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The Crystal Structure-Thermochromism Relationship for the Polydiacetylene ETCD

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The polydiacetylene of the bis-ethylurethane of 5,7-dodecadiyn-1,12-diol (ETCD) is the best defined example of a thermochromic polymer at present. Thermochromism in poly-ETCD is associated with an endothermic first-order phase transition involving an increase in unit cell volume. The conformer population of the side-chain methylene groups changes on heating from 23 to 130°C. Hydrogen bonding and backbone planarity do not appear to be significantly disrupted during the transition. Solid state thermochromism in other polymers and examples of reversible thermochromism in inorganic and molecular organic solids are discussed in relationship to poly-ETCD.

INTRODUCTION

Solid state thermochromism is a phenomenon readily detected by the human eye, yet the solid state structural changes underlying it may be quite subtle and diverse in character. Among reversible inorganic solid state thermochromics,[1] the red to yellow change in HgI_2 is accompanied by a change from a tetragonal to a rhombic solid. A planar to distorted tetrahedron change is associated with the green to yellow change of $CuCl_4^{-2}$, while a gauche-planar chelate ring conformational change accompanies the red to blue-violet change of Cu (N,N-deen)$^{+2}$(N,N-deen = 1,1-diethylethylenediamine).[1]

At present, solid state thermochromism has been observed in three classes of polymers: polydiacetylenes (PDA, *1*), poly-(3-alkylthiophenes) (P3AT), and polysilanes. In general, a comparison of the solid state structural changes accompanying thermochromism in these polymers to the situations observed in inorganic solids is of interest.

Since PDA are of special interest among polymers because they are available in several cases in the form of macroscopic single crystals, the crystal structure-thermochromism relationship is of particular importance because the properties of PDA have a higher degree of definition that those of less crystalline polymers. In this context, the reports[2,3] of thermochromism in PDA-ETCD (*1a*) in 1976–77 are particularly noteworthy, and their interpretation forms the bulk of the present discussion.

THERMOCHROMISM IN POLY-ETCD

In the initial report of thermochromism in poly-ETCD,[3] the electronic spectrum, studied by polarized specular reflectance, revealed a reflectance peak at 635 nm at 23°C which gradually shifted to 540 nm at 130°C. The effect is largely reversible with some hysteresis,[2,3] Several suggestions concerning bonding and crystallographic changes associated with this spectral shift emerged and are as follows:

1. There is a change in the backbone bond representation from acetylenic to butatrienic.[3]
2. For poly-ETCD, the crystallographic unit cell volume was reported to decrease as the temperature is raised above the thermochromic transition.[3]
3. From other urethane-substituted PDA, there may be a change in hydrogen bonding.[4]
4. A planar-nonplanar conformational change ("orbital-flip defect")[5] in the backbone results in a shorter "conjugation length." The visible absorption spectrum of poly-ETCD dispersed in KBr at room temperature was interpreted[2] to imply three "delocalization lengths" in the polymer.

Suggestion 1 has been ruled out on theoretical grounds[6] and by ^{13}C CP-MAS NMR studies[7] which revealed the usual acetylenic bonding at temperatures above and below the thermochromic phase transition. The second issue was resolved by an x-ray powder diffraction study which revealed that the unit cell of poly-ETCD expanded in volume by 3.7% on heating from 20 to 135°C.[8] This conclusion was confirmed by a subsequent x-ray study of poly-ETCD.[9] Table I summarizes the lattice constants for poly-ETCD at 20 and 130–135°C. Suggestion 3 was ruled out by both FTIR[4] and ^{13}CP-MAS NMR[7,9] spectral studies which revealed that the hydrogen-bonded network is not significantly changed by the thermochromic transition and that conformational changes occur in the methylene groups of the side chain. This conformational change may be analogous to that of a chelate conformational change noted above in the Introduction.

Suggestion 4 is now addressed. The observed solid state spectral transition energy, $E_{\overline{K}}$, for organic solids in general[10] and PDA in particular is typically discussed

TABLE I

Lattice Constants for Poly-ETCD[8]

Temperature	20°C[a]	130–135°C[a]	20°C[b]
a, Å	18.13	18.9	18.52(5)
b, Å	4.89	4.83	4.86(2)
c, Å	10.81	10.89	10.60(4)
β	94°	91°	94.2(3)
V, Å^3	956	994	952

[a]Powder data
[b]Single-crystal data

(Equation 1) in terms of ϵ_0, the gas phase transition energy for an isolated species, D, which summarizes the energetics of the gas-to-

$$E_{\bar{K}} = \epsilon_0 + D + I(\bar{k}) \quad (1)$$

crystal shift, and $I(\bar{k})$, which deals with the excition transfer interaction between translationally equivalent and nonequivalent moieties in the solid. D includes the effects of the local environment on a reference molecule or polymer chain, and it has been estimated that such effects comprise about 15% of $E_{\bar{K}}$ for PDA-PTS.[11] For a solid undergoing a thermochromic change, the relative contributions of changes in ϵ_0 and D to the spectral shift are relevant, ignoring $I(\bar{k})$. Figure 1 poses these questions and illustrates a main chain conformational change.

If the thermochromic phase transition in poly-ETCD involves a change in main chain conformation, the crystallographic repeat distance along the chain axis would be expected to change. Hence, the observed lattice constant for the *b* axis both below and above the phase transition in the 4.8–4.9 Å range strongly argues against a change in main chain conformation for poly-ETCD thermochromism.

Additionally, if a change in main chain conformation were involved in poly-ETCD thermochromism, it would require defects of the type shown in Figure 1 such that the length of planar segments would involve less than about eight repeat units. This conclusion follows from the work of Sixl,[12] who has shown that a growing polymer chain exhibits the spectrum of the complete polymer in about eight repeat units. In this view, a few defects on the main chain which leave the planar segments greater than eight repeat units in length would not change the optical properties of a PDA to a detectable extent.

Hence, thermochromism in poly-ETCD involves primarily changes in D in (1), and the "conjugation length" does not change.[13] Further indication of the significance of D in poly-ETCD comes from room-temperature resonance Raman (RR) studies.[14] When as-polymerized poly-ETCD single crystals are excited at 488 or 514.6 nm, the observed RR spectra reveal the presence of two PDA electronic states for the normal modes associated with both double-bond and triple-bond stretching. Extraction of residual monomer from such crystals reveals a marked diminution in the RR spectra of lines associated with the lower energy spectral state. Hence, the residual monomer in as-polymerized crystals contributes its intermolecular interactions to the overall environment.

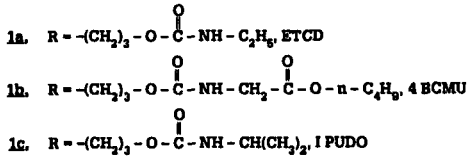
The above discussion does not include the possibility of changes in mechanical strains in the course of the thermochromic phase transition. As noted elsewhere,[15] it is not apparent what constitutes a definitive experimental manifestation of mechanical strains in PDA crystals.

The PDA-4BCMU (*1b*) has a crystal structure generally similar to poly-ETCD,[8] but its solid state thermochromic changes differ considerably in detail.[16] Solid state chromic changes from blue to red at 110°C and to yellow near 130°C are observed. The 110°C transition involves loss of hydrogen bonding, and new x-ray reflections are observed at 90–110°C.

Table II summarizes reversible solid state thermochromism for polymer systems.

Polydiacetylene
1

Polybutatriene

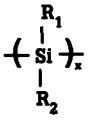


1a. R = -(CH$_2$)$_3$-O-C(=O)-NH-C$_2$H$_5$, ETCD

1b. R = -(CH$_2$)$_3$-O-C(=O)-NH-CH$_2$-C(=O)-O-n-C$_4$H$_9$, 4 BCMU

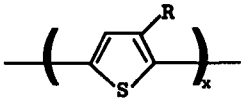
1c. R = -(CH$_2$)$_3$-O-C(=O)-NH-CH(CH$_2$)$_2$, I PUDO

Polysilanes



R_1 = n-C_3H_7; R_2 = CH_3 $(n\text{-ProMeSi})_x$

R_1 = R_2 = n-C_6H_{13} $[(n\text{-Hex})_2Si]_x$



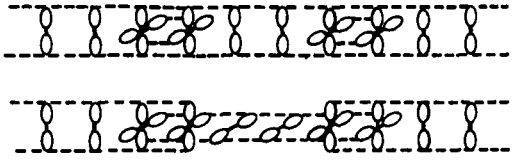
Poly(3-Alkylthiopenes) (P3AT): R = n-C_4H_9, P3BT; R = n-C_6H_{13}, P3HT; R = n-C_8H_{17}, P3OT; R = n-$C_{10}H_{21}$, P3DT

$E(k) = E_o + D + I(k)$

If the observed solid state electronic spectrum of a conjugated polymer shifts to higher energy, has

1) The main chain changed its conformation resulting in a shorter "effective conjugation length"?

Change in E_o.



OR

2) The local crystallographic environment changed without changing main chain conformation?

Change in D.

FIGURE 1 Schematic illustration of a main chain conformational change in a polydiacetylene.

TABLE II

Thermochromism in Solid Polymers

Polymer	λ_{max} (nm) Room Temperature	Thermochromic Transition Temperature, T_{TC} (°C)	λ_{max} (nm) at $T > T_{TC}$	Reference
poly-ETCD	635	125	540	2,3
poly-IPUDO(*1c*)	649	120	536	17
$[(n\text{-Hex})_2Si]_x$	374	40	313	21–23
$(nProMeSi)_x$	325	50	304	23
P3BT	510	>200	428	18
P3HT	510	180	428	18
P3OT	510	162	428	18
P3DT	510	85	428	18

OTHER THERMOCHROMIC POLYMERS

As noted above, several P3AT and polysilanes also display thermochromic behavior. Initial discussions of thermochromism in these materials involved changes in ϵ_0 in (1). For P3AT, thermochromism is manifested by a continuous blue shift of the wavelength of maximum absorption as the temperature is raised.[18] The phase transitions occur roughly in the same temperature region where melting occurs. In the specific case of poly(3-hexylthiophene) (P3HT), x-ray diffraction studies from ambient temperature up to 190°C reveal a reversible order-disorder transition.[19] The thermochromic effect in P3AT has been associated with thermally induced conformational defects in the Π-electron system of the aromatic backbone[20] or with a change in polymer conformation from rigid rod at low temperatures to random coil at high temperatures.[18] Of particular significance is the increase in intensity of the shake-up away from the main C(1s) peak in the X-ray Photoelectron Spectrum of P3HT with increasing temperature, indicating a localization.[20]

Thermochromism in $(n\text{-Hex}_2Si)_x$ is manifested by a decrease in intensity of the long wavelength band, while the shorter wavelength band increases in intensity as temperature is raised.[21–23] In contrast, $(n\text{-ProMeSi})_x$ reveals a continuous shift in absorption maximum.[23] Available x-ray data for $(n\text{-Hex}_2Si)_x$[24,25] reveal the presence of two phases at room temperature: a well-ordered phase with an all-trans Si backbone conformation with the side chains arrayed in a direction nearly perpendicular to the backbone with nearly all-trans conformations and a disordered phase with a trans backbone conformation and side chains which are conformationally disordered. The ordered phase is converted to the conformationally disordered phase above 40°C. Also, there is a partial disordering of the backbone conformation with significant remaining trans sequences, and an increase in intermolecular order.

CONCLUSIONS

While a complete crystal structure of a thermochromic polymer is not available at present, the detailed structural information for poly-ETCD from both x-ray dif-

fraction, FTIR, and solid state NMR studies render it the best defined thermochromic polymer at present. Available information about the first-order thermochromic phase transition in poly-ETCD suggests that it is primarily concerned with changes in the environment around the conjugated backbone rather than with the backbone itself. Available data for both polysilanes and P3AT suggests that thermochromism in these polymers involves changes in both the polymer backbones as well as the environment surrounding the backbones. Progress in the further understanding of thermochromism in polymers appears to require materials with improved crystallographic definition.

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