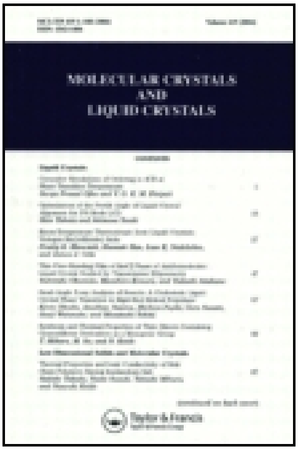

# Molecular Crystals and Liquid Crystals

# Solid-State Polymerization of Monophenylbutadiyne Derivatives

Jun-ichi Watanabe [a], Harumi Yokoyama [a], Shuji Okada [a], Shigeru Takaragi [b], Hiro Matsuda [c] & Hachiro Nakanishi [d]

[a] Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, Yonezawa, Japan

[b] Toda Kogyo Corp., Otake, Hiroshima, Japan

[c] National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

[d] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Aoba, Sendai, Japan

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# Solid-State Polymerization of Monophenylbutadiyne Derivatives

**Jun-ichi Watanabe[1], Harumi Yokoyama[1], Shuji Okada[1], Shigeru Takaragi[2], Hiro Matsuda[3], and Hachiro Nakanishi[4]**
[1]Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, Yonezawa, Japan
[2]Toda Kogyo Corp., Otake, Hiroshima, Japan
[3]National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan
[4]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Aoba, Sendai, Japan

*Solid-state polymerization of phenylbutadiyne derivatives with* o-*nitro,* m-*nitro or* p-*nitro group was investigated. All monomers in bulk crystals could be thermally polymerized to become black suggesting formation of extended* π-*conjugation system. However, no regular polydiacetylene structures were confirmed by the structural analysis. Nanocrystals of the* m-*nitro derivative were prepared, and the different polymerization behavior compared with in the bulk crystals was observed.*

**Keywords:** nanocrystal; polydiacetylene; solid-state polymerization

## INTRODUCTION

Polydiacetylenes (PDAs) are quite unique π-conjugated polymers prepared by solid-state polymerization of butadiyne monomers [1] and they are promising materials for photonics such as third-order nonlinear optics [2]. In order to improve their optical properties, extension of the π-conjugation system is an interesting challenge. PDAs with aromatic rings directly bound to the main chain are the good examples, and higher third-order nonlinear optical properties have

Address correspondence to Shuji Okada, Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510, Japan. E-mail: okadas@yz.yamagata-u.ac.jp

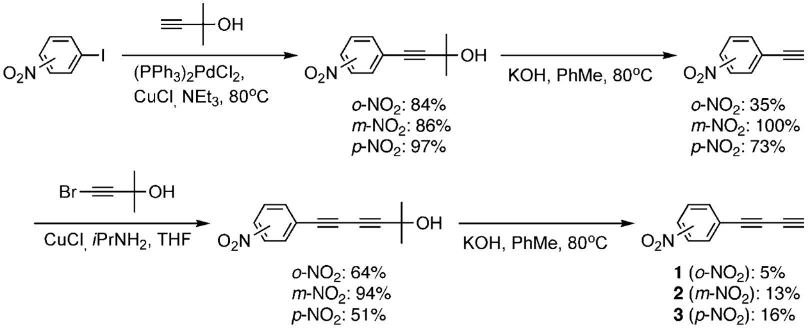

**FIGURE 1** Synthesis scheme of (nitrophenyl)butadiyne derivatives **1** through **3**.

already been reported in some compounds [3]. However, the corresponding monomers, e.g., butadiyne derivatives with two aromatic substituents, are often not polymerizable in crystals. Generally, molecular engineering, such as introduction of intermolecular hydrogen bonding, fluorinated substituents with effective electrostatic interaction, etc., is required to achieve their solid-state polymerization [4]. In this connection, solid-state polymerization of monomers with simpler structures, i.e., monophenylbutadiyne derivatives **1**, **2** and **3** in Figure 1, was investigated in both bulk crystals and nanocrystals in the present study. Although polymerizability of **1-3** has already been confirmed in our preliminary experiments [5], details of the polymer structures and nanocrystallization have not been reported.

## EXPERIMENTAL

Monomers **1-3** were synthesized according to Figure 1. The structures were confirmed by IR spectra and $^1$H- and $^{13}$C-NMR spectra. Melting points of **1**, **2** and **3** are 123–124°C, 97–98°C and 142–143°C, respectively. For photopolymerization, UV at 254 nm was irradiated to the monomer bulk crystals or the monomer nanocrystal dispersions using a 4-W UV lamp (UVP UVG-254). For thermal polymerization, samples were kept at 85°C. IR spectra of the bulk crystals were recorded for KBr-pelletized samples using a Horiba FT-210 spectrometer. Monomer conversions to the corresponding polymers were calculated from the decreasing ratio of the relative intensity of the peak assigned to $\nu_{\equiv\text{C-H}}$ after UV irradiation. UV-visible spectra were obtained using a Jasco V-560 spectrophotometer. For UV-visible spectral measurement of bulk crystals, the KBr-pelletized samples were also used. Solid-state $^{13}$C-NMR spectra were measured using a Bruker MSL-300 spectrometer. Powder X-ray diffraction patterns were measured by using a Mac Science M18XHF$^{22}$-SRA diffractometer with a Cu $K\alpha$ source.

By using the reprecipitation method [6], nanocrystals of **2** were prepared as water dispersion. THF solution of **2** (5 mmol/L, 200 μL) was injected into 10 ml of stirred pure water. The microwave-assisted method [7] was also applied. Average crystal sizes in dispersion were evaluated by dynamic light scattering (DLS) using an Otsuka DLS-6000 photometer.

## RESULTS AND DISCUSSION

Solid-state polymerization of **1**-**3** could be monitored by decrease of an absorption peak corresponding to $\nu_{\equiv \text{C-H}}$ in IR spectra. Figure 2 shows IR spectral change of **2** in the course of thermal annealing as a typical example. All monomers showed thermal reactivity and time to complete the thermal polymerization at 85°C was 1 h for **2**, 2 h for **1** and

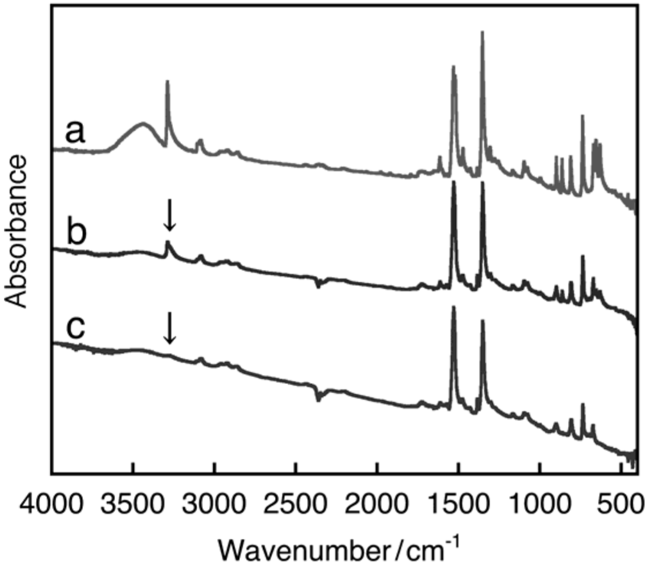

**FIGURE 2** IR spectral change of **2** in the course of solid-state polymerization at 85°C. Spectrum a is for the monomer, and spectra b and c were obtained after heating for 20 min and 1 h, respectively. The arrows indicate the position of the decreased peak for $\nu_{\equiv \text{C-H}}$.

12 h for **3**. By UV irradiation, **1** and **2** could be polymerized although *p*-substituted compound **3** was not reacted. From these results, alignment of monomer **3** in the bulk crystals is slightly deviated from the appropriate condition for solid-state polymerization, and molecular motions activated by annealing seem to stimulate the polymerization. The order of difference between melting point and thermal polymerization temperature was $\mathbf{3} > \mathbf{1} > \mathbf{2}$, suggesting that the order of relative magnitude of molecular motion at 85°C was $\mathbf{3} < \mathbf{1} < \mathbf{2}$. This relation seemed to be reflected to the time to complete thermal polymerization. Diffuse reflectance spectra of **2** during UV irradiation are shown in Figure 3. Other compounds also showed similar spectral change in the course of polymerization whether UV irradiation or thermal treatment. Although all monomers changed to black after polymerization, typical excitonic absorption peaks often observed for regularly polymerized PDAs were not observed. In the solid-state $^{13}$C-NMR spectra, acetylenic carbon peaks decreased and all aromatic carbon peaks were broadened after polymerization (Fig. 4). In addition, polymers from **1–3** were confirmed to be amorphous by powder X-ray diffraction experiments (Fig. 5). Thus, crystal structures of the monomers in this study are disordered during solid-state polymerization and PDAs with

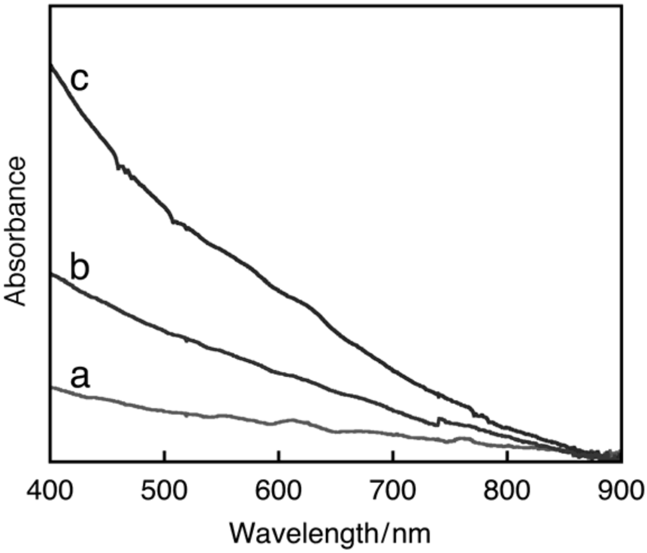

**FIGURE 3** Variation in visible absorption spectra of **2** with UV irradiation time. Spectrum a is for the monomer, and spectra b and c were obtained after UV irradiation for 1 h and 2 h, respectively.

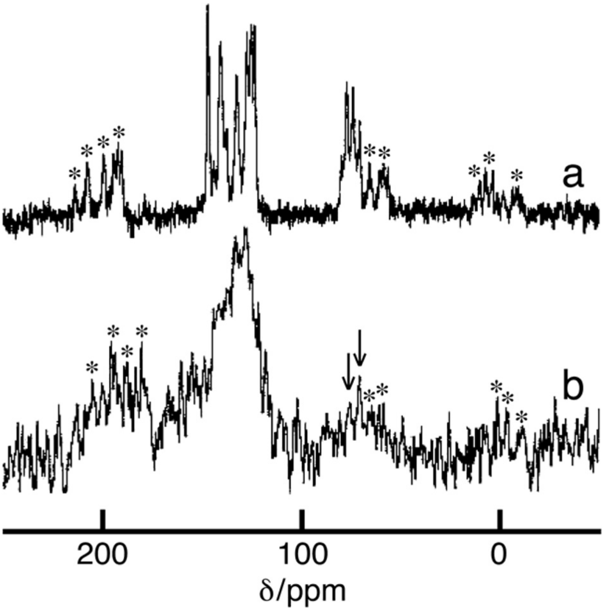

**FIGURE 4** Solid-state $^{13}$C-NMR spectra (CP/MAS) of **2**. Spectra a and b are for before heating and after heating for 20 min, respectively. The arrow indicates the decreased peaks for monomer acetylenic carbons. Spinning sidebands are marked with asterisks.

regular structures were not obtained although extended $\pi$-conjugation system was produced after polymerization.

Nanocrystals of **2** could be prepared using its THF solution. Although crystal size just after reprecipitation could not be measured by DLS, crystal size gradually increased and it became about 250–300 nm after one day. Microwave irradiation just after reprecipitation was found to accelerate the nucleation and rapid crystal-size increase up to 70 nm was observed at the initial stage. However, the size still increased depending on time even in this case, and the final size reached to about 250 nm. Its UV polymerization was confirmed by the UV-visible absorption change as shown in Figure 6. Large absorption bands in the wavelength range shorter than 300 nm decreased and absorption cutoff was extended to around 450 nm. However, absorption increase in visible region was limited in the shorter-wavelength range compared with the bulk crystals (cutoff $\sim$900 nm) and the effective conjugation length of the polymers in the nanocrystals was suggested to be shorter than that of bulk crystals.

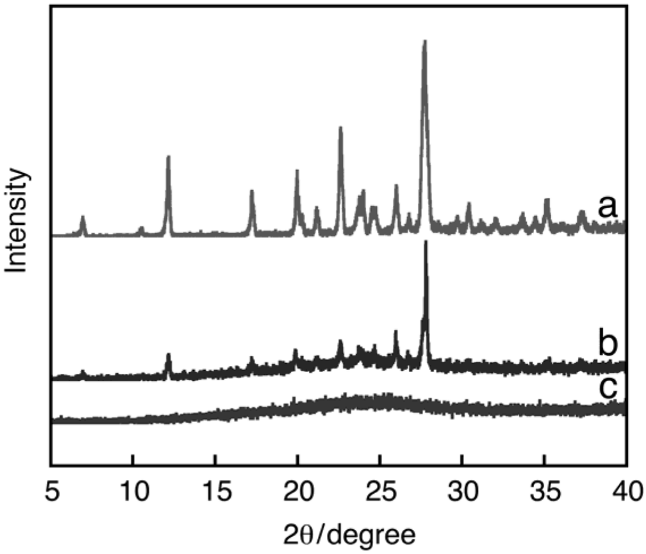

**FIGURE 5** Powder X-ray diffractograms of monomer **2** (a) and **2** after heating for 1 h (b) and 2 h (c).

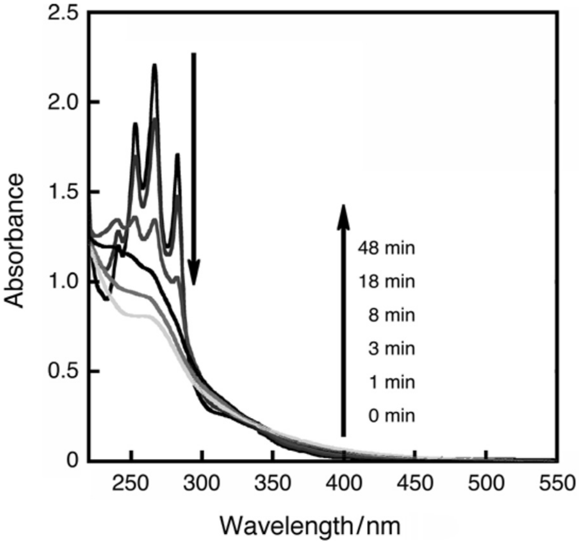

**FIGURE 6** Variation in UV-visible absorption spectra of **2** as nanocrystals in water with UV irradiation time.

UV irradiation at 302 nm also showed the similar spectral change. Although bulk crystals of **2** are thermally polymerizable as mentioned above, thermal polymerization was not observed for the nanocrystals even at 90°C. From these results, crystal structures of **2** seem to be different between bulk crystals and nanocrystals, resulting in different solid-state polymerization behaviors. In the previous study, we found that 1,4-di(3-quinolyl)butadiyne (DQ) also showed different polymerization behavior between bulk crystals and nanocrystals [8]. Common feature between **2** and DQ is their plane molecular shapes, and there may be several metastable molecular stacking structures in crystals by slipping adjacent molecules on the molecular $\pi$-electron surfaces.

In conclusion, monophenylbutadiyne derivatives **1-3** was prepared and solid-state polymerization behaviors were studied. In bulk crystals, all monomers showed thermal polymerizability and black polymers with extended $\pi$-conjugation system were obtained. However, their structures are not regular PDAs and $\pi$-conjugation structures are disordered. Nanocrystals of **2** with size of around 250 nm were successfully prepared by the reprecipitation method, and their polymerization behavior was found to be different from that of bulk crystals. Although the regular PDA structures were not obtained in this study, PDAs from monophenylbutadiynes are interesting because electronic perturbation of polymer backbone may be caused by not only $\pi$-conjugation effect from the attached aromatic ring but also intermolecular interaction from the non-substituted side. Thus, further extension on this series of compounds is worth investigating as future works.

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