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Synthesis and Solid-State Polymerization of L-Alanine Derivatives with a (1-Pyrenyl)butadiynyl Group

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*(1-Pyrenyl)butadiyne derivatives **5** and **6** with a methylene chain and a L-alanine moiety as a chiral group were synthesized, and the end group of **5** and **6** was ethyl ester and carboxylic acid, respectively. These compounds could be polymerized in the crystals by UV irradiation at 365 nm. The regular solid-state polymerization was confirmed for **5** although **6** showed irregular polymerization. Their nanoaggregate water dispersions were obtained by the reprecipitation method. Morphology of their nanoaggregates was studied by SEM, and helical nanoribbons and circle domains were observed for **5** and **6**, respectively.*

Keywords Butadiyne; L-alanine; nanoaggregates; pyrene; solid-state polymerization

1. Introduction

Polydiacetylene (PDA) has highly extended π-conjugation systems along the polymer chains in their solid state [1,2]. However, the high crystallinity avoids interaction between a π-conjugated backbone and dopant molecules, and their chemical doping is not easy [3]. Pyrene is known to show a long lifetime of its singlet excited state, and its fluorescent excimers can be utilized to study its mobility and aggregation behaviors [4–7]. Pyrene is also known as an electron donor, which gives conducting charge-transfer (CT) complexes when proper acceptors are combined [8]. Since combination of PDA and pyrene seemed to show some interesting electronic properties, we already synthesized a polymerizable (1-pyrenyl)butadiyne derivative in the previous study [9]. In this paper, we designed (1-pyrenyl)butadiyne derivatives with a relatively long methylene chain and a L-alanine moiety as a chiral group to investigate their solid-state polymerization and formation of the nanoaggregates.

2. Experimental

L-Alanine derivatives **5** and **6** with a (1-pyrenyl)butadiynyl group were synthesized according to Scheme 1.

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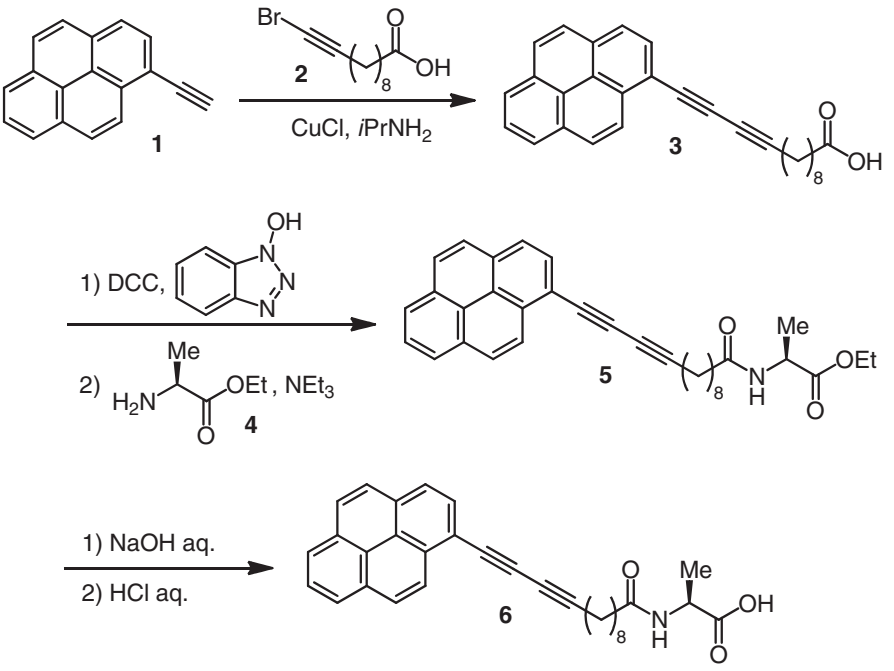

Scheme 1. Synthesis of L-alanine derivatives with a (1-pyrenyl)butadiynyl group.

Synthesis of **3**. Compound **1** [10], copper(I) chloride (21.9 mg, 0.22 mol), isopropylamine (14 mL, 0.16 mol), and hydroxylammonium chloride (1.0 g, 4.42 mol) were placed in a round bottom flask with 14 mL of THF under a nitrogen atmosphere. Compound **2** (2.31 g, 14.2 mol) [10] in 14 mL of THF was dropped to the stirred mixture for 3 h and further stirring was continued overnight. Hydroxylammonium chloride was added when the color of the mixture was changed. After solvent evaporation of the reaction mixture, chloroform was added and washed with water. The organic layer was dried over anhydrous magnesium sulfate. After filtration and removing solvent from the filtrate, the residue was purified by column chromatography (SiO_2, chloroform), and recrystallization from mixture of chloroform and hexane afforded **3** as brown powder (0.27 g, 15.3%). Mp. 128°C. ^{1}H NMR (400 MHz, $CDCl_3$) = δ_H: 1.35 (m, 8H); 1.47 (m, 2H); 1.64 (m, 2H); 2.37 (t, J = 7.8 Hz, 2H); 2.45 (t, J = 6.9 Hz, 2H); 8.08 (m, 8H); 8.55 (d, J = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) = δ_C: 133.5, 131.8, 131.4, 131.2, 130.8, 128.8, 128.7, 127.4, 126.5, 126.0, 125.9, 125.6, 124.7, 124.6, 124.4, 116.8, 86.7, 80.1, 74.4, 65.8, 31.9, 29.38, 29.30, 29.2, 29.1, 28.5, 24.9, 20.0.

Synthesis of **5**. Compound **3** (126 mg, 0.31 mmol) was placed in a round bottom flask with 30 mL of dichloromethane and the mixture was refluxed to solve the solid. Then, the mixture was cooled to 0°C, and stirring was continued for 30 min after adding dicyclohexylcarbodiimide (82.5 mg, 0.40 mmol) and 1-hydroxybenzotriazole (54.1 mg, 0.40 mmol). Compound **4** (42.9 mg, 0.31 mmol), which was prepared from L-alanine and ethanol using thionyl chloride [11], and triethylamine (43 μL, 0.31 mmol) were added to the mixture and it was stirred overnight at room temperature. The crude was filtered and the filtrate was washed with sodium hydrogen carbonate, sodium hydrogen sulfate and sodium hydrogen carbonate solutions. The organic layer was dried over anhydrous magnesium

sulfate and filtered. After solvent evaporation of the filtrate, the residue was purified by column chromatography (SiO_2, hexane:ethyl acetate = 1:1) to afford **5** as yellowish green powder (0.13 g, 84.8%). Mp. 109°C. ^{1}H NMR (400 MHz, $CDCl_3$) = δ_H: 1.27 (t, J = 7.3 Hz, 3H); 1.35 (m, 11H); 1.47 (m, 2H); 1.64 (m, 2H); 2.22 (t, J = 7.3 Hz, 2H); 2.45 (t, J = 7.3 Hz, 2H); 4.18 (q, J = 7.2 Hz, 2H); 4.58 (quint, J = 7.2 Hz, 1H); 8.08 (m, 9H); 8.55 (d, J = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) = δ_C: 173.1, 172.5, 133.0, 131.3, 130.9, 130.7, 130.3, 128.4, 128.3, 126.9, 126.1, 125.6, 125.5, 125.1, 124.2, 124.1, 123.9, 116.2, 86.3, 79.7, 73.9, 65.4, 61.3, 47.8, 36.3, 29.08, 29.05, 28.8, 28.7, 28.1, 25.4, 19.6, 18.4, 14.0.

Synthesis of **6**. Compound **5** (180 mg, 0.36 mmol) was placed in a round bottom flask with 10 mL of methanol. Then, sodium hydroxide solution (1 M, 1 mL) was added and the mixture was stirred for 4 h under N_2 at room temperature. After hydrochloric acid (1 M, 5 mL) was added, the solvent was removed. To the remaining portion, hydrochloric acid was (1 M, 6 mL) added again. The mixture was cooled using an ice bath, stirred for a few minutes and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate. After filtration and solvent evaporation of the filtrate, the crude product was purified by column chromatography (SiO_2, hexane:ethanol = 1:1) to afford **6** as pale brown powder (0.15 g, 87.6%). Mp. 78°C. ^{1}H NMR (400 MHz, $CDCl_3$) = δ_H: 1.34 (m, 8H); 1.47 (d, J = 6.9 Hz, 3H); 1.63 (m, 4H); 2.25 (t, J = 7.8 Hz, 2H); 2.45 (t, J = 7.1 Hz, 2H); 4.56 (quint, J = 7.1 Hz, 1H); 8.08 (m, 9H); 8.54 (d, J = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) = δ_C: 173.6; 172.9; 133.2; 131.5; 131.1; 130.9; 130.4; 128.5; 128.4; 127.0; 126.2; 125.7; 125.6; 125.3; 124.3; 124.2; 124.0; 116.4; 86.4; 79.8; 74.0; 65.5; 47.9; 36.3; 29.0; 28.88; 28.82; 28.2; 25.4; 19.7; 19.7.

Chemical structures of compounds were confirmed by ^{1}H- and ^{13}C-NMR spectra using a JEOL JNM-ECX 400 spectrometer. UV-visible diffuse reflectance spectra were recorded on a JASCO V-570 spectrophotometer equipped with an ILN-472 integrating sphere. Melting points were measured using a SII DSC 6220 differential scanning calorimeter. Photopolymerization of the samples was carried out by irradiating UV at 254 or 365 nm from a 4-W lamp (UVP, UVG-11 or UVL-21). For spectral measurements, monomer crystals were mixed with potassium bromide, ground and placed into a quartz-window cell.

For compounds **5** and **6**, their nanoaggregates were prepared by the reprecipitation method [12]. Acetone solution (5 mM) of the compound in a microsyringe was injected into 10 mL of pure water vigorously stirred. The temperature of water was room temperature, 60°C and 80°C for **5** and room temperature, 60°C and 90°C for **6**. Nanoaggregate sizes in dispersion were evaluated using an Otsuka FPAR-1000 fiber-optics particle analyzer. The nanoaggregate dispersion was dropped on to a substrate of highly ordered pyrolytic graphite (HOPG) and dried, and their SEM images were taken using a Seiko SPA 400 scanning probe microscope with an SPI 3800 probe station.

3. Results and Discussion

Change in UV-visible diffuse reflectance spectra of compounds **5** and **6** during UV irradiation was investigated. Since the large spectral differences were not observed between irradiation at 254 nm and 365 nm for both compounds, spectral changes by irradiation at 365 nm are shown in Fig. 1. Diacetylene monomers without π-conjugation to the substituents show no absorption in the wavelength region longer than 300 nm, and UV at 254 nm is generally used for the solid-state polymerization. However, both compounds showed the broad absorption bands at around 348 and 392 nm, which were assigned to be a pyrene moiety [13, 14] conjugated to the diacetylene part, and the photopolymerization at 365 nm was possible. In Fig. 1(a), compound **5** showed the maximum absorption at 624 nm,

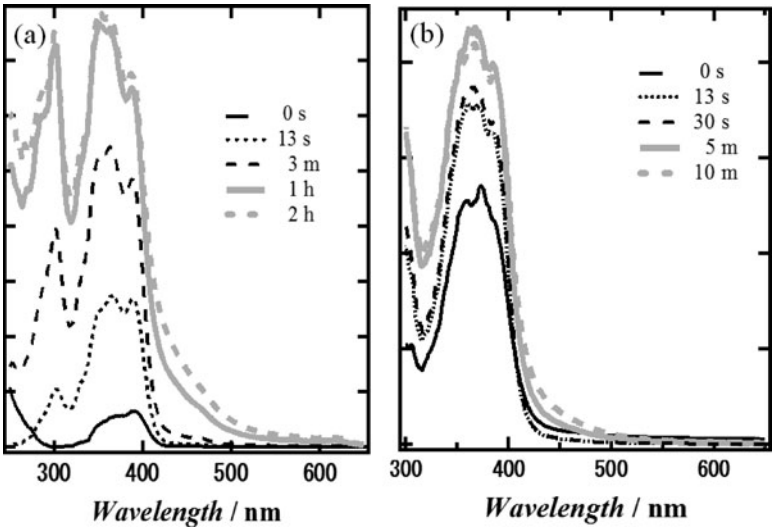

Figure 1. Change in UV-visible diffuse reflectance spectra of (a) **5** and (b) **6** depending on irradiation time of UV at 365 nm.

which was in the range of the characteristic excitonic absorption peak observed for PDAs, i.e., 520–640 nm [15, 16]. These peaks were generally obtained by the regular 1,4-addition polymerization in the crystals. On the other hand, **6** did not show the excitonic bands for the typical PDA although absorption increase in visible region was observed (Fig. 1(b)). This indicates that polymerization of **6** proceeded in an irregular manner.

By using the reprecipitation method, the nanoaggregate generation of **5** and **6** in dispersion was confirmed. The average sizes of the nanoaggregates of **5** prepared at room temperature, 60°C and 80°C were about 105 nm, 130 nm and 160 nm, respectively, while those of **6** at room temperature, 60°C and 90°C were about 50 nm, 90 nm and 130 nm, respectively. For both compounds, size of the nanoaggregates increased when the preparation temperature increased. At the same temperature, **5** gave larger structures than **6** in an average. Figure 2 shows SEM images of nanoaggregates composed of **5** and **6** prepared at 60°C. Compound **5** was apt to coagulate to give the uneven surfaces on the substrates.

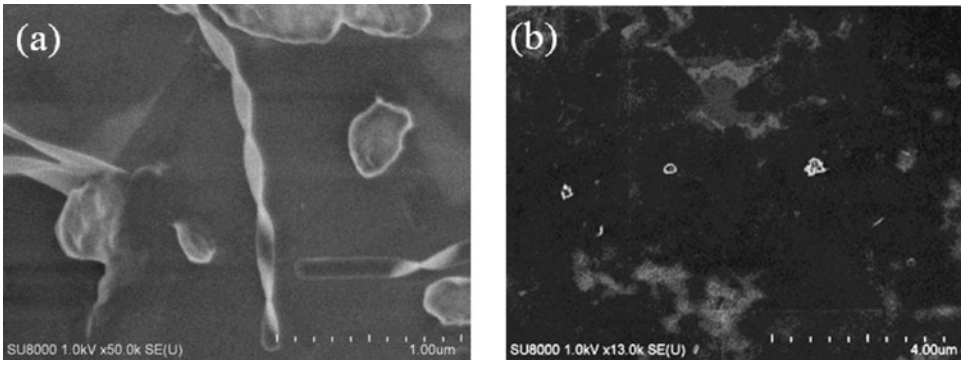

Figure 2. SEM images of nanoaggregates of (a) **5** and (b) **6** prepared at 60°C.

However, on such surfaces, we found one-dimensional nanoribbons with helical structures with typical width and length of about 100 nm and more than 1 μm, respectively (Fig. 2(a)). Since helicity of the nanoribbons may be related to the chiral center introduced by the alanine moiety, molecular modification around the chiral center of this compound seems to be interesting. At room temperature, the length of helical nanoribbons became shorter and number of nanoribbons decreased. At 80°C, torsion of nanoribbons seemed to be released to form flat structures and the width became wider although twisted nanoribbons were partially remained. When UV was irradiated to the nanoaggregate dispersion of **5**, excitonic absorption bands did not appear and absorption spectra similar to Fig. 1(b) was observed. This indicated that the molecular alignment of **5** was different between the crystals and nanoaggregates. In Fig. 2(b), compound **6** was found to form circle domains, whose sizes were hundreds of nanometers. In the magnified images, the rough surfaces of the domains were observed, suggesting that a domain was aggregates of the nanocrystals. This consideration coincided with the fact that the average size of nanoaggregates in dispersion was smaller than that of the domains on the substrate. Besides the domain structure, thin films, which can be seen as gray clouds in Fig. 2(b), were also deposited on the substrate. Photopolymerization behavior of the nanoaggregate dispersion of **6** was similar to that of the crystals.

4. Conclusion

We synthesized compound **5** and **6** as new (1-pyrenyl)butadiyne compounds with a L-alanine moiety. Both compounds could be polymerized in the crystals by UV irradiation even at 365 nm to give conjugated structures, clearly indicating the conjugation effect between diacetylene and pyrene moieties. Although **5** showed the characteristic excitonic absorption of PDA due to the regular polymerization by UV irradiation, irregular solid-state polymerization was observed for **6**. Their nanoaggregates were prepared by the reprecipitation method. Structures of **5** and **6** on HOPG substrates observed by SEM were helical nanoribbons and circle domains as nanocrystal aggregates, respectively, together with other aggregated structures. As future works, it is interesting to study about mechanisms of helical nanoribbon formation and conductivity of the CT complexes composed of these PDA derivatives and several acceptors.

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