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# Chromism in Polydiacetylene Solutions and Crystals

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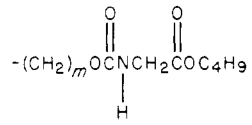
ABSTRACT: A planar–nonplanar conformational transition is reported for two weakly-soluble, urethane-substituted polydiacetylenes. These results strongly support the intramolecular hydrogen-bonding model which has been used to explain this conformational transition for highly soluble polymers of this type. A comparison of the chromism associated with the solution phase conformational transition with the thermochromism observed in crystalline polydiacetylenes suggests that the interplay of intra- and intermolecular interactions is importantly involved in the thermochromic phase changes.

A planar–nonplanar conformation transition has been reported recently[1] for solutions of polydiacetylenes, $(=RC-C\equiv C-CR=)$, with substituent groups (R) of the form



$$-(CH_2)_mOC(=O)N(H)CH_2C(=O)OC_4H_9$$

where $m$ = 3 (poly3BCMU) or $m$ = 4 (poly4BCMU). These materials are quite soluble in $CHCl_3$, yielding a yellow solution with a lowest energy optical transition ($E_0$) at ~21 500 cm$^{-1}$. This $E_0$ value is considerably blue shifted compared to the normal crystalline value ($E_0$ ~ 16 000 cm$^{-1}$)[2] due to a nonplanar backbone conformation. This nonplanar conformation probably consists of a statistical distribution of 90° rotations about the single bond in the backbone, which interrupts the backbone conjugation but allows maximum utilization of the entropy content of the R group in the stabilization of the solution phase. On addition of a nonsolvent such as hexane dramatic, reversible color changes occur: yellow → blue ($E_0$ = 21 300 → 16 000 cm$^{-1}$) for poly3BCMU and yellow → red ($E_0$ = 21 700 → 18 800 cm$^{-1}$) for poly4BCMU. The proposed mechanism for the chromism is based on *intramolecular* hydrogen bonding between the C=O and N—H groups on adjacent urethane substituents. This leads to a planar or near planar backbone configuration, hence the dramatic red shift in the $E_0$ transition. Strong evidence for this mechanism is provided by infrared spectroscopy.[1,2] The (butoxycarbonyl)methyl group plays no role in this mechanism.

In this paper, we demonstrate that polydiacetylenes with simple urethane substituents of the form $-(CH_2)_mOC(O)NHC_6H_5$ also show the chromic transition. Comparison to crystal spectra[3-5] yields some information on the origin of the different $E_0$ values for the $m$ = 3 and 4 cases. The relevance of these results to the thermochromic phase changes in polydiacetylene crystals is discussed.

The polydiacetylenes chosen for this investigation were polyTCDU ($m$ = 4) and polyDDU ($m$ = 3). Solutions were prepared by stirring the mixtures at 100 °C in dimethylformamide (DMF) for a few hours. The solutions were then filtered, since there was always an insoluble fraction of roughly 30%. Polymer concentrations of ~10$^{-4}$ mol/L were achieved in this manner (mol refers to mol of polymer repeat units). These solutions were stable with respect to precipitation for at least 6 months. No attempt was made to establish the molecular weights of the dissolved polymer, though it is likely that only the relatively low molecular weight portion of the sample is soluble. Both polymers were soluble to about the same extent in dimethyl sulfoxide. The spectroscopic experiments reported here were limited to the UV–visible portion of the spectrum, since solvent interference and low polymer concentrations prevented meaningful infrared spectroscopy.

Addition of a nonsolvent which is misible in DMF, such as $CHCl_3$ or methanol, produces color changes in an analogous manner to the BCMU polymers. Absorption spectra are shown in Figure 1 for polyDDU in DMF/$CHCl_3$ and in Figure 2 for polyTCDU in DMF/methanol for various volume fractions of DMF in $CHCl_3$ or methanol ($V_{DMF}$). The $V_{DMF}$ values for the color transitions are independent of polymer concentration. $E_0$ values are compared in Table I. In the nonplanar conformation, all

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Table I
Optical Transition Energies, $E_0$ (cm$^{-1}$), in Urethane-Substituted Polydiacetylenes, R = $(CH_2)_mOC(O)NHX$

| polymer | $m$ | X | $E_0$ (nonplanar)[a] | $E_0$ (planar)[b] | $E_0$ (crystal) |
|---|---|---|---|---|---|
| polyDDU | 3 | $C_6H_5$ | 21 100 | 17 100 | 15 800 |
| polyTCDU | 4 | $C_6H_5$ | 21 100 | 19 400 | 15 300/18 500[c] |
| poly3BCMU | 3 | $CH_2COOC_4H_9$ | 21 300 | 16 000 | 15 700 |
| poly4BCMU | 4 | $CH_2COOC_4H_9$ | 21 700 | 18 800 | 15 900/18 500[c] |

[a] Yellow solutions; good solvent. [b] Red or blue solutions; solvent plus nonsolvent. [c] Results for low- (I) and high-temperature (II) phases, respectively.

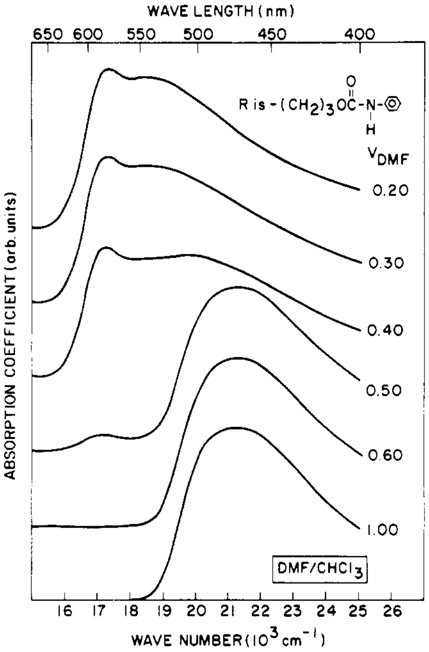

**Figure 1.** Optical absorption spectra for polyDDU solutions. The volume fraction of dimethylformamide (DMF) in $CHCl_3$ is indicated. Polymer concentrations (~$10^{-5}$ mol/L) are the same for all spectra. The spectra are arbitrarily offset.

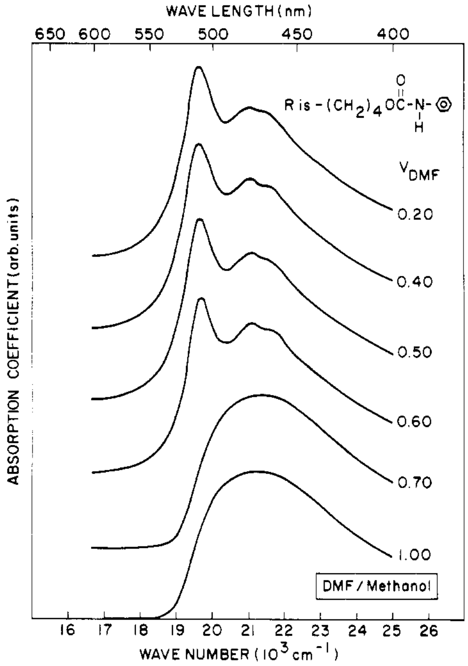

**Figure 2.** Optical absorption spectra for polyTCDU solutions. The volume fraction of dimethylformamide (DMF) in methanol is indicated. Polymer concentrations (~$10^{-5}$ mol/L) are the same for all spectra. The spectra are arbitrarily offset.

four $E_0$ values are nearly the same. In the planar conformation, $E_0$ values for polyTCDU and polyDDU are somewhat lower than their BCMU counterparts. This could be due to either of two effects: (1) shorter chain lengths in the polyTCDU and polyDDU cases or (2) interference of the phenyl ring with the formation of the ordered (planar) structure. Nevertheless, it is clear that the planar–nonplanar conformational transition is observed for these polymers. These results confirm that the only important role of the $-CH_2C(O)OC_4H_9$ functionality in the BCMU polymers is to allow substantial solubility in common organic solvents such as $CHCl_3$.

Similar experiments were attempted with the much studied[6] thermochromic polydiacetylene polyETCD (R is $(CH_2)_4OC(O)NHC_2H_5$). This polymer proved to be even less soluble with a maximum concentration of ~$10^{-5}$ mol/L achieved with DMF as a solvent. The room temperature spectrum of this solution, which was yellow in appearance at ~100 °C and orange in appearance at room temperature, showed evidence for both the planar and nonplanar conformations with a small peak at ~19 300 cm$^{-1}$ and a larger peak at ~21 200 cm$^{-1}$. On aging in a sealed vessel on a time scale of months, the lower energy peak grew at the expense of the higher energy peak and the polymer began to precipitate. (The precipitate had a absorption peak at ~18 900 cm$^{-1}$.) This behavior was not observed for polyTCDU and polyDDU, even in the presence of a nonsolvent. Though our experiments on polyETCD were limited, it seems clear that the behavior of this polymer in solution closely parallels that of polyTCDU.

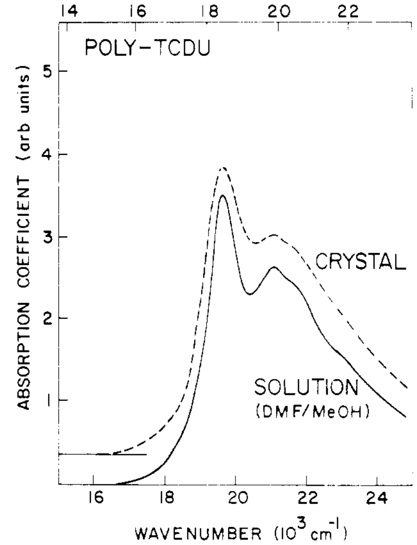

**Figure 3.** Comparison of crystal and solution spectra of polyTCDU. Note that the upper energy scale (crystal) is shifted to the right by 900 cm$^{-1}$ with respect to the lower scale (solution).

PolyTCDU crystals have been the subject of a number of spectroscopic studies.[3-5] Two phases of polyTCDU are known. The usual form obtained at room temperature has

$E_0^{II}$ = 18 500 cm$^{-1}$ and will be designated here as phase II. The absorption spectra for polyTCDU solution and crystal (phase II)[4] are compared in Figure 3. Except for a 900-cm$^{-1}$ shift, the spectra are essentially identical. A full X-ray structural determination is available for phase II of poly-TCDU; the results clearly show intramolecular hydrogen bonding as well as distortions in both the $-(CH_2)_4-$ linkage and in the polymer backbone.[7] In fact, the polymer backbone appears closer in structure to the butatriene structure ($-RC{=}C{=}C{=}CR-$) than to the lower energy acetylene structure ($=RCC{\equiv}CCR=$). Molecular models for the $m$ = 3 and 4 polymers suggest that the $-(CH_2)_4-$ distortion is required for the formation of intramolecular hydrogen bonds while no such distortion is required for a $-(CH_2)_3$ linkage.[1] Therefore, it seems that the unusually high $E_0$ value for the polyTCDU crystal is due to this backbone distortion rather than being a fundamental consequence of the butatriene backbone. (It may be, however, that the butatriene structure is the most stable structure in the strain field caused by the hydrogen-bond formation.) It follows that backbone distortion in the $m$ = 4 case is an attractive explanation for the large differences in $E_0$ values for the $m$ = 4 and 3 polymers in their planar conformations in solution.

Phase II of polyTCDU can be partially transformed into phase I by cooling the phase II polyTCDU to very low temperatures.[3] Complete conversion to phase I has been achieved only by strain.[5] The $E_0$ value for phase I is $E_0^{I}$ = 15 300 cm$^{-1}$, which is very close to that observed for other polydiacetylenes with no possibility of hydrogen bonding or other side group interactions which could distort the polymer backbone.[8,9] We take $E_0$ values in the range 15 000–16 000 cm$^{-1}$ to be indicative of a largely undistorted polydiacetylene backbone.

For this explanation to be correct, the strain energy required for a 3200-cm$^{-1}$ shift in $E_0$ must be comparable to the hydrogen-bond energy (8–14 kcal/mol for two hydrogen bonds per repeat unit). Batchelder and Bloor[10] have studied the strain dependence of $E_0$ for polyPTS (R is $-CH_2SO_3C_6H_4CH_3$) and find a blue shift of 1500 cm$^{-1}$ for a 5% strain. The energy cost for this degree of strain is about 5 kcal/mol.[11] Thus, rather large $E_0$ shifts can be induced at fairly low strain energies. The polyTCDU system is more complicated, since there is no significant elongation or contraction (<1%) associated with the phase I ↔ phase II conversion. (None is expected because the 4.9 Å repeat distance for the polymer backbone is nearly ideal for the hydrogen bonding of urethanes.[1,2]) Also out-of-plane distortion is not possible, since the molecular symmetry dictates the symmetry of the strain field. The X-ray results for polyTCDU[7] suggest that the distortion of the backbone, ($=RC_1C_2{\equiv}C_3C_4R=$), involves a substantial increase in the $C_4$–$C_1$–$C_2$ bond angle (as would also be the case for elongation), an increase in the $C_4$–$C_1$ bond length, and a decrease in the $C_1$–$C_2$ bond length, hence the "butatriene-like" backbone. It is difficult to estimate the energetics of this distortion though it seems reasonable that a dramatic variation in $E_0$ would result.

The thermochromism observed for many urethane-substituted polydiacetylenes with $m$ = 4[6,12] is almost certainly a consequence of backbone distortion caused by changes in side group packing on going from the low-temperature phase (I) to the high-temperature phase (II). Changes in side group packing are also believed to be responsible for similar color changes (blue → red) observed during the polymerization of multilayers of diacetylene monocarbonylic acids.[13] For the urethane-substituted polydiacetylenes, this side group packing is importantly influenced by hydrogen bonding. In environments free of important intermolecular constraints (solutions or films), the lowest energy conformation of the polymer chain is clearly very close to that of phase II (see Figure 3). Therefore, it follows that phase I is stabilized by intermolecular effects on side group packing, which are most likely dominated by effects due to hydrogen bonding. An attractive possibility is that the hydrogen bonding in phase I is *intermolecular* so that thermochromism involves a transformation from inter- to intramolecular hydrogen bonding. Examination of the X-ray structure[7] of phase II of TCDU suggests that this is at least feasible. If intramolecular hydrogen bonding is retained in phase I, we suggest that either the geometry of the hydrogen bonding is altered from the near optimal arrangement in phase II or the strain caused by the hydrogen bonding is taken up by other bonds in the side group so that the strain is not transmitted to the backbone. An X-ray structure determination on any of the $m$ = 4 urethane-substituted polymers whose optical properties clearly indicate phase I should prove definitive in choosing among these possibilities.

In summary, we have demonstrated the generality of previously reported "visual" conformation transition[1] by showing that this transition is also observed in solutions of the simpler urethane-substituted polydiacetylenes. Comparisons of solution and crystal spectra suggest that thermochromic phase transitions in these materials involve the interplay of inter- and intramolecular crystalline forces.

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