poly(ϵ-caprolactone) (PCL)[33] whose structures and chemical shifts are displayed in Figure 7.

A comparison of these solid-state chemical shifts makes it appear that the alkyl portions of the side chains in poly(ETCD) have the gt$\bar{g}$ conformation in the blue phase and the t′tt′ conformation in the red phase for bonds 3, 4, and 5, where g,$\bar{g}$ are gauche rotations of opposite sign and t′ represents an imperfect or nonplanar trans (t) conformation. This change in side-chain conformation is consistent with the expansion of the crystalline lattice in the side-chain direction observed to accompany the transition from the blue to the red phase by X-ray diffraction.[27,28] In addition, the conformational transition gt$\bar{g}$ $\leftrightarrow$ t′tt′ suggested for the alkyl portion of the side chains is of the Helfand type,[34] thought to be the most facile for alkane chains in condensed media.

Generally, the lowest energy conformation for an alkyl chain is the all-trans, planar zigzag, as is well-known.[35] The presence of gauche (g) conformations in the lower temperature blue phase may be the result of a compromise to achieve the lowest total free energy state that includes contributions from hydrogen bonding, backbone electronic energy, and side-chain conformational and packing energies.

The energy difference between t and g conformations in the allyl portion of the side chain is not substantial, ca. 0.5 kcal/mol. On the other hand, the energy gained by hydrogen bonding[36] may be ca. 5 kcal/mol. According to a simple calculation of the overlap integral between the π-electron clouds of sp and sp^2 backbone carbons, the energy change from a planar to a 90° rotational state around backbone bond 1 (see Figure 9) is 2 kcal/mol.

The gauche conformation of the lower temperature blue phase can be explained as a compromise between these energetic factors. This energy competition and the possible physical origin of the thermochromic phase transition will be discussed later. The possibility of different side-chain packings will also be mentioned in relation to the motional heterogeneity observed.

Motional States of the Poly(ETCD) Backbone and Side Chains. Figure 11 shows the temperature dependence of T_1 for several carbons. We can see the clear motional transition and the thermal hysteresis for all the carbons. The backbone carbons are apparently on the slow-motion side of their T_1 minima in both the blue and red phases. It is obvious that the backbone in the red phase is more mobile than the blue phase even at the same temperature. This may be consistent with a less conjugated backbone structure, because localization of the backbone π-electrons would result in a softer potential for single-bond rotation and a more mobile structure. This motional behavior is more consistent with the planar-nonplanar backbone transition model compared to the model based on distortion of the valence angles with retention of a planar backbone conformation. The backbone transforms from a planar to a nonplanar conformation at the transition point. In the red phase, the bottom of the potential well for rotation should be broader than in the blue phase because of less conjugation around the single bonds. Distortion of the backbone valence angles would not be expected to produce such a drastic change in the backbone motion.

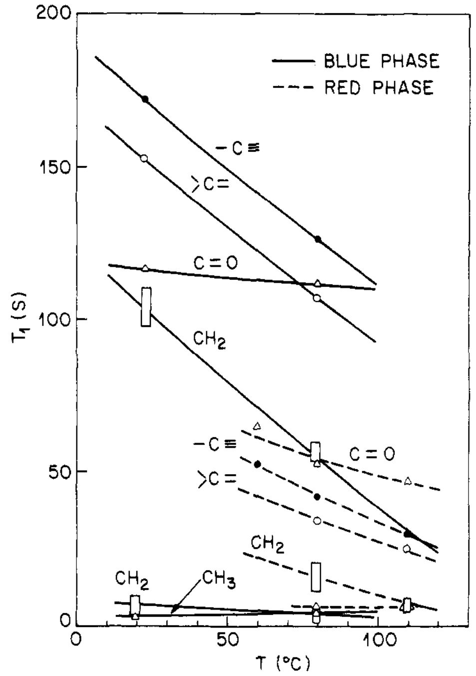

Figure 11. Temperature dependence of T_1 for the various carbons in poly(ETCD): (△) C═O; (○) >C═; (●) —C≡; (□) CH_2's; (△) CH_3. Solid lines denote data for the blue phase in the heating process, and dashed lines correspond to the red phase in the cooling process. Note that in the blue phase (see Table III) all CH_2 resonances exhibit two T_1 components.

The T_1 of the C═O carbon shows a weaker temperature dependence than those of the backbone carbons. There is an abrupt change in the mobility of C═O at the transition point. The mobility of the C═O carbon in the red phase may be produced by the mobility, or flexibility, of the side chains, especially the alkyl portion. The T_1 of C═O in the red phase is still long and has almost the same temperature dependence as in the blue phase. Therefore, the behavior observed is consistent with the retention of the hydrogen-bonding network of side chains in both the blue and red phases.

The side chains also become more mobile in the red phase. This means an increase in the flexibility of the side chains in the red phase, which might produce a stronger entropic spring causing strain on the backbone.

As can be seen from Table III, all the CH_2 carbons in the blue phase relax in two T_1 processes. One is very short (ca. 5 s) and the other is quite long (ca. 100 s). This suggests a motional heterogeneity, which might be related to the shoulder on the C═O resonance. According to the proton $T_{1\rho}$ measurements, all the carbons relax exponentially with the same $T_{1\rho}$. This implies that the heterogeneity is on a scale smaller than 10 Å based on spin-diffusion concepts.[19] The absence of splitting in the observed CH_2 resonances suggests that the heterogeneity does not have a conformational origin. The single-component T_1 of the backbone carbons means that the heterogeneity does not affect the backbone motions.

Among available candidates for this heterogeneity is the possibility of two manners for the packing of side chains which probably would not affect the backbone electronic structure. Additional evidence for two kinds of side-chain packing have been recently obtained from electron microscope observations by Tanaka et al.[28]

The T_1 decay processes in the pure red phase are well expressed by single exponential functions. This suggests that the red phase does not have significant heterogeneity, which is consistent with the single observed C═O resonance and the electron microscope observations.[28]

In the cooling process, at temperatures between 60 and 80 °C, there are two components observed in the T_1 processes, which probably reflect the coexistence of blue and red phases.

^{13}C NMR Powder Pattern Spectra. The ^{13}C CP/DD powder pattern spectra reflect[19,37] the chemical shift anisotropy tensors for each carbon, the distribution of electron clouds, and their motional averaging. As can be seen in Figure 4, a significant change is observed in the C═O region between the two phases. In the blue phase, a much more anisotropic chemical shift pattern is clearly observed compared to that in the red phase. This suggests that the motions of the C═O carbons are faster in the red phase than in the blue phase, thereby averaging the chemical shift anisotropy, and may indicate a weakening of the side-chain hydrogen bonding. This is consistent with our T_1 results for the C═O carbon and the slight decrease in the intensity and increase in frequency of N—H vibrations observed as a function of temperature by FTIR.[11]

Physical Interpretation of the Thermochromic Phase Transition in Poly(ETCD). As has been discussed in the section on side-chain conformation, the side-chain alkyl group is in a higher conformational energy state (gauche bonds) in the low-temperature blue phase. This suggests that other energetic factors dominate the total free energy of the system. Other candidates for important energetic factors are the side-chain hydrogen-bonding energy, the backbone electronic energy, and the side-chain packing energy. The blue phase is a lower energy state because the thermochromic phase transition is reversible. The blue-phase structure is not the result of a high potential energy barrier that accompanies the transition from the blue to the red phase. However, the large hysteresis observed upon cooling (see Figure 8) suggests a mechanism analogous to a ferroelectric phase transition of first order.

First we will discuss the competition between side-chain hydrogen-bonding and conformational energies. To stabilize hydrogen bonding,[36] the inter-urethane C═O to H—N distance tends to be minimized. This requires a distortion of the alkyl chain conformation and results in a nonplanar alkyl group conformation in the blue phase. With increasing temperature, the hydrogen bonding weakens due to increased thermal motion. The temperature dependence of the powder pattern spectra and FTIR[11] data on N—H vibration suggests a slight decrease in the hydrogen-bonding strength with increasing temperature. At a certain temperature (the thermochromic phase-transition temperature), the energy lost due to side-chain nonplanarity becomes more important than the energy gained from the most stable hydrogen bonding of side chains, as characterized by small distances between the N—H and O═C groups. At this point the side chains relax to their lower energy all-trans, planar conformation. The thermal motion of side chains may also be partially responsible for this transition.

In this model of the thermochromic phase transition of poly(ETCD), the change in the backbone electronic structure may result from the backbone strain[11,29] produced by the hydrogen-bonding side chains. First let us assume that the side-chain organization dominates the backbone structure. We must consider the origin of the backbone strain produced by the side chains. In the lowest energy hydrogen-bonding state, however, there may not be enough motion to create an entropic spring. One possibility is the more planar, more extended, side-chain conformation causes more strain on the backbone. This may result in a nonplanar backbone conformation produced by slight rotation around the single bond.[22,26] Recent theoretical calculations[22,26] indicate that only a slight rotation from a planar conformation around the single bond can cause a drastic decrease in the π-electron conjugation length. The energy difference between these two backbone structures was estimated to be <2 kcal/mol. In this model, the backbone is in a higher energy state in the high-temperature, red phase, and the side-chain packing energy is probably lower in this phase because of their planar conformation.

Another possibility is that the whole thermochromic transition is dominated by the transition in the backbone structure. However, this possibility is not likely because of the fact that some polydiacetylenes, such as PTS-6 and PTS-12, which have the same backbone structure, do not show any thermochromic transition. It is more likely that the transition of the backbone is triggered by strain coming from the side chains. In particular, the only difference between poly(ETCD) and PTS-12 is in the terminal part of the side chains. Poly(ETCD) has intramolecular hydrogen bonding between side chains in contrast to PTS-12. This is further evidence that the inter-side-chain hydrogen bonding plays an important role in the thermochromic phase transition and may be necessary to create the strain on the backbone.

Because the ^{13}C resonances observed for the —C≡ carbons in a variety of PDA's always occur, like poly(ETCD), at ca. 107 ppm in their blue phases and at ca. 103 ppm in their red phases, the model we have just suggested may be more generally applicable to the solid-state thermochromic phase transitions in PDA's. This work will be discussed in a subsequent publication.[38]

Conclusions

We have studied the thermochromic phase transition in solid poly(ETCD) by application of high-resolution ^{13}C NMR methods. Primarily on the basis of the chemical shifts and spin–lattice relaxation times observed for the backbone and side-chain carbons in the blue and red phases of poly(ETCD), we conclude that the thermochromic phase transition (i) does not involve a change in conjugation from the acetylenic to the butatrienic form, (ii) is accompanied by a planar to nonplanar backbone conformational change about the ≡C—C═ bonds, (iii) does not significantly disrupt the inter-side-chain hydrogen-bonding, and (iv) results in the extension of the side chains via a $gt\bar{g}$ to $t'tt'$ conformational transition.

Registry No. ETCD (homopolymer), 63809-82-5; ETCD (SRU), 83441-81-0.

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Hindered Diffusion of Porphyrins and Short-Chain Polystyrene in Small Pores

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ABSTRACT: The role of configurational effects on diffusion of solutes through pores of comparable dimension has been examined for two molecular geometries: disklike molecules (porphyrins) and short-chain polymers (low-MW polystyrenes). Rates of diffusion were measured as a function of pore size in thin membranes for tetraphenylporphyrin and tetrabiphenylporphyrin in chloroform and for three narrow molecular weight fractions (2000, 3700, and 7000 MW) of polystyrene in tetrahydrofuran. The diffusion properties of the porphyrins resembled those of hard spheres of the same Stokes–Einstein radius. The diffusion of short-chain polystyrenes was hindered to a greater extent than the porphyrins but less than long-chain (10^5–10^6 MW) polystyrenes of equivalent ratio of Stokes–Einstein radius-to-pore radius.

Introduction

The diffusion coefficient of a solute in a small, liquid-filled pore is smaller than the value for bulk (unbounded) solution when the molecule and pore are of comparable dimension. This retardation of diffusion is important to membrane processes associated with cell biology and medical physiology, as well as heterogeneous catalysis in microporous supports. Furthermore, the sharp decline in diffusion rate with increasing ratio of molecule/pore size makes membrane dialysis a potentially useful separation technique for macromolecules.

There are two mechanisms responsible for diffusional hindrance by small pores.[1] First, the mobility of the molecule is smaller because of viscous retardation caused by the pore wall, and second, the molecule is excluded from regions near the pore wall because of its size, so it is partitioned unfavorably within the pores. For diffusion through straight, capillary-like pores, the diffusional transport is parallel to the pore walls, and a diffusion coefficient (D) is defined in terms of the rate of molecular transport (M), the pore area (A_p) and length (l), and the difference in solute concentration (ΔC) of the bulk solutions that bathe opposite ends of the pore:

$$M = D(A_p/l)\Delta C \qquad (1)$$

For a membrane having identical pores, M would be the total rate of transport across the membrane, and C would be the concentration of solute at the membrane/fluid interface. Effects of boundary layers ("unstirred layers") at the membrane surfaces can be minimized by using membranes of low porosity and by vigorous stirring of the fluid.[2]

Of basic interest is the relationship between D/D_0 and λ, where D_0 is the diffusion coefficient in bulk solution and λ is the ratio of molecule-to-pore size. Deen[3] reviews the current state of understanding hindered diffusion. Most of the work to date has focused on spherical, compact solutes. Experiments with polystyrenes of high molecular weight indicate that linear, flexible macromolecules are

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