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Two-Dimensional Supramolecular Assemblies of a Polydiacetylene. 2. Morphology, Structure, and Chromic Transitions

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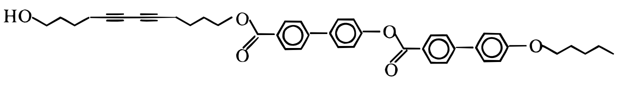
ABSTRACT: A mesogen-substituted polydiacetylene which self-assembles into stacks of bilayered two-dimensional structures was investigated by X-ray and electron diffraction as well as electron microscopy. The multilayered stacks of bilayers were found to organize into single crystals with an orthorhombic unit cell. Within each two-dimensional structure, the polyconjugated backbones are oriented along either of the two *ab* plane face diagonal directions, and the substituted side chains are oriented parallel to the layer normal (*c*-axis direction). The layered single-crystal structures form blue solids at room temperature but undergo the well-known thermochromic and solvatochromic transitions which produce red, orange, and yellow solids. In this work we have established links among chromic transitions, molecular organization, and morphology of these two-dimensional assemblies. Their thermochromic transition from blue to red solids at elevated temperature was found to be accompanied by reversible fracturing of the large single crystals. However, the red to orange transition at even higher temperatures was found to be associated with the irreversible twisting of fractured crystals and the lengthening of the chemical repeat. Based on electron diffraction, this twisting is accompanied by rotations of mesogenic side chains substituting the polydiacetylene backbone. On the other hand, our studies suggest that conformational changes do not play a role in the reversible blue to red transitions of these two-dimensional assemblies. Electronic delocalization perpendicular to the backbone may be a factor in these reversible changes linked to the fracturing of crystals.

Introduction

More than 2 decades ago Wegner reported that substituted diacetylene monomers polymerize topochemically in the solid state forming polymer crystals with nearly defect-free structures.[1] The polymerization proceeds in the crystalline state and converts monomers with conjugated triple bonds into the familiar conjugated polydiacetylenes.[1−4] Since the original discovery many other investigators have contributed to this field.[3−33] Over the past few years our laboratory has been interested in two-dimensional (2D) polymers formed by the chemical reaction among self-assembled monomers.[34,35] In this context we became interested in the use of polydiacetylene backbones as a way to covalently stitch 2D structures. Furthermore, we have also been interested in the use of hydrogen bonds to create 2D assemblies of molecules. In the previous paper, in this issue,[36] we reported on the synthesis of a diacetylene compound and its layered structures upon polymerization by UV photons. We also reported in this paper on the chromic transitions and third-order nonlinear optical properties of these 2D structures. The chemical structure of the compound is shown below:



In fact, polydiacetylene single crystals are known to have large third-order nonlinear optical susceptibilities due to their extended π systems,[23,25,37,38] and some substituted polydiacetylenes exhibit second-harmonic generation.[39−42] Furthermore, many polydiacetylenes have been reported to exhibit chromic transitions.[9,16,17,21−24,27−31,36] The origin of the chromic transitions has been studied by a number of investigators and attributed to many different phenomena. For example, Chance et al. attributed it to an acetylene to butatriene transformation in the bonding sequence of the backbone.[9] On the other hand, other authors linked the transition to a planar to nonplanar conformational change (conjugation length change) of the backbone[27−31] or to a conformational disorder of the backbone.[24] In our view, this phenomenon in polydiacetylenes is still not fully resolved.

The purpose of this paper has been to study in detail the morphology and structure of the layered single crystals formed by our monomer. Each layer in these single crystals is a 2D assembly of hydrogen-bonded polydiacetylene molecules. Hydrogen bonding is formed by hydroxyl groups present at the terminus of the side chain substituting the diacetylene group. These layered single-crystal structures form blue solids at room temperature but undergo thermochromic and solvatochromic transitions to produce red, orange, and yellow solids. Thus, we have been particularly interested in characterizing the morphological and structural changes associated with these chromic transitions. The experiments of the present study have involved the use of X-ray and electron diffraction as well as electron microscopy.

Experimental Section

Sample Preparation. Samples were prepared by solution casting films of the diacetylene monomer, placing a few drops of a dichloromethane solution (~0.1% by weight) on a surface of glycerin. The solution was spread over this surface and the solvent allowed to evaporate. After the solvent had evaporated, large white crystals of the diacetylene monomer appeared on the glycerin surface. The crystals were then rinsed in deionized water to remove residual glycerin and picked up either on 3 mm copper grids covered with a carbon substrate or on microscope slides and dried in air. All the preparation procedures described above were performed in darkness in

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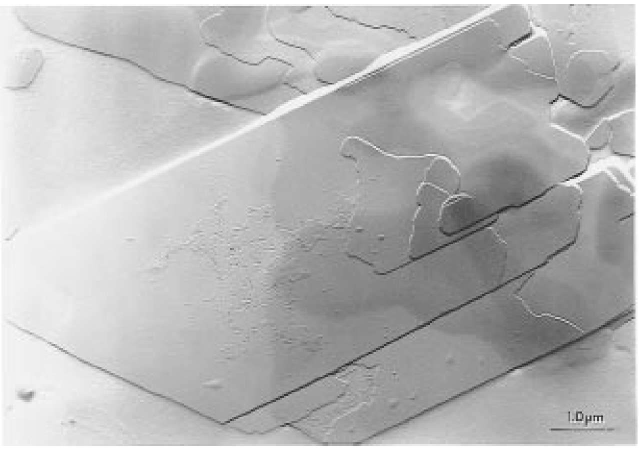


Figure 1. Transmission electron micrograph of the polydiacetylene single crystals shadowed with Pt/C.

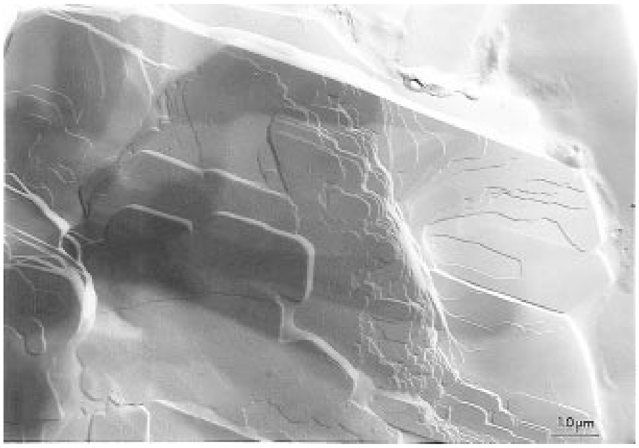


Figure 2. Transmission electron micrograph showing a multilayered structure of the two-dimensional bilayer assemblies (shadowed with Pt/C).

order to avoid premature polymerization. The monomer crystals on copper grids or microscope slides were polymerized by exposure to UV irradiation which led to a color change from white to blue at room temperature.

Characterization. Electron microscopy of samples was carried out in a Philips CM-12 electron microscope operated at 120 kV. Some of the samples were shadowed with Pt/C in order to enhance image contrast. Experiments above room temperature to study thermochromic transitions utilized a Philips EM420 electron microscope, equipped with a hot stage. The samples examined at elevated temperatures were not shadowed with Pt/C. The camera lengths of the two microscopes were calibrated using TlCl or Au evaporated onto the crystals. Characterization of samples on glass slides by X-ray diffraction was carried out using a Rigaku/D-Max diffractometer in the reflection mode using Cu Kα radiation.

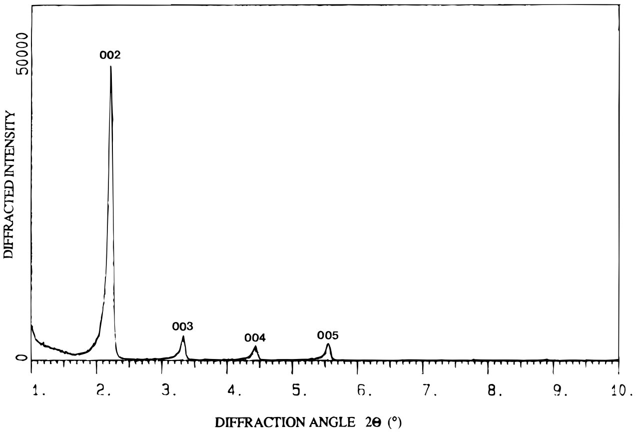


Figure 3. X-ray diffraction scan of a blue polydiacetylene film obtained at room temperature.

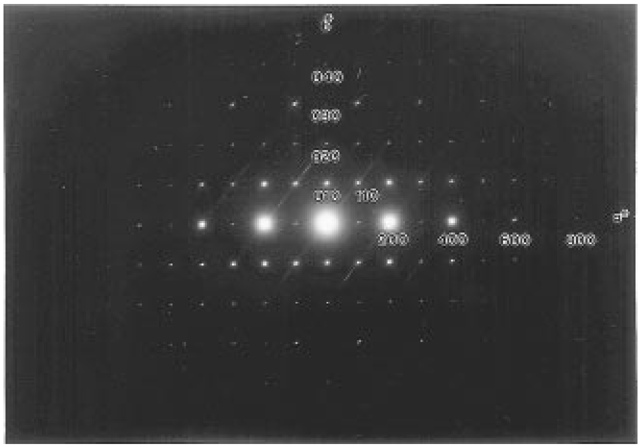


Figure 4. Electron diffraction pattern of a polydiacetylene single crystal, revealing an orthorhombic *a***b** reciprocal lattice plane and a series of sharp streaks on the layer lines parallel to the [110]* reciprocal vector direction.

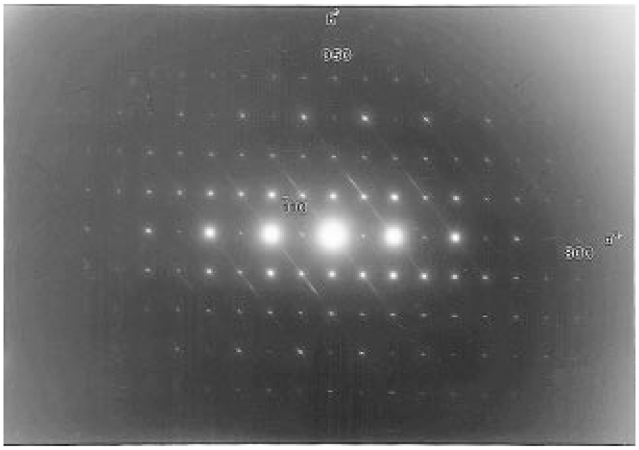


Figure 5. Electron diffraction pattern of a polydiacetylene single crystal, showing the same orthorhombic *a***b** reciprocal lattice plane shown in Figure 4. In this case the sharp streaks on the layer lines are parallel to the [1̄10]* direction instead of the [110]* direction.

Results and Discussion

Morphology and Structure of the Polydiacetylene Single Crystal. Figure 1 is an electron micrograph of the polydiacetylene sample shadowed with Pt/C, showing flat and thin structures with sharp edges. Figure 2 is another electron micrograph of the sample clearly showing its multilayer morphology containing stacked sheets. Those structures have two-dimensional nature since their $x-y$ dimensions can be as large as 10 μm and their characteristic period based on X-ray diffraction is only 80 Å. This periodicity is demonstrated by the X-ray diffraction scan in Figure 3 showing four sharp peaks corresponding to 002, 003, 004, and 005 reflections (up to 14 orders of reflection can be observed in these films; see previous article in this issue[36]). As reported in our previous publication,[36] the length of a fully extended monomer molecule is ~40 Å; thus each of the observed layers must have a bilayer structure with two sublayers. On the basis of FTIR spectra reported before, these two sublayers must be linked by hydrogen bonds.[36] Thus we envision the central region of the bilayer as being composed of

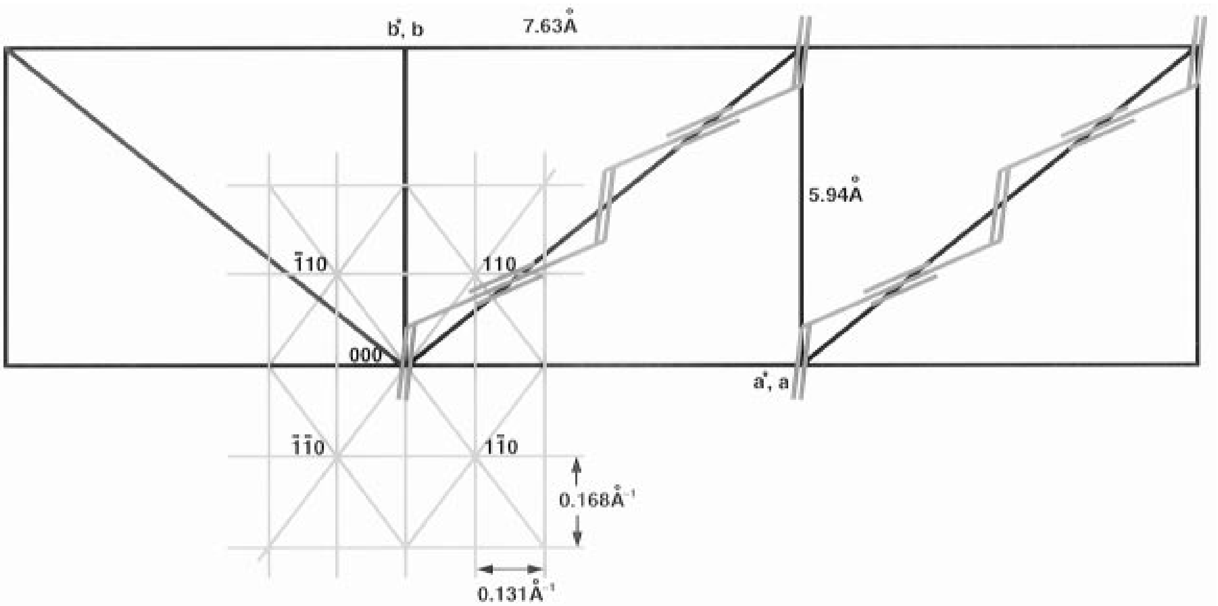


Figure 6. Schematic representation of the orthorhombic a^*b^* reciprocal lattice plane and the orthorhombic *ab* lattice plane in real space. The lines along the $[110]^*$ and $[\bar{1}10]^*$ directions represent the layer lines.

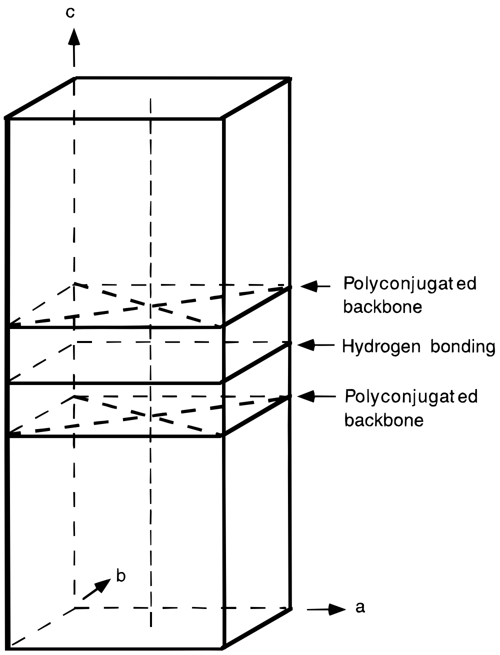


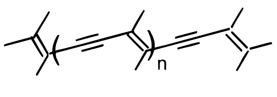
Figure 7. Schematic representation of the orthorhombic unit cell of the polydiacetylene single crystal, showing two half-unit cells linked by hydrogen bonds. The polyconjugated backbones are oriented along either of the two *ab* plane face diagonal directions, and side chains are situated in the corners and center of the unit cell and oriented along the *c*-axis.

hydrogen-bonded side chains through their terminal −OH groups and outer regions of the bilayers containing the mesogenic segments.

Figure 4 is a typical electron diffraction pattern revealing the single-crystal nature of a multilayered stack. This pattern reveals an a^*b^* reciprocal lattice plane with an orthorhombic unit cell. All the reflections in the pattern are very sharp, and the resolution is less than 1 Å since the 800 reflection is observed, indicating a high degree of perfection in the single-crystal structure. In addition to these sharp reflections there are also sharp streaks along the layer lines parallel to the $[110]^*$ reciprocal vector direction. Figure 5 is an electron diffraction pattern obtained from another single crystal of the polydiacetylene. This pattern shows the same orthorhombic a^*b^* reciprocal lattice plane as that shown in Figure 4. However, the sharp streaks on the layer lines are not parallel to the $[110]^*$ direction but parallel to the $[\bar{1}10]^*$ direction. Figure 6 is a schematic representation of the orthorhombic a^*b^* reciprocal lattice plane and the orthorhombic *ab* lattice plane in real space. The lines along the $[110]^*$ and $[\bar{1}10]^*$ directions represent the layer lines. Because the streaks appear on these layer lines, there must be periodic structures in real space along directions perpendicular to the layer lines. These directions correspond to two *ab* plane face diagonal directions, and the periodic structures in these directions must correspond to the conjugated backbones of the polydiacetylene chains. The reflections from the conjugated backbones appearing as streaks on the layer lines are due to a relative displacement of parallel backbones which are not correlated along the *ab* plane face diagonal direction.

The sharp, thin nature of the streaks indicate that the molecular backbones in these polydiacetylenes are fairly long. The intensity of the streaks along the layer lines is not uniform, showing some detailed structure of the alternating single−triple−single−double bonds along the backbone. According to the electron and X-ray diffraction results, the orthorhombic unit cell parameters are $a = 7.63$ Å, $b = 5.94$ Å, $c = 80.0$ Å, and $\alpha = \beta = \gamma = 90°$.

The *d*-spacing of the layer lines measured from the electron diffraction patterns is equal to 9.67 Å which is exactly equal to the length of the *ab* plane face diagonal. The length of one chemical repeat unit in the conjugated backbone:



calculated using standard bond length values is equal to 4.90 Å. Therefore, there must be two chemical repeat units per half-unit cell in each sublayer, and each chemical repeat unit is equal to 4.84 Å (one-half of 9.67 Å). The orthorhombic unit cell of the polydiacetylene single crystal is schematically represented in Figure 7. This figure shows two half-unit cells linked by hydrogen

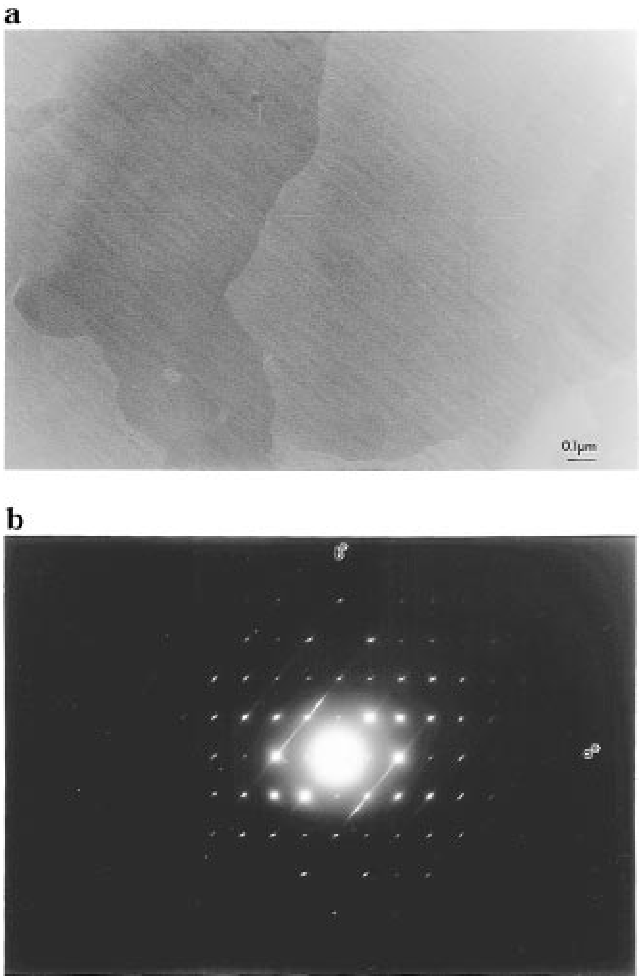


Figure 8. (a) Transmission electron micrograph of a polydiacetylene single crystal obtained at 77 °C, showing the fracturing into narrow strips of the single crystal along the backbone direction. (b) Electron diffraction pattern of the polydiacetylene single crystal taken at 77 °C, showing sharp reflections and streaks along the layer lines.

bonds. The conjugated backbones are in either of the two *ab* plane face diagonal directions, and the side chains are oriented along the *c*-axis direction in the corner and in the middle of the unit cell.

Chromic Transitions. As mentioned before, the polydiacetylene single crystals are blue solids at room temperature. Upon heating the following thermochromic transitions take place:[36]

$$\text{blue solid} \xrightleftharpoons{\sim 77\ ^\circ\text{C}} \text{red solid} \xrightarrow{\sim 125-150\ ^\circ\text{C}} \text{orange solid}$$

As shown earlier in Figures 1 and 2, the polydiacetylene single crystals have flat and smooth surfaces at room temperature. However, when heated to ~77 °C using the hot stage in the electron microscope, the crystals were observed to fracture into narrow strips along the molecular backbone direction. Figure 8a is an electron micrograph of a polydiacetylene single crystal obtained at 77 °C which shows the fracturing of the original single crystal. The corresponding electron diffraction pattern of the fractured single crystal is shown in Figure 8b. This pattern also shows sharp reflections and streaks, but as one might expect the spots are now elongated somewhat along the direction of the streaks. Figure 9a is an electron micrograph taken at 100 °C, revealing very clearly strips resulting from fracture along the backbone direction. Figure 9b is an electron diffraction pattern of the polydiacetylene single crystal taken at 100 °C, showing sharp reflections and streaks again as those shown in Figure 8b. Figure 10a is an electron micrograph of a polydiacetylene single crystal heated to 110 °C, showing strips parallel to the backbone direction. Most interestingly, when the single crystals are heated to 110 °C and subsequently cooled to room temperature, the intense fracturing appears to have healed and the original morphology is recovered. There are no longer narrow strips but large and flat crystals instead (Figure 10b), and at the same time the samples recover their original blue color. This healing solid state process associated with the reversible thermochromic transition is quite surprising, and we do not know at this time its mechanism.

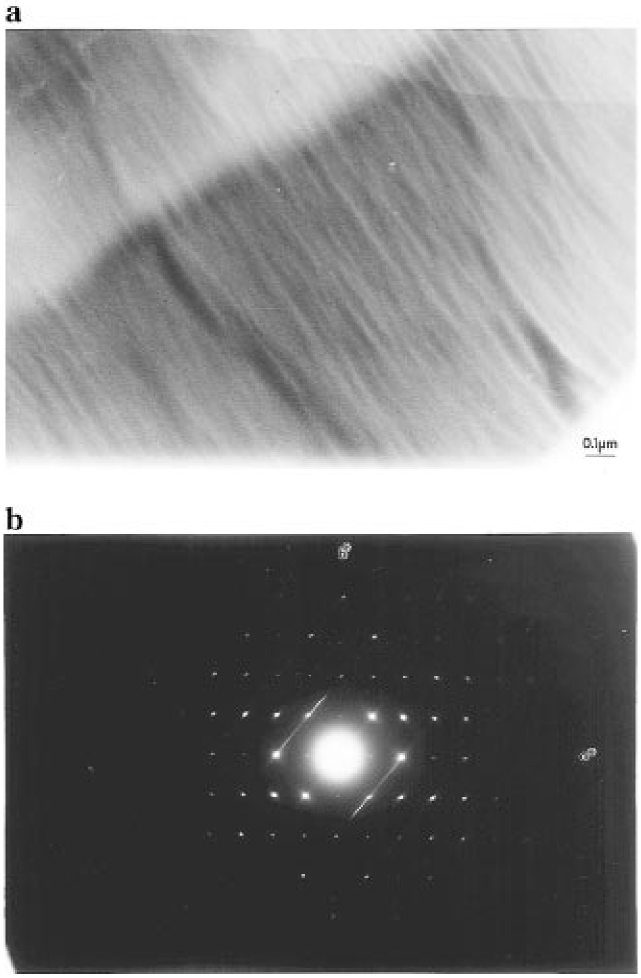


Figure 9. (a) Transmission electron micrograph of a fractured polydiacetylene single crystal obtained at 100 °C, showing clearly narrow strips along the backbone direction. (b) Electron diffraction pattern of the sample obtained at the same temperature.

In order to clarify the origin of the thermochromic transitions of the polydiacetylene single crystals, we analyzed the electron diffraction patterns taken at temperatures from 18 to 200 °C and calculated the orthorhombic unit cell parameters *a* and *b* at different temperatures. Figure 11 plots the temperature dependence of the *a* and *b* unit cell parameters, showing clearly their constant value as the temperature changes from ambient to 110 °C. Thus, the length of the chemical repeat in the polyconjugated backbone must remain constant as well (4.84 Å). We therefore believe the crystalline structure is geometrically the same in

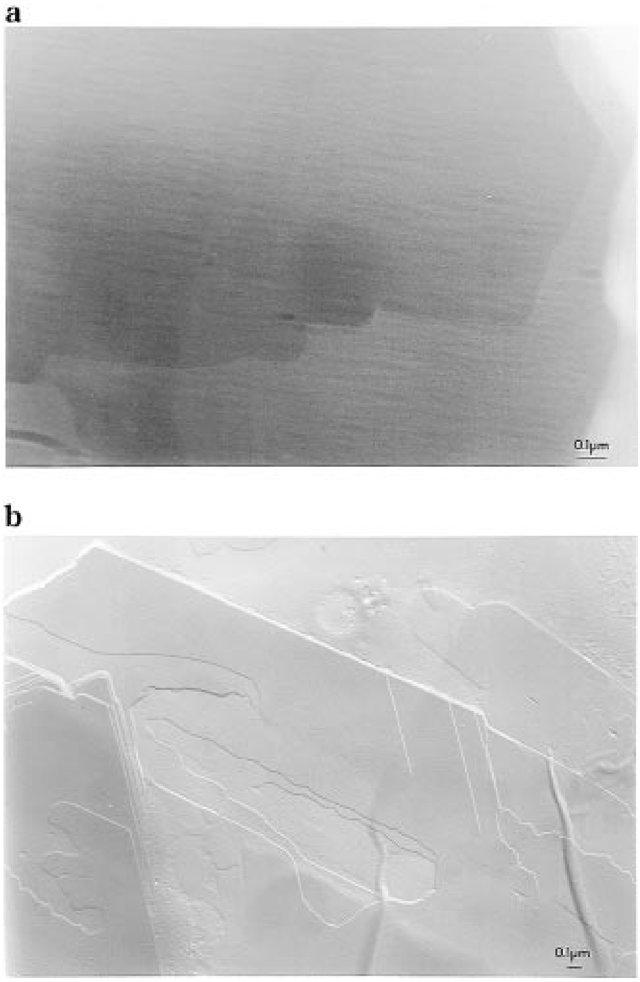


Figure 10. (a) Transmission electron micrograph of a fractured polydiacetylene single crystal obtained at 110 °C. (b) Electron micrograph of a similar sample heated to 110 °C and subsequently cooled to room temperature (shadowed with Pt/C), revealing the healing of the fracture observed in a.

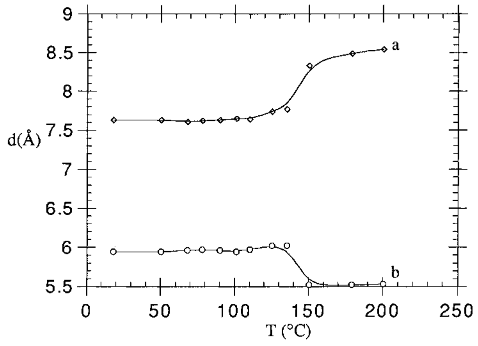


Figure 11. Temperature dependence of the orthorhombic unit cell parameters *a* and *b* in polydiacetylene samples.

both the red and blue forms of these polydiacetylene single crystals. However, their electronic structures (delocalization of π electrons) may be different.

In order to obtain more information on the morphology and structure of the red form, a different method was used to induce the chromic change, namely, immersing the blue solid material at room temperature in CH_2Cl_2.[36] It is interesting to observe the disappearance of the blue color in a couple of minutes as samples become bright red in color. As pointed out previously[36] this red color remains even after samples are removed from the CH_2Cl_2 and are visibly dried. Figure 12a is an electron micrograph of the red form obtained by CH_2Cl_2 immersion, revealing the same fractured morphologies observed in the heated sample. Figure 12b is an electron diffraction pattern of the red form polydiacetylene single crystal, showing sharp reflections and streaks similar to those in the blue-colored single crystals. Figure 13 is another electron micrograph obtained from

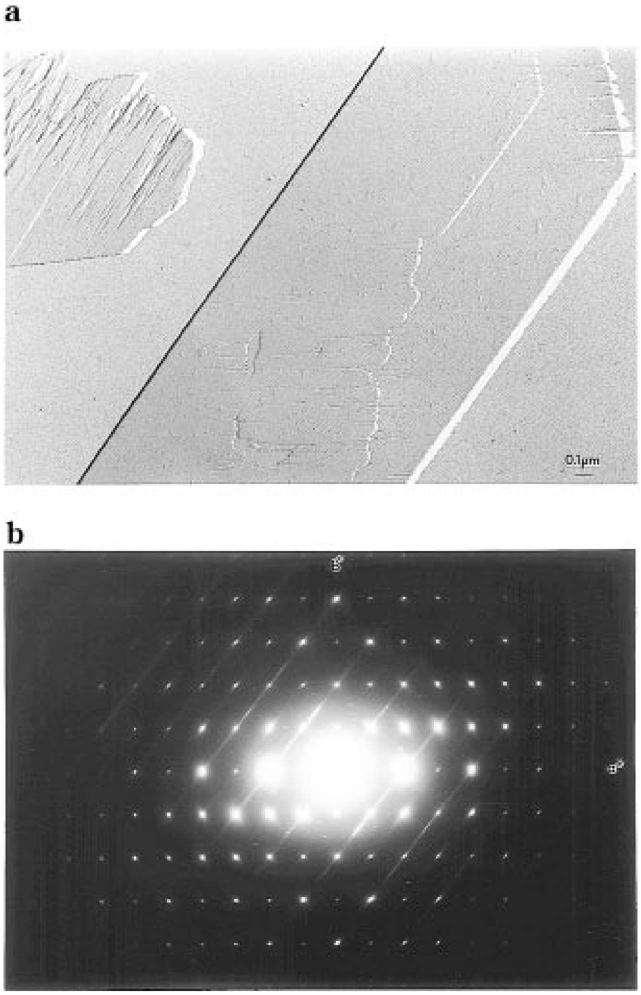


Figure 12. (a) Transmission electron micrograph of the red form polydiacetylene single crystals obtained from originally blue samples after immersion in CH_2Cl_2. The micrograph shows the fracturing of crystals parallel to the backbone direction. (b) Electron diffraction pattern of the same sample showing sharp reflections and streaks on the layer lines parallel to the [110]* direction.

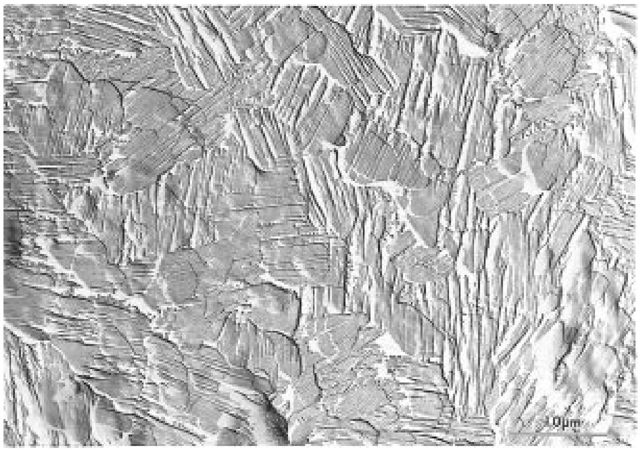


Figure 13. Transmission electron micrograph of many small crystals after immersion in CH_2Cl_2, revealing their fracture into narrow strips along the backbone direction.

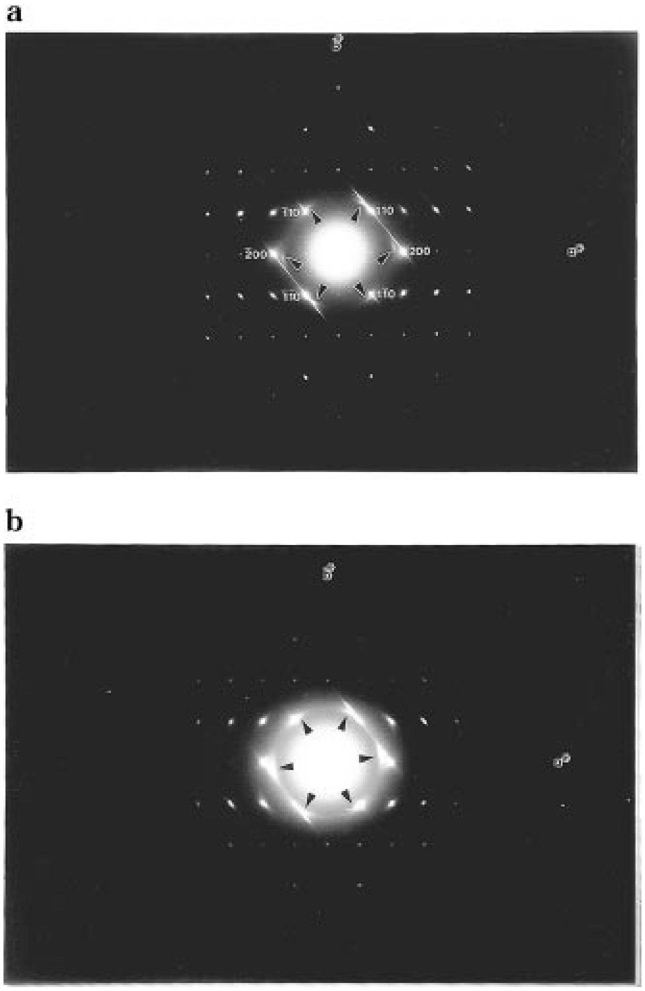


Figure 14. (a) Electron diffraction pattern of a polydiacetylene sample taken at 125 °C, showing six additional reflections (indicated by arrowheads) arranged in hexagonal geometry near the 110, 200, $1\bar{1}0$, $\bar{1}\bar{1}0$, $\bar{2}00$, and $\bar{1}10$ reflections. (b) Electron diffraction pattern obtained at 150 °C, showing six additional diffuse reflections (indicated by arrowheads) distributed in a hexagonal geometry.

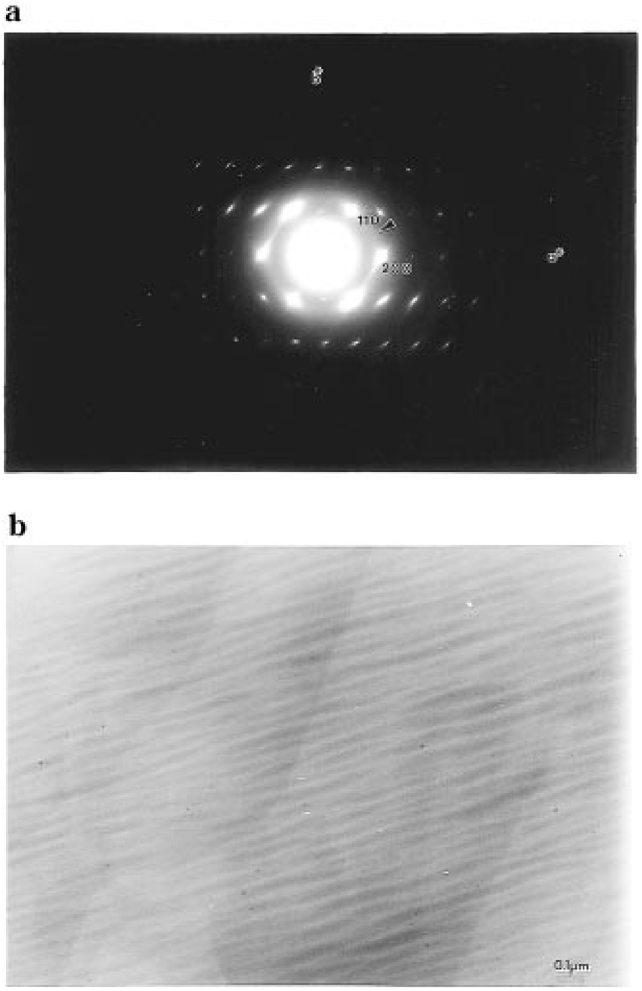


Figure 15. (a) Electron diffraction pattern of a sample obtained at 197 °C, showing an a^*b^* reciprocal lattice plane and a diffuse ring (indicated by an arrowhead). (b) Transmission electron micrograph of the same sample obtained also at 197 °C, showing crystal strips along the backbone direction.

a thin sample containing many small crystals and thus very clearly shows the fracturing of individual crystals. Each crystal reveals fracture lines along its polyconjugated backbone direction, as found in other samples upon heating. It is important to point out that the red form single crystals obtained by CH_2Cl_2 immersion also have the exact same unit cell parameters as those of the blue material. Thus the difference between the blue and red solids appears to be only in the planar dimension of crystals along a direction perpendicular to the backbone.

One could speculate that delocalization of π electrons in the layer plane occurs not only along the polyconjugated backbone direction but also in the direction perpendicular to the backbone. Alternatively, the color change could be linked to conformational changes in the boundary zones of narrow strip crystals. However, our observations do indicate that a homogeneous change in backbone "conjugation length" is not behind the observed chromic changes. Our images indicate that planar crystal dimensions parallel and perpendicular to the backbone direction are between 0.2 μm and several microns in the blue solid. However, in the red solid, dimensions perpendicular to the backbone are only on the order of 80 Å to several hundred angstroms.

When the material is heated in the temperature range between 125 and 150 °C, the red color disappears and the sample turns orange. As revealed by the plot of Figure 11, we found that the lattice parameter *a* increases very rapidly from 7.74 Å at 125 °C to 8.33 Å at 150 °C. Meanwhile the lattice parameter *b* decreases very rapidly from 6.02 Å at 125 °C to 5.52 Å at 150 °C. Correspondingly, the length of the chemical repeat unit increases from 4.90 Å at 125 °C to 5.00 Å at 150 °C. When the crystals are heated to temperatures higher than 150 °C, *b* does not change any more but *a* continues to expand slowly. This indicates that the thermochromic transition from red to orange is associated with changes in the crystal structure. In addition to the observed unit cell parameter changes, extra reflections appear in electron diffraction patterns. Figure 14a shows an electron diffraction pattern of a crystal taken at 125 °C. This pattern shows six extra reflections corresponding to a *d*-spacing of 4.40 Å arranged with hexagonal geometry. These six reflections are observed near 110, 200, $1\bar{1}0$, $\bar{1}\bar{1}0$, $\bar{2}00$, and $\bar{1}10$ reflections. This indicates that there are rotations of side chains about the *c*-axis in the crystal. Since we know that there are hydrogen bonds present in the center of each sheet, the side chains with $-$OH end groups probably cannot rotate at this temperature. Thus, the rotation must involve the mesogenic side chains which we believe exist

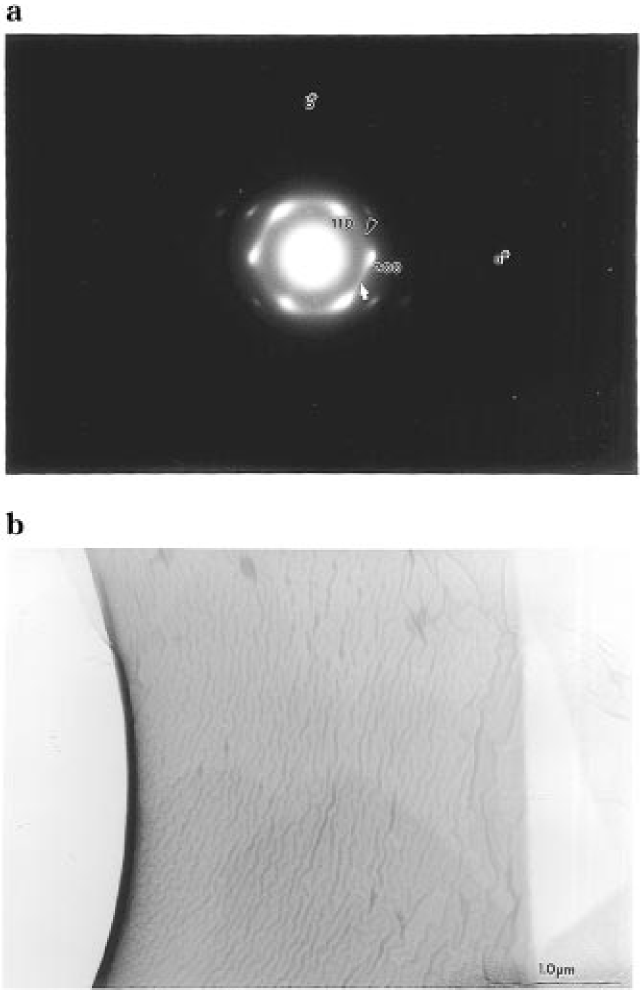


Figure 16. (a) Electron diffraction pattern of a sample obtained at 238 °C, showing only one diffuse streak on the second layer line (indicated by an arrow) and a diffuse ring (indicated by an arrowhead). (b) Transmission electron micrograph of the same sample obtained also at 238 °C, revealing twisted strips.

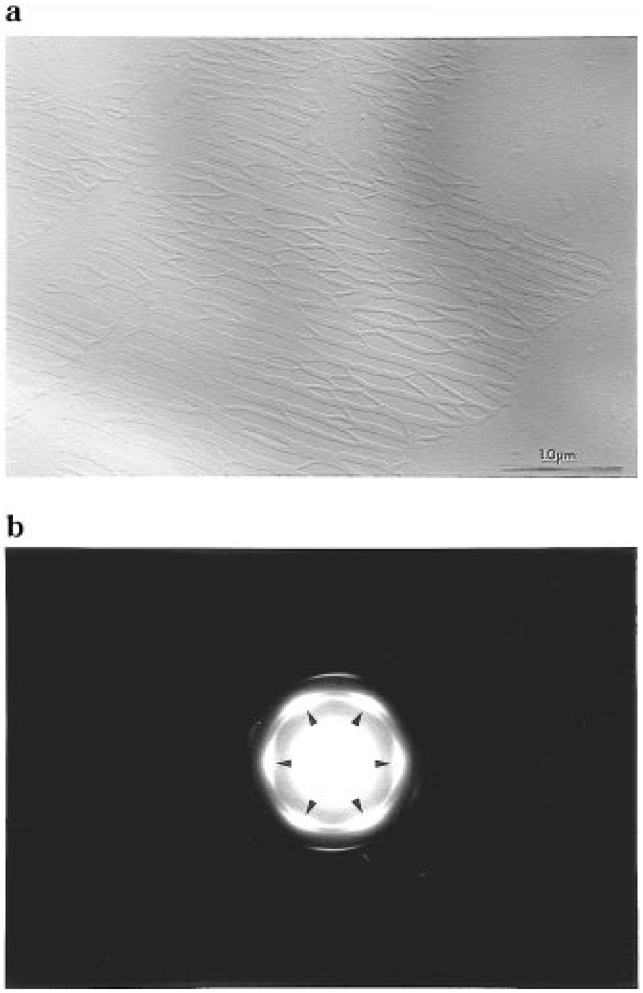


Figure 17. (a) Transmission electron micrograph of a sample heated to 200 °C and subsequently cooled to room temperature (shadowed with Pt/C). The micrograph reveals a network-like structure formed by twisted narrow strips. (b) Electron diffraction pattern corresponding to the same sample in panel a, revealing six innermost reflections distributed in a hexagonal geometry (indicated by arrowheads).

in a phase characterized by us before as a crystal E_h phase.[43] This phase contains three orthorhombic lattices with $a = \sqrt{3}b$ related to one another by rotations of ±60° about the c-axis. The orthorhombic unit cell parameters in this case are $a = 8.80$ Å and $b = 5.08$ Å, based on the 4.40 Å d-spacing measured from the six extra reflections. Once samples are heated to 125 °C, the rotations are presumably cooperative since the 4.40 Å spacing would be too small for independent rotation. The side-chain rotations probably twist the polyconjugated backbone, shortening the conjugation of repeats along the backbone direction. Figure 14b is an electron diffraction pattern obtained at 150 °C. This pattern also shows six extra reflections which are more diffuse corresponding to a d-spacing of 4.49 Å distributed in a hexagonal geometry. This enlarged distance is a possible indication that side chains with mesogenic segments are rotating independently about the c-axis of the crystal. The structure matches at this point the structure of a hexatic smectic B phase.[43,44]

Figure 15a is an electron diffraction pattern of a polydiacetylene single crystal taken at 197 °C. This pattern no longer shows the six hexagonally distributed additional reflections. Instead, a diffuse ring appears in the pattern indicating that side chains with mesogenic segments now exist in a smectic A phase. Figure 15b is an electron micrograph of the polydiacetylene single crystal taken at 197 °C, showing crystal strips parallel to the polyconjugated backbone direction. Increasing the temperature further to 238 °C results in the appearance of only one diffuse streak on the second layer line parallel to the [110]* direction (see Figure 16a). This indicates that the conjugation length along the backbone direction has been significantly shortened. The reflections in the pattern are not sharp, and the diffuse ring is clearly shown in the pattern. Figure 16b is an electron micrograph of the polydiacetylene single crystal taken at 238 °C, showing twisted strips quite different from the smooth-edge strips observed in the red solid. These morphological changes are not associated with chemical decomposition based on TGA experiments which indicate the material is stable below 300 °C.[45] In the orange solid consisting of twisted strips, there may be however less electronic delocalization along the backbone direction. Also, the parameter a in the crystal lattice increases from 8.33 Å at 150 °C to 8.54 Å at 200 °C (Figure 11), and correspondingly the length of the chemical repeat unit of the backbone increases from 5.00 Å at 150 °C to 5.09 Å at 200 °C. According to these electron diffraction and electron microscopy results, the thermochromic transition from the red form to the orange form could be accounted for by a reduction of electronic delocalization.

This compromised delocalization may be the result of backbone twisting and lengthening of the chemical repeat unit.

Finally, Figure 17a is an electron micrograph of a large polydiacetylene single crystal heated to 200 °C, subsequently cooled to room temperature, and then shadowed with Pt/C. This image shows twisted narrow strips connected to each other and forming a network-like structure. Thus, the morphological change is irreversible as is the thermochromic transition from red to orange color. Figure 17b is the corresponding electron diffraction pattern showing six innermost reflections distributed in a hexagonal geometry, confirming the irreversibility of the transformation.

Conclusions

We have characterized the solid state structure of a mesogen-substituted polydiacetylene capable of forming hydrogen bonds. The system was found to organize into two-dimensional bilayer assemblies, which in turn organize into multilayered single crystals. We have also established links among chromic transitions and molecular organization as well as morphology in these two-dimensional assemblies. Their thermochromic transition from blue to red solids at elevated temperature is accompanied by reversible fracturing of large crystals. However, the red to orange transition at even higher temperatures is associated with the irreversible twisting of fractured crystals and the lengthening of the chemical repeat. On the basis of electron diffraction, this twisting is accompanied by rotations of mesogenic side chains substituting the polydiacetylene backbone. On the other hand, our studies suggest that conformational changes do not play a role in the reversible blue to red transitions of these two-dimensional assemblies. Electronic delocalization perpendicular to the backbone may be a factor in these reversible changes accompanied by the fracturing of crystals.

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