



# Investigation on the photopolymerization possibility of 1,6-hexanediol diacrylate in crystalline-state



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## ABSTRACT

1,6-hexanediol diacrylate (HDDA) single crystal was grown by slow cooling method. The grown crystal was characterized by single crystal X-ray diffraction, and it showed that HDDA crystallizes in the triclinic system with space group P-1. The cell parameters are  $a = 6.4885(9) \text{ \AA}$ ,  $b = 6.945(2) \text{ \AA}$ ,  $c = 7.4890(12) \text{ \AA}$ ,  $\alpha = 96.43(2)^\circ$ ,  $\beta = 98.369(13)^\circ$ ,  $\gamma = 109.96(2)^\circ$  and  $Z = 1$ . The thermal properties of the HDDA was studied by differential scanning calorimetry (DSC) and showed just one crystalline form existed. A modelization method to judge the possibility of photoinitiating free-radical chain-reaction polymerization in crystal region was established based on the single crystal data, with which the polymerize possibility of HDDA in crystal region was studied.

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## 1. Introduction

Solid-state photopolymerization have been investigated for more than 100 years, and have the potential applications in photoswitching, optical recording and sensing [1–6]. “Solid-state photopolymerization” refers to the photoinitiating polymerization occurred in solid-state system, including polymerization of amorphous solid-state monomers and polymerization in the amorphous region or in the crystal region of crystalline monomers. Compared with the amorphous product manufactured from normal photopolymerization in liquid form, polymer from solid-state photopolymerization in crystalline state can obtain higher crystallinity and density. Especially, due to the tight and regular molecular arrangement, while the reactions performed in crystalline state, they can give regio- and stereospecific products [7]. Moreover, solid-state free radical photopolymerization can reduce oxygen inhibition by hinder oxygen diffusion and decrease the polymerization shrinkage due to the pre-shrinkage during solidification and crystallization.

In previous works, a series of solid-state photopolymerization system were studied, among which, the step-reaction solid-state photopolymerization based on [2+2] [8–10] and [4+4] [11,12] cycloaddition reactions were mostly investigated. The criteria for solid-state [2+2] cycloaddition was proposed by Schmidt and his co-workers [13,14]. They addressed that the centre-to-centre distance  $d$  between the nearest-neighbour double bonds is of the order of  $4 \text{ \AA}$  through topochemical rules, and the experimental observed limit is  $3.5 \text{ \AA} < d < 4.2 \text{ \AA}$  [13]. After that, numerous examples of solid-state [2+2] photo-dimerization were reported such as diene [15], diyne [16], heterocyclic derivatives [17] and metal-organic framework [10] systems. In addition, because of the high regularity of molecules and high homogeneity of materials, single crystal step-reaction photopolymerization was studied, and an ultimately thin molecular membrane with high density of monodisperse pores was obtained in the subnanometre range [12]. However, the research about chain-reaction solid-state photopolymerization seems much less than step-reaction polymerization. The solid-state photopolymerization of octadecyl acrylate and octadecyl methacrylate were investigated upon both  $\gamma$ -ray [18–21] and UV [22,23] irradiation. It was found that the polymerization reactivity is influenced by the molecular arrangement of monomers. Monomers in triclinic packing ( $\beta$ -form) show little tendency to polymerize while monomers in hexagonal packing ( $\alpha$ -form) polymerized well and achieved high conversion. Shibasaki [19] explained that monomers in hexagonal form are similar in the

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packing style to its polymer, thus it was easy to polymerize. However, the triclinic packing monomers must perform an expansion to reach hexagonal packing as polymer, which can't achieve in real situation, thus the polymerization in triclinic form is almost impossible. They also analyzed the entropy change for fusion ( $\Delta_f S$ ) of a series of long-chain monomers and concluded that when the value of  $\Delta_f S$  is smaller than a critical value ranging from 270 to 310 J/(K mol), solid-state polymerization may be allowed [24]. They explained that the value of  $\Delta_f S$  reflects the conformational freedom of the functional group, the lower the  $\Delta_f S$ , the more conformational freedom the functional group may have and the easier polymerization occurs. However,  $\Delta_f S$  seems to be more suitable to reflect the freedom of whole molecules, and the freedom of functional group may take a small part of it. Thus this method with the value of  $\Delta_f S$  to judge the polymerization possibility looks not entirely accurate. The solid-state photopolymerization of cyclic acetal-containing acrylates were also studied by Berchtold et al. [25] and the conversion achieved near 90% in 20 s. However, they did not distinguish whether the polymerization occurred in crystal region or amorphous region. In order to realize the indeed free-radical chain-reaction crystalline state photopolymerization, the place where the polymerization occurred must be clarified.

Due to the crystal can be easily obtained just around 0 °C, 1,6-hexanediol diacrylate (HDDA) was chose to be a kind of solid-state photopolymerizable monomer. In previous work, our lab reported the solid-state photopolymerization of HDDA exhibiting a certain conversion characterized by photo-DSC and real-time FTIR [26], but the place of polymerization wasn't assured whether or not in crystal region. To analyse the possibility of crystalline state polymerization, the crystal structure of HDDA is necessary, but no result was reported before and no data can be gained from the Cambridge Crystallographic Date Centre (CCDC) because this kind of organic monomer is difficult to grow a single crystal. Fortunately, we grew it and obtained the crystal structure successfully. In this article, the crystal data was used to explore the polymerization possibility of HDDA in crystal region. A curved surface model and a three-molecule model were established on the level of atoms to judge the possibility of free-radical chain-reaction polymerization in crystal region. The place, where the polymerization occurred, was inferred. It is believed that not only for HDDA, this method can also be a foundation to study the possibility of other systems in the later research of chain-reaction solid-state photopolymerization.

## 2. Experimental section

### 2.1. Materials

1,6-hexanediol diacrylate was purchased from Sartomer (Exton, PA, USA). After recrystallization by ethanol for several times until no impurities were detected by HPLC Waters 1525 (Waters, Milford, USA).



Fig. 1. Photograph of 1,6-hexanediol diacrylate single crystal.

### 2.2. Crystal growth

Crystal growth was performed by slow cooling method. 1,6-hexanediol diacrylate was firstly cooled down to 0 °C at the rate of 0.2 °C/h, and kept this low temperature for 48 h in low temperature thermostatic bath DC-8006 (FangRui Instrument CO., LTD, Shanghai, China). A transparent and colorless single crystal was obtained at the bottom of the beaker (Fig. 1).

### 2.3. Characterization

The grown crystal was subjected to single crystal X-ray diffraction studies using a diffractometer Gemini E (Agilent, USA), with  $MoK\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). Diffraction data was obtained by using SAINT and SADABS methods. The structure was solved by direct method and refined by the least-squares employing the SHELXTL-97 program. Thermal analysis was carried out by differential scanning calorimeter (DSC) Q2000 (TA Instruments, New Castle, DE). The sample weight was about 5 mg and scanning rate was 1 °C/min.

## 3. Results and discussion

The previous results of solid-state photopolymerization of HDDA showed that the conversion and rate increased with the content of photoinitiator increasing, and the conversion could achieve 37.11% with 2.5 wt% of photoinitiator [26]. It prove that the solid-state photopolymerization of HDDA is a typical free-radical initiated chain-reaction photopolymerization (Fig. 2), which have

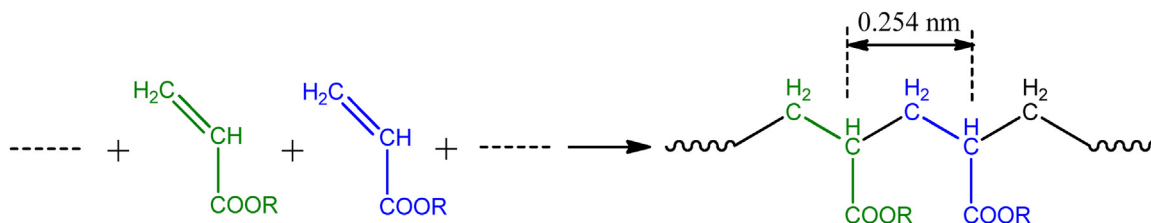


Fig. 2. The scheme for the process of chain-reaction polymerization, and an illustration of the distance between every adjacent methylene along main chain in polyacrylate.

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