Solid State Phase Transformation of a Diacetylene by Solvation. Crystal Structure of a Moderately Reactive Monomer Form

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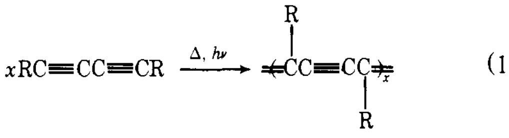
Abstract: The synthesis of a new diacetylene, 2,4-hexadiyne-1,6-bis(*m*-tolylurethane), $\mathrm{HD}_m\mathrm{TU}$ (I), is reported. $\mathrm{HD}_m\mathrm{TU}$ crystallizes in at least two different phases. Crystallization from acetone/hexane gives a moderately active "orange" phase while crystallization from *p*-dioxane/water gives a highly reactive "blue" phase. These colors are not the true colors of highly purified monomer but are produced by a 1,4-addition polymerization product, which forms a solid solution in the monomer via thermal reaction. Upon irradiation with γ-rays, the orange phase polymerizes to a limiting polymer conversion of about 35% while the blue phase polymerizes quantitatively. When exposed to *p*-dioxane vapor, the orange phase undergoes a solid state phase transformation to the blue phase by solvation. The crystals expand by about 25% in the lateral directions. The blue phase incorporates 0.5 molecule of *p*-dioxane per molecule of the diacetylene. The process can be expressed as orange phase of $\mathrm{HD}_m\mathrm{TU} + \frac{1}{2}p$-dioxane → blue phase of $\mathrm{HD}_m\mathrm{TU}\cdot\frac{1}{2}p$-dioxane in the solid state. Upon extraction of the unreacted monomer, the partially polymerized blue phase exhibits a blue shift while the partially polymerized orange phase exhibits a red shift. The crystal structure of the orange phase has been determined by X-ray structure analysis. The crystals are monoclinic with a = 21.908 (6) Å, b = 9.982 (3) Å, c = 9.352 (2) Å, and β = 108.03 (2)°; the space group is $C2/c$ with Z = 4. The structure was refined to an R factor of 0.078 on 1189 nonzero reflections. The molecule of I has C_i site symmetry. During X irradiation, formation of 7–8% polymer was observed. The shortest C(sp)---C(sp) distance in the crystal is 3.607 (7) Å, but the neighboring diacetylene vectors are not parallel but crossed at an angle of 72°. This unusual arrangement of diacetylene vectors in the crystal may be responsible for the low overall rate of formation of polymer (~35%) and the small amount of polymer incorporated as a solid solution (~7%).

Introduction

Diacetylenes, $\mathrm{RC{\equiv}CC{\equiv}CR}$, where R is a substituent group, polymerize in the solid state upon either thermal annealing or exposure to high-energy radiation[2,3] (eq 1). Typically, the monomers are colorless, partially polymerized diacetylenes are either blue or red, and polydiacetylenes are metallic, green-gold. The polymer chains are colored because the π-electron density is delocalized extensively along the conjugated backbone.[2a] The color of a polydiacetylene is determined mainly by the length of the conjugated chain and the planarity of the backbone.[4-6]

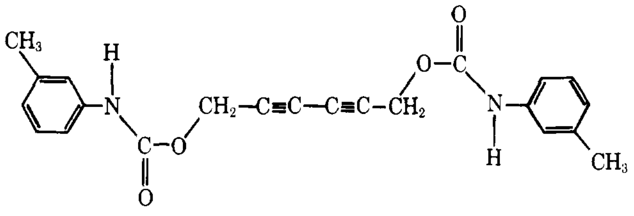


$$x\mathrm{RC{\equiv}CC{\equiv}CR} \xrightarrow{\Delta,\ h\nu} \left[=\!\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{C{\equiv}C}\underset{\mathrm{R}}{\underset{|}{\mathrm{C}}}\!=\right]_x \qquad (1)$$

(monomer) (polymer)

Diacetylenes are known to crystallize in more than one crystallographic modification.[7,8] In some cases, as many as five different modifications have been reported;[7,8] a few of these phases are inactive, some are moderately active, and the rest are highly reactive. The inactive phases do not polymerize, the moderately active phases usually polymerize to a limiting fractional conversion (~30%), and the reactive phases polymerize almost quantitatively upon either thermal annealing or exposure to γ rays. The reactivity of a diacetylene has been shown to depend upon the crystal packing of the monomer molecules.[2a,9]

Hadicke et al.[10] and others[2a,7,11] have reported that one half of a molecule of *p*-dioxane per monomer unit of 2,4-hexadiyne-1,6-bis(phenylurethane) is incorporated in the lattice during crystallization from *p*-dioxane/water. We have found that this monomer, HDPU, is not the only diacetylene which incorporates *p*-dioxane. The monomer, 2,4-hexadiyne-1,6-bis(*m*-tolylurethane) (I), referred to hereafter as $\mathrm{HD}_m\mathrm{TU}$, also incorporates *p*-dioxane in the crystals obtained from *p*-dioxane/water. Crystals of $\mathrm{HD}_m\mathrm{TU}$ containing *p*-dioxane are highly reactive and are always polymerized to an extent sufficient to give them a blue color. This reactive phase will be described hereafter as the "blue phase". Crystallization from acetone/hexane gives a moderately active phase of $\mathrm{HD}_m\mathrm{TU}$. Crystals of this moderately active phase polymerize to an extent sufficient to give them a light orange color; these crystals will be described hereafter as the "orange phase". We have discovered that the orange phase can be transformed to the blue phase upon exposure to *p*-dioxane vapor. In this paper, we report on this novel solid state phase transformation of a diacetylene by solvation and on the crystal structure of the monomer of the "orange phase".



I

Experimental Section

Synthesis. To a stirred solution of 11.0 g (0.1 mol) of 2,4-hexadiyne-1,6-diol, 0.5 g (0.001 mol) of di-*tert*-butyltin bis(2-ethoxyhexanoate), and 2 mL of triethylamine in 300 mL of THF was added 33.2 g (0.25 mol) of *m*-tolyl isocyanate dropwise over a period of 0.5 h. The temperature was maintained at 25 °C for a period of 2 h, after which 1500 mL of hexane was added. The colorless precipitate was collected and dried under vacuum. The yield was quantitative. Recrystallization from acetone/hexane gave mp 133 °C. Anal. Calcd for $\mathrm{C_{22}H_{20}N_2O_4}$: C, 70.21; H, 5.32; N, 7.45; O, 17.02. Found: C, 70.17; H, 5.20; N, 7.12; O, 17.21. Infrared (KBr pellet): 3320 (aromatic C–H, meta substituted) and 1005 and 1489 cm^{-1} (aromatic C=C stretch).

Orange Phase. $\mathrm{HD}_m\mathrm{TU}$ crystallizes in the moderately active orange phase from solvents such as acetone, tetrahydrofuran, chloroform,

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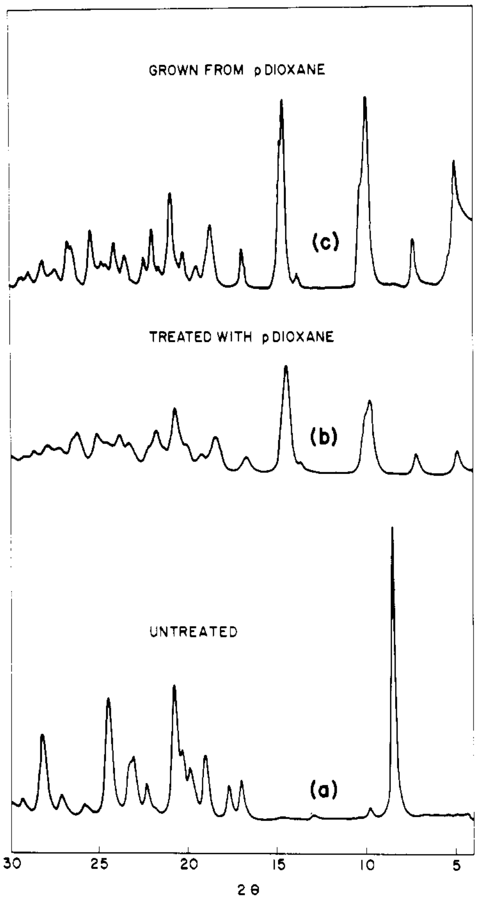

Figure 1. Powder X-ray diffraction patterns (Cu Kα radiation) of the orange phase (a), the blue phase obtained by exposing the orange phase to *p*-dioxane vapor (b), and the blue phase obtained by crystallizing HD$_m$TU from *p*-dioxane/water (c).

Table I. Final Atomic Coordinates for the Monomer of I in the "Orange Phase" in Fractions of the Unit Cell Edge

atom	*x*	*y*	*z*
C1	0.4791(2)	0.4603(5)	0.0233(5)
C2	0.4425(2)	0.3947(5)	0.0640(5)
C3	0.3983(3)	0.3118(6)	0.1148(7)
O4	0.3529(1)	0.3933(3)	0.1596(3)
C5	0.3002(2)	0.4325(4)	0.0448(5)
N6	0.2633(2)	0.5100(4)	0.1009(4)
C7	0.2070(2)	0.5791(4)	0.0162(4)
C8	0.1912(2)	0.6957(5)	0.0782(5)
C9	0.1368(2)	0.7670(5)	0.0021(5)
C10	0.0976(2)	0.7219(5)	−0.1362(5)
C11	0.1126(2)	0.6054(5)	−0.1977(5)
C12	0.1672(2)	0.5346(5)	−0.1211(5)
C13	0.0687(3)	0.5530(7)	−0.3458(6)
O14	0.2915(1)	0.4002(3)	−0.0836(3)
H3A	0.421(2)	0.271(5)	0.212(5)
H3B	0.372(2)	0.251(5)	0.023(5)
H6	0.277(2)	0.533(5)	0.193(5)
H8	0.218(2)	0.730(4)	0.168(4)
H9	0.376(2)	0.651(5)	−0.047(5)
H10	0.061(2)	0.782(4)	−0.184(4)
H12	0.177(2)	0.457(4)	−0.162(4)
H13A	0.040(3)	0.625(6)	−0.403(7)
H13B	0.090(2)	0.530(6)	−0.404(6)
H13C	0.037(3)	0.494(6)	−0.326(7)

and nitromethane when precipitated by nonsolvents such as hexane and petroleum ether. The orange phase can also be obtained by rapid evaporation of the above solvents.

Blue Phase. The highly reactive blue phase of HD$_m$TU can be obtained by crystallization from *p*-dioxane upon addition of sufficient water to precipitate the blue crystals.

Activation of the Orange Phase. *p*-Dioxane (5 mL) was placed in a 500-mL glass jar containing tissue paper in the bottom of the jar to aid in rapid formation of vapor. A small beaker containing single crystals of the orange phase (0.1 g) was placed inside the jar such that direct contact did not occur between the liquid and the crystals, and the jar was closed. Within 0.5 h the light orange colored crystals started turning blue. In order to determine the amount of *p*-dioxane incorporated in HD$_m$TU, the crystals were weighed before and after exposure to *p*-dioxane vapor for a period of 1 day at room temperature. The crystals after exposure to *p*-dioxane vapor were dried under high vacuum for at least 2 days before weighing and were found to retain the full stoichiometric amount of solvent.

Polymerization. Both the orange and the blue phases polymerize upon thermal annealing but the polymer conversion is usually less than 5%. Higher monomer-to-polymer conversion can be obtained by γ-ray irradiation. Both the orange and blue phases were irradiated with ^{60}Co γ rays in air at room temperature. The polymer conversion was determined by extracting with acetone using a Soxhlet extractor and weighing unreacted monomer. The orange phase also polymerized upon exposure to X-rays (see below).

X-ray Diffraction. Powder diffraction patterns were obtained on lightly ground crystals of both forms by using a Norelco diffractometer in parafocus geometry with copper Kα radiation. The traces are shown in Figure 1.

A single-crystal study was carried out on crystals of the monomer of the orange phase. Prior to data collection, cell data were obtained from a crystal 0.58 × 0.28 × 0.13 mm at ambient room temperature (20–23 °C) by a least-squares fit to the settings for 15 high-order reflections centered on a Syntex P2$_1$ diffractometer (Mo Kα, λ = 0.710 69 Å.[12] Crystal data follow: $C_{22}H_{20}N_2O_4$, mol wt 376.5, monoclinic, a = 21.908 (6) Å, b = 9.982 (3) Å, c = 9.352 (2) Å, β = 108.03 (2)°, V = 1944.7 Å^3, ρ_{calcd} = 1.29 g cm^{-3}, Z = 4, space group *C2/c or Cc;* the former was established by the results of the analysis; μ(Mo Kα) = 1.0 cm^{-1}. Intensity data ($hk\bar{l}$ and $\bar{h}k\bar{l}$ octants) were collected, 2θ = 55° (Mo Kα). The intensities of three standard reflections indicated an average drop of 10% by the end of the data collection (ca. 4 days); one of the standards (060) dropped by 20%. Of the 2252 independent reflections collected, 1189 were considered nonzero at the 1.5σ level of significance. The orange color of the crystal used for data collection appeared to have darkened during the 4-day period and the cell constants were observed to have changed significantly. However, examination of the crystal in the polarizing microscope indicated that it still extinguished polarized light and no other obvious changes could be noted.

The structure was solved using the MULTAN program.[13] After refinement, most of the hydrogen atoms were located from a difference map, the remainder being positioned following standard criteria. Full-matrix least-squares refinement on the positional and anisotropic thermal parameters for all nonhydrogen atoms and the positional and isotropic thermal parameters for all hydrogen atoms gave final values of R and R_w of 0.078 and 0.085 on all 1189 nonzero reflections. The "goodness of fit" was 1.33. The atomic scattering factors were taken from the analytical expressions given in "International Tables for X-ray Crystallography".[14] The final atomic coordinates are given in Table I.[15]

As changes were noted in the cell dimensions after data collection, the crystal of the orange phase used for data collection was subjected to further irradiation for two periods of 7 days, after each of which the cell dimensions were measured. In addition, the cell dimensions of crystals that had been subjected to 1 Mrad of ^{60}Co γ rays were measured. Further γ-irradiation provided material which did not give a single-crystal diffraction pattern. The values of the cell dimensions obtained at different levels of irradiation are presented in Table II.

It did not prove possible to obtain any single-crystal data on the blue phase on account of the very thin crystals and their great tendency to polymerize.

Spectrophotometry. A Perkin-Elmer UV-visible spectrophotometer, Model 200, with an integrating sphere attachment was used to record spectra in the visible region. The integrating sphere attachment was designed for a wavelength range of 400–700 nm in reflectance measurement. A piece of filter paper coated with partially polymerized HD$_m$TU was mounted in the holder of the integrating sphere and the absorption spectra were recorded. A piece of uncoated filter paper was used as the reference standard. The reflectivity, R, of the partially

Table II. Cell Constants for the Orange Form of I after Various Periods of Irradiation

	a, Å	b, Å	c, Å	β, deg	V, Å^3
initial values[a,b]	21.908(6)	9.982(3)	9.352(2)	108.03(2)	1945
after 4 days X irradiation	21.943(8)	9.990(3)	9.391(3)	108.25(2)	1955
after 11 days X irradiation	22.112(12)	10.033(5)	9.470(4)	109.03(4)	1986
after 18 days X irradiation	22.129(4)	10.038(6)	9.476(4)	109.12(4)	1989
after 1 Mrad of γ rays	22.161(8)	10.022(3)	9.486(3)	109.23(2)	1989

[a] The cell dimensions were obtained by a least-squares fit to the settings for 15 high-order reflections as described in the text. [b] See ref 12.

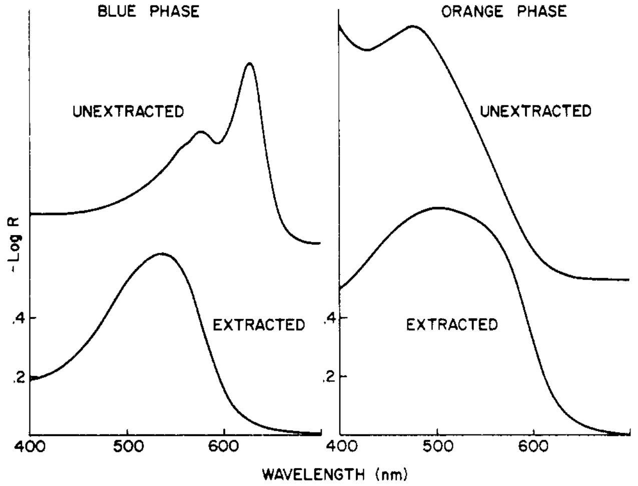

Figure 2. Reflectance spectra for the partially polymerized orange and blue phases of HD$_m$TU. The moderately active phase was partially polymerized to a light orange color by thermal annealing at room temperature for 1 month, while the highly reactive phase was partially polymerized to a light blue color by thermal annealing at room temperature for a few minutes. Both the phases were coated on filter papers. The filter papers were then dipped in acetone in order to get a thin coating of the residual polymers. Acetone extracts the unreacted monomer leaving the polymer on the filter papers. R is the reflectivity.

polymerized HD$_m$TU was recorded as $-\log R$, which is equivalent to the absorbance.

Discussion

Blue and Red Shifts. Visible spectra of partially polymerized orange and blue phases are shown in Figure 2. The color of polyconjugated systems such as polydiacetylenes is determined mainly by the conjugation length and by the planarity of the backbone.[4-6] Although the orange color suggests the presence of polymer chains as a solid solution in the monomer crystal,[9] they were not present in a concentration sufficient to affect seriously the structure determination to be discussed. The shade and intensity of the color suggest that the incorporated polymer chains are either short (about five repeat units) or are nonplanar. The blue color of the reactive phase suggests that the polydiacetylene chains are planar and long (more than 30 repeat units).[5,6] Upon extraction of unreacted monomer from the partially polymerized blue phase, the residual polymer chains turned red. A visible spectrum of the residual chains is also shown in Figure 2. This shift toward shorter absorption wavelength (blue shift) is common for partially polymerized diacetylenes, as they are solid solutions of unreacted monomer and polymer chains.[9] There is considerable strain in these crystals of partially polymerized diacetylenes owing to the mismatch (about 5% in specific cases) between monomer and polymer along the fiber axis.[2,9] The blue shift of the absorption maximum upon extraction of unreacted monomer is believed to be due to the release of intramolecular strain. The polymer chains in the partially polymerized crystals are held planar by the adjacent monomer molecules. When these molecules are removed, intramolecular strain is released with the result that the backbone becomes less planar (probably in a twisted conformation). The residual polymer chains turn red also upon extraction of unreacted monomer from the orange phase. A visible spectrum of the residual polymer chains is also shown in Figure 2. Although the red shift, i.e., the shift toward higher wavelength, is small, it is rather unexpected. The red shift suggests that the polymer chains in the partially orange phase are longer than five repeat units but are nonplanar. The origin of this red shift will be explained in the following sections.

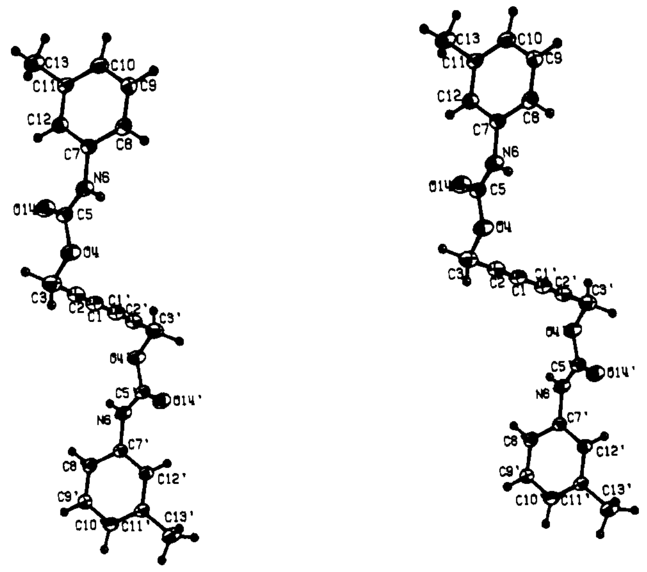

Figure 3. A stereoscopic view of the monomeric HD$_m$TU as found in the crystals of the orange phase.

Crystal Structure of the Monomer of the Orange Phase of HD$_m$TU. The molecule of I found in the orange phase is shown in Figure 3. Bond lengths and angles are given in Table III. They are in good agreement with the values obtained in previous investigations of monomeric diacetylenes.[16-24]

The molecules of I occupy centers of symmetry in the crystals. The molecular configuration is dominated by three types of planar groups: the diacetylene group (A), the urethane groups (B), and the phenyl rings (C). The angles between A and B and between B and C are 110.6 and 25.9°, respectively. The tolyl group is arranged such that the CCH_3 group lies to the same side of the molecule as the urethane C=O bond.

The molecular packing is illustrated in the stereoscopic Figure 4. The only close contacts involving acetylenic carbon atoms are in the c direction. However, neighboring molecules in this direction are not translationally related, but are related by a glide plane. Thus, the diacetylene groups are not required to be parallel and, in fact, deviate very dramatically from the parallelism of the diacetylene axis that is most frequently observed. Neighboring diacetylene vectors are crossed at an angle of 72°. A view of the overlap of one diacetylene group with its neighbors is shown in Figure 5. The shortest C(sp)---C(sp) contacts are of 3.607 (7) and 3.764 (7) Å between C(2) and C(1) in the reference molecule each with C(2) in the molecule

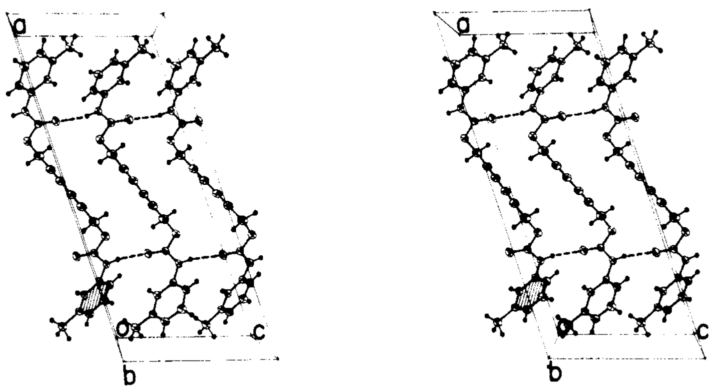

Figure 4. A view of the packing of molecules of HD_mTU in crystals of the orange phase. The phenyl ring in the reference half-molecule is shaded. The molecules related by the C centering are not shown.

Table III. Bond Lengths (Å) and Angles (deg) in the Monomer of I in the Orange Phase[a]

C(1)-C(1′)	1.380(7)	C(7)-C(8)	1.392(6)
C(1)-C(2)	1.186(7)	C(7)-C(12)	1.383(6)
C(2)-C(3)	1.460(8)	C(8)-C(9)	1.381(7)
C(3)-O(4)	1.445(7)	C(9)-C(10)	1.387(7)
O(4)-C(5)	1.368(5)	C(10)-C(11)	1.380(7)
C(5)-N(6)	1.339(6)	C(11)-C(12)	1.384(6)
C(5)-O(14)	1.200(5)	C(11)-C(13)	1.514(7)
N(6)-C(7)	1.420(6)	C(8)-C(7)-N(6)	117.3(4)
C(2)-C(1)-C(1′)	178.5(5)	C(12)-C(7)-N(6)	123.4(4)
C(3)-C(2)-C(1)	178.9(5)	C(9)-C(8)-C(7)	120.2(4)
O(4)-C(3)-C(2)	111.1(5)	C(10)-C(9)-C(8)	119.9(4)
C(5)-O(4)-C(3)	115.0(4)	C(11-C(10)-C(9)	120.3(4)
N(6)-C(5)-O(14)	128.3(4)	C(12)-C(11)-C(10)	119.5(4)
N(6)-C(5)-O(4)	108.8(4)	C(10)-C(11)-C(13)	120.4(4)
O(14)-C(5)-O(4)	122.9(4)	C(12)-C(11)-C(13)	120.4(4)
C(7)-N(6)-C(5)	126.0(4)	C(7)-C(12)-C(11)	120.8(4)
C(8)-C(7)-C(12)	119.2(4)		

[a] C-H lengths range from 0.93 (4) to 1.06 (5) Å.

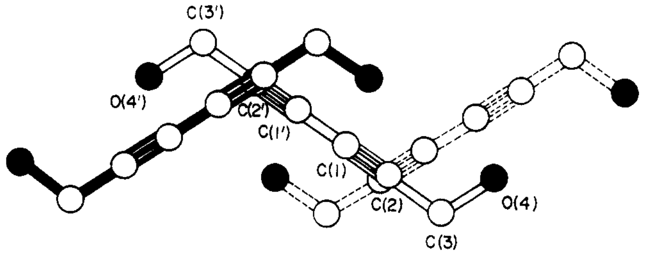

Figure 5. Drawing showing the overlap of the neighboring diacetylene vectors along the *c* axis. The reference diacetylene group is numbered, the glide-related one above it is shaded in black, and the glide-related one below it is shown with discontinuous lines. The oxygen atoms are blackened. Atoms are projected onto the best plane through the atoms C(1), C(2), C(3), O(4), and the centrosymmetrically related atoms.

at $1 - x, y, \frac{1}{2} - z$. Molecules that are related by the glide plane in the *c* direction and which have the shortest C(sp)---C(sp) contacts are linked by N-H---O hydrogen bonds. The N---O and H---O distances are 2.959 (5) and 2.12 (5) Å, respectively, and the N-H---O angles is 168 (4)°.[25] This hydrogen bonding may be the factor that causes glide-related rather than translationally related diacetylene groups to be in close contact.

Baughman[9] has given criteria for the formation of defect-free single crystals of polymer from diacetylene monomer, including a geometric requirement in terms of the repeat distance d_1 between reacting monomers and the angle γ that the vector of the diacetylene group makes with the stacking axis. However, his discussion dealt only with the case where the monomer diacetylene rods were parallel, a situation which is not applicable to the present example. Among the diacetylene monomers studied by X-ray structure analysis, all the reactive diacetylene groups have been translationally related or related by a center of inversion.[16,18,19,22,23,26] The present example provides the first case of reaction (albeit partial) between nonparallel neighboring diacetylene groups (Figure 5). As will be described below, reaction appears to take place at least to the extent of 7-8% resulting in solid solution formation between monomer and polymer. Unlike most of the totally unreactive diacetylene monomers studied,[16-18,20,21] the present structure contains C(sp)---C(sp) distances that are sufficiently short for reaction. It appears that the geometrical criteria for a moderate amount of polymerization of diacetylenes are less restrictive than those for [2 + 2]photoreaction of olefins to form cyclobutane derivatives; these latter are described by Schmidt's topochemical rules,[27] which apply to situations that do not require the formation of defect-free single crystals. In cases where cyclobutane ring formation could be expected on the basis of the separation distance of the potentially reactive olefin groups, reactivity was reduced or inhibited if the olefin vectors were not parallel.[28,29]

Polymerization in the Crystal. When the orange and blue phases were irradiated with ^{60}Co γ rays, polymerization occurred. Figure 6 shows plots of polymer conversion vs. a period of irradiation for both phases. The orange phase reaches a limiting polymer conversion of about 35% while the blue phase polymerizes rapidly to 100% polymer; however, the 11% of *p*-dioxane that is interstitially bound in the blue phase cannot be extracted with acetone.

Reactivity of the orange phase under the influence of X-rays was apparent by changes in the cell dimensions. On the basis of the plot in Figure 5, it appeared that there was 7-8% conversion to polymer before single-crystal diffraction dropped effectively to zero. It is significant that the cell dimensions of the solid solution of polymer in monomer increased over those of monomer, with the greatest changes being in the *a* and *c* axes. In other cases, where much less motion of reacting monomer is required for polymerization, some cell dimensions decrease as polymerization takes place.[19,26,30]

Polymerization of the orange phase and subsequent incorporation of the polymer in a solid solution of the monomer must lead to a highly nonplanar polymer backbone. As incorporated in the crystal of the monomer, the polymer backbone will be highly strained. The orange color (λ 510 nm) must be due to the nonplanar backbone. Upon extraction of the unreacted monomer from the solid solution, the strain is released, the crystal is destroyed, and the backbone will tend to acquire the familiar trans-planar conformation, thus giving rise to the red shift.

Phase Transformation under the Influence of *p*-Dioxane Vapor. Small single crystals of the orange phase were exposed

Table IV. Activation of Inactive Phases of Some Diacetylenes by Solvent Vapors

diacetylene, RC≡CC≡CR	R group	color of the inactive phase	solvent vapor for activation	color of the partially reacted activated phase
HD_oCPU	$-CH_2OCONHPhCl$-*o*	white[a]	*p*-dioxane	violet
HD_pCPU	$-CH_2OCONHPhCl$-*p*	white[b]	dimethylformamide	blue
HD_oMPU	$-CH_2OCONHPhOCH_3$-*o*	white[a]	*p*-dioxane	pink[c]
HDPU	$-CH_2OCONHPh$	white[a]	*p*-dioxane	blue

[a] Acetone/hexane system was used for crystallization. [b] Tetrahydrofuran/hexane system was used for crystallization. [c] Only the surfaces of the crystals are activated.

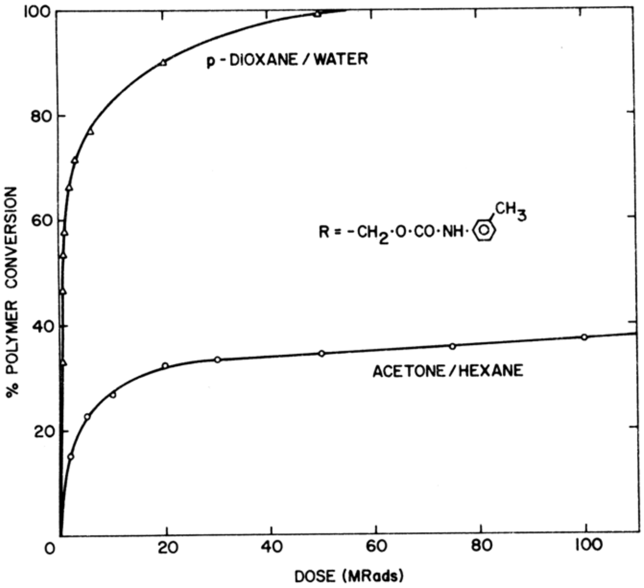

Figure 6. Plots of polymer conversion (%) vs. dose (Mrad) for HD_mTU crystallized either from acetone/hexane (the orange phase) or from *p*-dioxane/water (the blue phase).

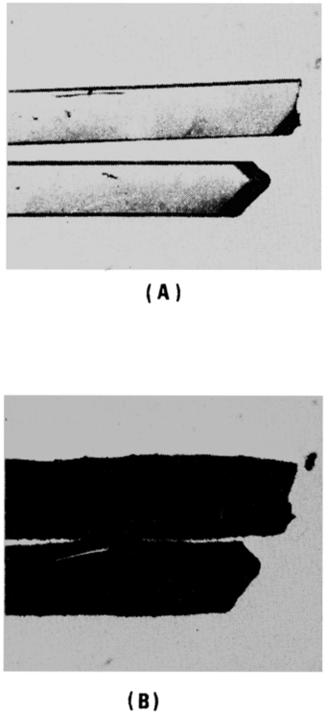

Figure 7. Microphotographs of the orange phase of HD_mTU before (A) and after (B) exposure to *p*-dioxane vapor for 30 min. The crystals expand by about 25% in the lateral directions.

to the vapors of a number of organic solvents for 2 days at room temperature. Vapors of carbon tetrachloride, chloroform, dichloromethane, 1,2-dichloroethane, chlorobenzene, benzene, toluene, xylene, cyclohexane, carbon disulfide, petroleum ether, hexane, methanol, ethanol, nitromethane, methyl formate, ethyl formate, methyl acetate, ethyl acetate, and diethyl ether did not affect the orange crystals while vapors of acetone, 1,2-dimethoxyethane, dimethylformamide, and dimethylacetamide dissolved the crystals. When exposed to vapor of *p*-dioxane and pyridine, the light-orange colored crystals started turning blue within 0.5 h. The phase transformation undoubtedly occurs before the crystals turn blue as the development of blue color is due to the solid-state polymerization of the new phase. The blue color intensifies with the time and the temperature of annealing. The greater intensity of the blue color is due to increasing polymerization of the reactive phase. The crystals turn from a very light blue to dark blue within a few hours. If left under the ambient light, they turn metallic green-gold within 1 week.

A number of inactive diacetylenes were also exposed to vapors of the solvents listed above. Only four of the inactive diacetylenes underwent phase transformation into reactive phases. These results are summarized in Table IV. In the present paper, only the phase transformation of HD_mTU will be discussed.

During the phase transformation, the crystals of HD_mTU pick up 11% weight and the crystals expand by 25% in their lateral directions. HD_mTU picks up the same weight if crystallized from *p*-dioxane or from *p*-dioxane/water. An 11% increase in weight corresponds to 0.5 mol of *p*-dioxane per mol of HD_mTU, the same relative amount as was found in the case of HDPU (R = $-CH_2OCONHPh$).[31] In the structure of the polymer of HDPU,[31] the *p*-dioxane molecule sits on a crystallographic center of symmetry and is involved in two centrosymmetrically related N-H---O hydrogen bonds.

HD_mTU crystallizes in the same blue phase whether obtained by crystallization from *p*-dioxane/water or by activation of the orange phase from the blue phase as can be seen from the powder traces (Figure 1), which also show that the orange and blue phases are crystallographically distinct.

The phase transformation of the orange phase of HD_mTU by *p*-dioxane vapor occurs in the solid state, as indicated by the following points: (1) The crystals retain their original shape even after the phase transformation. The molecules in the optically anisotropic single crystals of the orange phase rearrange to produce a polycrystalline blue phase (Figure 7). The transparent crystals of the orange phase turn blue and opaque. (2) Vapors of a number of solvents do not affect the orange phase, as mentioned in a previous section. Some of these solvents, such as chloroform, ethyl acetate, and nitromethane, dissolve the crystals if direct liquid contact is made. *p*-Dioxane (liquid) also dissolves the crystals if direct contact is made. Vapors of certain solvents such as acetone, glyme, and dimethylformamide are capable of dissolving the crystals. As the vapor of *p*-dioxane does not dissolve the crystals, we believe that phase transformation occurs without dissolution.

It is clear from the above arguments that the orange phase of $\mathrm{HD}_m\mathrm{Tu}$ undergoes the solid state phase transformation to the blue phase by incorporation of *p*-dioxane. This phase transformation produced by solvent vapor is similar to that found for hydration of inorganic salts and can be expressed as

$$\begin{matrix}\text{orange phase}\\ \text{of } \mathrm{HD}_m\mathrm{TU}\end{matrix} + p\text{-dioxane} \rightarrow \begin{matrix}\text{blue phase}\\ \text{of } \mathrm{HD}_m\mathrm{TU}\end{matrix} \cdot \frac{1}{2}\, p\text{-dioxane}$$

The solid-state rearrangement of molecules of organic compounds is well known.[32,33] Such rearrangement is often initiated by thermal annealing. However, the phase transformation of diacetylenes by solvent vapors is more properly described as a gas-solid reaction.[34] Instead of a chemical reaction of a gas with a solid, the solvent vapor forms a solvate with the diacetylene in the solid state. When heated, the diacetylene-*p*-dioxane solvate loses the *p*-dioxane between 80 and 110 °C.

The present study reveals several novel features about the polymerizable diacetylene $\mathrm{HD}_m\mathrm{TU}$ (I). It is the first diacetylene which undergoes significant polymerization accompanied by solid solution formation in a crystal environment where the diacetylene vectors of the monomer are not parallel. The increase in *all* the cell parameters upon solid solution formation is also atypical. The unusual red shift upon removal of unreacted monomer is due to the release of strain caused by the formation of polymer in the crystal of nonparallel monomers. Another remarkable property of this compound is the transition that is brought about by incorporation of dioxane in the crystal in a process that is reminiscent of a solid-gas reaction.

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Supplementary Material Available: Values of structure factors and thermal parameters for I (13 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Allied Chemical Corp.; (b) University of Illinois.
(2) (a) G. Wegner, *Z. Naturforsch. B*, **24**, 824 (1969); *Makromol. Chem.*, **134**, 219 (1970); **145**, 85 (1971); **54**, 35 (1972). (b) D. Bloor, L. Koshi, G. C. Stevens, F. H. Preston, and D. J. Ando, *J. Mater. Sci.*, **10**, 1678 (1975); G. C. Stevens and D. Bloor, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 2411 (1975).
(3) R. R. Chance and G. N. Patel, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 859 (1978); G. N. Patel, R. R. Chance, E. A. Turi, and Y. P. Khanna, *J. Am. Chem. Soc.*, **100**, 6644 (1978).
(4) I. A. Drabkin, V. I. Tsaryuk, M. I. Cherkashin, P. P. Kisilitsa, M. G. Chauser, A. N. Chigir, and A. A. Berlin, *Vysokomol. Soedin, Ser. A*, **10**, 1727 (1968).
(5) G. N. Patel, R. R. Chance, and J. D. Witt, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 607 (1978).
(6) G. N. Patel, R. R. Chance, and J. D. Witt, *J. Chem. Phys.*, **70**, 4389 (1979).
(7) J. Kaiser, G. Wegner, and E. G. Fischer, *Isr. J. Chem.*, **10**, 157 (1972).
(8) K. Takeda and G. Wegner, *Makromol. Chem.*, **160**, 349 (1972).
(9) R. H. Baughman, *J. Chem. Phys.*, **68**, 3110 (1978); R. H. Baughman, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1511 (1974).
(10) E. Hadicke, E. C. Mez, C. H. Krauch Sowie, G. Wegner, and J. Kaiser, *Angew. Chem.*, **83**, 253 (1971).
(11) R. H. Baughman and E. A. Turi, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 2453 (1973).
(12) It should be borne in mind that the crystal used for determination of the cell data had been subjected to 3 or 4 days of irradiation during preliminary X-ray studies.
(13) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
(14) J. A. Ibers and W. C. Hamilton, Eds., "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, pp 99–102.
(15) See paragraph at end of paper regarding supplementary material.
(16) V. Enkelmann and H. J. Graf, *Acta Crystallogr., Sect. B*, **34**, 3715 (1978).
(17) B. Morosin and L. Harrah, *Acta Crystallogr., Sect. B*, **33**, 1760 (1977).
(18) A. W. Hanson, *Acta Crystallogr., Sect. B*, **31**, 831 (1975).
(19) V. Enkelmann and G. Wegner, *Angew. Chem.*, **89**, 432 (1977).
(20) J. J. Mayerle and T. C. Clarke, *Acta Crystallogr., Sect. B*, **34**, 143 (1978).
(21) J. J. Mayerle and M. A. Flandera, *Acta Crystallogr., Sect. B*, **34**, 1374 (1978).
(22) D. A. Fisher, D. N. Batchelder, and M. B. Hursthouse, *Acta Crystallogr., Sect. B*, **34**, 2365 (1978).
(23) E. Hadicke, K. Penzien, and H. W. Schnell, *Angew. Chem.*, **83**, 1024 (1971).
(24) J. D. Dunitz and J. M. Robertson, *J. Chem. Soc.*, 1145 (1947).
(25) If the N-H bond is extended from the value of 0.85 (5)° Å found to a more realistic value of 1.00 Å, then the H---O distance is 1.98 Å and the N-H---O angle is 167°.
(26) V. Enkelmann, G. Schleier, G. Wegner, H. Eichele, and M. Schwoerer, *Chem. Phys. Lett.*, **52**, 314 (1977).
(27) G. M. J. Schmidt, *Pure Appl. Chem.*, **27**, 647 (1971); *J. Chem. Soc.*, 2014 (1964).
(28) L. Leiserowitz and G. M. J. Schmidt, *Acta Crystallogr.*, **18**, 1058 (1965).
(29) J. K. Frank and I. C. Paul, *J. Am. Chem. Soc.*, **95**, 2324 (1973).
(30) D. Day and J. B. Lando, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 2453 (1973).
(31) E. Hadicke, E. C. Mez, C. H. Krauch, G. Wegner, and J. Kaiser, *Angew. Chem.*, **83**, 253 (1971).
(32) I. C. Paul and D. Y. Curtin, *Acc. Chem. Res.*, **6**, 217 (1973).
(33) D. Y. Curtin, I. C. Paul, E. N. Duesler, T. W. Lewis, B. J. Mann, and W.-I. Shiau, *Mol. Cryst. Liq. Cryst.*, **50**, 25 (1979).
(34) I. C. Paul and D. Y. Curtin, *Science*, **187**, 19 (1975).