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# Preparation and Solid-State Polymerization of Dipyridyloctatetrayne Derivatives

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## Summary

Three symmetrical dipyridyloctatetrayne monomers, i.e., 1,8-di(*x*-pyridyl)octatetrayne: $x$=2, 3 and 4, were synthesized and their solid-state polymerization was investigated. In addition, a salt prepared from 1,8-di(3-pyridyl)octatetrayne and *p*-nitrobenzoic acid was found to be polymerized via 1,4-addition in the solid state.

## Introduction

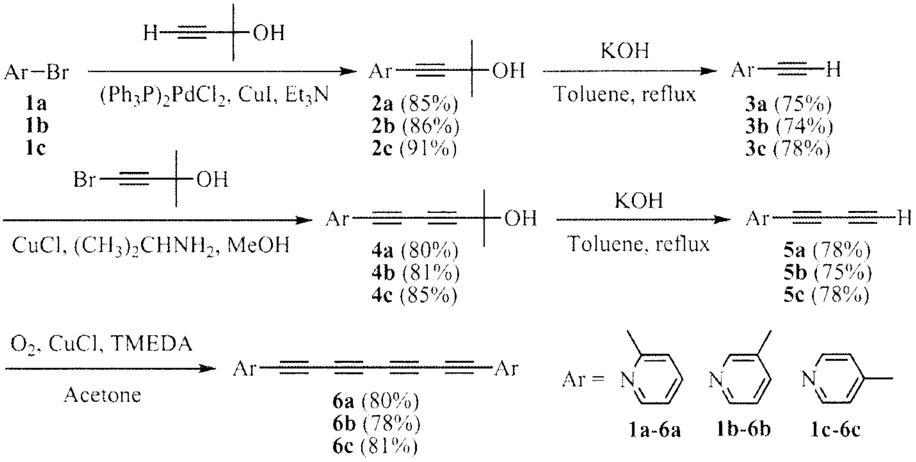
Polydiacetylene (PDA) can be obtained by the topochemical solid-state polymerization of butadiyne compounds [1]. When the appropriate alignment of the butadiyne monomers in crystals is achieved, monomer single crystals can be transformed into polymer single crystals in their entirety. The investigation of PDA covers various aspects such as electrical properties [2], solution properties [3], nonlinear optical (NLO) properties [4] and mechanical properties [5]. Due to the immense application fields of PDA, further studies on the solid-state polymerization to PDA and their properties are deemed worth investigating.

Among them, we have been focusing on enhancement of third-order NLO properties of PDA by increasing the effective π-conjugation length. It can be realized by attaching aromatic and/or acetylenic substitutents directly bound to the conjugated backbone of PDA [6,7]. In our previous studies, we have succeeded in preparation of polymerizable butadiynes substituted by one or two aromatic rings using the several structural characteristics of the substituents [8-11]. Moreover, the PDAs with conjugated acetylenic substituents could be synthesized from the monomers with more than three conjugated acetylenic units to achieve absorption maximum at longer wavelength [12-14]. We report here tetrayne compounds having pyridyl groups directly bound to the conjugated acetylenes as a combination of the above two systems. Pyridyl groups have some advantages on expansion of the compound system since they can be derived into the corresponding salts or metal complexes. In the present study, three symmetrical dipyridyloctatetrayne monomers, i.e., 1,8-di(*x*-pyridyl)octatetrayne: $x$=2, 3 and 4, were prepared and their solid-state polymerization behavior was investigated. The properties of a salt prepared from 1,8-di(3-pyridyl)octatetrayne and *p*-nitrobenzoic acid were also investigated.

## Experimental

### *Synthesis of compounds*

New dipyridyloctatetraynes **6a**, **6b** and **6c** were synthesized according to the route shown in Scheme 1. Preparation of **3a**, **3b** and **3c** has been reported previously [15]. They were coupled with 4-bromo-2-methyl-3-butyn-2-ol and the following acetone removal gave **5a**, **5b** and **5c**, which were so active at ambient temperature that they are better to be used for the next-step reaction as soon as possible. Tetraynes **6a, 6b** and **6c** were obtained by the oxidative coupling reaction of **5a**, **5b** and **5c**, respectively, using CuCl/TMEDA as a catalyst. The reaction procedures were referred to the previous report [16]. **6a**: M.p. 118°C, IR (KBr), $cm^{-1}$: 3030, 2200, 1600, 1580, 1050. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.32 (1H, ddd), 7.55 (1H, ddd), 7.69 (1H, ddd), 8.62 (1H, ddd). Anal, Calcd for $C_{18}H_8N_2$: C, 85.57; H, 3.17; N, 11.11. Found: C, 85.49; H, 3.21; N, 10.97. **6b**: M.p. 165°C, IR (KBr), $cm^{-1}$: 3030, 2200, 1600, 1580, 1050, $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.30 (1H, ddd), 7.82 (1H, ddd), 8.61 (1H, ddd), 8.70 (1H, ddd). Anal, Calcd for $C_{18}H_8N_2$: C, 85.57; H, 3.17; N, 11.11. Found: C, 85.39; H, 3.12; N, 10.94. **6c**: M.p. 168°C, IR (KBr), $cm^{-1}$: 3030, 2200, 1600, 1580, 1050. $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.37 (1H, d), 8.64 (1H, d). Anal, Calcd for $C_{18}H_8N_2$: C, 85.57; H, 3.17; N, 11.11. Found: C, 85.19; H, 3.22; N, 10.86. 4,4′-(1,8-Octatetraynylene)dipyridinium) bis(*p*-nitrobenzoate) **7b** was prepared as follows: To the methanol solution (500 mL) of **6b** (2.52 g, 10 mmol) was added the methanol solution (500 mL) containing *p*-nitrobenzoic acid (3.59 g, 20 mmol). After evaporating the solvent, the residue was recrystallized from methanol to give **7b** as a yellow powder. Yield: 95%. M.p. 191°C, IR (KBr), $cm^{-1}$: 3030, 2250, 2180, 1700, 1600, 1580, 1520, 1420, 1350, 1050. Anal, Calcd for $C_{32}H_{18}N_4O_8$: C, 65.53; H, 3.07; N, 9.56. Found: C, 65.57; H, 3.30; N, 9.32.



**Scheme 1.** Synthetic procedure of **6a**, **6b** and **6c**.

### *Solid-state polymerization*

Grinded monomer samples of **6a**, **6b** and **6c** were prepared and their solid-state polymerization was stimulated by annealing or UV irradiation at 254 nm by use of a 4-W lamp. The annealing temperatures for **6a**, **6b** and **6c** were set at 80°C, 110°C and 120°C, respectively, which were about 40-50°C lower than their melting points. FTIR and UV-visible-near IR spectra were measured for KBr-dispersed samples. Powder X-ray diffraction (XRD) patterns were recorded using CuK$_\alpha$ radiation.

## Results and discussion

IR spectra of the monomers were measured before and after annealing. As shown in Figure 1, the peak intensity of the stretching vibration band of the acetylenic triple bonds ($\nu_{C\equiv C}$) at 2180 cm$^{-1}$ for **6b** gradually decreased during heat treatment. After heating for 24 h, the sharp peak originated from $\nu_{C\equiv C}$ could not be clearly observed. When the regular 1,4-addition topochemical polymerization proceeds, disappearance of the $\nu_{C\equiv C}$ peak is a good indication for the quantitative conversion to PDA. However, in this case, the polymer yield determined by the weight ratio of the chloroform insoluble portion was 31%. This result suggested that the solid-state polymerization reaction did not proceed in 1,4-addition but in irregular 1,2-addtion or other manners to react C≡C bonds. In the polymerization scheme of **6b**, reacted monomer units may move from their lattice points to prevent the chain-reaction polymerization in the solid state. This behavior resulted in the low-molecular weight oligomers and the slightly remaining monomers, which could be soluble in chloroform. This result was contrast to that for 1,8-substituted octatetrayne by 2-

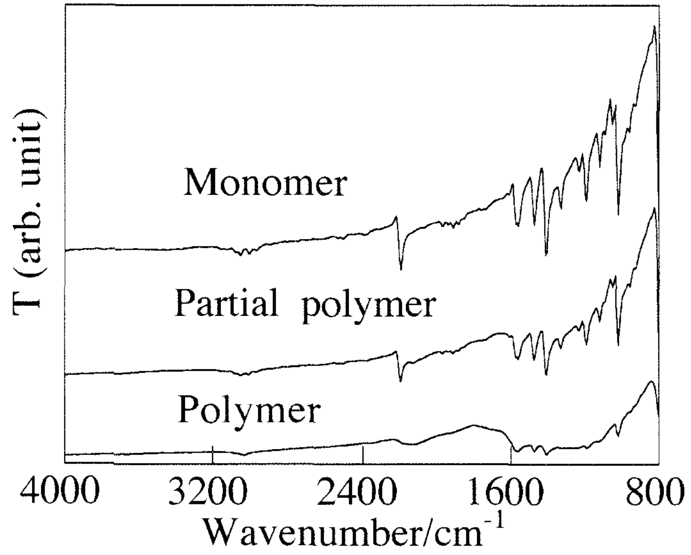


**Figure 1.** IR spectra of **6b** (upper), its partial polymer obtained by heating at 110°C for 3 h (middle), and its polymer obtained by heating at 110°C for 24 h (lower).

thienyl or 3-quinolyl groups, which was considered to polymerize in irregular 1,2-addition followed by cyclization reaction to form π-conjugated system but their polymer yield is quantitative [16]. The molecular alignment differences in crystals seem to cause polymer yield variation even in the irregular polymerization process. When UV was irradiated to **6b** for 60 h, only a slight decrease of the $\nu_{C\equiv C}$ peak was found, and the polymer yield was only 10%. The reason for the lower yield compared with the annealed sample is that UV light could not penetrate through the crystals due to colored polymers produced on their surfaces. Thus, thermal treatment is the better method to stimulate the polymerization of **6b**.

As mentioned above, the color of **6b** changed from yellow to green, brown and finally black during polymerization. It proved that polymerization took placed with extension of π-conjugation. Figure 2 shows the UV-visible-near IR diffuse reflectance spectra of the monomer and polymer of **6b** before and after heating. The absorption tail of the polymer extends to the near IR region, and the bands at 352, 376 and 408 nm of the conjugated pyridyl groups became broad after heating. Figure 3 shows the XRD patterns of **6b** and the corresponding polymer after heating at 110°C. The sharp XRD peaks of **6b** indicate its crystalline nature. After heating for 21 h, the monomer and polymer were both present in the product. When heated for 41 h, the monomer crystalline peaks completely disappeared, and only broad amorphous patterns were observed. These data support the large movement of the monomer units from their lattice points to decrease the crystallinity in the course of the solid-state polymerization.

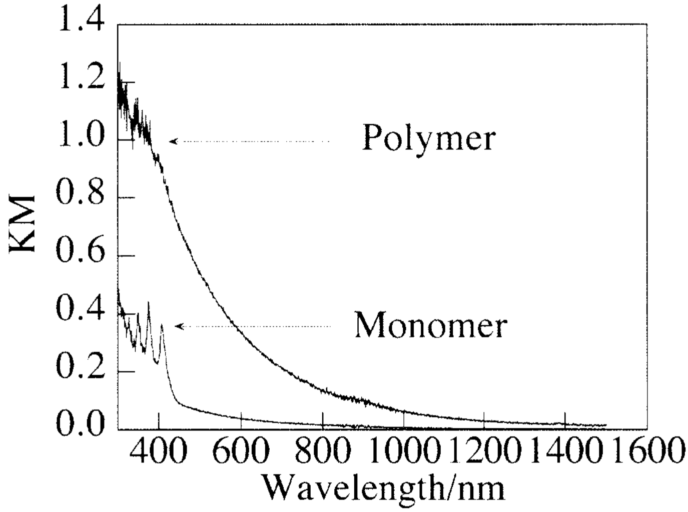


**Figure 2.** UV-VIS-NIR diffuse reflectance spectra of **6b** monomer and its polymer obtained by heating at 110°C for 40 min.

Similar spectral and XRD changes during annealing or UV irradiation to those of **6b** were also observed for **6a** and **6c**, suggesting that these three monomers polymerize in the similar manner in the solid state.

It has been established that the regular 1,4-addition polymerization of butadiyne

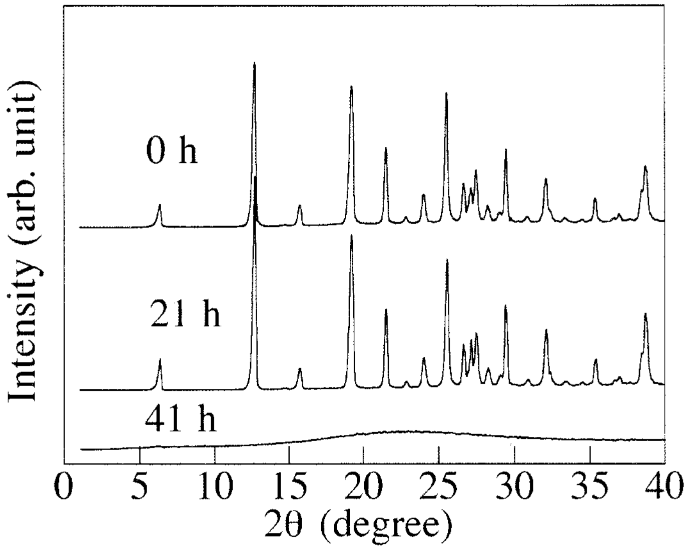


**Figure 3.** Powder XRD patterns of **6b** (upper), its partial polymer obtained by heating at 110°C for 21 h (middle), and its polymer obtained by heating at 110°C for 41 h (lower).

derivatives in crystals only occurs when the stacking distance of monomers in the array is around 5 Å and the angle between the butadiyne rod and the stacking axis is around 45° [17]. Therefore, in order to align the monomers into the polymerizable stack for 1,4-addition, we prepared some salts of **6a**, **6b**, and **6c** by reacting with derivatives of benzoic acid or benzenesulfonic acid. Among the salts obtained, we found that the salt **7b** composed of **6b** and *p*-nitrobenzoic acid could be polymerized in regular 1,4-addition. From IR spectra, **7b** was confirmed to be polymerized quantitatively by heating at 110°C for 40 min. Figure 4 shows the powder XRD patterns of **7b** before and after heating. Although the peak positions were changed between monomer and polymer, the diffraction peaks were also observed in its polymer, suggesting that regular polymerization proceeded.

Figure 5 displays UV-visible-near IR diffuse reflectance spectral change of **7b** in the course of the solid-state polymerization by annealing. There is a broad band in the region shorter than about 900 nm after heating at 110°C for 2 min. Then, an absorption band at around 700 nm appeared. This is considered to be an excitonic band, which is generally observed for the PDA structure obtained by 1,4-addition polymerization of butadiynes. These XRD and spectral results for the polymer from **7b** are striking contrast to those for **6b**. It is interesting that we can utilize pyridyl groups to adjust the structure suitable for 1,4-addition reaction by salt formation.

## Conclusion

We have succeeded in the preparation of a series of octatetrayne derives having directly bound pyridyl groups. The monomers **6a**, **6b** and **6c** can be polymerized by heating or UV irradiation in the solid state to form extended π-conjugation structures. However, irregular polymerization other than 1,4-addition was suggested due to no

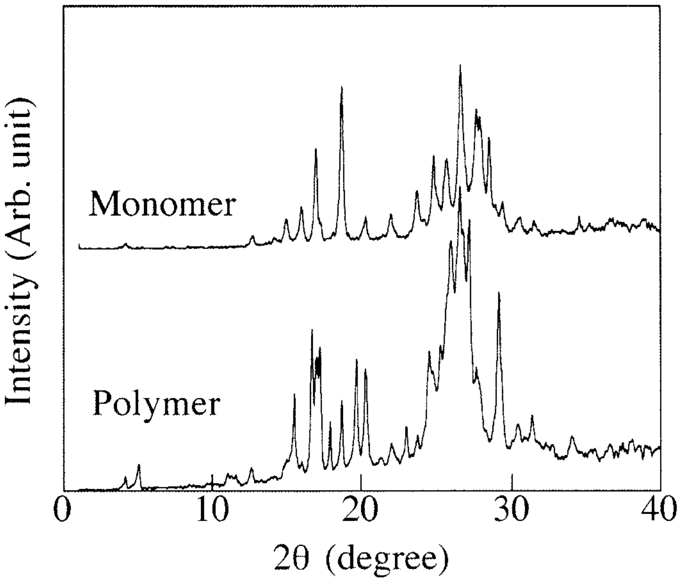


**Figure 4.** Powder XRD patterns of **7b** and its partial polymer obtained by heating at 110°C for 40 min.

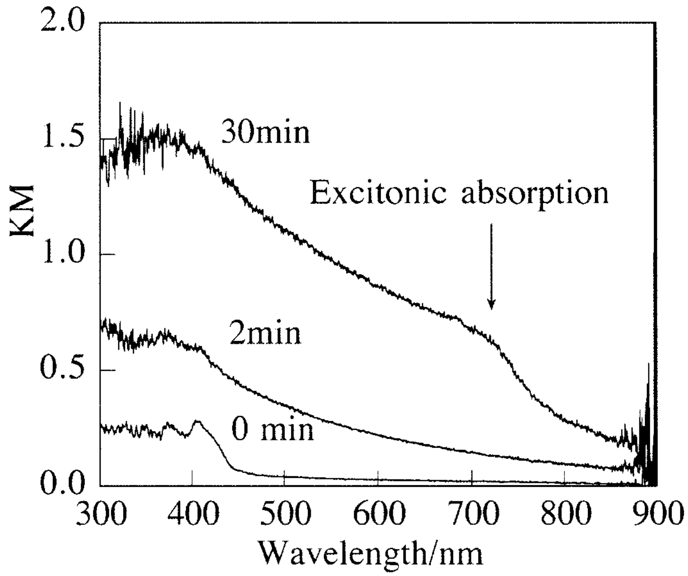


**Figure 5.** UV-VIS-NIR diffuse reflectance spectra of **7b** depending on heating time at 110°C.

excitonic bands and deteriorated crystallinity in the polymers. Then, the presence of pyridine moieties was utilized to form salt with organic acid to change the crystal structure appropriate for the 1,4-addition reaction. When **6b** was combined with *p*-nitrobenzoic acid, such a structure was realized. This work demonstrates that by using the merits of pyridyl side group directly bound to the butadiyne moiety, we can adjust the structure to reach our proposal. Further synthesis of the related compounds and the detailed structural analysis of the polymers are now in progress.

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