Optical, Calorimetric, and Mass Spectroscopic Study of Nonthermochromic Crystalline Forms of the Polydiacetylene Bis(ethylurethane)-5,7-Dodecadiyne-1,12-diol (ETCD)[†]

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Exposure of single crystals of the thermochromic polydiacetylene bis(ethylurethane)-5,7-dodecadiyne-1,12-diol (ETCD) to boiling chlorobenzene leads to nonthermochromic crystalline materials whose structures are similar to that of pristine ETCD. X-ray powder diffraction, differential scanning calorimetry (DSC), and room-temperature specular reflection and absorption spectra are reported for two nonthermochromic forms of ETCD. In addition, electron impact and fast atom bombardment mass spectrometric measurements were performed on the chlorobenzene extracts to determine substances removed by the boiling chlorobenzene along with a calorimetric study to correlate the loss of thermochromism with time of extraction. The mass spectrometry data indicate that ETCD monomer and possibly ETCD oligomer are removed during the extraction process. The crystallographic and optical data show that extraction with boiling chlorobenzene not only removes the interactions responsible for observable thermochromic behavior but also implies that both forms' electronic and lattice structure is significantly altered. The anisotropic reflection and corresponding absorption spectra show a dramatic blue-shift of the most intense spectral transitions by approximately 3500 cm^{-1} along the long axis, while spectra along the short axis remain essentially featureless. The X-ray data of both forms indicate an expansion of the lattice in the direction of the urethane side groups that significantly reduces the restriction to motion of the side groups and allows for a concomitant relaxation of the backbone. Results are also presented indicating the presence of residual thermochromic ETCD in the two nonthermochromic forms.

Introduction

Considerable progress has been made in recent years in the elucidation of the structural changes which occur in the course of thermochromic phase transitions in polydiacetylenes such as ETCD and IPUDO.[1-4] The high degree of crystallinity in urethane-substituted polydiacetylenes makes these systems excellent models for the study of thermochromism which, in ETCD and IPUDO, is associated with a first-order phase transition involving an increase in the volume of the crystallographic unit cell.[3,5-7] Infrared[4] and ^{13}C CP-MAS NMR[8] spectral studies reveal that the conformer population of the methylene groups of ETCD changes as the material is heated from 23 to 130°C with an accompanying transmission color change from green to red. While the melting point of the monomer and the thermochromic transition temperature are similar for many polydiacetylenes, recent calorimetric studies of IPUDO ruled out the possibility that monomer melting plays a significant role in the phase transition.[3]

FTIR studies of urethane-substituted polydiacetylenes have shown that the hydrogen bonding between polymer chains and the planarity of the conjugated backbone to not appear to change significantly in the course of the transition.[4] It has been proposed, however, that in urethane-substituted polydiacetylenes some distortion of the molecular structure is needed to accommodate the intramolecular hydrogen bonding which leads to a mechanical strain on the backbone.[10] Quantum chemical computations supporting this proposal have been published.[11,12] To quantitatively assess the potential mechanical strain, it is desirable to have a complete crystal structure of a thermochromic polydiacetylene above and below the thermochromic transition temperature. How-

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[†] The authors are pleased to dedicate this paper to the memory of the late Professor Margaret Etter.

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ever, crystals of sufficient quality for this purpose are not yet available.[6]

It was recently noted that samples of ETCD exposed to *N,N*-dimethylformamide (DMF) and chlorobenzene held at temperatures above the thermochromic transition remained red after return to room temperature.[1] Further, precipitates of ETCD from DMF are reported to have an absorption maximum near 18 870 cm^{-1} which is comparable to the high-temperature phase of ETCD.[10,13] While the precipitates of ETCD from DMF are powders which are shown to be largely amorphous by X-ray diffraction, the samples isolated after exposure to boiling chlorobenzene are crystalline.[1] Additionally, these latter materials generally retain their original shape and have an appearance somewhat reminiscent of the polydiacetylene THD. Two different forms of ETCD extracted with boiling chlorobenzene have been isolated and characterized: material exposed for a short time (2 min) is designated ETCD-SE and material exposed for 48 h is designated ETCD-LE. Neither of these new forms exhibits thermochromism. The preparation and characterization of ETCD-SE has been previously reported.[1]

Probing the electronic structure of solid-state organic compounds such as polydiacetylene crystals with conventional optical methods is inherently difficult because of these compounds' high molar concentrations and their large extinction coefficients. Polarized specular reflection spectroscopy at normal incidence on single crystals gives extensive information about a crystal's electronic structure. The reflectivity, R, of a sample at a given frequency of light is related to the refractive index, *n*, and the absorption coefficient, *k*, through the Fresnel equation:[14]

$$R(\bar{\omega}) = (n^* - 1)^2/(n^* + 1)^2$$

where the complex refractive index $n^* = n + ik$. The optical constants, and thus the absorption spectra, are determined by employing a fast-Fourier transform.[15]

Reflectivity measurements of ETCD and IPUDO reveal the temperature dependence of the spectra of these materials as well as the hysteresis which occurs upon temperature cycling.[2,13] The high-temperature spectra exhibit considerably less vibronic structure than those near room temperature. Between 25 °C and temperatures above the thermochromic transition, the spectral maxima of ETCD and IPUDO shift 2750 and 3250 cm^{-1} to higher energy, respectively.

A particularly noteworthy feature of the room-temperature spectra of ETCD, IPUDO and related thermochromic urethane-substituted polydiacetylenes is the similarity of the position of the reflection maximum to those of polydiacetylene crystals such as DCH and PTS.[5,16] It is widely accepted that polydiacetylene side group polarizability is an important factor in determining the wavelength of maximum absorption.[16-19] Thus, the resemblance in the reflection maximum position for ETCD and IPUDO, which have four methylene groups between the conjugated backbone and the urethane function, and DCH and PTS, which have only one methylene group between the backbone and a polarizable π-electron system, is worthy of further investigation.

Herein, we describe the preparation and characterization of ETCD-LE and the study of ETCD-SE and ETCD-LE by specular reflection along with comparison of the observed structural and spectral properties to those of thermochromic ETCD. In addition, a calorimetric study was undertaken to correlate the loss of thermochromism in ETCD to the exposure to chlorobenzene along with a mass spectral determination of the ETCD-LE chlorobenzene extract.

Experimental Section

The ETCD monomer was synthesized and polymerized as previously described.[20] X-ray powder diffraction, recorded on a Philips diffractometer with a Philips three kilowatt generator using Cu Kα radiation, established that the crystals of ETCD were the reported thermochromic phase.[5-7,13] Infrared spectra were recorded on a Brüker FTIR spectrometer. A Model-4 Perkin-Elmer differential scanning calorimeter was used to measure thermal properties. High-resolution electron impact mass spectrometry experiments were performed using a Kratos MS-50 double-focusing, high-resolution mass spectrometer. Fast atom bombardment (FAB) mass spectrometry was done with a Kratos MS-50 triple-focusing mass spectrometer using a 3-nitrobenzyl alcohol matrix. Flotation density was measured using a chlorobenzene:*o*-dichlorobenzene mixture.

Preparation of the Nonthermochromic PDA-ETCD (ETCD-LE). Crystals of ETCD (86 mg) in chlorobenzene (5 mL) were refluxed for 48 h. Crystals with specular surfaces were isolated by suction filtration and washed with chloroform to give ETCD-LE, 70 mg (81.4% recovery). The X-ray powder pattern of these crystals exhibited the following lattice spacings: 19.5, 9.7, 6.65, 5.02, 4.33, 4.04, 3.36, 2.88, 2.25, 2.03, 1.813, 1.683, 1.555 Å. The flotation density is 1.13–1.14 g/cm^3. The FTIR spectrum of these crystals was quite similar to those of ETCD and ETCD-SE.[1]

Reflection Spectra. The room-temperature, near-normal incidence specular reflection spectra of thermochromic ETCD, ETCD-SE, and ETCD-LE were obtained with light polarized along the principal directions which are both parallel and perpendicular to the polymer chain axis. In the analysis of the reflection and subsequent transformed absorption spectra, the polarization direction parallel to the main chain axis is designated as the long axis and the polarization direction perpendicular to the chain axis as the short axis. A double-channel reflection spectrometer was utilized to take spectra with a bandwidth of 100 cm^{-1} in the range 10 500–40 000 cm^{-1} along each of the principal directions. The apparatus, data collection and processing are reported elsewhere.[15,21,22] Reflection spectra were taken from at least three different crystals of each of the three different forms of ETCD. This established reproducibility of the reflection curves both in magnitude of reflectivity and structure. All reflection data presented are averages obtained from 9 to 18 individual determinations.

Results and Discussion

Structural and Thermal Properties of ETCD-LE. The X-ray powder patterns of various forms of ETCD at 2θ values less than 20° are dominated by the intense *h*00, *h* = 1, 2, 3 reflections.[1,6,7] Changes in these reflections are

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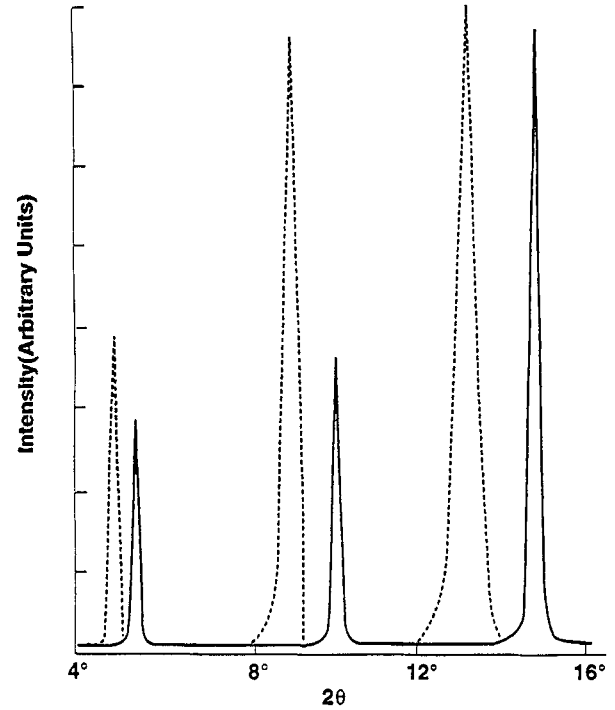

Figure 1. X-ray powder diffraction at 20 °C of pristine ETCD (—) and ETCD-LE (- - -).

Table 1. X-ray Powder Diffraction of PDA-ETCD

PDA	temp, °C	*h*00 (2*θ*), deg	density, g/cm^3
ETCD	20	5.1, 10.0, 14.8	1.16
ETCD-SE	20	4.8, 5.0, 5.5; 9.1, 9.3, 10.2; 13.3, 13.6, 15.2	1.14–1.15
ETCD-LE	20	4.6, 8.9, 13.1	1.13–1.14
ETCD	130–135	4.7, 9.4, 14.0	1.12[a]

[a] Calculated from the lattice constants in ref 6.

a valuable diagnostic of alterations in the crystal structure. Figure 1 displays the relevant portion of the powder pattern of ETCD and ETCD-LE. Table 1 summarizes the available powder diffraction information and sample density for the different forms of ETCD.

Examination of the data in Figure 1 and Table 1 reveals a continual shift of the position of the *h*00 reflections of the nonthermochromic forms of ETCD to smaller angles and hence larger lattice spacings. Also there is a regular decrease in the density of the crystal until the calculated density of the high-temperature form of ETCD is approached. Note that the available crystallographic and spectral data for ETCD-SE suggest that this material is not a single crystallographic phase.[1] Single-crystal photographs of ETCD at 20 °C indicate that more than one phase is present in the crystal.[6] Compared to ETCD, the positions of the *h*00 reflections indicate an expansion of the lattice at least in the direction of the side group. Inspection of the diffraction peaks of ETCD-LE in Figure 1 reveal that they are somewhat broader than the corresponding reflections of ETCD. This increased breadth is attributed to either smaller crystallite size or increased disorder as a result of the penetration of the macroscopic crystal by chlorobenzene in ETCD-LE compared to ETCD.

A calorimeteric study was undertaken to correlate the disappearance of observable thermochromism as a function of exposure time to boiling chlorobenzene. This effect was measured by noting the disappearance of the thermochromic endotherm near 120 °C. The DSC measurements for thermochromic ETCD and ETCD-SE have been presented elsewhere and both systems show a distinct thermochromic endotherm.[1,7] Crystals exposed for 5, 10, 20, and 25 min and 48 h to boiling chlorobenzene were prepared and isolated as discussed in the Experimental Section. The DSC thermograms for these five exposure times are shown in Figure 2. The most noticeable feature of these thermograms is the marked diminution of the thermochromic endotherm for increasing exposure time to boiling chlorobenzene until the 25-min exposure time where the thermochromic endotherm has disappeared completely.

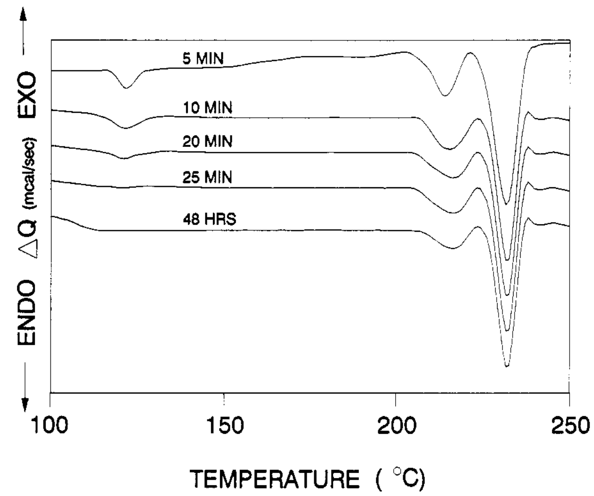

Figure 2. DSC thermograms of ETCD at 5-, 10-, 20-, and 25-min and 48-h exposure times to boiling chlorobenzene.

Mass Spectrometry Results. Extraction of polydiacetylenes with solvents such as chlorobenzene and ethyl acetate has been used extensively to remove any unreacted monomer still present in the lattice. In this study fast atom bombardment (FAB) and high-resolution electron impact (EI) mass spectrometries were employed to determine what compounds are removed from ETCD crystals upon the extraction process. Determination of the causes for the absence of observable thermochromism in these crystals may be better understood by identification of these compounds.

Upon filtering of the ETCD-LE crystals, the recovered filtrate was evaporated to dryness yielding orange, powdery crystals. The high-resolution EI spectrum of these crystals shows a molecular ion of 336.203 74 *m*/*z*, which corresponds to the M$^+$ ion of the ETCD monomer. A mass deviation analysis comparing the experimentally found mass with the ETCD monomer's exact mass yielded a deviation of only 3.48 ppm, a value within the limits of experimental error. The FAB spectrum supports the presence of monomer in the extracts by showing an intense mass to charge peak at 337, which corresponds to the [M + H] peak of the monomer, and a peak at 637.7 which corresponds to a dimer of ETCD. Several higher mass peaks were also observed and could be due to oligomers of ETCD. These peaks, however, could not be unambiguously assigned.

Reflection and Absorption Spectra. The absolute reflectivity spectra and their corresponding absorption spectra along both the long and short axes of the three forms of ETCD are shown in Figures 3 and 4. The long axis absorption intensities of the two modified forms of ETCD are clearly comparable to those of thermochromic ETCD and to other polydiacetylenes found in the literature.[13,18] Furthermore, the reflection and transformed absorption spectra for the two nonthermochromic

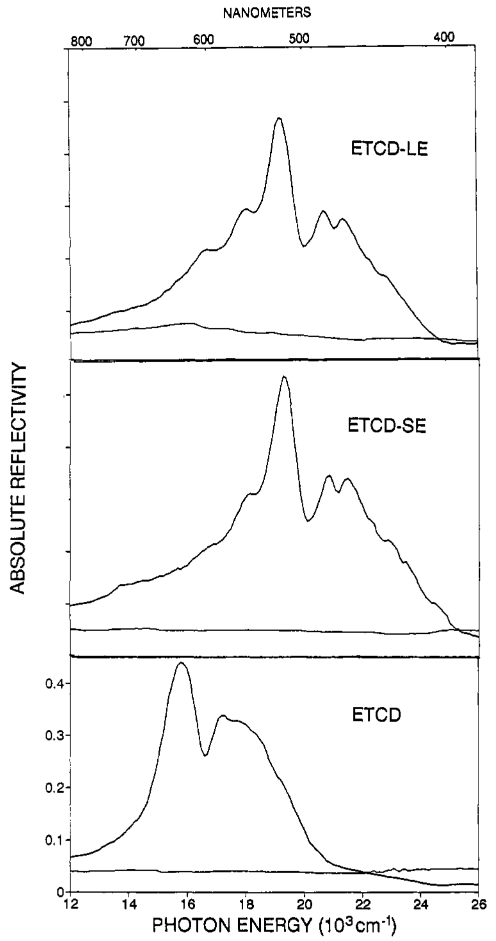

Figure 3. Room-temperature, near-normal incidence specular reflection spectra of ETCD, ETCD-SE, and ETCD-LE along the long and short axis.

forms of ETCD exhibit similar shape and vibronic structure with peak absorptivities for ETCD-LE and ETCD-SE at 19 000 and 19 200 cm^{-1}, respectively. The short-axis spectra of the nonthermochromic forms remain essentially featureless, indicating that the material retains a highly anisotropic structure. Comparison of the absorption spectra of thermochromic ETCD to those of the two nonthermochromic forms of ETCD shows that the most distinguishing feature is the dramatic blue shift of the main absorption peaks along the long axis by 3600 and 3400 cm^{-1}. These two energy shifts are significantly greater than the 2750 cm^{-1} shift found for the thermochromic phase transition of ETCD.[13] This implies that the diffusion of hot chlorobenzene into the lattice of ETCD not only causes destruction of the thermochromic behavior but substantially changes the structure of the conjugated backbone and its surroundings resulting in decreased delocalization of the π-electron system.

Both ETCD-SE and ETCD-LE exhibit structure on the high-energy side of the most intense transition which is more pronounced than that found in thermochromic ETCD and its high-temperature phase. The energy difference between the three most prominent vibrons in this high energy progression is the same for both nonthermochromic forms and corresponds to values of 1600 and 2200 cm^{-1}. This anomalous structure can be further analyzed by comparing it to structure found in thermochromic ETCD, DCH, and THD. With reference to Table 2, the vibrons at about 1600 and 2200 cm^{-1} (determined with the most intense absorption peak as their origin) correspond to backbone double-bond and triple-bond stetching, respectively. These modes are the most intense vibrations in polydiacetylenes.[23] The structure in the spectra of ETCD-SE and ETCD-LE is sufficiently similar to that of other polydiacetylenes that it may be assigned to a similar origin.

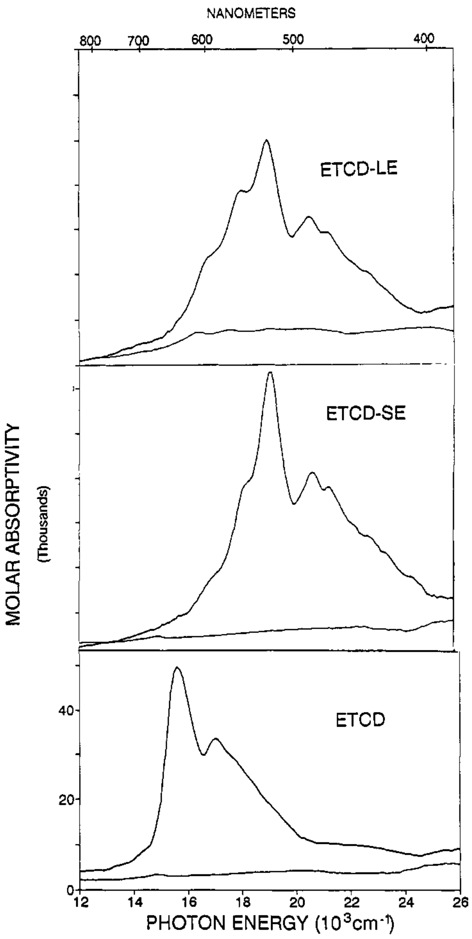

Figure 4. Molar absorptivity (L/mol cm) of ETCD, ETCD-SE, and ETCD-LE along the long and short axis.

Table 2. Vibronic Progression on the High-Energy Side of the Most Intense Absorption Peak in the Long-Axis Absorption Spectra of Representative Polydiacetylene Crystals. Differences in Energy, Δenergy, Listed Are Peak Minus Origin

PDA	energy (cm^{-1})	Δenergy (cm^{-1})
DCH	15 250	
	16 700	1450
	17 350	2100
THD	17 575	
	19 175	1600
	19 725	2150
ETCD	15 600	
	17 000	1400
	17 800	2200
ETCD-SE	19 200	
	20 800	1600
	21 400	2200
ETCD-LE	19 000	
	20 600	1600
	21 200	2200

A second feature in the spectra of the two nonthermochromic forms of ETCD is the presence of structure of the low energy side of the most intense absorption peaks. This is usually not found in polydiacetylene crystals. Vibronic peaks are observed at 16 900 and 18 300 cm^{-1} for ETCD-

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SE and at 16 700 and 18 100 cm^{-1} for ETCD-LE. The energies of these two sets of vibrons are essentially the same. Comparing this value of 1400 cm^{-1} with the energy difference between the two most intense peaks in thermochromic ETCD, 15 600 and 17 000 cm^{-1}, yields the same value. However, if one compares the energy difference of these two sets of vibrons on the low-energy side of the most intense peaks in the two nonthermochromic forms with that of the energy difference between the first vibronic on the high-energy side and the most intense peak, a difference of 900 cm^{-1} is found. These anomalous vibrons present on the low-energy side of the most intense peak are not attributed to transitions within the nonthermochromic ETCD electronic manifold. Instead, they are ascribed to transitions in the electronic manifold of residual thermochromic ETCD. This occurs because some of the original thermochromic ETCD is apparently present in the two new forms of nonthermochromic ETCD.

This argument is strengthened by the X-ray powder diffraction data for ETCD-SE listed in Table 1.[1] Comparison of the diffraction patterns of thermochromic ETCD with ETCD-SE along the (h00) face, where $h = 1$, 2, and 3, shows three distinct features. The first, which has already been mentioned, is the shifting of the most intense diffraction peaks to smaller values of 2θ, indicating an expansion of the lattice in ETCD-SE along the direction of the urethane side groups. The second is the splitting of the main diffraction peaks in ETCD-SE, suggesting the presence of more than one crystallographic phase. And finally, some diffraction intensity near the position of the h00 reflection of the original thermochromic ETCD is observed. We assign this diffraction intensity to the presence of thermochromic ETCD still present in ETCD-SE.

The DSC thermogram of ETCD-SE also supports the hypothesis that some of the original thermochromic ETCD is still present in ETCD-SE. The thermogram of ETCD-SE and the first three shown in Figure 2 show a highly diminished yet clearly observable endotherm near the thermochromic transition of pristine ETCD. This fact is in direct agreement with the available physical, crystallographic, and electronic spectral data that show destruction of the observable thermochromism but yet predicts the presence of residual thermochromic ETCD still present in ETCD-SE.

In contrast, the presence of thermochromic ETCD in ETCD-LE is not supported by the X-ray diffraction and DSC data. As mentioned previously, the reflection and corresponding absorption spectra for ETCD-LE indicate the presence of some residual thermochromism still present in ETCD-LE. However, the DSC thermogram for ETCD-LE (Figure 2) shows no presence of the expected thermochromic endotherm implying that the boiling chlorobenzene has removed all thermochromic interactions. In addition, the X-ray diffraction pattern for ETCD-LE shows no diffraction intensity at values of 2θ corresponding to that of thermochromic ETCD, nor does it show any splitting of the main diffraction peaks as observed for ETCD-SE. However, the X-ray data does show that the main diffraction peaks are shifted to lower values of 2θ, indicating an expansion of the lattice. The absence of observable thermochromic ETCD in the X-ray diffraction and DSC data of ETCD-LE can be attributed to the increased exposure time to boiling chlorobenzene compared to that of ETCD-SE. It appears that increased exposure times allow the boiling chlorobenzene to extensively penetrate enough of the crystal to destroy the long-range order of any remaining thermochromic material in the lattice. This is seen quite dramatically in the DSC thermograms where a decrease in the observable thermochromic endotherm for increased exposure time to boiling chlorobenzene is seen. With reference to the X-ray diffraction pattern of ETCD-LE, it should be noted that the diffraction data are an average of the collected reflections, so destruction of long-range order will prevent observable diffraction by residual thermochromic ETCD. It is apparent that the concentration of residual pristine ETCD in ETCD-LE is low, accounting for the lack of observation by either DSC or X-ray diffraction, and that it is concentrated in regions near the crystal surface where it is more readily observed in reflection spectra. Recall that diffusion in solids in general requires defects, especially vacancies. The chlorobenzene extraction process begins with penetration of the ETCD crystal at defects and proceeds to remove monomer and oligomer, creating unoccupied volume inside the crystal leading to the observed expanded lattice. Since the extraction process removes more than 15% of the weight of the crystal, the extensive expansion of the lattice is not overly surprising. The proposed presence of small concentrations of residual pristine ETCD is consistent with the general notion that diffusion in polymers is not facile in the crystalline regions of a sample. These considerations can account for a residual low concentration of pristine ETCD.

Conclusions

The thermal, electronic spectral, and crystallographic data for ETCD-SE and ETCD-LE indicate that chlorobenzene extraction results in the irreversible loss of the conditions which give rise to the thermochromic behavior of ETCD and dramatically alters both forms' electronic and lattice structure. The reason for this loss of thermochromic behavior and the significant blue shift compared to pristine ETCD is attributed to the method of ETCD-SE and ETCD-LE preparation. In both cases, refluxing in chlorobenzene resulted in partial weight loss of the material, 16% for ETCD-SE and 18% for ETCD-LE, which in conjunction with mass spectroscopic analysis confirms that the chlorobenzene removes unreacted monomer and oligomer. In doing so, it increases the volume of the lattice by expansion in the direction of the side groups. This increased volume manifests itself in a marked decrease in the restriction to motion of the urethane side groups. This situation can result in the reduction of a mechanical strain imposed on the backbone of ETCD by the polymerization process and subsequently result in partial relaxation of the conjugated chain and its surroundings. If a compressive mechanical strain is the reason that the reflectivity maxima of ETCD and IPUDO are comparable to those of DCH and PTS, then relief of the strain should shift the maximum to higher frequency, as observed herein for ETCD. The relaxation of the conjugated chain could include the situation of a less planar configuration. These possibilities collectively can reduce the degree of delocalization and shift the corresponding electronic spectra to higher energies, as observed.

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