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# **Solid-State Polymerization Behaviors of Polydiacetylene Nanofibers**

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# Solid-State Polymerization Behaviors of Polydiacetylene Nanofibers

The conversion curve of solid-state polymerization in polydiacetylene (PDA) nanofibers (NFs) was so different from that of PDA nanocrystals (NCs). PDA NFs clearly showed the longer induction period, and the conversion rate was much higher than that of PDA NCs. These differences have been discussed on the basis of thermally softened crystal lattice in PDA NFs and/or PDA NCs. In addition, the excitonic absorption peak position of PDA NFs was red-shifted, compared with PDA bulk crystals. This fact suggests that PDA chains inside PDA NFs would be almost strain-free and the effective  $\pi$ -conjugation is fully extended possibly to the maximum level.

Keywords: polydiacetylene, nanofibers, nanocrystals, solid-state-polymerization, conversion rate, excitonic absorption peak

## INTRODUCTION

Polydiacetylene (PDA) is a unique one-dimensional  $\pi$ -conjugated polymer, which is usually synthesized by topochemical solid-state polymerization of diacetylene (DA) monomer in a crystal state [1-3], and one of the most promising organic nonlinear optical (NLO) materials [4-7]. In fact, PDA exhibits large third-order NLO susceptibility, so-called  $\chi^{(3)}(\omega)$ , and femto-second order of highly optical response. Some NLO effects induced and emerged through optoelectronic interaction are very important and key technology toward optoelectronic and/or photonic devices applications such as optical shutter, optical circuits, optical memory, and so on [8-10].

On the other hand,  $\pi$ -conjugated organic and polymer nanocrystals (NCs) (hereinafter, organic NCs), including PDA NCs, have been extensively investigated so far by developing the reprecipitation method [11-12]. Crystal size- and shape-controlled organic NCs could be successfully fabricated by experimentally optimizing the reprecipitation conditions. The crystal size is typically in the range of several tens nanometers to sub-micrometers. These well-defined organic NCs have interestingly

provided crystal size-dependence of linear optical properties in the extinction (excitonic absorption) and/or fluorescence emission spectra [11-14]. In a word, an electron state including exciton and lattice interaction is so strongly influenced by crystal size and shape in organic NCs, due to thermally softened crystal lattice structure with decreasing crystal size [13-15]. As part of morphological (crystal size and shape)-controlled organic NCs, PDA nanofibers (NFs) have been recently produced successfully and highly reproducibly, when a surfactant such as sodium dodecyl sulfate (SDS) was suitably added to the reprecipitation process [11,12,16]. However, solid-state polymerization behaviors and linear optical properties (excitonic absorption spectrum) are still unclear until now in the case of PDA NFs.

In the present article, the dependence of solid-state polymerization behaviors and linear optical properties on morphological effects will be discussed in detail by monitoring the extinction (excitonic absorption) spectral changes during the formation process of PDA NFs.

## **EXPERIMENTAL SECTION**

### ***Materials***

Diacetylene (DA) monomer used was 1,6-di(*N*-carbazolyl)-2,4-hexadiyne (DCHD) [2]. DCHD and sodium dodecyl sulfate (SDS) were purchased from Wako Pure Chemical Industries Ltd. and Sigma-Aldorich Co. LLC, respectively. All the solvents were also purchased from Wako Pure Chemical Industries Ltd. with 99% purity or greater, and used without purification.

### ***Fabrications of PDA NCs and PDA NFs, and their characterization***

PDA NCs were prepared by the ordinary reprecipitation method [11-12], and PDA NFs

were also fabricated by the reprecipitation process as follows [16]. A 200  $\mu\text{L}$  of DCHD - acetone solutions (5 mM) containing SDS (1 mM) was quickly injected into vigorously stirred pure water (10 mL) as a poor medium at given temperature, after the retention time for about 30 min, followed by UV-irradiation ( $\lambda = 254 \text{ nm}$ ,  $1.55 \text{ W m}^{-2}$ ) to convert DA into the corresponding PDA [poly(DCHD)] through solid-state polymerization [1-3], which behaviors were monitored by means of UV-Vis spectrometer (JASCO, V-570). The resulting PDA NCs and PDA NFs were characterized with scanning electron microscope (SEM: JEOL, JSM-6700F) after platinum sputtering.

## RESULTS AND DISCUSSION

Figure 1 displays the typical SEM images of PDA NCs and PDA NFs. The crystal size of PDA NCs is *ca.* 100 nm, whereas the diameter and counter length of PDA NFs are about 50 nm and more than several  $\mu\text{m}$ , respectively. It was especially necessary to control water temperature as a poor medium in the reprecipitation method so as to produce well-defined PDA NFs [11,12,16]. In addition, the crystal lattice structure of PDA NFs was the same as those of PDA NCs and/or PDA bulk crystals from the measurement with powder X-ray diffraction (XRD) patterns [16].

As illustrated in Figure 2, PDA provides the excitonic absorption peak around at  $\lambda = 650 \text{ nm}$  in wavelength, which is originated from  $\pi$ -conjugation along PDA backbone formed by solid-state polymerization [1-3,17-19]. The small and broad absorption peak from  $\lambda = 580 \text{ nm}$  to  $620 \text{ nm}$  is assigned to phonon-side band [1-3]. The intensity of excitonic absorption peak became simply stronger without changing the peak positions with increasing UV-irradiation time during solid-state polymerization in the present case.

Figure 3 exhibits the characteristic conversion curves of PDA NCs and PDA NFs, which displays the plots of normalized extinction calculated from intensity changes of

excitonic absorption peak vs. UV-irradiation time during solid-state polymerization. Compared with PDA NCs, one can see some characteristic behaviors in the case of PDA NFs, that is to say, clearly long induction period at the initial stage, quiet quick and rapid conversion rate at the middle stage, and the relatively short completion time of solid-state polymerization at the latter stage. Actually, these experimental results in Figure 3 could be well reproduced by means of so-called Sigmoid function, Eq. (1), in any PDA NCs and PDA NFs as drawn with solid lines.

$$f_{Extinction}(t) = C_{Base} + \frac{C_{Max}}{1 + \exp\{-\alpha(t - t_{1/2})\}} \quad (1)$$

Where,  $C_{Base}$  and  $C_{Max}$  are adjustable parameters to produce a fitting curve. The gain constant,  $\alpha$ , in Eq. (1) was  $1.39 \times 10^{-2} \text{ s}^{-1}$  for PDA NFs, and much larger than that of PDA NCs ( $5.97 \times 10^{-3} \text{ s}^{-1}$ ). In addition, the half time of completion time for solid-state polymerization,  $t_{1/2}$ , was 622.5 s in PDA NFs, and was shorter than that of PDA NCs (724.5 s). These obtained parameters in Eq. (1) would evidently reflect the difference in dynamics of solid-state polymerization between PDA NFs and PDA NCs, which will be discussed in details later, relating to the rigidity of crystal lattice structure.

On the other hand, the excitonic absorption peak position of PDA NFs ( $\lambda_{exc, PDA NFs} = 660 \text{ nm}$ ) was red-shifted obviously, rather than typical PDA NCs with *ca.* 100 nm in crystal size ( $\lambda_{exc, PDA NCs} = 643 \text{ nm}$ ) and/or PDA bulk crystals ( $\lambda_{exc, PDA bulk crystal} = 655 \text{ nm}$ ) (not shown) as shown in Figure 4. The  $\pi$ -conjugation of PDA backbone is practically parallel to the long axial direction of PDA NFs [11-14], which corresponds to the b-axis in the unit cell of DA monomer crystal [2]. Such kind of obvious red-shift in excitonic absorption peak suggests that the effective  $\pi$ -conjugation is more fully extended and its length becomes longer possibly to the maximum level in PDA NFs [2,19]. This provides

the possibility that  $\chi^{(3)}(\omega)$  would be more enhanced in accordance to the so-called three-state model [20,21], in which  $\chi^{(3)}(\omega)$  is proportional to band gap energy to the power of -6. Thus, PDA NFs, *i.e.*, poly(DCHD) NFs, are expected as one of the most promising organic third order NLO materials among PDA derivatives.

As mentioned in Introduction, crystal lattice structure in organic NCs is thermally softened by comparison with the corresponding bulk crystals on the basis of crystal size-dependence of linear optical properties [11-14], owing to highly large specific surface area and reduction of intermolecular interactions in a crystal lattice [13-15]. Probably, the rigidity of crystal lattice structure for PDA NFs is an intermediate state between PDA NCs and the corresponding PDA bulk crystals, because the nanometer-scale diameter of PDA NFs is almost the same as the typical crystal size of PDA NCs [11,12], whereas the counter length along long axial of PDA NFs corresponds to bulk-like micrometer scale. In addition, solid-state polymerization proceeds through DA monomer crystal - to - PDA crystal phase transition in the case of poly(DCHD) bulk crystal [2,3]. Table 1 lists the crystallographic lattice parameters of DCHD and poly(DCHD) in bulk crystal state [22]. This kind of phase transition would occur as the same manner even in poly(DCHD) NCs and/or poly(DCHD) NFs [11-13], and the difference in lattice parameters between DA monomer and PDA is responsible for crystal lattice strain induced and accumulated during solid-state polymerization.

As demonstrated in Figure 5, the following mechanisms are now speculated from the difference in dynamic behaviors of solid-state polymerization between PDA NCs and PDA NFs. Probably, crystal lattice strain induced inside PDA NFs would be efficiently accumulated at the initial stage of solid-state polymerization, and afterward promptly released with increasing UV-irradiation time at the latter stage, because of properly (or moderately) intermediate rigidity of crystal lattice structure, compared with PDA NCs

and/or PDA bulk crystals. In other words, the size of phase transition domain induced in PDA NFs would be relatively larger than that of PDA NCs, which would lead to some peculiar dynamic behaviours of solid-state polymerization as shown in Figure 3. On the contrary, the size of phase transition domain is relatively small in PDA NCs, and then the solid-state polymerization would proceed gradually (or relatively slowly).

Namely, the most important and interesting results in PDA [poly(DCHD)] NFs are the quiet rapid conversion rate and the more red-shift of excitonic absorption peak, corresponding to relatively longer effective  $\pi$ -conjugation length along PDA chains inside PDA NFs, than that of PDA bulk crystals. These behaviours are probably caused by the effective accumulation and quick release of strain induced during crystal - to - crystal phase transition type solid-state polymerization [2,3], owing to moderate rigidity of crystal lattice in one-dimensional PDA NFs between PDA NCs and PDA bulk crystals [23]. As a result, there is little residual strain in PDA chains inside PDA NFs, that is to say, “almost strain-free” in the present study.

## **CONCLUSIONS**

The dynamic behaviors of solid-state polymerization have been investigated in PDA NFs by comparison with PDA NCs and/or PDA bulk crystals. The resulting PDA chains formed inside PDA NFs would be almost strain-free, and the effective  $\pi$ -conjugation is fully extended possibly to the maximum level, which would lead to red-shift of excitonic absorption peak in PDA NFs. Namely, PDA NFs [poly(DCHD) NFs] and their oriented thin films have morphologically much advantageous to provide excellent NLO properties as one of the most promising organic third-order NLO materials toward photonic devices application [15,23,24].

## **ACKNOWLEDGEMENTS**



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#### CONFLICTS OF INTEREST

There are no conflicts to declare.

#### REFERNCES

[1] Wegner, G. (1997). *Pure & Appl. Chem.*, 49, 443.

- [2] Enkelmann, V. (1984). *Adv. Polym. Sci.*, *63*, 91.
- [3] Oldenburg, S. J., Averitt, R. D., Westcott, S. L., & Halas, N. J. (1998). *Chem. Phys. Lett.*, *288*, 243.
- [4] Miller, D. A. B., Chemla, D. S., Eilenberger, D. J., Smith, P. W., Gossard, A. C., & Tsang, W. T. (1982). *App. Phys. Lett.*, *41*, 679.
- [5] Sauteret, C., Helmann, J.-P., Frey, R., Pradère, F., Ducuing, J., Baughman, R. H., & Chance, R. R. (1976). *Phys. Rev. Lett.*, *36*, 956.
- [6] Matsuda, M., Molyneux, S., Kar, A. K., Wherrett, B. S., Okada, S., & Nakanishi, H. (1993). *J. Photopolym. Sci. Technol.*, *6*, 261.
- [7] Giorgetti, E., Margheri, G., Sottini, S., Chen, X., Cravino, A., Comoretto, D., Cuniberti, C., Dell'Erba, C., & Dellepiane, G. (2000). *Synth. Met.*, *115*, 257.
- [8] Bäessler, H. (1984). *Adv. Polym. Sci.*, *63*, 1.
- [9] Oikawa, H., Onodera, T., Masuhara, A., Kasai, H., & Nakanishi, H. (2010). *Adv. Polym. Sci.*, *231*, 147.
- [10] Yarimaga, O., Jaworski, J., Yoon, B., & Kim, J.-M. (2012). *Chem. Commun.*, *48*, 2469.
- [11] Oikawa, H., Kasai, H., & Nakanishi, H. (2001). *Fabrication of Organic Microcrystals and Their Optical Properties*, eds. by Glaser, R., & Kaszynski, P. *Anisotropic Organic Materials –Approaches to Polar Order-*, ACS Symposium Series 798, ACS, Washington, 158.
- [12] Oikawa, H., & Nakanishi, H. (2003). *Reprecipitation Method for Organic Nanocrystals*, eds. by Masuhara, H., Nakanishi, H., & Sasaki, K. *Nano Science and Technology -Single Organic Nanoparticles-*, Springer, Berlin, 17.
- [13] Oikawa, H. (2011). *Bull. Chem. Soc. Jpn.*, *84*, 233.
- [14] Oikawa, H., Mitsui, T., Onodera, T., Kasai, H., Nakanishi, H., & Sekiguchi, T. (2003). *Jpn. J. Appl. Phys.*, *42*, L111.
- [15] Volkov, V. V., Asahi, T., Masuhara, H., Masuhara, A., Kasai, H., Oikawa, H., & Nakanishi, H. (2004). *J. Phys. Chem. B*, *108*, 7674.
- [16] Iimori, Y., Onodera, T., Kasai, H., Mitsuishi, M., Miyashita, T., & Oikawa, H. (2017). *Opt. Mater. Exp.*, *7*, 2218.
- [17] Weiser, G. (1992). *Phys. Rev. B: Condens. Matter.*, *45*, 14076.
- [18] Hood, R. J., Müller, H., Eckhardt, C. J., Chance, R. R., & Yee, K. C. (1978). *Chem. Phys. Lett.*, *54*, 295.

- [19] Exarhos, G. J., Risen Jr., W. M., & Baughman, R. H. (1976). *J. Am. Chem. Soc.*, *98*, 481.
- [20] Agrawal, G. P., Cojan, C., & Flytzanis, C. (1978). *Phys. Rev. B*, *17*, 776.
- [21] Bubeck, C., Kaltbeitzel, A., Grund, A., & LeClerc, M. (1991). *Chem. Phys.*, *154*, 343.
- [22] Enkelmann, V., Leyrer, R. J., Schleier, G., & Wegner, G. (1980). *J. Mater. Sci.*, *18*, 168.
- [23] Tashiro, K., Nishimura, H., & Kobayashi, M. (1996). *Macromolecules*, *29*, 8118.
- [24] Wong K. Y., & Garito, A. F. (1986). *Phys. Rev. A Gen. Phys.*, *34*, 5051.
- [25] Gu, B., Zhao, C., Baev, A., Yong, K.-T., Wen, S., & Prasad, P. N. (2016). *Adv. Opt. Photonics*, *8*, 328.

## CAPTIONS

**Table 1** Crystallographic lattice parameters of diacetylene (DA) [DCHD] monomer and the corresponding polydiacetylene (PDA) [poly(DCHD)] in bulk crystal state.

\* Difference in lattice parameters before and after solid-state polymerization

**FIGURE 1** SEM images of (a) polydiacetylene (PDA) [poly(DCHD)] nanocrystals (NCs) and (b) PDA [poly(DCHD)] nanofibers (NFs).

**FIGURE 2** Schematic illustrations of extinction (excitonic absorption) spectral changes during solid-state polymerization with increasing UV-irradiation time to convert diacetylene (DA) monomer into the corresponding PDA in a crystal state.

**FIGURE 3** Plots of normalized extinction evaluated from changes of excitonic absorption peak intensities vs. UV-irradiation time for solid-state polymerization in PDA [poly(DCHD)] NCs (closed circles) and PDA [poly(DCHD)] NFs (open circles). The solid lines were simulated by using Eq. (1) in any case.

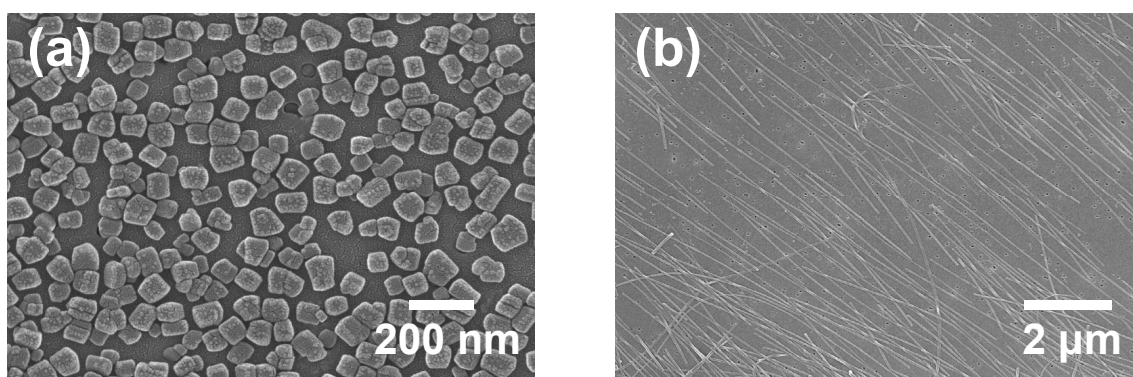
**FIGURE 4** Normalized extinction (excitonic absorption) spectra for aqueous dispersion liquids of PDA [poly(DCHD)] NCs (broken line:  $\lambda_{\text{exc, PDA NCs}} = 643 \text{ nm}$ , *ca.* 100 nm in crystal size) and PDA [poly(DCHD)] NFs (solid line:  $\lambda_{\text{exc, PDA NFs}} = 660 \text{ nm}$ ). PDA [poly(DCHD)] bulk crystals exhibit  $\lambda_{\text{exc, PDA bulk crystal}} = 655 \text{ nm}$ .

**FIGURE 5** Proposed mechanisms for solid-state polymerization processes in the cases of PDA NCs and PDA NFs. The areas surrounded by the dotted lines display to phase transition domains.

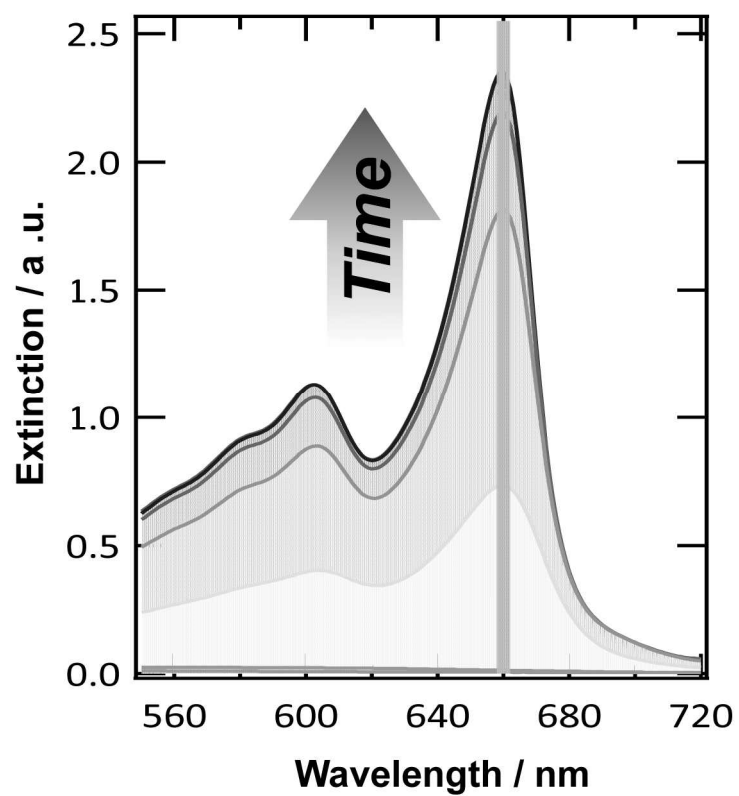
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	<i>DCHD</i>	<i>Poly(DCHD)</i>	<i>Variations</i> <sup>*</sup>
<i>a (nm)</i>	1.360	1.287	5.4% down
<i>b (nm)</i>	0.455	0.491	7.9% up
<i>c (nm)</i>	1.760	1.740	1.1% up
$\beta$ (°)	94.60	108.3	14° up
<i>Z</i>	4	4/n	
<i>Space group</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	
<i>d (kg m<sup>-3</sup>)</i>	$1.25 \times 10^{-3}$	$1.30 \times 10^{-3}$	

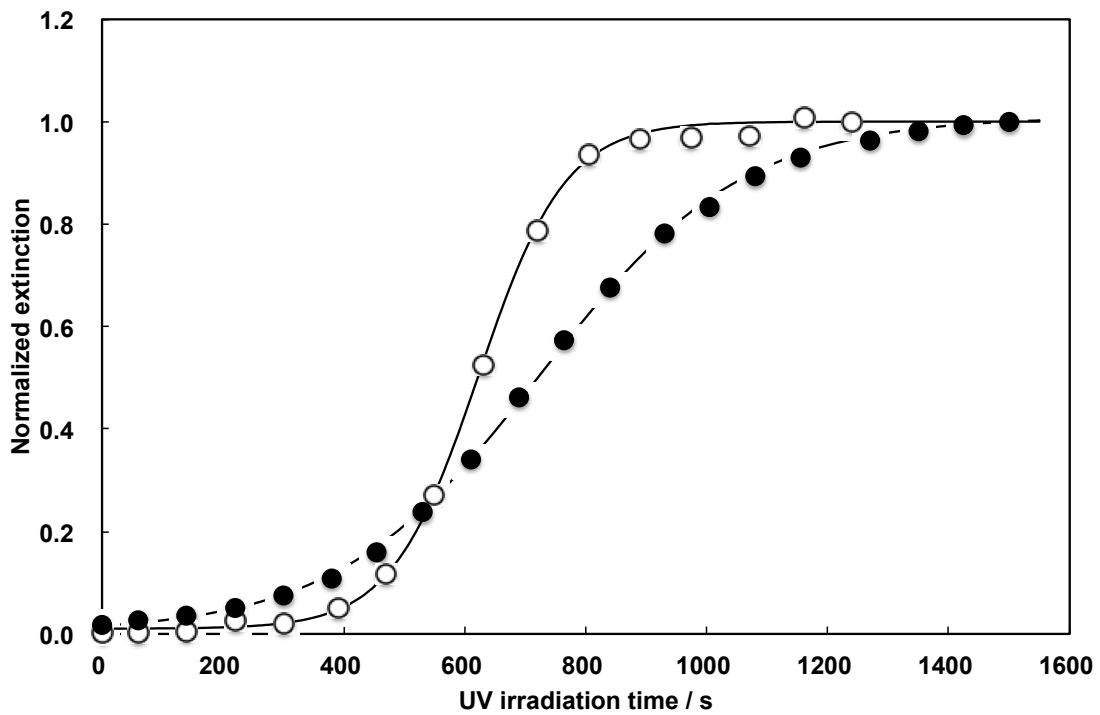
\* Difference in lattice parameters before and after solid-state polymerization



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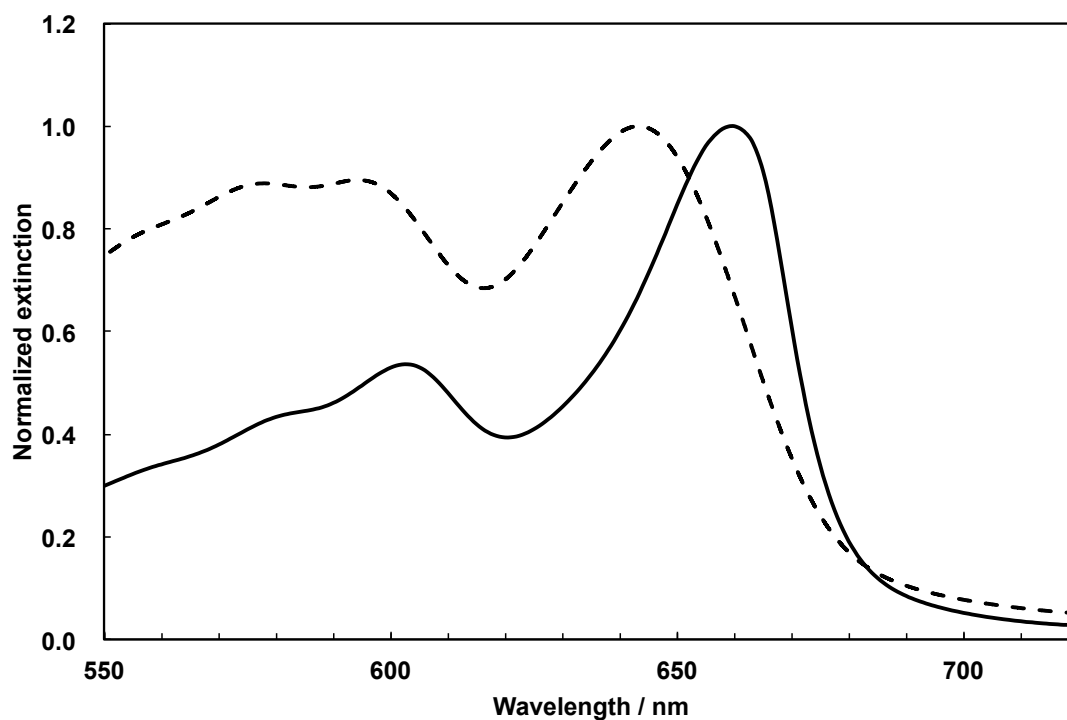


**FIGURE 2** Schematic illustrations of extinction (excitonic absorption) spectral changes during solid-state polymerization with increasing UV-irradiation time to convert diacetylene (DA) monomer into the corresponding PDA in a crystal state.

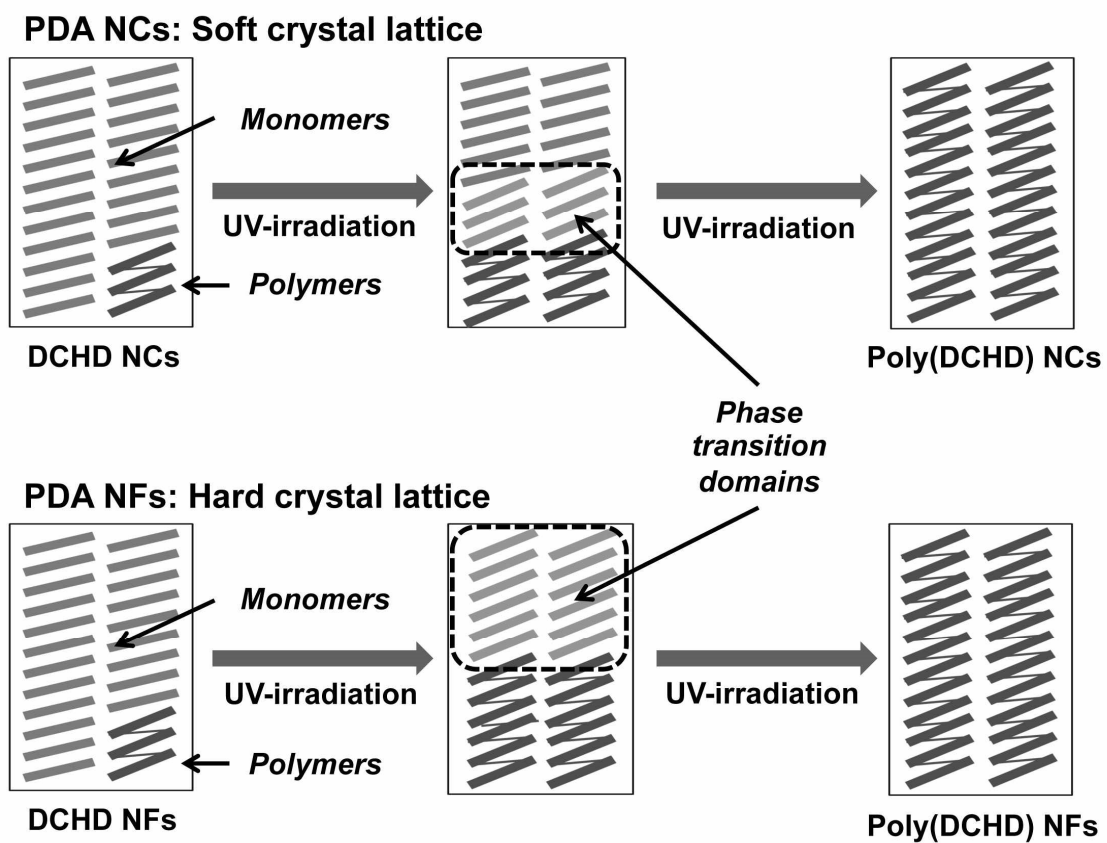


**FIGURE 3** Plots of normalized extinction evaluated from changes of excitonic absorption peak intensities vs. UV-irradiation time for solid-state polymerization in PDA [poly(DCHD)] NCs (closed circles) and PDA [poly(DCHD)] NFs (open circles). The solid lines were simulated by using Eq. (1) in any case.





**FIGURE 4** Normalized extinction (excitonic absorption) spectra for aqueous dispersion liquids of PDA [poly(DCHD)] NCs (broken line:  $\lambda_{\text{exc, PDA NCs}} = 643 \text{ nm}$ , *ca.* 100 nm in crystal size) and PDA [poly(DCHD)] NFs (solid line:  $\lambda_{\text{exc, PDA NFs}} = 660 \text{ nm}$ ). PDA [poly(DCHD)] bulk crystals exhibit  $\lambda_{\text{exc, PDA bulk crystal}} = 655 \text{ nm}$ .



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