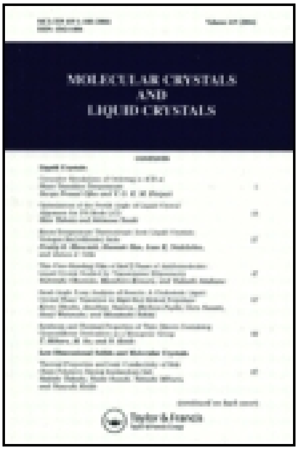

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Fabrication of Diacetylene Nanofibers and their Dynamic Behavior in the Course of Solid-State Polymerization

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Fabrication of Diacetylene Nanofibers and their Dynamic Behavior in the Course of Solid-State Polymerization

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The size-controlled diacetylene nanocrystals and/or nanofibers are fabricated by the reprecipitation-microwave irradiation method. It is found that the worm-like monomer nanofibers are converted into straight-like ones during the solid-state polymerization.

Keywords: diacetylene; microwave; nanocrystal; nanofiber; polydiacetylene; reprecipitation; solid-state polymerization

INTRODUCTION

The research of the topochemical polymerization has been reported extensively since the 1960s [1,2]. In this context, polydiacetylenes, a π-conjugated polymer system has received much attention as conductive and non-linear optical materials [3]. Because of the accumulation of strain in bulk crystal during the solid-state polymerization, the resulting crystals are often crushed, and the rate of polymeric conversion does not occur with high efficiency. We find that the polymerization

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taking place in the nanocrystal state of this polymer has scope to give rise to high quality polymeric crystal because the strain accumulated in nanocrystals is easily released [4]. Recently, we have been reporting that many kinds of organic nanocrystals are fabricated by a facile technique "the reprecipitation method" and/or the advanced ones [5,6]. The size of crystal is controlled by changing the experimental condition. In particular, nanofibers with an average length of 10 μm and an average width of 50 nm are obtained [7,8]. In this paper, we introduce "the reprecipitation-microwave (RMI) method" [9,10] for the fabrication of diacetylene nanofibers. Furthermore, we report the interesting behavior of morphology change of nanofibers at the stage of the solid-state polymerization.

EXPERIMENTAL

The monomeric diacetylene compound used in this study was 1,6-di(*N*-carbazoly)-2,4-hexadiyne (DCHD). Poly(DCHD) nanofibers were fabricated by the RMI method as described below. DCHD monomer was dissolved in acetone to give a 0.1 mM solution. First, 200 μl of this acetone solution was rapidly injected to 10 ml of water under vigorously stirring, taken in a glass container. The entire reaction mixture was subsequently transferred from the glass container to a Teflon sealed vessel (P-25, San-ai Kagaku). The Teflon sealed vessel was under microwave irradiation (2.45 GHz, 500 W, EMO-C4-(TB), SANYO) for a given time, typically 40 s. After cooling down to room temperature in few minutes, the resulting DCHD monomer nanofibers in water dispersion were solid-state polymerized by irradiation of UV ($\lambda = 254\,\mathrm{nm}$) light to obtain the poly(DCHD) nanofibers. The crystal size and shape were evaluated by scanning electron microscopy (SEM: JSM-6700F, JEOL). Visible (VIS) absorption spectra were measured by UV-VIS spectrometer (550 V, JASCO).

RESULTS AND DISCUSSION

Figure 1 shows the relationship between the concentration of DCHD monomer in acetone solution and the sizes of the obtained nanocrystals. When the concentration of the acetone solution is 9.0 mM, the shape of the obtained crystals is roughly cube-like with the size *ca.* 150 nm. Upon the concentration of the acetone solution becoming lower to 5.0 mM, the shape changes to rod-like with size *ca.* 300 nm along long axis. When the concentration is lowered down to 0.1 mM,

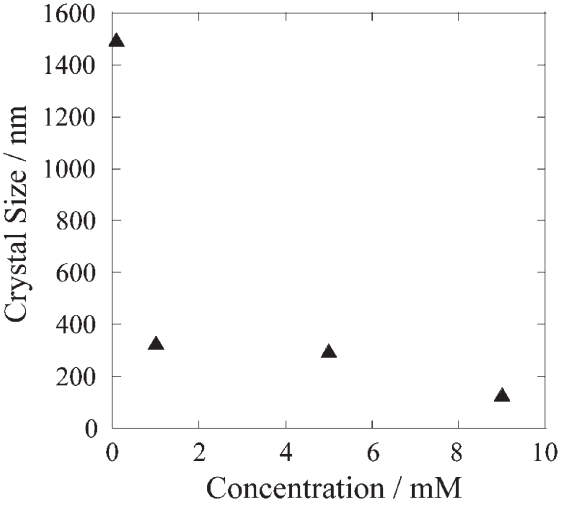

FIGURE 1 Relationship between concentration of injected acetone solution and the size of poly(DCHD) nanocrystals and/or nanofiber.

the shape of products becomes fibrous, with the length of the fibers approximating few micrometers in the direction of long axis. It appears that at a very dilute concentration regime of the DCHD monomer,

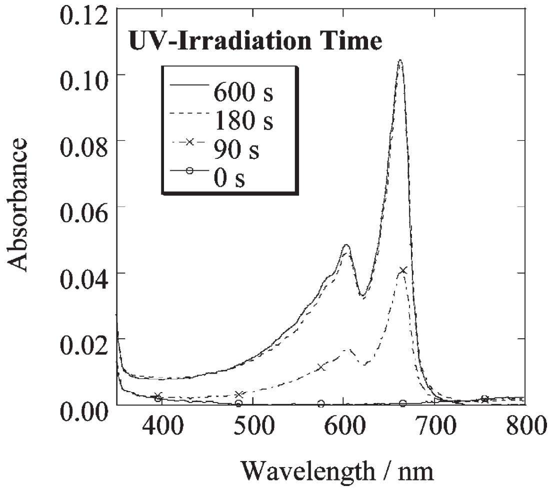

FIGURE 2 Absorption spectra of DCHD nanofiber water dispersion after irradiating of UV light. Irradiation time of UV light was (a) 0 s, (b) 90 s, (c) 180 s, and (d) 600 s.

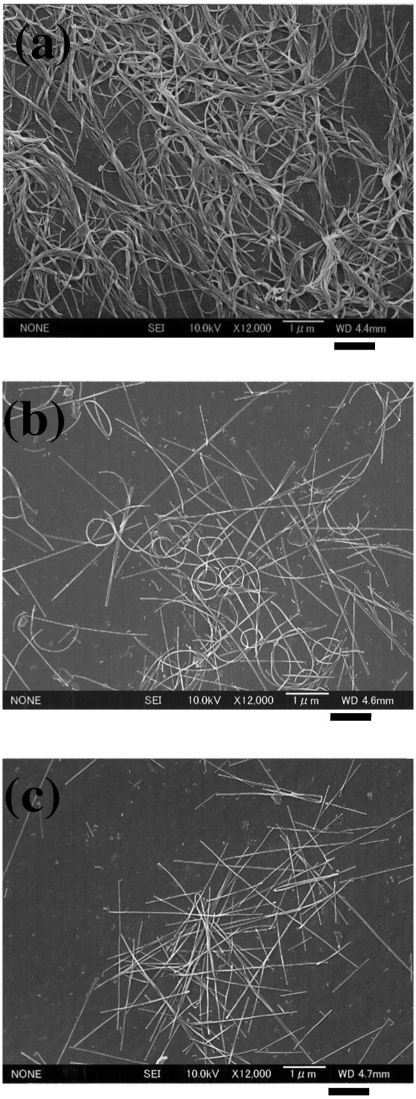

FIGURE 3 SEM images of DCHD nanofiber which were exposed by UV light for given time. Irradiation time of UV light was (a) 0 s, (b) 90 s, (c) 180 s, and (d) 600 s. The scale bar is 1 μm.

one-dimensional crystal growth in the direction of the long axis occurs. From a materials science view point, it is remarkable that we can control the contour length by simply changing the initial concentration of DCHD monomer in acetone solution.

When an aqueous dispersion of DCHD nanofibers is put under UV-light irradiation, the excitonic absorption peak gradually appears around 662 nm (Fig. 2). Thus, the solid-state polymerization does not occur in amorphous state of DCHD, polymerization of DCHD nanofibers proceeds as in the crystalline state. As shown in Figure 2, the polymerization is completed in 10 min of UV-irradiation because the exciton peak is saturated. Furthermore, the rate of conversion of monomer into polymer is recognized to proceed to almost 100% completion as determined by the measurement of absorbance of residual monomer eluted by acetone from poly(DCHD) nanofibers. We observed a morphological change of DCHD nanofibers in the course of solid-state polymerization (Fig. 3). DCHD monomer nanofibers which are fabricated by the RMI method are worm-like before solid-state polymerization as shown in Figure 3(a). Interestingly, worm-like nanofibers are converted into straight-like ones through the solid-state polymerization, as shown in Figures 3(b) and (c). It is inferred that morphological change of nanofibers is based on the strain-induced deformation in the direction of the one-dimensional π-conjugate main chains. In other words, this phenomenon also underscores the fact that the lattice in nanofibers and/or nanocrystals is generally soft, compared with that of bulk crystals.

CONCLUSION

The size-controlled poly(DCHD) nanocrystals and/or nanofibers are successfully fabricated by the RMI method. We observe that the worm-like monomer nanofibers are morphologically changed into rigid polymer nanofibers in the course of solid-state polymerization. Thus, the final products of crystalline nanofibers are composed of many π-conjugate polymer chains which can be useful for the estimation of cohesion of molecules, bond energy of π-conjugated system and/or the conductivity of a single polymer chain.

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