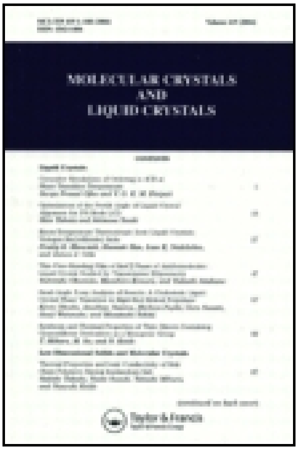

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Fabrication of Polydiacetylene Fibrous Microcrystals by the Reprecipitation Method

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Version of record first published: 24 Sep 2006

To cite this article: Toshiyuki Oshikiri, Hitoshi Kasai, Hideyuki Katagi, Shuji Okada, Hidetoshi Oikawa & Hachiro Nakanishi (1999): Fabrication of Polydiacetylene Fibrous Microcrystals by the Reprecipitation Method, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 337:1, 25-30

To link to this article: http://dx.doi.org/10.1080/10587259908023370

Mol. Cryst. and Liq. Cryst., 1999, Vol. 337, pp. 25-30
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Fabrication of Polydiacetylene Fibrous Microcrystals by the Reprecipitation Method

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The size and morphology control of polydiacetylene microcrystals has been investigated by changing preparation conditions such as temperature and added surfactant in the reprecipitation method. As a result, fibrous microcrystals (diameter: 50 nm, length: 5–10 μm) of conjugated polymers were interestingly fabricated under an optimum condition. The formation mechanism of polydiacetylene fibrous microcrystals and their optical properties were also investigated.

Keywords: microcrystals; polydiacetylene; fibrous microcrystals; reprecipitation method

INTRODUCTION

Polydiacetylene, which is an unique one-dimensional π-conjugated polymer, is much of interests in both linear and nonlinear optics (NLO). For example, the bulk single crystals of poly[1,6-di(*N*-carbazolyl)-2,4-hexadiyne (DCHD)] are reported to exhibit large third-order nonlinear optical susceptibilities in the resonant region[1]. However, it is extremely difficult to bring out the high performance in its device configuration, because of poor transparency, fabricatability and so on. On the contrary, microcrystal dispersion systems are considered to be one of the most promising materials in nonlinear optics and microelectronics, owing to low scattering loss. Therefore, we have studied the preparation of organic microcrystals and evaluated their NLO properties[2]. Especially, the microcrystallization processes of DCHD monomer and perylene were investigated in detail[3,4]. As the result, fibrous microcrystals of solid-state polymerizable DCHD could successfully be fabricated under an optimum condition. In the present paper, the formation mechanism of poly-DCHD fibrous microcrystals and their linear optical properties are described.

EXPERIMENT

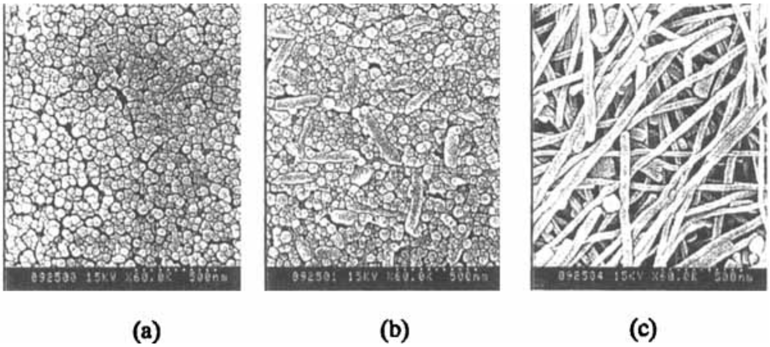
The compound used in the present study was DCHD, which was synthesized by reference to the literature[5]. The fibrous microcrystals of DCHD were prepared by the conventional reprecipitation method as follows[6]. Firstly, 200 μl of DCHD acetone solution (5.0 mM) was injected into vigorously stirred water (10 ml) at 60 ℃ using a microsyringe. After a given retention time (t_r), DCHD fibrous microcrystals was solid-state polymerized by UV-irradiation (254 nm) for 20 minutes. Similarly, the same procedures were carried out at 20 ℃ in the presence of the added surfactant such as anionic sodium dodecylsulfate (SDS).

The size and shape of UV-irradiated DCHD microcrystals were estimated by scanning electron microscope (SEM; Hitachi, S-900). The optical properties were measured with UV-VIS spectrometer (JASCO, V-570 DS).

RESULTS AND DISCUSSION

It was reported that the crystallization of DCHD amorphous microparticles formed at the initial stage has been completed in 20 minutes after the reprecipitation in the case that the water as poor solvent was kept at 20 ℃, and that the final size of DCHD microcrystals was approximately the same as that of initial microparticles[3,7]. These processes were totally confirmed by the measurements with SEM photographs, absorption spectra, powder X-ray diffraction patterns and so on.

On the other hand, when DCHD microparticles were prepared in water at 60 ℃, the crystallization required 90 minutes and then the resulting DCHD microcrystals were fibrous. The diameter and the length were about 60 nm and 5-10 μm, respectively. Figure 1(c) shows SEM photograph of fibrous DCHD microcrystals, depending on t_r. The size of initial microparticles as shown in Fig. 1(a) was dependent not on water temperature but on the concentration of solution. The size of the initial microparticle was about 60 nm at $t_r=0$. This value nearly corresponds to the diameter of fibrous microcrystals.



(a) (b) (c)

FIGURE 1 SEM photographs of DCHD fibrous microcrystals depending on t_r:(a) 0 min, (b) 20 min, and (c) 90 min in water at 60 ℃.

After adding SDS to DCHD acetone solution to stabilize the initial microparticles, the reprecipitation in the same manner was carried out at 20 ℃. Figure 2 shows SEM photographs of DCHD fibrous microcrystals thus obtained at various t_r. In this case, DCHD rod-like microcrystals (diameter: 50 nm, length: 500 nm) were fabricated finally. The rate of crystallization was considerably slow, and it took more than 10 weeks to crystallize completely. It was considered that the DCHD molecules were hard to reorientate in the DCHD amorphous microparticles stabilized by SDS.

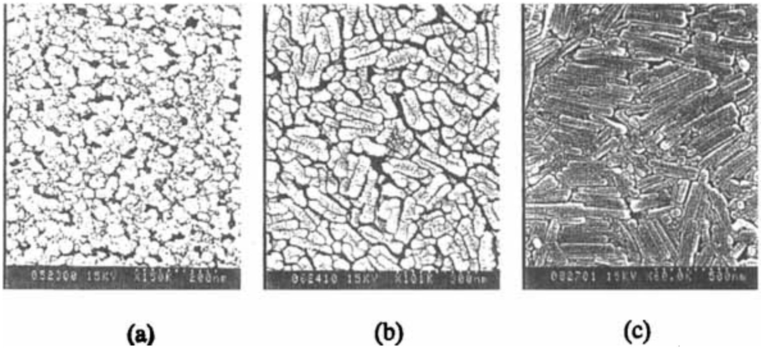

(a) (b) (c)

FIGURE 2 SEM photographs of DCHD fibrous microcrystals depending on t_r:(a) 0 min, (b) 3 weeks, and (c) 10 weeks in water under existence of SDS at 20 ℃.

From the results in Figs. 1 and 2, it was revealed that DCHD microcrystals have grown up one-dimensionally through the collisions between DCHD microparticles and microcrystals, as shown in Fig. 3, at high temperature (60 ℃) or in the presence of SDS. The microcrystals initially formed are considered to play a role as nucleus for growing fibrous microcrystals. And, DCHD microparticles are considered to be adsorbed only on the one specific surface of fibrous microcrystals. Whole these DCHD microcrystals were quantitatively converted into the poly-DCHD microcrystals with the same shape and dimension as the monomer microcrystals by UV-irradiation.

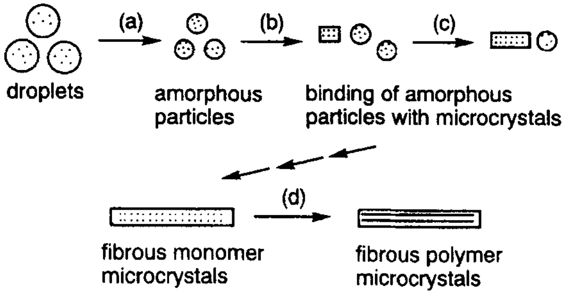


FIGURE 3 The schematic model for the preparation process of fibrous microcrystals after reprecipitation treatment: (a) removing of acetone from droplets and dissolution into surrounding water; (b) reorientation of molecules in the amorphous particles and crystallization; (c) binding between microcrystals and amorphous particles, and then crystallization; (d) solid-state polymerization by UV-irradiation.

Figure 4 shows the absorption spectra of poly-DCHD microcrystals. The crystal size were 70 nm, 150 nm, and fibrous microcrystals. We have already reported that linear optical property of some organic microcrystals was dependent on crystal size[3,8]. For example, the high energy shift of

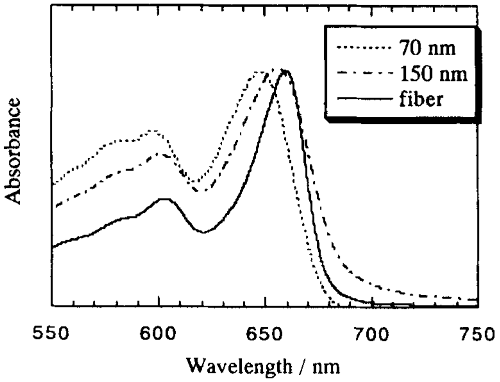


FIGURE 4 Optical absorption spectra of poly-DCHD microcrystals with different crystal size.

the excitonic absorption of peak was strikingly observed in perylene microcrystal, which crystal size was less than about 200 nm. The excitonic absorption peak position of fibrous microcrystals was *ca.* 660 nm, which was almost the same as that of bulk crystals. This fact implies the direction of π-conjugation was the one along the long axis of fibrous microcrystals. The cause of the size effect peculiarly observed in organic microcrystals is presumed to be due to the changes in lattice hardness, but now it is in investigation.

In conclusion, for the first time, we have obtained diacetylene fibrous microcrystals (diameter: 60 nm, length: 5-10 μm), and have clarified the formation mechanism. In addition, linear optical properties were also revealed.

ACKNOWLEDGMENTS

This research was supported by Research Center of Interdisciplinary Science, Tohoku University.

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