Synthesis of Polydiacetylene-Based Ladder Polymer

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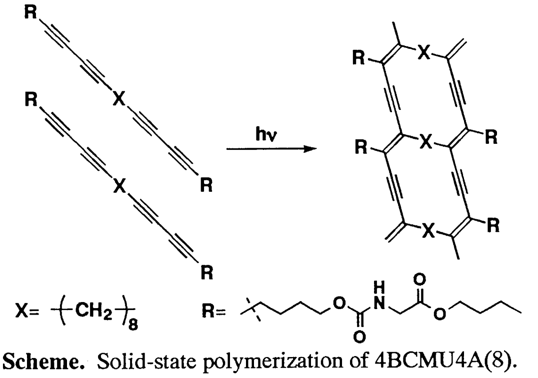
(Received July 17, 1997; CL-970558)

A novel polydiacetylene (PDA) was prepared from the monomer having two butadiyne parts linked by a chain of methylene units. Polymerization in solid state was performed by UV or γ-ray irradiation. From ^{13}C NMR spectra measured using CP/MAS technique, the structure of the ladder polymer composed of two PDAs linked by methylene chains was confirmed. By X-ray diffraction experiment, crystallinity was found to be preserved even for the ladder polymer.

PDA[1] has received considerable attention as third-order nonlinear optical materials due to its one-dimensional π-conjugated main chain.[2-4] In order to enhance the third-order nonlinear optical properties by increasing the density of π-conjugated PDA chain per unit volume without change in absorption wavelengths, ladder polymer having two PDA chains linked by methylene chains seems to be promising. When we look back at the previous studies from the point of above mentioned view, several compounds have already been reported[5,6] to undergo such polymerization. However, none of them has attained high crystallinity in the ladder-type PDA, and quantitative conversion of butadiyne moiety has not been reported. Here, we report a new monomer, i.e. 5,7,17,19-tetracosatetraynylene bis(*N*-butoxycarbonylmethyl)carbamate [4BCMU4A(8)], which gives a highly crystalline ladder polymer as shown in the following Scheme.



Scheme. Solid-state polymerization of 4BCMU4A(8).

The diacetylene monomer 4BCMU4A(8) was obtained as follows. 1,11-Dodecadiyne was coupled with 6-bromo-5-hexyn-1-ol in the presence of Cu(I) catalyst with 2-aminopropane. The reaction was carried out at ambient temperature for several hours and 5,7,17,19-tetracosatetrayne-1,24-diol was prepared.[7] Then, this diol was reacted with butyl isocyanatoacetate at 80 °C in the presence of pyridine catalyst to give 4BCMU4A(8) as colorless crystals.[8] As the compound polymerized spontaneously in the solid state, it was stored in solution state and was recrystallized just before starting the experiments. The thin film was prepared on a glass plate by spin-coating method. Bulk crystals and thin film samples of monomer were polymerized by γ-ray with 0.2 kGy dosage and UV light, respectively.

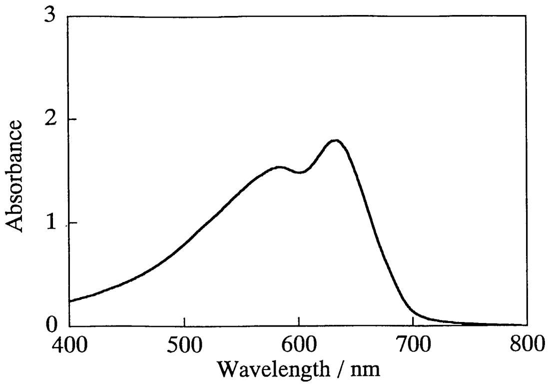


Figure 1. Visible absorption spectrum of 4BCMU4A(8) polymer obtained from spin-coated and polymerized by UV irradiation.

To investigate its polymerization behavior in the solid state, the visible absorption spectrum of the 4BCMU4A(8) polymer was measured and is shown in Figure 1. After polymerization, the colorless sample turned blue. In the spectrum, characteristic excitonic absorption of the PDA structure was observed at 635 nm together with its vibronic side band at 585 nm. However, from the absorption spectrum, it was difficult to ascertain whether both the butadiyne moieties at the two ends of the methylene chain are involved in the polymerization to form two PDA main chains or not.

Therefore, chemical structure of the polymer was investigated by means of high-resolution solid-state ^{13}C NMR spectroscopy and powder X-ray diffractometry. The CP/MAS ^{13}C-NMR spectra of 4BCMU4A(8) crystals before and after irradiation of γ-ray are shown in Figure 2(a) and 2(b), respectively. Quantitative conversion of the monomer by the γ-ray irradiation was confirmed because no monomer was extracted by boiling hexane from the sample. In Figure 2(a), the peaks of four acetylenic carbons of the monomer are observed at δ=79.5 ppm, 79.0 ppm and around 65.9 ppm where two of them overlap with the peaks of methylene carbons adjacent to the oxygen atoms. In Figure 2(b), several new peaks appear. The peak at δ=131 ppm corresponds to the olefinic carbon of the PDA backbone and that at 109 ppm corresponds to the acetylenic carbon of the PDA backbone. The peak at 37 ppm corresponds to the methylene carbon adjacent to the olefinic carbon of the PDA backbone. The intensity of peaks around 79 ppm assigned to the acetylenic carbons and that of peak at 22 ppm assigned to the methylene carbon adjacent to the acetylenic carbon in Figure 2(a) decreased markedly in Figure 2(b), indicating that there are almost no unreacted butadiyne part. The chemical shifts of backbone carbons of this PDA-based ladder polymer agree with those of

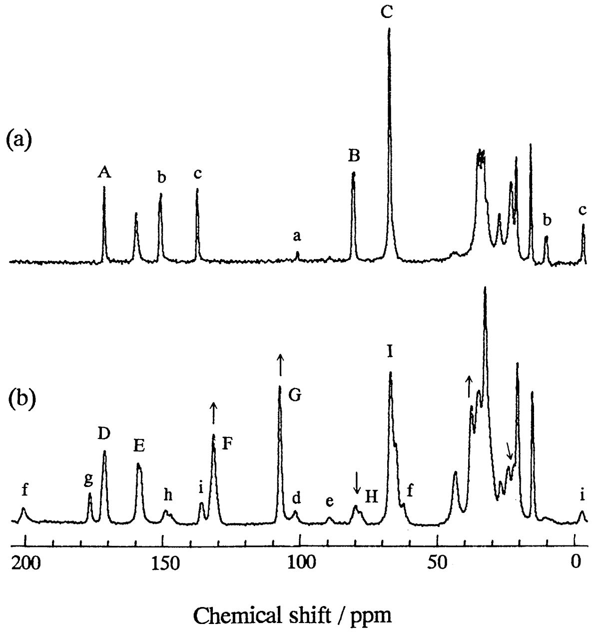


Figure 2. CP/MAS spectra of 4BCMU4A(8) before (a) and after γ-ray irradiation (b). The peaks labeled with capital letters have spinning side bands. The spinning side band(s) for each of these peaks are distinguished using small letter of the corresponding alphabets. Arrows ↑ and ↓ indicate decreasing and increasing peaks during polymerization.

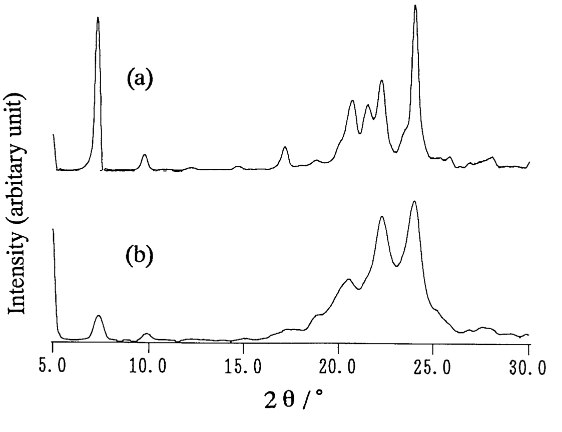


Figure 3. X-ray diffraction patterns (CuK$_\alpha$) of 4BCMU4A(8) (a) monomer and (b) polymer obtained by γ-ray irradiation.

conventional PDA derivatives.[9] Thus, it is confirmed that the polymerization took place at the both butadiyne moieties and the ladder polymer composed of two PDAs linked by methylene chains was formed.

X-ray diffraction patterns of 4BCMU4A(8) monomer (a) and γ-ray irradiated one (b) are shown in Figure 3. Although the peaks of polymer became broad compared with those of monomer, its high crystallinity is still maintained even after polymerization. The peak positions were not much different between the monomer and the polymer, indicating that the monomer crystal transforms to polymer crystal without significant mismatch in their crystalline lattices.

In conclusion, 4BCMU4A(8) was found to be polymerized to give highly crystalline ladder polymer having two PDA backbones.

References and Notes

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8 Satisfactory spectral data for 4BCMU4A(8) were obtained. Selected data are as follows: Mp 91.0-92.0 ℃; ^{1}H-NMR (400 MHz, CDCl$_3$) δ=0.94 (6H, t, J=7.4 Hz), 1.26-1.78 (28H, m), 2.24 (4H, t, J=7.3 Hz), 2.30 (4H, t, J=7.0 Hz), 3.96 (4H, d, J=5.6 Hz), 4.10 (4H, t, J=6.3 Hz), 4.16 (4H, t, J=6.7 Hz), 5.13 (2H, broad); ^{13}C-NMR (100 MHz, CDCl$_3$) δ=13.34, 18.52, 18.71, 18.80, 24.44, 27.78, 27.94, 28.42, 28.56, 30.23, 42.36, 64.27, 64.87, 64.95, 65.54, 76.26, 77.32, 156.32, 169.96; IR (KBr) 3326, 2959, 2849, 1752, 1690, 1541, 739 cm^{-1}; Found: C, 68.14; H, 8.35; N, 4.10%. Calcd for $C_{38}H_{56}N_2O_8$: C, 68.23; H, 8.44; N, 4.19%.
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