



Solid-state polymerization of 1,4-bis(hexatriynyl)benzene derivatives

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Abstract

Two 1,4-bis(hexatriynyl)benzene derivatives with urethane groups, i.e., 10,10'-(1,4-phenylene)bis(5,7,9-decatriynyl *N*-(butoxycarbonylmethyl)carbamate) **1** and its perfluorophenylene derivative **2**, were synthesized, and their solid-state photopolymerization was investigated. Upon UV irradiation, both of them showed excitonic absorption characteristic of polydiacetylene (PDA). In particular, **2** showed an absorption maximum at 743 nm, which was approximately 100 nm longer than that of conventional PDAs because of the effective conjugation between the polymer backbone and π -conjugated substituents. The conversion of **1** to the corresponding polymer was quite low. On the other hand, more than half of the hexatriynyl moieties of **2** were found to polymerize, indicating that most of the monomers were converted to the polymer upon prolonged UV irradiation.

Introduction

Among π -conjugated polymers, polydiacetylenes (PDAs) with a backbone composed of an ene-yne sequence are very unique in their synthesis; for example, butadiyne monomers generally are crystallized and then polymerized in the solid state using a photo- or thermostimulus [1]. Some of the derivatives showed a single-crystal-to-single-crystal transition resulting in single-crystal polymers [2–4], while crystallinity degradation during polymerization was observed for some other derivatives [5, 6]. However, many butadiyne derivatives do not polymerize because the monomer molecules are not aligned in an appropriate condition for polymerization in the crystalline state. The condition for regular 1,4-addition polymerization has been established: The distance between adjacent two monomers must be approximately 0.5 nm, and the angle between the translation axis of the monomers and the butadiyne rod must be approximately 45° [7, 8]. Similar to other π -conjugated polymers, PDAs

have been extensively investigated as materials for electronics and photonics [9–11].

Substituent modification of PDAs is interesting from the point of view of the electronic state tuning of the π -conjugated system. We have synthesized PDAs with conjugated substituents directly bound to the backbone [12–14]. Furthermore, monomers with more than two sets of butadiyne moieties are expected to form ladder-type PDAs, in which two PDA backbones can be formed for each monomer unit. We have introduced acetylenes [15–18], a triene moiety [19], and aryls as the conjugated substituent sandwiched with two butadiyne moieties [17, 20, 21]. Among these groups, only decapentayne and dodecahexayne derivatives were found to give ladder-type PDAs in which two PDA backbones were linked by acetylene moieties. A ladder-type PDA with π -conjugated linkages composed of a *p*-phenylenediamine moiety has also been reported [22]. On the other hand, when methylene chains were introduced between butadiyne moieties, the formation of ladder-type PDAs was confirmed depending on the methylene number [23]. Solid-state polymerization of other monomers having two butadiyne moieties without conjugation between them has also been investigated [24, 25].

In the present study, we prepared 1,4-bis(hexatriynyl)benzene derivatives, which have one more acetylene unit in each substituent than the 1,4-bis(butadiynyl)benzene derivatives studied previously [21]. Their solid-state polymerization behavior was investigated by visible, FT-IR and ¹³C-NMR spectroscopies and powder X-ray diffraction.

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Experimental procedure

Materials

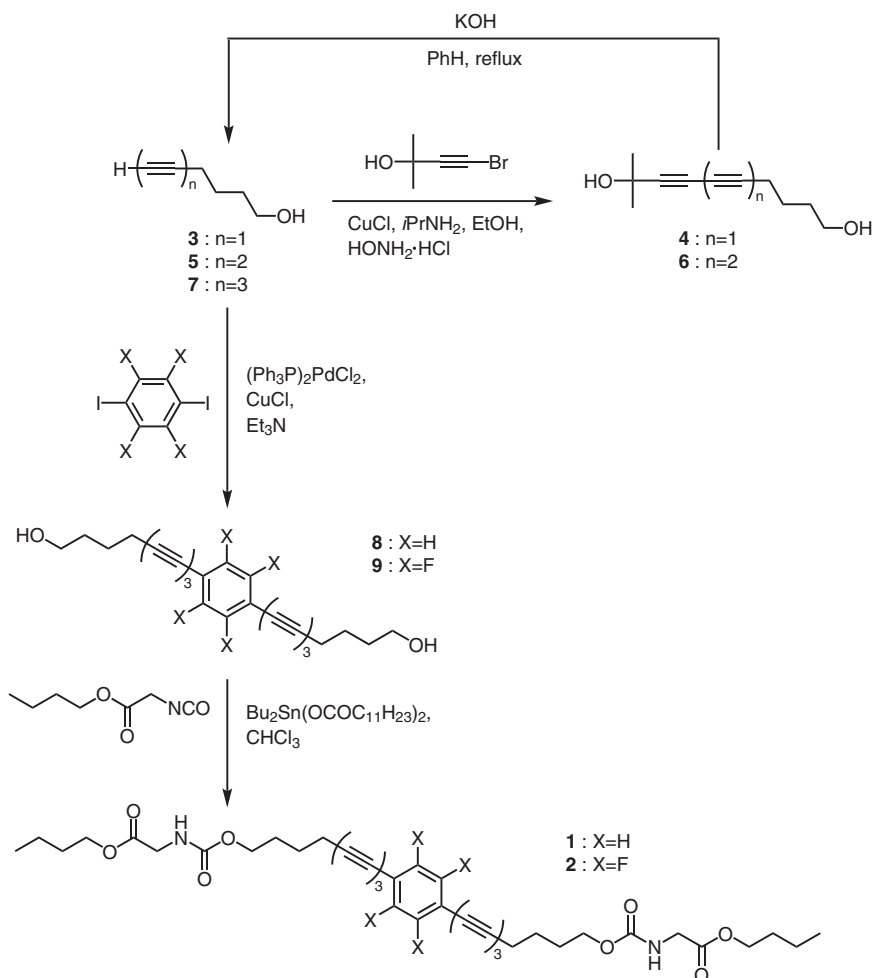
Commercially available reagents and solvents were used as received. Although 1,4-bis(hexatriynyl)benzene derivatives have been synthesized via alkyne migration in vinylidene carbenoid species [26, 27], we prepared those compounds with urethane groups (**1** and **2**) via a step-by-step connection of acetylene units as shown in Fig. 1. The procedure to synthesize **5** from **3** has been reported in a previous study [28]. Details of the synthesis of **1** and **2** from **5** are described below.

11-Methyl-5,7,9-dodecanetriyne-1,11-diol 6. To a mixture of copper(I) chloride (0.12 g), ethanol (5 mL) and 2-aminopropane (30 mL), 1.65 g (13.5 mmol) of 5,7-octadiyn-1-ol **5** was added under a nitrogen atmosphere. Then, 3.31 g (20.3 mmol) of 4-bromo-2-methyl-3-butyn-1-ol was added dropwise. During this addition, a small portion of hydroxyammonium chloride was added when the color of the mixture became dark. After stirring overnight, hydrochloric acid (2 mol L⁻¹) was added, and the mixture was extracted

with chloroform. The collected organic layer was dried over anhydrous magnesium sulfate. After filtration and solvent evaporation from the filtrate, the residue was purified using column chromatography (silica gel, chloroform-ethyl acetate (3:1)) to give 2.05 g (10.5 mmol, yield 74%) of **6** as a yellowish powder: ¹H-NMR (400 MHz, CD₃OD, δ) 1.51 (6H, s), 1.65–1.68 (4H, m), 2.42 (2H, t, *J* = 6.6 Hz), 3.61 (2H, t, *J* = 5.9 Hz); ¹³C-NMR (100 MHz, CD₃OD, δ) 19.67, 25.65, 31.16, 32.68, 59.79, 62.18, 64.38, 65.77, 66.06, 67.30, 81.79, 82.82.

5,7,9-Decanetriyn-1-ol 7. First, 1.2 g (5.88 mmol) of compound **6** was dissolved in benzene (40 mL). After keeping the solution temperature at 80 °C, 0.50 g (8.82 mmol) of ground potassium hydroxide was added, and the mixture was refluxed for approximately 90 min and filtered. The solvent in the filtrate was evaporated, and the residue was purified by column chromatography (silica gel, chloroform-ethyl acetate (3:1)) to give 0.37 g (42%) of **7** as a pale yellow liquid. This compound was kept in solution because of its instability when purified: ¹H-NMR (400 MHz, CDCl₃, δ) 1.62–1.74 (4H, m), 2.08 (1H, s), 2.36 (2H, t, *J* = 6.4 Hz), 3.67 (2H, t, *J* = 5.5 Hz); ¹³C-NMR

Fig. 1 Synthesis scheme of bis(hexatriynyl)benzene derivatives **1** and **2**



(100 MHz, CDCl_3 , δ) 19.02, 24.25, 31.57, 59.50, 60.90, 61.89, 65.43, 65.97, 68.48, 79.67.

1,4-Bis (10-hydroxy-1,3,5-decanetriynyl) benzene **8**. Copper(I) chloride (8.5 mg, 0.085 mmol) was added to a mixture of **7** (0.50 g, 3.42 mmol), *p*-diiodobenzene (0.56 g, 1.71 mmol), bis(triphenylphosphine)palladium(II) dichloride (24 mg, 0.034 mmol) and triethylamine (30 mL) at ambient temperature under a nitrogen atmosphere and stirred overnight. Hydrochloric acid (2 mol L^{-1}) was added to the mixture, and it was extracted with ether. The organic layer was washed with brine, and the solvent was evaporated. The residue was purified by column chromatography (silica gel, chloroform-ethyl acetate (3:1)) to give 0.10 g (16%) of **8** as a colorless solid: $^1\text{H-NMR}$ (400 MHz, CD_3OD , δ) 1.60–1.74 (8H, m), 2.47 (4H, t, $J = 6.6$ Hz), 3.62 (4H, t, $J = 5.9$ Hz), 7.56 (4H, s); IR (KBr) 3400, 2937, 2868, 2212, 1622, 1063, 835, 542 cm^{-1} . The $^{13}\text{C-NMR}$ spectrum was hard to obtain because of the low solubility of **8**. During column chromatography, 0.31 g (54%) of 10-(4-iodophenyl)-5,7,9-decanetriyn-1-ol, a monosubstituted compound, was also obtained just before the fraction containing **8**.

1,4-Bis(10-hydroxy-1,3,5-decanetriynyl)-2,3,4,6-tetrafluorobenzene **9**. Copper(I) chloride (7.7 mg, 0.077 mmol) was added to a mixture of **7** (0.50 g, 3.42 mmol), 2,3,5,6-tetrafluoro-1,4-diiodobenzene (0.62 g, 1.55 mmol), bis(triphenylphosphine) palladium(II) dichloride (21 mg, 0.031 mmol) and triethylamine (30 mL) at ambient temperature under a nitrogen atmosphere and stirred overnight. Hydrochloric acid (2 mol L^{-1}) was added to the mixture, and it was extracted with ether. The organic layer was washed with brine, and the solvent was evaporated. The residue was purified by column chromatography (silica gel, chloroform-ethyl acetate (3:1)) to give 0.12 g (22%) of **9** as a colorless solid: $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ) 1.64–1.74 (8H, m), 2.44 (4H, t, $J = 6.4$ Hz), 3.68 (4H, t, $J = 6.0$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ) 19.38, 24.22, 31.58, 58.21, 59.84, 61.89, 65.45, 72.11, 85.46, 87.93, 104.37 (m), 148.09 (d, $J_{\text{CF}} = 252$ Hz); IR (KBr) 3327, 2924, 2852, 2197, 1755, 1687, 1493, 1055, 985 cm^{-1} . During column chromatography, 0.24 g (45%) of 10-(2,3,5,6-tetrafluoro-4-iodophenyl)-5,7,9-decanetriyn-1-ol was also obtained just before the fraction containing **9**.

10,10'-(1,4-Phenylene)bis(5,7,9-decatriynyl *N*-(butoxycarbonylmethyl)carbamate) **1**. To a mixture of **8** (0.10 g, 0.27 mmol) and butyl isocyanatoacetate (90 μL) in chloroform (20 mL), two drops of dibutyltin dilaurate was added, and the mixture was stirred overnight at ambient temperature. After solvent evaporation from the mixture, the residue was purified by column chromatography (silica gel, chloroform-ethyl acetate (3:1)) to give 0.13 g (72%) of **1** as a colorless solid: Mp 145 $^\circ\text{C}$; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ) 0.94 (6H, t, $J = 7.5$ Hz), 1.38 (4H, m), 1.58–1.79 (12H, m), 2.40 (4H, t,

$J = 6.8$ Hz), 3.96 (4H, d, $J = 4.1$ Hz), 4.12 (4H, t, $J = 5.9$ Hz), 4.16 (4H, t, $J = 6.8$), 5.13 (2H, broad), 7.43 (4H, s); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ) 13.63, 19.02, 19.28, 24.47, 28.08, 30.53, 42.71, 59.48, 64.51, 65.36, 66.06, 68.70, 74.65, 82.73, 122.20, 132.85, 156.39, 170.12 (one of the peaks corresponds to two overlapping peaks); IR (KBr) 3328, 2958, 2871, 2214, 1755, 1687, 1537, 1192, 1095, 829 cm^{-1} ; UV-vis (CHCl_3), λ_{max} nm (ϵ_{max} $\text{cm}^2 \text{mol}^{-1}$) 369 (1.1×10^5), 342 (7.2×10^4), 319 (2.9×10^4). Found: C, 70.20%; H, 6.50%; N, 4.14%. Calcd for $\text{C}_{40}\text{H}_{44}\text{O}_8\text{N}_2$: C, 70.57%; H, 6.51%; N, 4.11%.

10,10'-(2,3,5,6-Tetrafluoro-1,4-phenylene)bis(5,7,9-decatriynyl *N*-(butoxycarbonylmethyl)carbamate) **2**. To a mixture of **9** (0.10 g, 0.23 mmol) and butyl isocyanatoacetate (120 μL) in chloroform (20 mL), two drops of dibutyltin dilaurate was added, and the mixture was stirred at 40 $^\circ\text{C}$ for 1 day. After solvent evaporation from the mixture, the residue was purified by column chromatography (silica gel, chloroform-ethyl acetate (3:1)) and recrystallization from a hexane-chloroform mixture. Since impurities were still detected in the resulting material, it was ultimately purified by preparative TLC (silica gel, chloroform) to obtain 20 mg of **2** in 12% yield as a colorless solid: Mp 141 $^\circ\text{C}$; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ) 0.94 (6H, t, $J = 7.3$ Hz), 1.38 (4H, m), 1.58–1.78 (12H, m), 2.42 (4H, t, $J = 6.6$ Hz), 3.96 (4H, d, $J = 4.6$ Hz), 4.12 (4H, t, $J = 6.8$ Hz), 4.17 (4H, t, $J = 6.4$ Hz), 5.13 (2H, broad); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ) 13.63, 19.00, 19.31, 24.33, 28.06, 30.51, 42.67, 58.42, 59.85, 64.41, 65.35, 65.71, 72.11, 85.04, 87.99, 104.62 (m), 147.95 (d, $J_{\text{CF}} = 254$ Hz), 156.36, 170.13; IR (KBr) 3327, 2962, 2924, 2852, 2197, 1755, 1689, 1543, 1495, 1298, 1200, 1055, 985 cm^{-1} ; UV-vis (CHCl_3), λ_{max} nm (ϵ_{max} $\text{cm}^2 \text{mol}^{-1}$) 375 (1.0×10^5), 347 (7.0×10^4), 324 (3.5×10^4). Found: C, 61.32%; H, 5.54%; N, 3.87%. Calcd for $\text{C}_{40}\text{H}_{40}\text{O}_8\text{N}_2$: C, 61.36%; H, 5.68%; N, 3.97%.

Characterization and apparatus

Melting points were determined from the endothermic peak temperature of differential scanning calorimetry (DSC) thermograms obtained by using an SII DSC 6220 calorimeter. The heating rate was 5.0 $^\circ\text{C min}^{-1}$. NMR spectra in both solution and the solid state were measured using a JEOL ECX-400 spectrometer. In solution, the internal standards used were for the ^1H and ^{13}C spectra tetramethylsilane (0 ppm) and CDCl_3 (77 ppm), respectively. For the solid-state ^{13}C spectra, the methylene carbon of adamantane at 29.5 ppm was used as an external standard. FT-IR spectra were recorded on a Horiba FT-720 spectrometer. UV-visible absorption spectra of solutions were obtained using a JASCO V-560 spectrophotometer. Visible diffuse reflectance spectra were obtained using a JASCO

V-570 spectrophotometer equipped with an integration sphere (JASCO ILN-472). Elemental analysis was performed using a PerkinElmer 2400II analyzer. Powder XRD was measured using a Rigaku Ultima IV diffractometer, whose X-ray source was $\text{CuK}\alpha$ radiation. The applied voltage and current were 40 kV and 40 mA, respectively. The UV sources for solid-state polymerization were a 4 W lamp at 254 nm (UVG-11, UVP) and a 4 W lamp at 365 nm (UVL-21, UVP).

Results and discussion

When **1** was irradiated with UV light at 254 nm, absorption peaks at 637 and 586 nm developed (*a* and *b* in Fig. 2(a)), and a shoulder band was observed at a longer wavelength of approximately 690 nm at the initial stage (*c* in Fig. 2(a)).

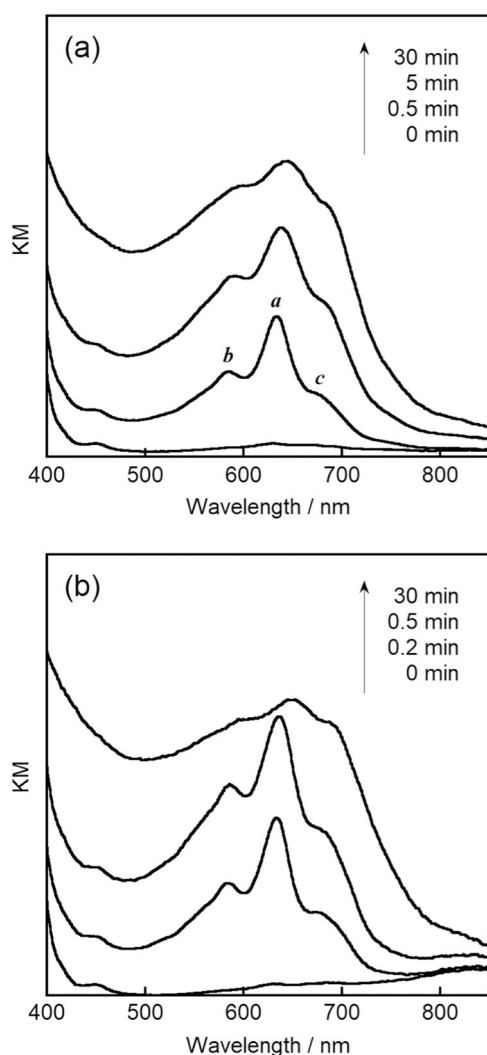


Fig. 2 Visible diffuse reflectance spectra of **1** depending on UV irradiation time. The irradiation wavelengths were (a) 254 nm and (b) 365 nm. Details on bands *a*–*c* are described in the text

The peaks at 637 and 586 nm are often observed for PDA derivatives, and they have been assigned as the excitonic band and the phonon sideband, respectively. These absorption peaks are a good indication of regular 1,4-addition polymerization of butadiyne to form the PDA structure. Solid-state polymerization of hexatriyne derivatives has been reported to occur as 1,4-addition [29–31] except for one example [32], in which supramolecular chemistry was applied to achieve 1,6-addition polymerization. When UV irradiation to **1** was continued, the absorption bands increased and broadened, and the maximum wavelength became 646 nm after 30 min. Since the corresponding bis(butadiynyl)phenylene derivative of **1** did not polymerize [21], the extension of the conjugated acetylene portions from butadiyne to hexatriyne was effective in increasing the probability of solid-state polymerization. The presence of the shoulder band at the longer wavelength suggested that there was an extended component of the effective π -conjugation length. Since **1** has an absorption maximum at 369 nm (see Experimental procedure), polymerization using UV light at 365 nm was also possible (Fig. 2(b)). The absorption change during irradiation at 365 nm was almost the same as that when UV light at 254 nm was used. Thus, we concluded that polymerization behaviors at both wavelengths were the same, and the polymerization experiments of **1** hereafter were performed using UV light at 254 nm.

The absorption changes during UV-stimulated polymerization were also investigated for **2**. Upon UV irradiation at 254 nm, the absorption maximum and the shoulder peak were observed at 622 nm and approximately 580 nm, respectively (*a* and *b* in Fig. 3(a)). These characteristic bands clearly signify the formation of the PDA structure, although compared with those of **1**, the band positions were blueshifted. Interestingly, the polymerization behavior of **2** was different when UV irradiation at 365 nm was performed. At the initial stage of polymerization, a small band at 743 nm was observed along with the broad band at 654 nm (*c* and *d* in Fig. 3(b)). Continuous UV irradiation enhanced both bands, and their intensities became similar after 60 min. Some polymers synthesized from conjugated acetylene compounds via solid-state polymerization are known to show absorption profiles exceeding 700 nm [15–18, 22, 33, 34]. However, this behavior is not normal: π -conjugated and/or electron-donating substituents directly bound to the PDA backbone are generally required to achieve such long-wavelength absorption. In the present case, conjugation of the aromatic groups seemed to affect the electronic state of the PDA backbone. The reason why UV irradiation of **2** at 254 nm did not give PDA with absorption beyond 700 nm is unclear. One of the plausible explanations is that the polymer component obtained from **2** with absorption beyond 700 nm is not stable in the presence

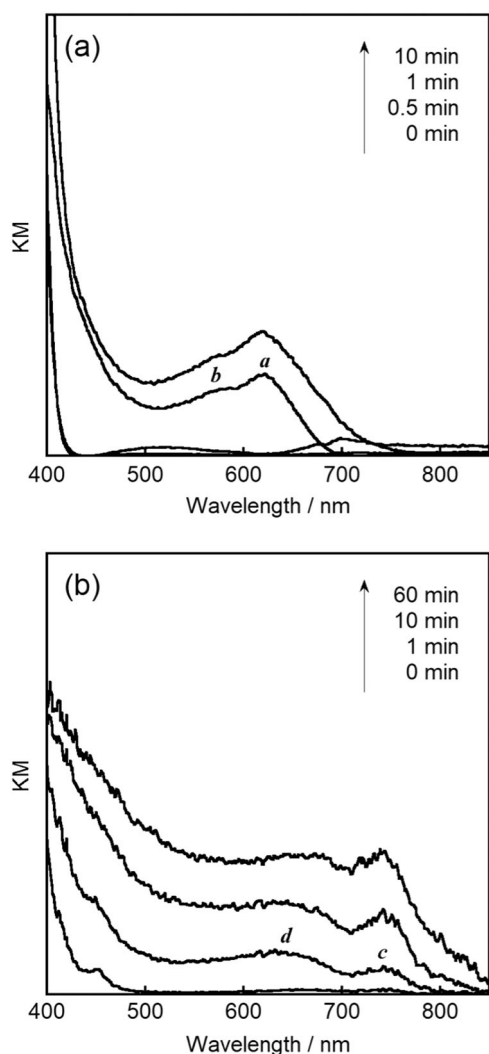


Fig. 3 Visible diffuse reflectance spectra of **2** depending on UV irradiation time. The irradiation wavelengths were (a) 254 nm and (b) 365 nm. Details on bands *a–d* are described in the text

of UV light at 254 nm. Accordingly, UV light at 365 nm was used in the subsequent photopolymerization experiments of **2**. As mentioned above, since the polymerization behaviors of **1** at 254 nm and 365 nm are the same, we believe that it is valid to compare the polymerization behaviors between **1** irradiated at 254 nm and **2** irradiated at 365 nm despite the difference in irradiated wavelengths.

During photopolymerization, FT-IR spectra were monitored to estimate the conversions of **1** and **2** (Fig. 4). Both compounds showed a stretching vibration peak of C≡C at 2214 cm⁻¹ and 2197 cm⁻¹ for **1** and **2**, respectively (*a* in Fig. 4). The intensity of these peaks decreased according to the progress of polymerization. Thus, the conversion from a monomer to the corresponding polymer was calculated from the decreasing ratio of the C≡C peak. Since both compounds have two polymerizable sites, quantitative transformation from the monomer to the single-chain-type PDA

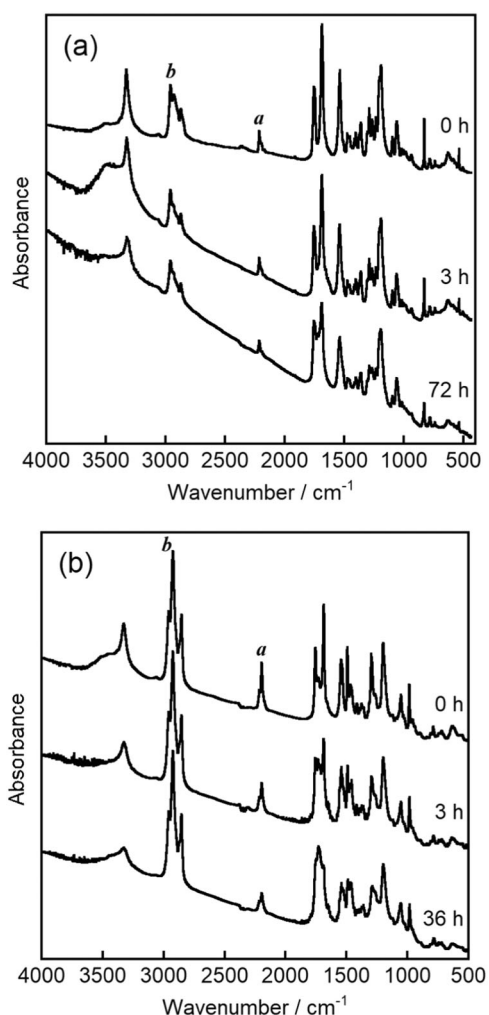


Fig. 4 FT-IR spectra of (a) **1** and (b) **2** depending on UV irradiation time. The irradiation wavelengths were 254 nm for **1** and 365 nm for **2**. Details on peaks *a* and *b* are described in the text

can be achieved by polymerization of one of two hexatriyne parts in a monomer, resulting in at least 50% reduction in the C≡C peak intensity. To avoid peak intensity fluctuation caused by a small difference in the measuring conditions, the intensity of the C≡C peak was normalized to that of the C–H stretching vibration peak at 2960 cm⁻¹ for **1** and 2924 cm⁻¹ for **2** (*b* in Fig. 4), which seemed to be unchanged during polymerization. Although a significant decrease in the peak intensity was not observed for **1**, an approximately 60% reduction in the peak of **2** was observed after UV irradiation for 36 h. That is, most of the monomers of **2** were included in the polymer. However, the production of the ladder-type polymer was not clearly confirmed, and its amount would be quite small even if it existed.

These conversion differences were also confirmed by the solid-state ¹³C-NMR spectra (Fig. 5). As shown in Fig. 5(a), the spectrum of **1** after UV irradiation is quite similar to the original spectrum, indicating that the polymerization had

only slightly progressed. On the other hand, the intensity of several peaks of **2** apparently changed after UV irradiation (Fig. 5(b)). The peak assignment of **2** was first conducted on the CDCl₃ solution spectrum according to previous studies [30, 35, 36], and then the solid-state spectrum was assigned. For explanation, the carbon numbering of **2** is shown in

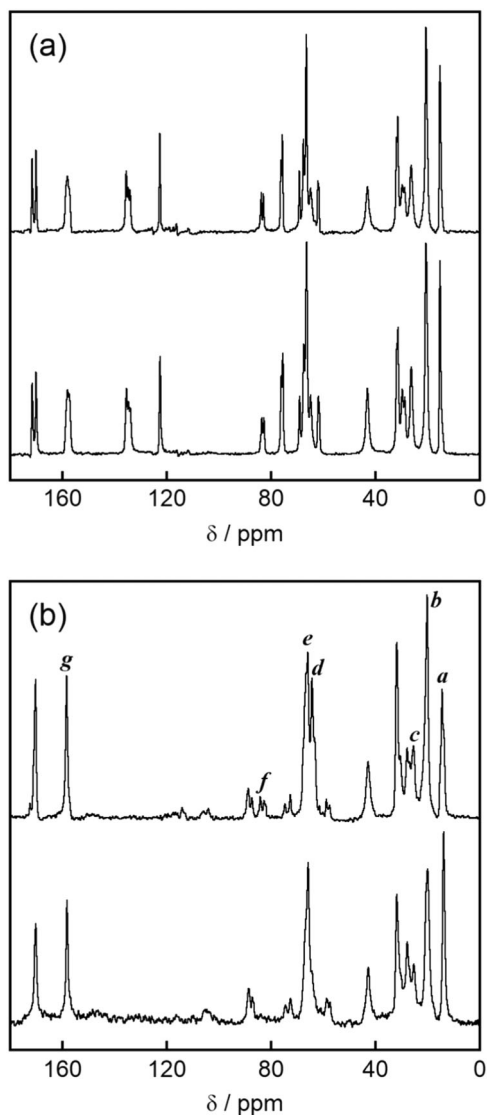


Fig. 5 Solid-state ¹³C-NMR spectra of (a) **1** and (b) **2** obtained using the pulse sequence of total suppression of spinning sidebands (TOSS). The upper and lower spectra correspond to those before and after UV irradiation, respectively. The irradiation wavelengths were 254 nm for **1** and 365 nm for **2**. The irradiation time was 240 h for **1** and 135 h for **2**. Details on peaks *a*–*g* are described in the text

Fig. 6 Carbon numbering of **2** for assignment

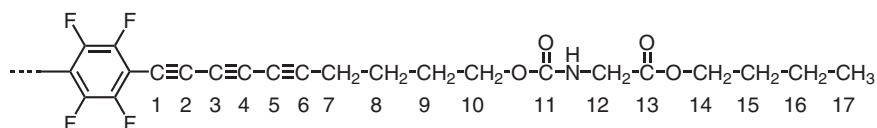


Fig. 6. Among the peaks in the monomer spectrum (upper line in Fig. 5(b)), peak *g* at 158.5 ppm, corresponding to C11, which irrelevant to the polymerization reaction, was used as a peak-intensity standard. Unfortunately, it was difficult to find the polymerization sites from the acetylenic peaks since some peaks were split and remained unchanged except for peaks *f* assignable to C6 or C2, which almost disappeared after UV irradiation. In addition, new peaks for the polymer produced were not clearly detected. The conversion of the sample determined from the NMR spectra seemed to be much lower than that determined from the FT-IR spectra because uniform UV irradiation to a larger amount of the sample was not easy and UV light did not fully penetrate into the crystalline powder. However, the polymerization sites were estimated from indirect evidence from other peak changes. Peak *a* at 14.6 ppm of C17 became sharper and higher and slightly shifted upfield to 14.1 ppm after UV irradiation. This type of change is often observed during polymerization and suggested that the terminal methyl group became more mobile after polymerization [36]. Peak *b* at 20.3 ppm consists of two carbons, i.e., C7 and C16 at 19.31 ppm and 19.00 ppm, respectively, in the solution spectrum. Since C16 in the terminal butyl group should not change during UV irradiation, the intensity reduction in peak *b* after UV irradiation was due to environmental changes around C7. The intensity reduction in peak *c* at 25.4 ppm corresponding to C8 was also prominent after UV irradiation. These changes in peaks *b* and *c* suggested that structural transformation occurred at the position next to C7 and C8 and that 1,4-addition polymerization at the C3 and C6 positions probably occurred (Fig. 7). Peak *d* at 64.5 ppm and peak *e* at 66.1 ppm corresponding to C10 and C14, respectively, were combined into one peak at 65.9 ppm during UV irradiation.

Powder X-ray diffraction patterns were compared between **1** and **2** (Fig. 8). Both monomers showed a peak at approximately 21° (*a* in Fig. 8), corresponding to a spacing of 0.42 nm. This is attributed to the molecular stacking distance. On the other hand, a difference was found in the small-angle peaks. For **1**, two large peaks were observed at 5.63° and 8.47° (*b* and *c* in Fig. 8), which could be assigned to the second- and third-order diffraction peaks, respectively, of 3.14-nm spacing for the layered structure. Moreover, **2** showed peaks at 5.62° and 7.53° (*d* and *e* in Fig. 8) corresponding to the third- and fourth-order diffraction peaks, respectively, of approximately 4.2-nm spacing. Although the molecular lengths of these two compounds are

Fig. 7 Most probable solid-state polymerization scheme of **2**

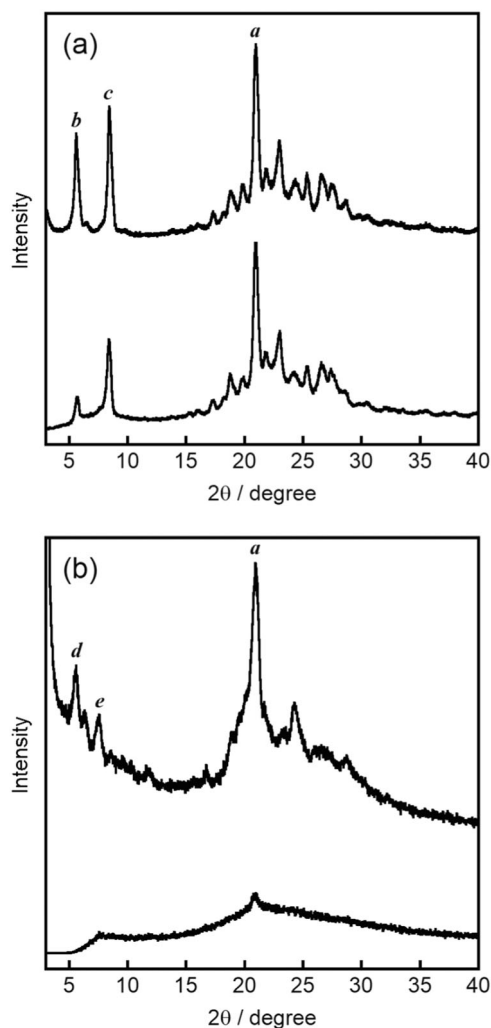
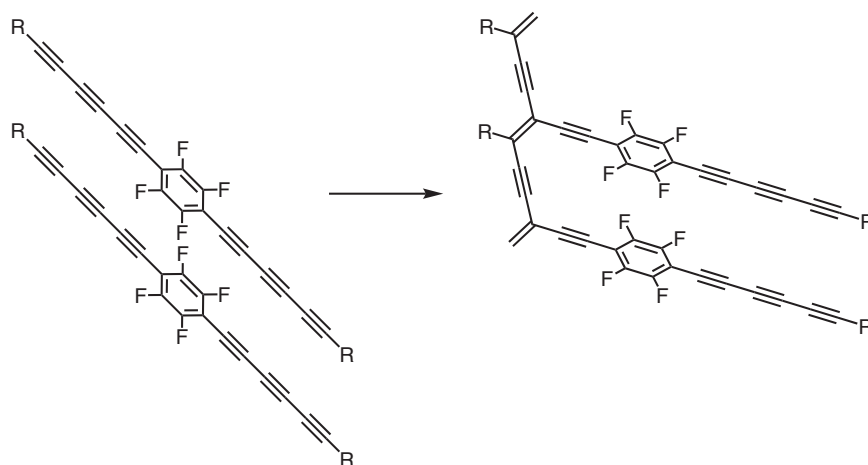


Fig. 8 Powder X-ray diffractograms of (a) **1** and (b) **2**. Upper and lower diffractograms correspond to those before and after UV irradiation, respectively. The irradiation wavelengths were 254 nm for **1** and 365 nm for **2**. The irradiation time was 240 h for **1** and 135 h for **2**. Details on peaks *a–e* are described in the text

almost the same, molecules of **1** inclined more within a layer than those of **2**. The different polymerization behaviors between **1** and **2**, irrespective of their similar structures, must be caused by the above-mentioned difference in molecular arrangement. After prolonged UV irradiation, the crystallinity of **1** remained with little degradation. This is because the crystalline monomer maintained its structure due to the low conversion. However, the crystallinity of **2** was virtually lost upon UV irradiation, indicating that in the course of polymerization, molecular motion within the crystalline lattice was not limited. This structural disorder is considered the reason why solid-state polymerization of the remaining hexatriyne portions did not progress to form ladder-type PDA.

CONCLUSION

Two bis(hexatriynyl)benzene derivatives, **1** and **2**, were synthesized, and their photoinduced solid-state polymerization was investigated. Because the conjugated acetylene portions were elongated to triynes, polymerization of both compounds was confirmed. They showed absorption bands characteristic of PDA, indicating that the main polymerization scheme was regular 1,4-addition. The excitonic absorption peak was observed at 646 nm for PDA obtained from UV irradiation of **1**. However, low conversion of **1** was found in the FT-IR and ^{13}C -NMR spectra. On the other hand, the color of the polymer obtained from **2** varied depending on the irradiation wavelength. When 254-nm light was used, the excitonic absorption maximum was observed at 622 nm. Furthermore, upon irradiation with UV at 365 nm, the excitonic absorption peak appeared at 743 nm, which was approximately 100 nm longer than that of conventional PDAs. Electronic interaction between the PDA backbone and π -conjugated substituents may play an important role in the redshift of the excitonic band. The

conversion of **2** after prolonged UV irradiation was estimated from FT-IR spectra, and one of two hexatriyne moieties completely reacted, indicating that single-chain-type PDA was formed. ^{13}C -NMR analysis suggested that 1,4-addition polymerization progressed mainly at the C3 and C6 positions. From X-ray diffraction, the crystallinity of **2** was found to deteriorate after UV irradiation, and further polymerization was difficult; thus, the ladder-type polymer was not obtained.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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