Polymerization of a Butadiyne Derivative in Crystalline State Stimulated by Radical Initiators

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Solid-state polymerization of a butadiyne derivative initiated by radical species was investigated for the first time. In the nanocrystals, monomers were fully converted to the polydiacetylenes as the case of conventional photopolymerization. In bulk crystals, polymerization occurred only the parts near the specific crystal surfaces.

Butadiyne derivatives are known to be polymerized in crystalline state to give polydiacetylenes (PDAs) when the butadiyne monomers are aligned in proper conditions in crystals.[1] PDAs are considered to be one of the promising materials for third-order nonlinear optical applications,[2] and modifications of the electronic structures[3] and crystal fabrication in a variety of sizes[4,5] have been investigated. Usually polymerization of butadiyne crystals is initiated by high-energy electromagnetic waves, such as UV or γ-ray, or by thermal annealing irrespective of the crystal size. In this study, we investigated polymerization of butadiyne crystals stimulated by radical initiators because modification of crystal surfaces for additional functionality to PDA may be possible if we can attach the radical species on the crystal surfaces.

1,6-Di(*N*-carbazolyl)-2,4-hexadiyne (DCHD) used as a butadiyne monomer was synthesized referring to the literature[6] and recrystallized from THF. Uniform water dispersion of DCHD nanocrystals was prepared by the reprecipitation method[5] as follows: 200 µL of DCHD acetone solution (5 mmol/L) was injected using a microsyringe into 10 mL of pure water stirred vigorously at room temperature, and the resulting dispersion was kept at ambient temperature for 20 min.[7] After bubbling nitrogen gas into the dispersion, a water-soluble radical initiator such as potassium peroxodisulfate (KPS) or 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AMPAD) was dissolved in water in concentration of 18.5 mmol/L and, in the typical case, 50 µL of the solution was added to the nanocrystal dispersion. The mixture was heated at 90 °C for polymerization. For comparison, thermal polymerization at 90 °C and photopolymerization using a 4-W UV light (254 nm) at ambient temperature were performed for DCHD nanocrystal dispersion without initiators.

When UV irradiated the DCHD nanocrystal dispersion, the color turned blue. In the UV–vis absorption spectra, the excitonic absorption band of the PDA structure was observed at 645 nm (Figure 1a). Similar color change of the DCHD nanocrystal dispersion into blue by PDA production was observed for both radical initiators (Figures 1b and 1c). Since the DCHD nanocrystal dispersion was not polymerized only by heating at 90 °C without initiators (Figure 1d), it can be concluded that KPS and AMPAD initiate DCHD solid-state radical polymerization in nanocrystals. During heat treatment with radical initiators, absorbance of the excitonic band of PDA increased depending on time and finally saturated as shown in Figure 1. It should be noted that the final absorbance was the same for two radical initiators and coincided with that obtained by UV irradiation, for which quantitative conversion to PDA has already been confirmed by DSC measurements;[8] i.e., the exothermic peak corresponding to heat of polymerization was not observed for UV-irradiated nanocrystals obtained from the dispersion with the absorption spectrum as shown in Figure 1a. Time to reach the absorption saturation can be shortened by increasing the amount of KPS added as shown in Figure 2. Although polymerization was almost terminated after 3 h when 50 µL of KPS solution

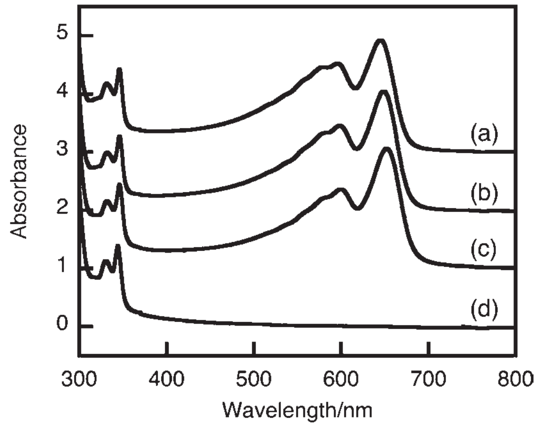

Figure 1. UV–vis absorption spectra of DCHD nanocrystal dispersion: (a) After UV irradiation, (b) after heating with KPS, (c) after heating with AMPAD, and (d) after heating without initiators. All spectra shown are the final ones after continuous changes have been completed. Base lines of each spectrum are shifted by absorbance 1.

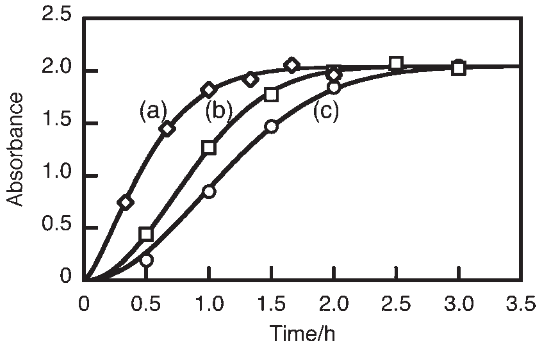

Figure 2. Absorbance changes at the excitonic absorption maximum of DCHD nanocrystal dispersion depending on time after adding KPS solution (18.5 mmol/L). KPS solution amounts added were (a) 200, (b) 100, and (c) 50 µL.

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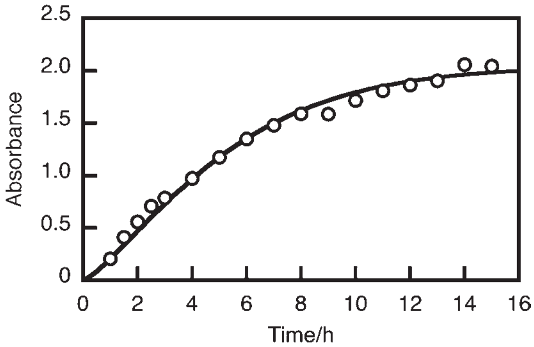

Figure 3. Absorbance changes at the excitonic absorption maximum of DCHD nanocrystal dispersion depending on time after adding 50 µL of AMPAD solution (18.5 mmol/L).

was added, the same polymerization process was finalized after 1.5 h by adding the fourfold amount of KPS solution. In the case of AMPAD, it took 14 h to complete polymerization when 50 µL of the solution was injected (Figure 3). However, reduction of the reaction time for AMPAD failed because precipitation due to coagulation of DCHD nanocrystals occurred when more than 100 µL of AMPAD solution was added. Since initiators used in the present study were electrolytes, the salting-out effect became prominent to aggregate colloidal nanocrystals when the initiator amount was increased. One of the plausible reasons on difference in the absorption saturation time of the excitonic band for two initiators is decomposition rate difference under the present experimental condition.

Since we confirmed that DCHD nanocrystals were able to be polymerized by radical initiators, the same polymerization scheme was applied for DCHD bulk crystals, which had a needle shape when recrystallized from THF. The long-side direction of the crystals corresponds to crystallographic *b* axis, along which solid-state polymerization proceeds.[9] DCHD bulk crystals were soaked in degassed KPS solution and heated at 90 °C for 3 h. The appearance of the resulting crystal is shown in Figure 4. Interestingly, color change of the crystal due to polymerization was observed only both ends of the long-side direction. It can be explained that radical species attacked the end of long-side direction, i.e., the crystal surfaces perpendicular to the polymerization direction, only work as initiators. Since almost no polymerization was observed in the middle part of the crystals regarding to the long-side direction, side attack of radical species is not effective for solid-state polymerization of this crystal.

From these results on solid-state polymerization of DCHD crystals induced by radical initiators, we can conclude that only radical species attacked on the specific crystal surfaces can start the solid-state polymerization. In the case of nanocrystals, the crystal sizes are several hundreds nanometer in side, and radical polymerization can propagate from both end surfaces in one direction and whole monomers in nanocrystals are finally converted to PDA. Since synthesis of PDA with the molecular length corresponding to the crystal size has been reported for UV-induced solid-state polymerization,[10] most of monomer arrays were converted to PDA linearly extending from one crystal end to the other end. On the other hand, polymerization of bulk crystals was stopped by defects randomly existing in the crystals, and only edge portions were polymerized after the radical initiator attack on the specific crystal surfaces. To the best of our knowledge, solid-state polymerization initiated by radical attack from the media surrounding the crystals is reported for the first time. Detailed polymerization mechanisms are being investigated. Since end-modified PDA was produced in crystals, their chemical and physical properties are worth investigating in future works.

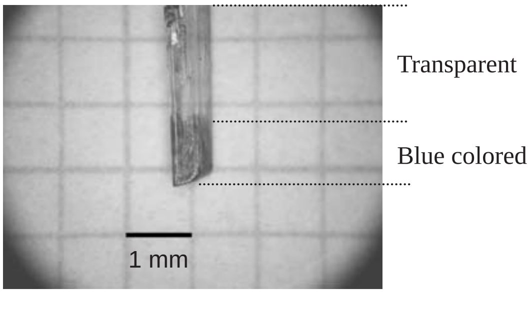

Figure 4. Appearance of a DCHD bulk crystal after the reaction in KPS solution.

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References

1 G. Wegner, *Z. Naturforsch.* **1969**, *24b*, 824; V. Enckelmann, in *Polydiacetylenes, Adv. Polym. Sci.*, *63*, ed. by H.-J. Cantow, Springer-Verlag, Berlin, **1984**, p. 91.
2 C. Sauteret, J.-P. Hermann, R. Frey, F. Pradère, J. Ducuing, R. H. Baughman, R. R. Chance, *Phys. Rev. Lett.* **1976**, *36*, 956; G. I. Stegeman, in *Nonlinear Optics of Organic Molecules and Polymers*, ed. by H. S. Nalwa, S. Miyata, CRC Press, Boca Raton, **1997**, p. 799.
3 H. Nakanishi, H. Matsuda, S. Okada, M. Kato, *Polym. Adv. Technol.* **1990**, *1*, 75; S. Okada, M. Ohsugi, A. Masaki, H. Matsuda, S. Takaragi, H. Nakanishi, *Mol. Cryst. Liq. Cryst.* **1990**, *183*, 81; S. Okada, K. Hayamizu, H. Matsuda, A. Masaki, H. Nakanishi, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 857; S. Okada, K. Hayamizu, H. Matsuda, A. Masaki, N. Minami, H. Nakanishi, *Macromolecules* **1994**, *27*, 6259.
4 M. Thakur, S. Meyler, *Macromolecules* **1985**, *18*, 2341.
5 H. Kasai, H. S. Nalwa, H. Oikawa, S. Okada, H. Matsuda, N. Minami, A. Kakuta, K. Ono, A. Mukoh, H. Nakanishi, *Jpn. J. Appl. Phys.* **1992**, *31*, L1132.
6 V. Enkelmann, G. Schleier, G. Wegner, H. Eichele, M. Schwoerer, *Chem. Phys. Lett.* **1977**, *52*, 314; K. C. Yee, R. R. Chance, *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 431.
7 H. Katagi, H. Kasai, S. Okada, H. Oikawa, K. Komatsu, H. Matsuda, Z. Liu, H. Nakanishi, *Jpn. J. Appl. Phys.* **1996**, *35*, L1364; H. Kasai, H. Katagi, R. Iida, S. Okada, H. Oikawa, H. Matsuda, H. Nakanishi, *Nippon Kagaku Kaishi* **1997**, 309; H. Katagi, H. Kasai, S. Okada, H. Oikawa, H. Matsuda, H. Nakanishi, *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 2013; H. Oikawa, T. Oshikiri, H. Kasai, S. Okada, S. K. Tripathy, H. Nakanishi, *Polym. Adv. Technol.* **2000**, *11*, 783.
8 R. Iida, Master Thesis, Tohoku University, **1994**.
9 V. Enkelmann, R. J. Leyrer, G. Schleier, G. Wegner, *J. Mater. Sci.* **1980**, *15*, 168.
10 R. Iida, H. Kamatani, H. Kasai, S. Okada, H. Oikawa, H. Matsuda, A. Kakuta, H. Nakanishi, *Mol. Cryst. Liq. Cryst.* **1995**, *267*, 95; S. Okada and H. Nakanishi, *Int. J. Nonlinear Opt. Phys.* **1994**, *3*, 501.
11 Z. Wei, H. Miura, A. Masuhara, H. Kasai, S. Okada, H. Nakanishi, *Jpn. J. Appl. Phys.* **2003**, *42*, L1213; Z. Wei, K. Ujiiye-Ishii, A. Masuhara, H. Kasai, S. Okada, H. Matsune, T. Asahi, H. Masuhara, H. Nakanishi, *J. Nanosci. Nanotechnol.* **2005**, *5*, 937.

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