Single-crystal-to-Single-crystal Polymerization of 4,4′-Butadiynedibenzylammonium Disorbate

Toru Odani, Shuji Okada,[†] Chizuko Kabuto,[††] Tatsumi Kimura,[†††] Hiro Matsuda,[†††] Akikazu Matsumoto,[††††] and Hachiro Nakanishi
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577
[†]*Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992-8510*
[††]*Graduate School of Science, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8578*
[†††]*National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565*
[††††]*Graduate School of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585*

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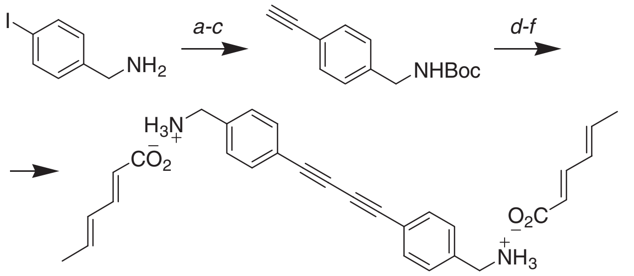
Solid-state polymerization of 4,4′-butadiynedibenzylammonium disorbate was investigated. The quantitative polymer yield of the diene moieties was achieved under UV-, X-ray, and γ-ray irradiation, whereas the conversion of diyne moieties was low. X-ray crystal structure analyses of monomer and polymer crystals show the polymerization proceeded under topochemical polymerization mechanism indeed.

Topochemical polymerization in the crystalline state is one of the most important methods in terms of the control of the resulting polymer structure. By the topochemical polymerization, we can obtain a stereoregular polymer as a crystal. Several polymerizable compounds in the crystalline state have been known since late 1960s.[1] Among them, the polymerization of diacetylene derivatives provides colored polymer based on their π-conjugated polymer backbone.[2] In a recent decade, topochemical polymerization of 1,3-diene derivatives such as sorbic and muconic acid have been reported.[3] The diene polymerization gives colorless and non-conjugated polymer. The diene moieties in the polymerizable crystals are oriented similarly to the fashion of diacetylene,[4] i.e., aligned with a translation distance of 5 Å. When both of diyne and diene groups are incorporated in one system, they are expected to be polymerized in a crystal. As a result, we can obtain the highly regulated polymer network composed of the diyne and diene polymers.[5] The combination of carboxylic acids and primary alkylamines were effective for the solid-state polymerization of diacetylene[6] and diene derivatives,[7] respectively. In this paper, we demonstrate the single-crystal-to-single-crystal polymerization of 4,4′-butadiynedibenzylammonium disorbate. The molecular alignments of the monomer and polymer are described. Especially, X-ray crystal structure analysis of the polymer from ammonium salts of diene derivatives is the first time to be reported.



Scheme 1. Preparation of 4,4′-butadiynedibenzylammonium disorbate: (a) Boc$_2$O in CHCl$_3$, (b) TMS-acetylene, Pd(PPh$_3$)$_2$Cl$_2$, CuCl in triethylamine, (c) (n-Bu)$_4$NF in THF, (d) CuCl, TMEDA, O$_2$ bubbling in acetone, (e) HCl aq/THF, (f) sorbic acid in CHCl$_3$.

4,4′-Butadiynedibenzylammonium disorbate was prepared as shown in Scheme 1. 4,4′-Butadiynebenzylamine was synthesized from 4-iodobenzylamine as a starting material. The ammonium salt of sorbic acid was prepared by the reaction of sorbic acid and diamine in chloroform as precipitant. Following recrystallization from hot methanol gave plate crystals. Crystalline-state polymerization of 4,4′-butadiynedibenzylammonium disorbate was carried out under UV irradiation using high-pressure mercury lamp attached a U340 filter at room temperature for 8 h. The recrystallized plate crystals became blue by UV irradiation, indicating the formation of polydiacetylene. However, the as-prepared powdery crystals were inert at the same condition. The difference of reactivities is due to polymorph, which was confirmed by powder X-ray diffraction. We used the monomer after recrystallization from methanol for further experiments described below. The polymerization also underwent by X-ray and ^{60}Co γ-ray irradiations. The maximum wavelength for the exitonic band of the polydiacetylene was observed at 686 nm in diffuse reflectance UV–vis spectrum as shown in Figure 1. CP/MAS ^{13}C NMR measurement was carried out to confirm the conversion of each reaction group. After photoirradiation for 8 h, the peak at 174.2 ppm assigned to the carbonyl carbon of the monomer sorbate anions completely disappeared, and new carbonyl peak was observed at 182.5 ppm. The peaks due to the methine carbons were also appeared at 60.8 and 49.9 ppm. These results show that the polymerization of the sorbate moieties underwent almost quantitatively. On the other hand, the peaks at 80.7 and 74.2 ppm assigned to *sp*-carbons in the diyne moiety still remained and peaks due to the polydiacetylene backbones were too weak to be detected in the spectrum. Similar CP/MAS spectrum was obtained even after γ-ray irradiation of 500 kGy dose. The results indicate that the conversion of the diacetylene moie-

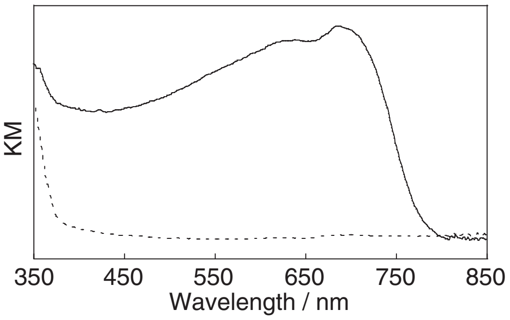


Figure 1. Diffuse reflectance UV–vis spectra of 4,4′-butadiynedibenzylammonium disorbate before and after polymerization. Dotted line: monomer, solid line: after UV irradiation for 8 h.

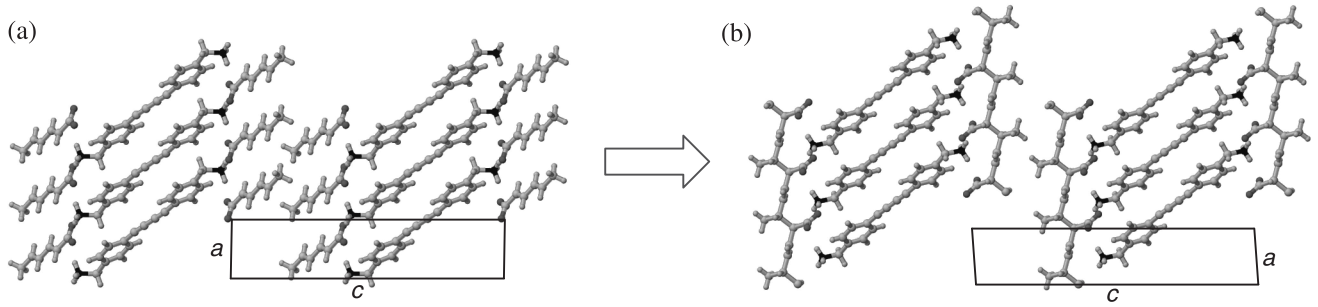


Figure 2. Crystal structure of 4,4′-butadiynedibenzylammonium disorbate viewed from crystallographic *b* axis. (a) Monomer recrystallized from methanol, (b) after X-ray irradiation for 48 h (Mo Kα, 40 kV, 200 mA).

ties was low, although the exitonic band of polydiaetylene was observed.

X-ray single-crystal analysis of the monomer was carried out and result is shown in Figure 2a.[8] The polymerization reactitvity of dienes was evaluated by the following four parameters of the alignment of diene moieties proposed by Matsumoto et al:[4] the repeating distance along the polymerization direction (d_s), the distance between two carbons to make new bond during polymerization (d_{cc}), and the angles between the diene plane and the polymerization direction (θ_1, θ_2). These parameters in the monomer crystal are $d_s = 4.88$ Å, $d_{cc} = 5.38$ Å, $\theta_1 = 26^\circ$, and $\theta_2 = 61^\circ$, respectively. These distances and angles are very similar to those of the polymerizable crystals of alkylammonium sorbates that have already been reported.[7b] Therefore, the diene moieties polymerized smoothly in the crystalline state. On the other hand, the diacetylene polymerization requires the molecular orientation with translation distance of 5 Å and the angle of 45° between the translation axis and diyne moieties in the crystalline state.[2] For the present compound, the translation distance was also 4.88 Å, which was suitable for their polymerization in the crystalline state. However, the tilt angle of the diyne moieties against the translation axis was 60°, and the value is different from the ideal angle 45°. It causes low conversion of the diyne moieties.

We also succeeded the structure analysis of the polymer single crystal that prepared by X-ray irradiation (40 kV, 200 mA, 48 h).[8] The crystal structure after irradiation was solved as the diene polymers with diyne monomers. The unit cell parameters of these crystals were very similar, indicating that the polymerization proceeded by the topochemical polymerization mechanism indeed. The polymerization underwent along the crystallographic *a* axis, and the repeating distance of diene polymer chains is 4.82 Å, which is slightly shorter than the translation distance of the precursor monomers.

We demonstrated that the polymerization of 4,4′-butadiynedibenzylammonium disorbate proceeded under topochemical reaction mechanism. With regard to ammonium salts of diene derivatives, this is the first success of X-ray crystal structure analysis of the polymer. Although the conversion of diyne moieties was low, the polymer networks composed of two kinds of polymer were partially formed. The conversion of diyne moieties would be higher by the improvement of tilt angle.

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8 Crystal data for monomer: $C_{15}H_{16}NO_2$, fw = 242.29, triclinic, space group $P\bar{1}$, $T = 173$ K, $a = 4.883(3)$ Å, $b = 5.781(3)$ Å, $c = 22.520(14)$ Å, $\alpha = 89.000(14)^\circ$, $\beta = 89.011(18)^\circ$, $\gamma = 84.398(16)^\circ$, $V = 632.5(7)$ Å^3, $Z = 2$, $D_{calcd} = 1.272$ g/cm^3, $F(000) = 258$, μ(Mo Kα) = 0.084 mm^{-1}. A total of 4481 reflections was measured, 2240 was unique. 2129 ($I > 2\sigma(I)$) were used in the refinement of 163 parameters. $R_1 = 0.045$, $wR_2 = 0.126$, GOF = 1.04. For polymer: $C_{15}H_{16}NO_2$, fw = 242.29, triclinic, space group $P\bar{1}$, $T = 293$ K, $a = 4.818(3)$ Å, $b = 5.609(2)$ Å, $c = 23.803(10)$ Å, $\alpha = 89.02\ (3)^\circ$, $\beta = 85.43(4)^\circ$, $\gamma = 80.22(4)^\circ$, $V = 631.9(5)$ Å^3, $Z = 2$, $D_{calcd} = 1.273$ g/cm^3, $F(000) = 258$, μ(Mo Kα) = 0.085 mm^{-1}. 2917 reflections was measured. 1456 ($I > 2\sigma(I)$) were used in the refinement of 165 parameters. $R_1 = 0.091$, $wR_2 = 0.256$, GOF = 1.06. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 248012 and 248013.