Polymer Bulletin

Solid-State Polymerization Behavior of 1,3-Bis(3-quinolyl)-1,4-butadiyne

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Summary

1,4-Bis(3-quinolyl)-1,3-butadiyne (DQ) is known to be polymerized in solid state to give the corresponding polydiacetylene. However, the polymer yield of DQ bulk crystals is low. Thus, we prepared several types of DQ crystals by different procedures to find the reason for the low polymer yield. We found three modifications of DQ crystals and they were evaluated by spectroscopic measurements and X-ray diffraction. DQ bulk crystals (Crystal I) and thermally grown DQ crystals on Crystal I (Crystal II) have the same structure classified to Type A, which gives regular polydiacetylene structure in low polymer yields. DQ crystals grown on glass plates by sublimation (Crystal III) belong to the second modification of Type B. DQ nanocrystals prepared by the reprecipitation method (Crystal IV) are Type B, and thermally grown DQ crystals on nanocrystals (Crystal V) are Type C. Crystals of Types B and C could be polymerized in low yields without showing excitonic absorption of polydiacetylene indicating irregular polymerization other than 1,4-addition. For crystals of Type A, we found that the 1,4-addition polymerization proceeded only in near-surface portions of the crystals. It can be plausibly explained that mobile monomers in the near-surface portion are only able to take part in their polymerization, resulting in low polymer conversion.

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Introduction

Polydiacetylenes are unique π-conjugated polymers with a highly crystalline feature obtained by the solid-state polymerization of butadiynes [1], and their π-conjugated structure has attracted much attention for applications [2-4]. Thus, their design and synthesis closely related to the monomer structure and the alignment in the crystals were extensively investigated [5]. In principle, when the molecular alignment satisfies the following conditions, i.e., the translation distance d between adjacent monomers along the stacking direction of about 0.5 nm and the angle ϕ between the stacking direction and the butadiyne rod of about 45˚, butadiyne monomers can be polymerized in the topochemical manner [6]. However, in some cases, high polymer yields cannot be achieved even if the condition is realized. A symmetrically substituted butadiyne, 1,4-bis(3-quinolyl)-1,3-butadiyne (DQ) [7], is one of the examples(Scheme1).
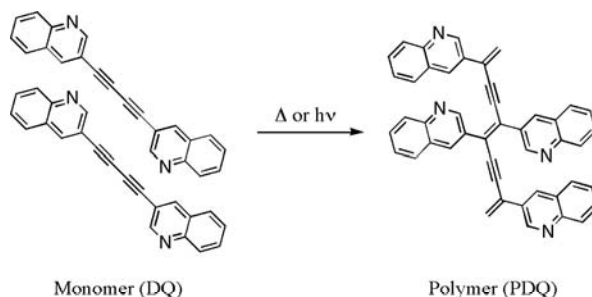
Scheme 1. Solid-state polymerization of DQ.

Although the DQ crystal has d of 0.4807 nm and ϕ of 47.5˚ [8], which are quite near the appropriate conditions, it showed low polymer yield when stimulated by γ-ray irradiation or thermal annealing. In order to examine this fact in detail, we prepared various types of DQ crystals in this study, and their structures and properties were investigated.

Experimental

Monomer DQ was synthesized as reported [7]. The obtained DQ was recrystallized from acetone. Partially polymerized samples of DQ bulk crystals were obtained by UV irradiation from an 8-W UV lamp at 254 nm or thermal annealing at 190˚C in an ambient atmosphere. Polymer of DQ (PDQ) was obtained by extracting the unreacted monomer from the partially polymerized DQ using chloroform as the monomer solvent, and the polymer yield was calculated from the PDQ weight divided by the weight of the partially polymerized DQ. γ-Ray-induced polymerization was also performed for vacuum-sealed samples using a ^{60}Co source with the dose rate of about 10 kGy/h. DQ nanocrystals were fabricated by the reprecipitation method [9]. 1 mmol/l DQ acetone solution (200 μl) was injected into vigorously stirred pure water (10 ml) at ambient temperature to give DQ nanocrystal dispersion. Nanocrystals were collected by the suction filtration using Millipore filter (TYPE VS) with a pore size of about 200 nm. The collected nanocrystals were irradiated by UV or γ-ray.
UV-visible-NIR diffuse reflectance spectra in solid state were recorded for the samples dispersed in KBr powder crystallites on a Jasco V-570 spectrometer. IR

spectra were measured using a Nicolet Avatar-360 spectrometer. High-resolution solid-state ^{13}C NMR spectra were recorded on a Bruker MSL-300 spectrometer with the cross polarization/magic angle spinning (CP/MAS) method. The methylene-carbon peak of external adamantane was set at 29.5 ppm from TMS as a ^{13}C chemical shift in the solid state. The spinning sidebands were clearly distinguishable by using a TOSS (total suppression of spinning sideband) pulse sequence. Dipolar dephasing spectra were also measured to find quaternary carbons. The X-ray diffraction patterns were measured using a Mac Science M19XHF[22]-SRA diffractometer with a CuK$_\alpha$ radiation source. DSC was performed using Rigaku DSC 8240. Optical micrographs were obtained using an Olympus BH2 microscope. A scanning electron microscope (Hitachi S-900) was used to observe the size and shape of nanocrystals

Results and discussion

Solid-State Polymerization of DQ Bulk Crystals

By UV irradiation or annealing, DQ bulk crystals could be polymerized to form polydiacetylene as a blue product as was reported previously [7]. Figure 1 shows the UV-visible-NIR diffuse reflectance spectra of DQ bulk crystals when annealing at 190°C. Since polymerization has been started even at the initial stage of the measurement, the excitonic absorption peak at 672 nm was observed at 0 min. When the sample was annealed, the peak at 672 nm grew fast and almost saturated after 20 min. After 130 min, this peak decreased. On the other hand, the peak at 752 nm continued to increase up to 130 min. This observation was similar to the previous report [10] suggesting the polydiacetylene structure via regular 1,4-addition polymerization.
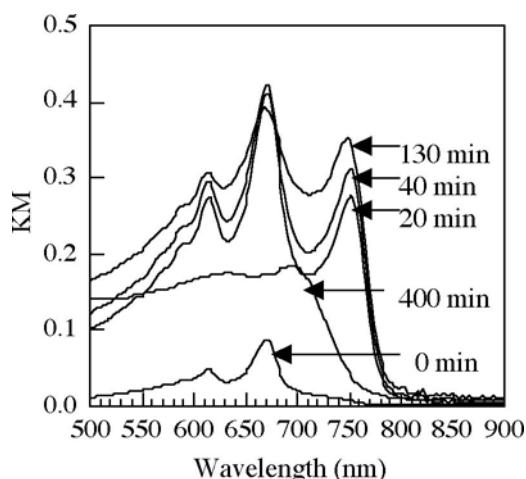

Figure 1. UV-visible-NIR diffuse reflectance spectra of DQ bulk crystals depending on annealing time at 190°C.

However, in IR spectrum of the polymerized sample, the peak corresponding to stretching vibration of C≡C did not disappeared at all. Solid-state ^{13}C CP/MAS NMR

spectra of DQ bulk crystals were also measured before and after annealing in order to gain an insight into the polymer structure (Figure 2). When the 1,4-addition polymerization of butadiyne moieties proceed to give polydiacetylene backbones, a ^{13}C peak of acetylenic carbon within the polymer backbones appears in the range of 101-108 ppm in the solid state [11]. However, in the present case, no clear peak corresponding to acetylenic carbon in the polydiacetylene backbones was observed in the DQ bulk crystals annealed at 190°C, and the peaks for monomer acetylenic carbons of DQ at 78 and 81 ppm remained. This was simply due to low polymer conversion, and actually the polymer yield was less than 5% in our experimental condition.

To confirm the structure of PDQ, we also investigated the ^{13}C NMR spectra of the purified PDQ after extracting the monomer (Figure 3). Comparing the ^{13}C CP/MAS spectrum and the dipolar-dephasing spectrum with TOSS (DD-TOSS), we could find that the two peaks at 78 and 81 ppm for monomer acetylenic carbons disappeared indicating that PDA was formed. At 104 ppm, a new peak corresponding to acetylenic carbons of the PDA backbone appeared in DD-TOSS spectrum. The original peak of monomer DQ at 111 ppm (Figure 2) assigned to the carbon at 3-position of the quinoline ring disappeared in Figure 3. Presumably it shifted to 125 ppm during polymerization due to the change in the conjugation between quinolyl groups and the polymer backbone.

In order to investigate the origin of the lower polymer yield, we irradiated γ-ray to DQ bulk crystals. With 1 MGy dose, yield of the blue polymer was only 8.0%. The changes of UV-visible-NIR diffuse reflectance spectra and ^{13}C CP/MAS NMR spectra
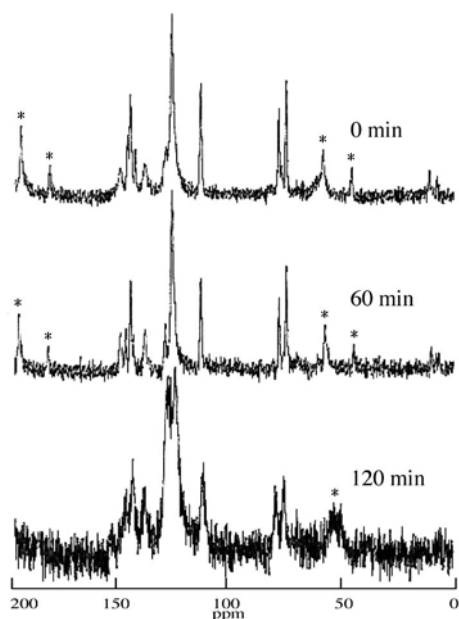

Figure 2. ^{13}C CP/MAS NMR spectra of DQ bulk crystals depending on annealing time at 190°C. Asterisks indicate spinning sidebands.
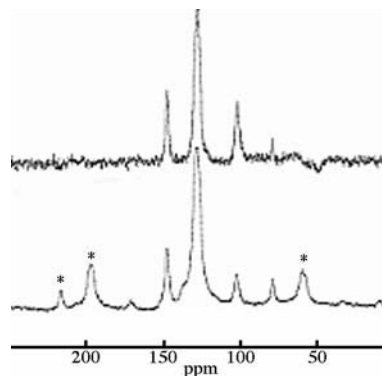

Figure 3. ^{13}C NMR spectra of purified PDQ: Upper, dipolar depasing with TOSS; Lower, CP/MAS. Asterisks indicate sidebands. A peak at around 80 ppm in the upper figure is considered to be due to an impurity incorporated in the polymer or an artifact.

of bulk DQ crystals irradiated by γ-ray showed the similar results with those obtained by the above annealing experiments (Figures 4 and 5). Although the polymer yield was slightly improved up to 8.0% by γ-ray irradiation, it was still lower than we expected.

During the annealing experiment of DQ bulk crystals, interesting phenomena were observed. Upon heating the DQ bulk crystals at 190°C, crystal growth of DQ on the DQ bulk crystals was observed. This seemed to be due to partial sublimation. Hereafter, we call the original DQ bulk crystals as Crystal I and the grown crystals on
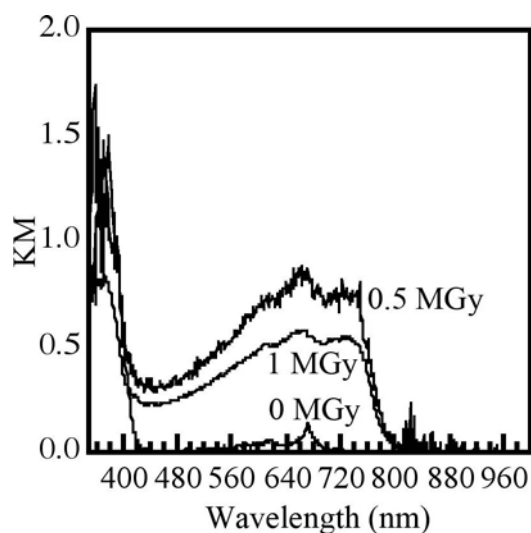
Figure 4. UV-visible-NIR diffuse reflectance spectra of DQ bulk crystals depending on γ-ray dose.
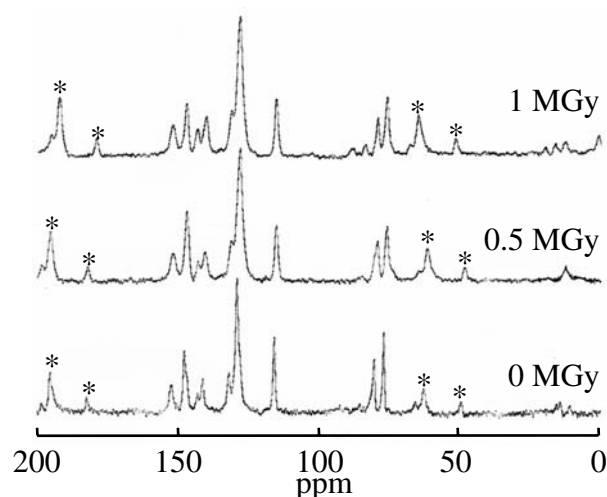
Figure 5. ^{13}C CP/MAS NMR spectra of DQ bulk crystals depending on γ-ray dose. Asterisks indicate spinning sidebands.

Crystal I as Crystal II. Crystal II has a needle shape and it could be polymerized to become blue after annealing. When the DQ crystals were further heated at 190˚C for more than one day or heated at higher temperature than 190˚C, another crystals (Crystal III) were grown on a glass plate, which was placed just above the DQ crystals. This is really gas-phase crystal growth by sublimation. These behaviors are schematically shown in Figure 6 together with the photographs of the crystals. Powder XRD patterns of Crystal II were the same as those of Crystal I, and we call this modification as Type A (Figure 7 (a)). Crystal III was found to have a different crystal structure compared with Type A crystals. Hereafter this modification is called Type B (Figure 7 (b)). The absorption change of Type B crystals in the course of polymerization was similar to that of nanocrystals discussed later.
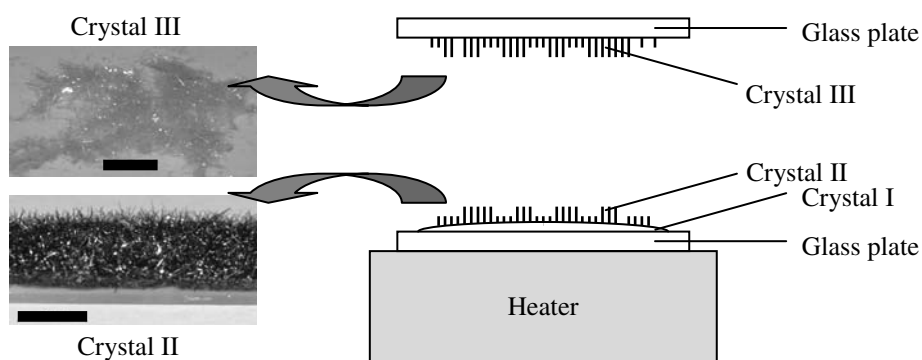

Figure 6. Photographs of DQ bulk crystals (Crystal I) sample after annealing at 190˚C for a prolonged time. The sample surface was covered with needle-shape crystals of Crystal II and crystals (Crystal III) were also formed on a glass plate above the bulk crystals. The bars in the photographs indicate 5 mm length.
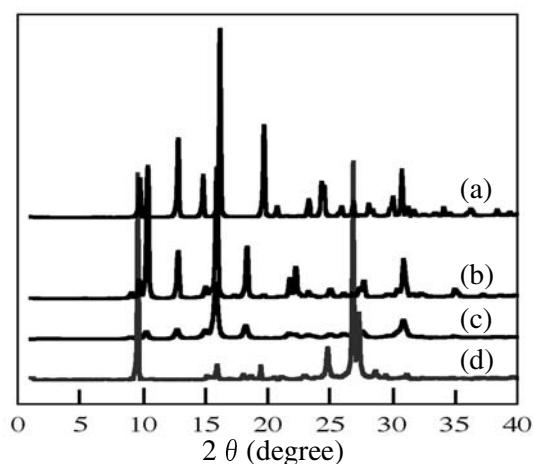

Figure 7. Powder XRD patterns of DQ modifications: (a) bulk crystals (Type A), (b) crystals grown on a glass plate by sublimation (Type B), (c) nanocrystals (Type B), and (d) crystals grown on nanocrystals by heating (Type C).

Interestingly, thermal polymerization of Crystal II was predominantly recognized near the surface of the crystals and inner parts of the crystals remained to be colorless. When a partially polymerized crystal was washed with chloroform under an optical microscope, crystal outlines were almost retained even after monomer extraction (Figure 8). If the polymer chains were produced randomly within the crystals, the shape of the crystal should not be maintained. Thus, it was confirmed that polymerization of Crystal II occurred only in near-surface portions of the crystals. Plausible explanation of this phenomenon is that mobility of the molecules is different between near surface and inside, and more mobile near-surface monomers can only take part in their polymerization.
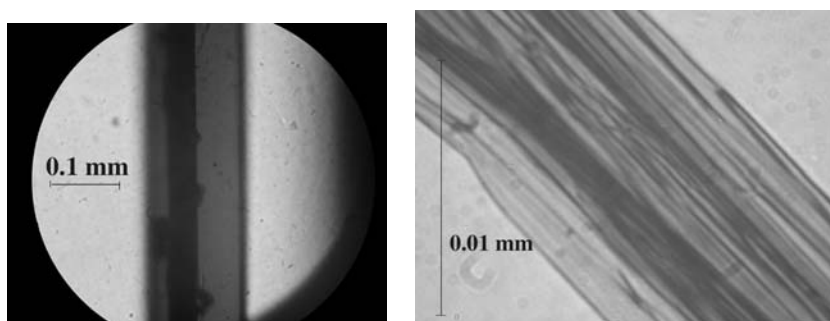

Figure 8. Optical micrographs of a bulk DQ crystal heated for 1 h: (a) just after heating and (b) after extracting unpolymerized monomer from the heated sample with chloroform.

Solid-State Polymerization of DQ nanocrystals

Since polymerization of Type A crystals only proceeded in the near-surface portions, we thought that increasing the surface area of the crystals could enhance the polymer conversion. In order to achieve larger surface areas respect to the unit volume, we applied a nanocrystallization technique for DQ. DQ nanocrystals (Crystal IV) prepared by the reprecipitation method had a size of about 200 nm as shown in Figure 9. The UV-visible-NIR diffuse reflectance spectra of Crystal IV were recorded before and after γ-ray irradiation (Figure 10). After irradiation, the absorption tail extended to the NIR region and the color of the samples became dark brown. Since there was no excitonic absorption band in visible region, Crystal IV seemed to polymerize in irregular polymerization other than regular 1,4-addition polymerization to give PDA. The irregular polymerization suggested that DQ monomer alignment in nanocrystals were not fully suitable for solid-state polymerization, and it caused the low polymer yield less than 5%. From powder XRD patterns, Crystal IV was found to have the same crystal structure as Crystal III, i.e., Type B (Figure 7 (c)). Difference between Type A and Type B crystals was also observed in their ^{13}C chemical shifts. The monomer acetylenic peaks at 78 and 81 ppm of Type A crystals are overlapped at 79ppm as a broad peak in Type B crystals. Even in the case of DQ nanocrystals, crystal growth was observed on the nanocrystal surfaces upon heating (Figure 11). The grown crystals (Crystal V) with a thin plate shape were found to have a crystallographic structure different from the former two modifications. This

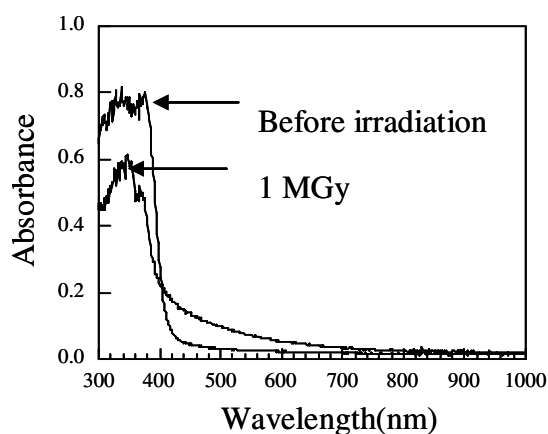**Figure 9.** Scanning electron micrograph of DQ nanocrystals (Crystal IV).

Figure 10. UV-visible-NIR diffuse reflectance spectra of DQ nanocrystals before and after γ-ray irradiation.
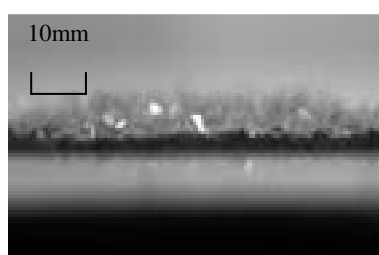

Figure 11. Photograph of DQ nanocrystals (Crystal IV) sample after annealing at 190˚C for a prolonged time. The sample surface was covered with plate-shape crystals of Crystal V.

modification is called Type C (Figure 7 (d)). The absorption change is similar to that of Crystal IV, indicating that irregular polymerization took place. When the DQ crystals were further heated at 190˚C for more than one day or heated at higher temperature than 190˚C, crystals were also grown on a glass plate placed above the

crystals, just as the case of the DQ bulk crystals. This crystal structure was confirmed to be Type B by powder XRD. Table 1 summarizes the obtained DQ crystals and their structures and properties.

Table 1. Various DQ crystals prepared and their properties

Crystal	Preparation method	Modification	Shape	Melting point / °C	Polymerization[a]
I	Recrystallization from acetone	A	Needle	231	Regular
II	Growth on Crystal I by heating	A	Needle	231	Regular
III	Growth on glass by heating	B	Silk	229	Irregular
IV	Reprecipitation	B	Ellipsoid	230	Irregular
V	Growth on Crystal IV by heating	C	Thin plate	236	Irregular

[a] Regular polymerization indicates production of the polydiacetylene structure with the excitonic absorption.

Conclusions

We investigated polymerization behaviors of DQ using various spectroscopic measurements and X-ray diffraction. Although DQ bulk crystals (Type A) were polymerized in the 1,4-addition manner, the polymer yield was low not only after annealing but also after γ-ray irradiation. We found DQ crystals grown on a glass plate by sublimation (Type B). We also fabricated DQ nanocrystals (Type B), and found DQ crystals thermally grown on DQ nanocrystals (Type C). These crystal structures were different each other and crystals of Types B and C were polymerized in low yields without showing excitonic absorption of polydiacetylene, indicating irregular polymerization other than 1,4-addition. Polymorphism of DQ has not been reported so far. From observation of a polymerized DQ bulk crystal under an optical microscope, we confirmed that 1,4-addition polymerization proceeded only in near-surface portions. Plausible explanation of this phenomenon is that mobility of the molecules are different between near surface and inside of the crystals and only mobile near-surface monomers can take part in their regular polymerization resulting in low polymer conversion.

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