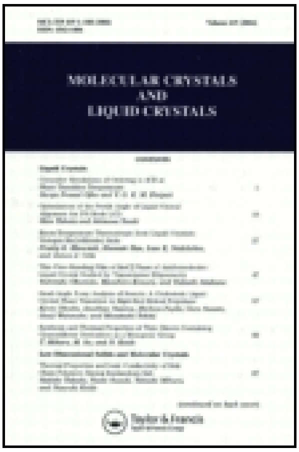

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Rieko Iida , Hirokazu Kamatani , Hitoshi Kasai , Shuji Okada , Hidetoshi Oikawa , Hiro Matsuda , Atsushi Kakuta & Hachiro Nakanishi (1995): Solid-state Polymerization of Diacetylene Microcrystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 95-100

To link to this article: http://dx.doi.org/10.1080/10587259508033979

Mol. Cryst. Liq. Cryst. 1995, Vol. 267, pp. 95–100
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SOLID-STATE POLYMERIZATION OF DIACETYLENE MICROCRYSTALS

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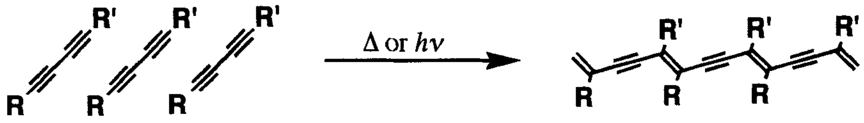
Abstract Microcrystals of two different types of diacetylene monomers, *i.e.* 4BCMU known for giving a soluble polydiacetylene and 14-8 ADA known as an amphiphilic diacetylene, were prepared and in their solid-state polymerization behaviors were investigated. The polymerization of 4BCMU proceeded quantitatively in the perfect crystalline lattice to give blue-colored polymer crystals. Averaged molecular weight of poly-4BCMU was found to be proportional to microcrystal size, implying that the solid-state polymerization proceeds from one end to the other end of microcrystals. 14-8 ADA microcrystals gave very stable water dispersion even after polymerization, so that the detailed analysis of polymerization behaviors was possible. Size-dependent spectral change and final conversion found for 14-8 ADA were discussed in terms of strain and thermal motion of the crystal lattice.

INTRODUCTION

Microcrystals of inorganic semiconductor and metals have been studied because of some possibilities in nonlinear optical properties caused by quantum confinement effect and so on. However, even the method how to fabricate organic microcrystals has not been established so far, owing to their instability at elevated temperature. Recently, we have obtained some organic microcrystals easily at room temperature by the reprecipitation method,[1] which makes use of the difference in solubilities of organic compounds between in organic good solvent and in water (poor solvent). Organic microcrystals were dispersed in water, and their crystal sizes, say several nanometer to several micrometer, could be controlled by the reprecipitation conditions.

We are much interested in the relationship between crystal structure and solid-state polymerization behavior,[2] as shown in Fig. 1, of microcrystals of diacetylene (DA), which are expected to be connected along main chain up to the both ends of microcrystals of the resulting polydiacetylenes (PDA). The two factors *i.e.* the crystal size and the extension of π-conjugation are closely related to nonlinear optics.

In this article, we will describe the preparations of microcrystals of so-called 4BCMU and amphiphilic 14-8 ADA, and discuss solid-state polymerization behaviors of these DA microcrystals in detail, depending on crystal size. 4BCMU was selected for molecular weight investigation of resulting polymers and 14-8 ADA was supposed to give stable dispersion of the polymer microcrystals in water.



4BCMU : **R**- = **R'**- = $CH_3(CH_2)_3OCONHCH_2COO(CH_2)_4$-
14-8 ADA : **R**- = $CH_3(CH_2)_{13}$- , **R'**- = $HOCO(CH_2)_8$-

FIGURE 1 Illustration of solid-state polymerization in diacetylene crystal

EXPERIMENTAL

The DA derivatives used in the present study were 5,7-dodecadiyne-1,12-diyl bis (N-(buthoxycarbonylmethyl)carbamate) (4BCMU), and heptacosa-10,12-dinoic acid (14-8 ADA), which were synthesized by reference to the literatures.[3,4] Both DA microcrystals were prepared by the conventional reprecipitation method.[1] Under the typical condition, the acetone solution of 14-8 ADA (2.0×10^{-2} M, 50 mL) was dropped into 10 mL of purified water stirred vigorously at 20 °C, and then microcrystal, whose size was several nanometer, was obtained as milky dispersion. Here after, in the present paper, we call this microcrystal "several nanometer microcrystal". For preparing "submicrometer microcrystal", the water dispersion obtained at ice-water temperature was further frozen in liquid nitrogen, and was thawed out spontaneously at room temperature. 4BCMU microcrystals were also produced by the same technique. These microcrystals dispersed in water were solid-state polymerized by UV (254 nm : high pressure mercury lamp) or γ-ray (^{60}Co source) irradiation.

The size of microcrystals was evaluated by means of DLS (dynamic light scattering : Otsuka electronics DLS-7000) and SEM (scanning electron microscopy : Hitachi S-900). Platinum was lightly sputtered onto dried microcrystals before SEM observation. The crystal structure of microcrystals was identified by XRD (X-ray diffraction : Shimadzu XD-D1 diffractometer).

Poly-4BCMU microcrystal prepared by γ-ray irradiation was dissolved in chloroform for the measurement with GPC (gel permeation chromatography : Shimadzu LC-8A, Shodex GPC K-80M). Mono-dispersed polystyrene (Toso) was used as standard sample.

On the other hand, solid-state polymerization of 14-8 ADA microcrystal irradiated by UV-light for a given time was monitored from the changes of UV absorption spectrum

(Shimadzu UV-240 spectrometer) and DSC (Differential scanning calorimetry : Rigaku DSC 8240B) thermograms. UV-absorption spectra of water dispersion liquid were recorded at room temperature. For DSC measurements, the irradiated microcrystals were taken out from dispersion liquid by freezing-dry method while shielding from room light. The conversion was estimated from the endothermic peak of molten residual monomer crystal in partially polymerized 14-8 ADA microcrystal.

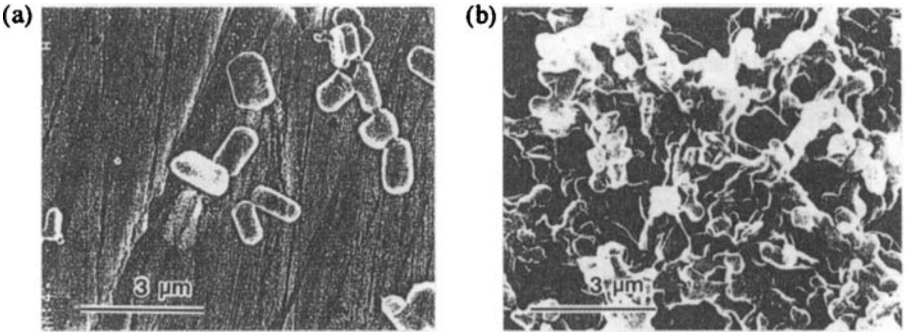


FIGURE 2 SEM photogaphs of two kinds of poly-4BCMU microcrystals : a) 1 μm and b) 300 nm.

RESULTS

Two kinds of poly-4BCMU microcrystals with different crystal sizes (300 nm and 1 μm, respectively) were obtained as shown in Fig. 2. These microcrystals were blue, reflecting well-expanded π-conjugation in the perfect crystalline lattice, but didn't disperse well in water. The value of Mw of poly-4BCMU, whose crystal size was 300 nm, was 0.55 x 10^6, while the same quantity was 1.6 x 10^6 in the case of 1 μm. The polydispersities were 3.1 and 3.4, respectively.

Fig. 3 indicates both DLS results and SEM photographs of submicrometer and several nanometer microcrystals of 14-8 ADA. These microcrystals were dispersed stably in water even after UV-irradiation. The spectral changes of both type of microcrystals are exhibited in Fig. 4. With UV-irradiation time, the intensity of the excitonic absorption peak increased, and at the same time, the peak was shifted. The hypsochromic shift in the initial stage of polymerization was observed in both bulk crystal and microcrystal. However, the characteristic bathochromic shift occurred subsequently in the case of microcrystals. This bathochromic shift of submicrometer microcrystals was pronounced.

The area of the endothermic peak decreased with UV-irradiation time as illustrated in Fig. 5. The ratio of residual monomer of several nanometer microcrystal (25 %) was nearly eight times as much as that of submicrometer microcrystal (3 %).

Poly-14-8 ADAs from submicrometer and several nanometer microcrystals gave the same XRD patterns as that from bulk crystals.

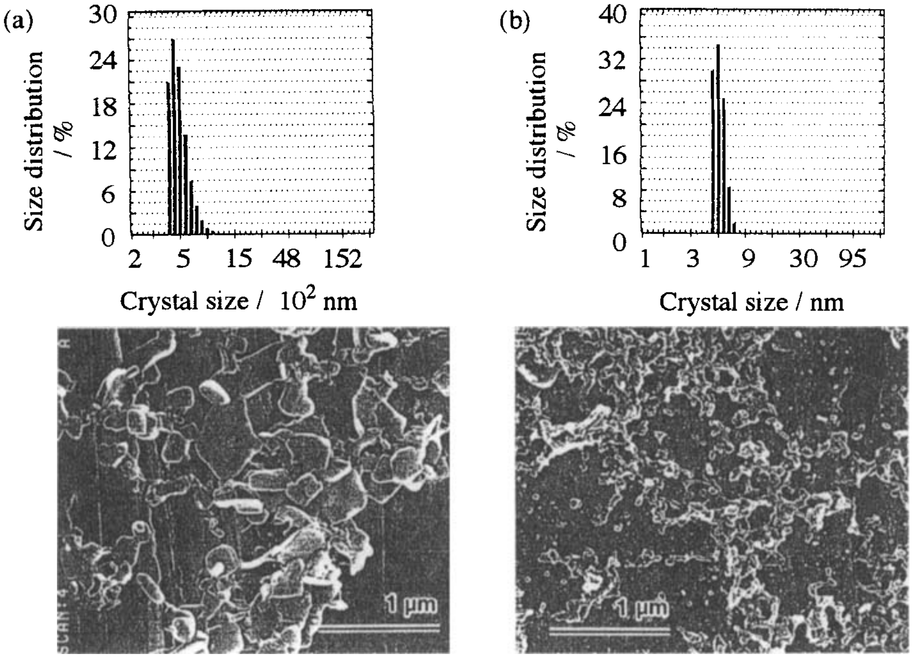


FIGURE 3 Size distribution of 14-8 ADA microcrystals evaluated by DLS (upper figures) and SEM photogaphs (lower figures) : (a) submicrometer and (b) severalnanometer microcrystals.

DISCUSSION

Investigations of solid-state polymerization of DA microcrystal could give us useful information about crystalline lattice of microcrystal. The measured Mw of poly-4BCMU was approximately proportional to crystal sizes. Subsequently, these values coincide well with those calculated from their crystal sizes on the assumption that the repeat length of

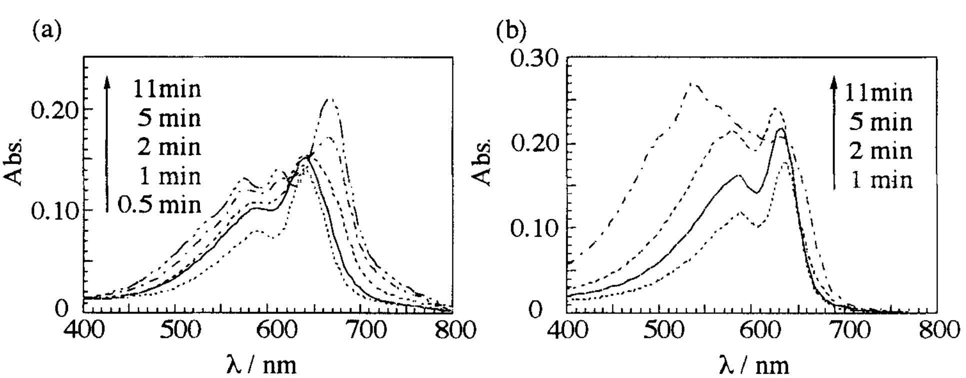


FIGURE 4 Visible spectral changes of 14-8 ADA microcrystals dispersed in water depending on UV irradiation time at r.t.. : (a) submicrometer and (b) several nanometer microcrystals.

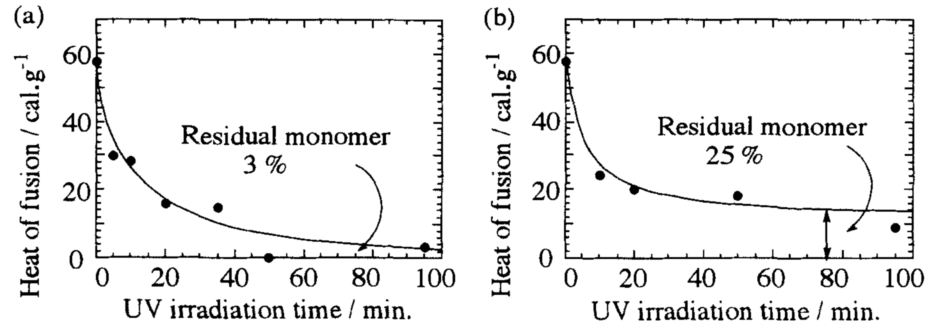


FIGURE 5 Change of heat of fusion of residual 14-8 ADA monomer normarized by weight of microcrystals, depending on UV irradiation time : (a) submicrometer and (b) several nanometer microcrystals.

poly-4BCMU is ca. 0.5 nm. Thus, poly-4BCMU main chain is considered to be connected up to the both ends of microcrystals.

The polymerization behaviors of 14-8 ADA microcrystals are summarized in Table I. Concerning solid-state polymerization of 14-8 ADA microcrystals, we have considered the following mechanism of the two steps : the first step is the polymerization in monomer crystal lattice ; the second step is the sequent polymerization in the resulting polymer crystal lattice. The hypsochromic and bathochromic shift may correspond to the first and second steps, respectively. Naturally, this mechanism is influenced by the lattice mismatch between monomer and polymer crystals as well as the lattice rigidity. At the first step, the planer conformation of poly-14-8 ADA must be disturbed and strained in monomer crystal lattice. According to Tieke *et al.*,[5] in the bulk crystal, the strain is relieved by a phase transition at same extent, in which the continuous phase is transformed from monomer rich region to polymer rich one in the course of the polymerization. Such phase transition is thought to occur easily in the microcrystal, rather than the bulk crystal, because the crystal lattice becomes loose with decreasing crystal size.

In several nanometer microcrystal, however, the conversion of 75 % is not higher than that of submicrometer microcrystal, in spite that the crystal size is smaller. In addition, as described previously in RESULTS, the bathochromic shift was not so remarkable, compared with the submicrometer microcrystal. This is due to enhancement of thermal vibration of crystal lattice of this type of long-alkyl-substituted diacetylenes. That is to say, it is considered to be a kind of dynamic defect in crystal lattice that disturbs solid-state polymerization.

Some additional experimental evidence with regard to the effect of this thermal vibration could be obtained. When polymerized at 50 °C (usually at room temperature), the excitonic absorption peak of submicrometer microcrystals was shifted to far longer wavelength of 673 nm (cf. 666 nm at r.t.), and the absorbance increased, too. In the case of

TABLE 1 Solid-state polymerization of 14-8 ADA crystal

	Bulk crystal		Submicrometer microcrystal		Several nanometer microcrystal		Polymerization condition
	b. s.[a]	r. s.[b]	b. s.	r. s.	b. s.	r. s.	
The shift of excitonic absorption peak.	633	—	640	666	630	637	at r.t.
			638	673	627	643	at 50 °C
			637	662			in PVA film at r.t. (40 wt. % : thin)
			637	—			in PVA film at r.t. (15 wt. % : thick)
Conversion	35 %		97 %		75 %		at r.t.

a) Position of excitonic absorption peak after b. s. (blue shift) at first step.
b) Position of excitonic absorption peak after sequent r. s. (red shift) at second step.(in the unit of nm).

several nanometer microcrystals, however, this heat treatment made no effect upon absorption spectral changes, indicating that the microcrystals at room temperature are already under the effect of enough thermal vibration. Furthermore, the bathochromic shift was not observed for several nanometer microcrystals embedded in PVA film. We believe that the rigid PVA matrix may suppress the phase transition which requires volume change.

CONCLUSIONS

The blue color of poly-4BCMU microcrystal demonstrates its perfect crystalline lattice, which is also supported from the fact that the Mw was proportional to crystal sizes. On the other hand, in the case of microcrystals of 14-8 ADA with long alkyl substituents, spectral change and conversion in the course of polymerization depend on crystal size, which can be explained by the looseness or thermal vibration of the crystal lattice.

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