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Synthesis and Solid-State Polymerization of a New Diacetylene: 1-(*N*-Carbazolyl)penta-1,3-diyn-5-ol

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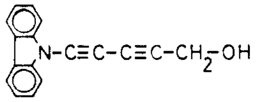
ABSTRACT: A new unsymmetrical diacetylene having a carbazolyl group directly bound to an acetylene moiety, i.e., 1-(*N*-carbazolyl)penta-1,3-diyn-5-ol, was synthesized. This diacetylene can be topochemically polymerized in the solid state and the visible absorption edge of the polymer is expanded to nearly 800 nm, suggesting longer π-conjugation than the so-far-known polydiacetylenes.

Introduction

Solid-state polymerization of diacetylenes is known to give single crystals of conjugated polymers[2] and has attracted attention on their physical properties, such as conductivity,[3–6] optical nonlinearity,[7] and mechanical strength.[8] Especially, it is interesting that the value of the third-order nonlinear optical susceptibility is very large ($\chi^{(3)} = 10^{-9}$–10^{-10} esu) and the response is very fast (less than picosecond order).[9,10] However, since these interesting nonlinear optical properties are due to the π-conjugation, there must be little difference among most polydiacetylenes which have methylene groups next to diacetylene moiety and have the same number of π-electrons per repeating unit, such as poly[2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate)] (poly-PTS),[11] poly(1,6-di(*N*-carbazolyl)-2,4-hexadiyne) (poly-DCHD),[12] poly[5,7-dodecadiyne-1,12-diol bis(phenylurethane)] (poly-TCDU),[13] and so on. To achieve higher susceptibility, a polydiacetylene with aromatic substituents directly bound to the main chain, and therefore with increased numbers of π-electrons per repeating unit through the π-conjugation between the main chain and substituents, might be a better candidate. However, few such polydiacetylenes are known: e.g., diphenyldiacetylene and dicarbazolyldiacetylene[14] are not polymerizable, and several substituted diphenyldiacetylens give polymers only in low conversion.[15] In fact, the conductivity of poly(bis(*m*-acetamidophenyl)butadiyne) upon iodine doping was 10^3 order higher than those of polydiacetylenes with methylene groups next to the polymer backbone.[16,4] This is evidence that directly bound aromatic substituents are effective for expanding π-conjugation of poly-DAs.

In polymerizable diacetylene crystals packing parameters, *d* and ϕ shown in Figure 1, are known to be near 5 Å and 45°, respectively.[17,18] Such a crystal structure is usually observed in diacetylenes which have methylene groups next to diacetylene moiety. In these crystals, bending in the methylene units seems to produce the polymerizable stacks. So, in order to obtain the polydiacetylene with expected conjugation between polymer backbone and side groups, the synthesis of unsymmetrical diacetylenes which have both an aromatic ring and a methylene group directly bound to acetylene moieties seems to be promising.

In this paper, we report the synthesis and the solid-state polymerization of such a new diacetylene: 1-(*N*-carbazolyl)penta-1,3-diyn-5-ol.



Experimental Section

Synthesis of 1-(*N*-Carbazolyl)penta-1,3-diyn-5-ol (CPDO). CPDO was prepared by the Chodkiewicz and Cadiot coupling[19] of *N*-ethynylcarbazole[20] and 1-bromopropargyl alcohol.[21] Catalyst solution was made from Cu(I)Cl (0.1 mmol), 70% aqueous solution

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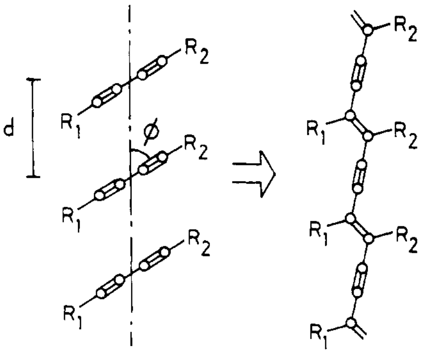

Figure 1. Solid-state polymerization scheme of diacetylenes: $d \approx 5$ Å, $\phi \approx 45°$.

of ethylamine (1 mL), and ethanol (2 mL) under an Ar atmosphere. *N*-Ethynylcarbazole (1 mmol) was dissolved in the catalyst solution and then 1-bromopropargyl alcohol (1.2 mmol) was added dropwise at 35 °C for 2 h. When the solution became blue due to the presence of the Cu^{2+} ion, a little $NH_2OH \cdot HCl$ was added for reduction of Cu^{2+} to form Cu^{1+}. The reaction mixture was evaporated and extracted with benzene. The products were isolated by column chromatography on silica gel with benzene. The yield was 21% of *N*-ethynylcarbazole. Elem. Anal. Calcd for $C_{17}H_{11}NO$: C, 83.25; H, 4.52; N, 5.71. Found: C, 83.54; H, 4.68; N, 5.66. Mp 132 °C; IR (KBr) 3340 (O—H), 2258 (2246), 2172 (C≡C), 1450 cm^{-1} (C=C of carbazole ring); ^1H NMR ($CDCl_3$) δ 1.75 (br, 1 H, OH), 4.45 (s, 2 H, CH_2), 7.35 (t, 2 H), 7.50 (t, 2 H), 7.66 (d, 2 H), 7.99 (d, 2 H).

Solid-State Polymerization. CPDO was polymerized by heating the crystals in a vacuum vessel below the melting point or γ-ray or UV irradiation of the crystals at room temperature. ^{60}Co γ-ray with the dose rate of 1 Mrad/h or a low-pressure mercury lamp (4 W) was used for the polymerizations. Polymer conversion was determined by IR spectra change of triple bond stretching vibration. Graviometry after extraction of monomer was also used for confirmation of conversion.

X-ray Crystallography. X-ray powder diffraction patterns were recorded on a Phillips PW-1700 system by using the Cu Kα line (λ = 1.542 Å). Cell parameters and full intensity data for crystal structure analysis were obtained at room temperature on a Nicolet P3F 4-circle diffractometer, using a $2\theta/\omega$ scanning routine and graphite-monochromatized Cu Kα radiation (λ = 1.54178 Å). Full details of molecular and crystal structures will be published elsewhere.

Spectroscopy. IR absorption spectra were measured with a KBr pellet by a Hitachi 260-30. Visible absorption spectra were measured with a KBr pellet and a thin film of micro crystallites on a glass plate by Varyan Cary 17D. ^1H NMR spectrum was measured with $CDCl_3$ solution by a Nicolet NT-360.

Results and Discussion

CPDO has two crystal forms. Modification I was obtained in the form of large hexagonal plates (~1 cm) by recrystallization from benzene or chloroform, whereas modification II in very thin needle from methanol or acetone. Difference in molecular arrangements between these two modifications was confirmed by X-ray powder diffraction. Triple bond stretching vibrations of modification I exist at 2258 and 2172 cm^{-1}, and those of modification II at 2246 and 2172 cm^{-1}. Since the absorption bands at the higher wavenumber are assigned to the triple bond near the hydroxymethyl group (CH_2OH), this polymorphism seems to be caused by a difference in interactions among hydroxy groups.

Modification I was revealed to crystallize in the monoclinic space group $P2_1/a$, with a = 16.249 (3), b = 4.951 (1), c = 17.360 (4) Å; β = 113.53 (2)°; F_w = 245.3, V = 1280.4 (5) $Å^3$, z = 4, D_x = 1.273, D_m = 1.27 Mg/m^3. As shown in Figure 2, the molecules are stacked with a repeating distance of 4.951 Å and inclination angles of 46.11° to the b-axis. These parameters are well in the range of highly polymerizable packing. As expected, the bending in methylene units plays an important role in causing polymerizable stacks. The crystal structure of modification II could not be analyzed because of the small size of the thin needles.

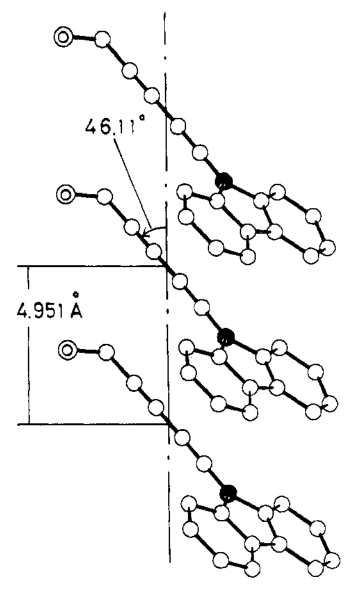

Figure 2. Molecular arrangement of CPDO along the b-axis in modification I: ○ C; ◎ O; ● N.

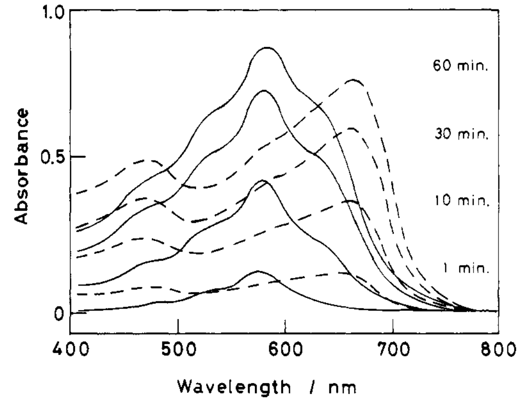

Figure 3. Changes in the visible absorption spectra of CPDOs in the course of UV polymerization: (—) modification I; (- - -) modification II.

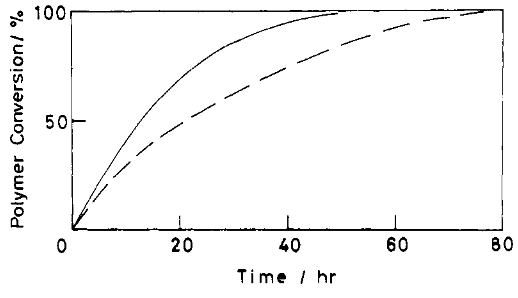

Figure 4. Time–conversion curves of the thermal polymerization of CPDOs at 80 °C: (—) modification I; (- - -) modification II.

Visible absorption spectrum changes in the course of UV polymerization are shown in Figure 3. The absorption maximum of modification I exists at 580 nm, whereas that of modification II is at 670 nm. Time conversion curves of thermal polymerization at 80 °C are shown in Figure 4, where the polymer conversion was determined by IR absorption intensity of triple bond stretching vibration in comparison with that of carbazole carbon skeleton. Since two triple bond stretching vibrations decreased in the same proportion, it is obvious that the polymerization proceeds

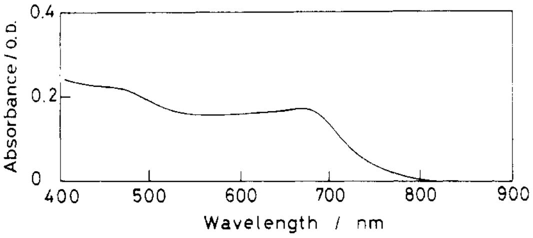

Figure 5. Visible absorption spectrum obtained with the thin film of microcrystallites of poly-CPDO at complete conversion.

by 1,4-addition. As seen from Figure 4, both modifications reached 100% conversions via thermal polymerization. The quantitative conversion was also confirmed by gravimetry; no monomer was extracted by any organic solvents. By γ-ray irradiation with a 1 Mrad/h dose rate, it took about 600 h to reach 100% conversion. By UV irradiation with a low-pressure mercury lamp (4 W), the polymerization was saturated at 60% conversion. This may simply be because the polymer formed near the crystal surface absorbs UV light.[22] Some other reasons, like quenching of excited monomers,[23] have been proposed for this kind of saturation.

As was often found for other diacetylenes, a single-crystal-to-single-crystal transition was observed in the polymerization of both modifications. The crystallographic data of the polymer from the modification I are as follows: monoclinic, space group $P2_1/a$, with a = 16.494 (6), b = 4.873 (3), c = 19.513 (8) Å; β = 124.27 (3)°; F_w of repeating unit = 245.3, V = 1296 (1) Å^3, z = 4, D_x = 1.256, D_m = 1.26 Mg/m^3. Since the space group of the polymer is the same as that of the monomer, this polymerization can be concluded to be a typical topochemical reaction. However, the crystal structure of the polymer could not be analyzed because X-ray diffraction peaks were diffuse and only small numbers of intensity data were available. In the case of modification I, X-ray powder diffraction patterns became broad after polymerization. On the other hand, in modification II, the polymer patterns stay as sharp as in the stage of the monomer. This fact indicates that the molecular arrangement in modification II is far more suitable for a single-crystal-to-single-crystal transition, though the reaction rate itself becomes slower, compared with those of modification I.

At the initial stage of the polymerizations, modification I became red, whereas modification II became green as can be seen from Figure 3. However, the absorption spectra of polymers at the complete conversion of both modifications became almost the same spectra as shown in Figure 5. This absorption spectrum was obtained with the thin film, ca. 0.1 μm thick, of microcrystallites on a glass plate. The absorption coefficient could not be determined because of the rough surface of the thin film. The absorption maximum of poly-CPDO is expanded to the 675 nm, i.e., longer wavelength than those of poly-PTS (620 nm),[24] poly-DCHD (650 nm),[25] and poly-TCDU (540 nm).[26] Furthermore, the absorption edge of poly-CPDO is expanded to near 800 nm. In other words, the band gap (the energy difference between HOMO and LUMO) of the present polydiacetylene becomes smaller than those of hitherto-known polydiacetylenes. This must be an indication of longer π-conjugation. So, it can be considered that the directly bound carbazolyl group donates some electron density to the conjugated main chain. The π-conjugation between the polymer backbone and carbazolyl group should be proportional to $\cos^2\theta$, where θ is the internal rotation angle between the main chain and carbazole plane. Studies to evaluate the θ value are currently in progress experimentally and theoretically.

In conclusion, a novel polydiacetylene with aromatic substituents directly bound to the main chain has been synthesized with complete conversion in the manner of a topochemical single-crystal-to-single-crystal transition, and judged from the longer π-conjugation, it is expected that the nonlinear optical susceptibility of poly-CPDO is larger than that of other polydiacetylenes.[7] The measurements of the action spectrum of the photocurrent and the nonlinear optical properties of poly-CPDO are in progress, together with larger crystal growth of modification II.

Registry No. CPDO, 113274-97-8; CPDO (homopolymer), 113274-98-9; N-ethynylcarbazole, 26157-62-0; 1-bromopropargyl alcohol, 2060-25-5.

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