Novel Polydiacetylenes Containing Crown Ether Groups

Satoru Shimada,* Atsushi Masaki, Kikuko Hayamizu, Hiro Matsuda,* Shuji Okada,† and Hachiro Nakanishi†
National Institute of Materials and Chemical Research, 1-1-4 Higashi, Tsukuba, Ibaraki 305-8565
†Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980

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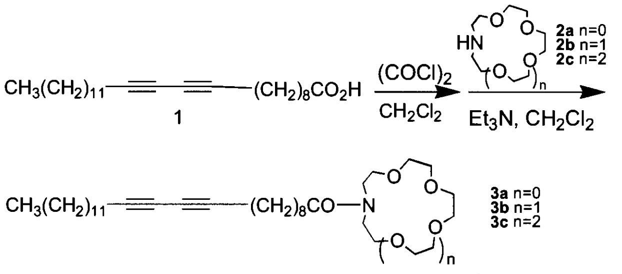
Polydiacetylenes containing crown ethers in the substituent were synthesized by the solid-state polymerization of the corresponding diacetylenes derived from 1,10-pentacosadiynoic acid in the manner of 1,4-addition.

Polydiaceteylenes (PDAs)[1] have been attracting much attention because of their electrical transportation and third-order nonlinear optical properties,[2] which come from the highly regular conjugated main chain. In order to modulate the electronic structures and, thereby, modify the electrical and optical properties of the main chain, we developed the syntheses of PDAs having aromatic,[3] alkynyl groups,[4] and hetero atoms[5] directly bound to sp^2 carbons of the main chain.

Recently we tried to incorporate the functionalized side group in the substituent of a PDA, which would form the side columns in the PDA crystals. Such a molecular design would have resulted in a conjugated polymer containing electron donating side columns which would be expected to have the correlation between the main chain and the side columns. On the basis of this design, the PDA with tetrathiafulvalene (TTF) moieties contained in the side groups[6] was synthesized, which was revealed to have a fairly good conductivities with doped iodine.[7]

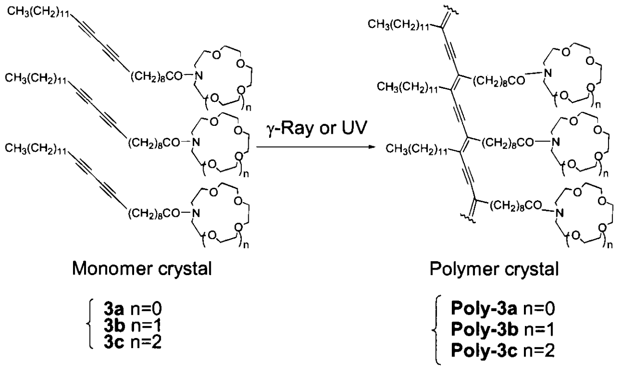
On the other hand, crown ethers are well known to form ion conducting channels in charge-transfer salts.[8] Therefore in this communication, we tried the incorporation of crown ether to polydiacetylene side groups. However, there is no precedent about the synthesis of PDAs having crown ethers in the substituent. This is the first example of PDA derivatives containing crown ether groups in the substituents.

The monomers **3a–c** for PDA were prepared in 2 steps as shown in Scheme 1. Treatment of 1,10-pentacosadiynoic acid (**1**) with oxalyl chloride in dichloromethane quantitatively afforded the corresponding acid chloride. Addition of the acid chloride of **1** to the dichloromethane solution of 1-aza-12-crown-4 (**2a**), 1-aza-15-crown-5 (**2b**), and 1-aza-18-crown-8 (**2c**) with triethylamine at room temperature gave the diacetylene derivative **3a–c**[9] in 58, 62, 65% yield, respectively, as oil at room temperature.



Scheme 1. Synthesis of diacetylene monomers **3** having crown ether groups.

The color of the white bulk crystals of the monomers **3a–c** at –18 °C changed to red after exposure to UV with a low-pressure mercury lamp (4W) or ^{60}Co γ-ray irradiation. It indicated clearly that the crystal structures of the monomers were favorable for solid-state polymerization proceeding by 1,4-addition as shown in Scheme 2. A further study of the polymerization was performed with the monomer **3c** because of its highest melting point (6.1 °C).



Scheme 2. Schematic representation of solid-state polymerization of diacetylene **3**.

The solid-state polymerization of the monomer **3c** stimulated by ^{60}Co γ-ray irradiation (The dose rate was ca. 9.8 kGy/h) at 0 °C was investigated by the gravimetry after extraction of the unreacted monomer by benzene, the polymer being insoluble in this solvent, as shown in Figure 1. The polymer content of the crystals increased with γ-ray dose up to 90 kGy, to about 72% conversion to polymer. However the rate of polymerization became slow for doses in excess of 100 kGy. This behavior of the polymerization of the monomer **3c** is similar to that reported before for diacetylene with TTF.[7]

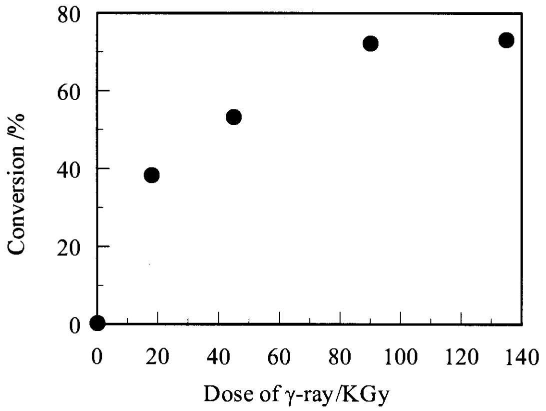


Figure 1. Time-conversion curve of solid-state polymerization of diacetylene **3c** caused by ^{60}Co γ-ray irradiation.

The solid-state high-resolution ^{13}C NMR spectrum of the reaction product after 100-kGy-dose radiation was measured at 50.2 MHz with cross-polarization, ^{1}H decoupling method under the magic-angle sample spinning. The spectrum is consistent with the chemical structure of the polymer **poly-3c** in Scheme 2. In particular, the carbon signals at 102 and 130 ppm correspond to the acetylenic and olefinic carbons of the conjugated backbone of the polymer **poly-3c**, respectively, and are characteristic of poly(5,7-dodecadiyne-1,12-diol bis[((butoxycarbonyl)methyl)urethane]) in the red phase.[10]

By X-ray diffraction measurements, the polymer **poly-3c** produced by 100-kGy radiation still has the similar crystal structure to the monomer **3c**.

The absorption spectrum of **poly-3c** is shown in Figure 2, in which the maxima were observed at 540 and 470 nm, which come from the conjugated backbone of the PDA.

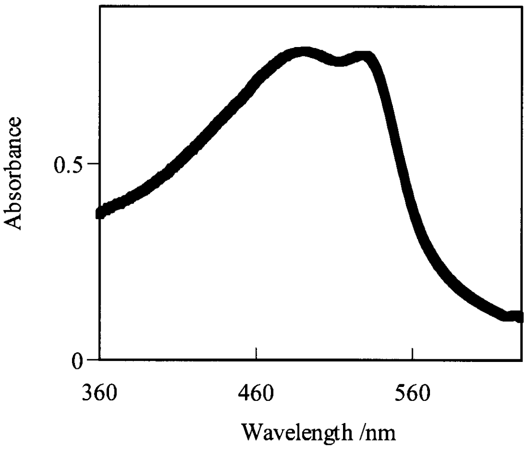


Figure 2. Absorption spectrum of thin film (thickness: 15 nm) of **poly-3c** obtained from **3c** after exposure to ^{60}Co γ-ray with 100 KGy dose.

All of the monomers **3a–c** form complexes[11] with alkali metal (Li, Na, K) halide (Cl, Br, I) salts. The complexes have much higher melting points than **3a–c** and can be isolated as a white powder at room temperature. The complexes between **3a–c** and Na and K salts cannot be polymerized by UV or γ-ray irradiation. But the complexes of the monomer **3a-c** and Li salts showed color changes (white to dark blue) on the basis of solid-state polymerization by a UV light exposure.

The PDA prepared here can be dissolved in DMF or DMSO to afford clear yellow solutions above 120 °C, which result in the red gels[12] containing the solvent after cooling. These gels form complexes with alkaline salts in the solutions. The color of the gels is changed by complexations, which suggests that the conformation of the conjugated main chain is modulated by the complexation in the side chain. Metal salts of chromophores can also be introduced into the gels in a same manner. A detailed study of optical nonlinearities of these complexes between the gels and salts will be published elsewhere.

In conclusion, a novel diacetylene containing crown ethers was synthesized for the first time, giving the PDA with crown ethers in the side chains after solid-state polymerization.

References and Notes

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9 Compound **3** gave satisfactory analytical and spectral data. Selected data for **3c**: white crystals (mp 6.1 °C). ^{1}H NMR ($CDCl_3$) δ 0.65 (t, 3H, J = 6.6 Hz), 1.25–1.64 (m, 32H), 2.23 (t, 4H, J = 6.8 Hz), 2.34 (t, 2H, J = 7.6 Hz), 3.59–3.70 (m, 24H); ^{13}C NMR ($CDCl_3$) δ 13.96, 19.04, 22.52, 25.15, 28.2, 28.66, 28.70, 28.81, 28.94, 29.15, 29.18, 29.27, 29.32, 29.46, 31.76, 32.93, 46.67, 48.79, 65.15, 65.17, 69.42, 69.90, 70.20, 70.41, 70.52, 70.61, 70.64, 70.68, 77.26, 77.35, 173.26.

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