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# Methods for the Preparation of Micro- and Nanocrystals of Urethane-Substituted Polydiacetylenes

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*Urethane-substituted polydiacetylene (PDA) crystals of bis(ethyl)-urethane of 5,7-dodecadiyne-1,12-diol (poly(ETCD)) with micronscale and nanoscale dimension were fabricated by either ultrasonication, surfactant addition or vapor phase processing approaches. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to evaluate the sizes and the shapes of the obtained poly(ETCD) microcrystals. Dynamic light scattering (DLS) was performed to investigate in situ size distributions of these crystals in aqueous suspension. A UV/Visible/NIR Spectrometer (UV/Vis/NIR) was used to study the electronic absorption of the poly(ETCD) microcrystals. Thermochromic phenomena for poly(ETCD) crystals still exist after their dimension was decreased to the nanoscale.*

**Keywords** polydiacetylene, bis(ethyl)-urethane of 5,7-dodecadiyne-1,12-diol, ultrasonication, surfactant, vapor phase processing, micron, nano, shape, size and size distribution, thermochromism

## Introduction

Polydiacetylenes (PDAs) are a unique class of polymeric material that combines structurally ordered conjugated backbones with tailorable pendant side groups and functionalities. Certain urethane-substituted PDAs exhibit intense optical absorption, which changes dramatically with various external stimuli, including applied mechanical stress (mechanochromism) (1, 2), temperature change (thermochromism) (3–6), chemical environment change or binding of a biological target (e.g. influenza virus) (affinochromism or biochromism) (7, 8).

In this research, PDA thermochromism has focused on poly(ETCD) crystals with micron-sized, submicron-sized and nano-sized dimension. These monomer crystals were prepared first and UV light (254 nm) was then used to polymerize them. We want to ascertain whether the thermochromism in solid conjugated polymers is a single chain phenomenon or a multi-chain phenomenon. In other words, we want to explore a

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potential relationship between crystal size and thermochromism for the urethane-substituted PDA (9, 10).

Currently, micron- and nano-structured materials are prepared by several methods, including mechanical attrition, high-energy milling, ultrasonication, gas evaporation, plasma deposition, electrochemical approach, etc. (11–13). Organic crystals attracted more attention after Nakanishi et al. reported a pioneering work to fabricate microcrystals by a reprecipitation technique (14–16). This method involves pouring a diacetylene solution into a poor solvent (water) under vigorous stirring. The micron-sized or nano-sized organic crystals formed immediately and they have good stability on dispersion for a long time (several days to several months). Adjusting the concentration of the solution, solution temperature, the mixing methodology, etc, control the size and shape of the crystals. Many crystals of  $\pi$ -conjugated monomers and polymers can be prepared in sizes ranging from a few tens of nm to one  $\mu\text{m}$  by using this approach. Sandman and coworkers built a poly(1,6-bis(N-carbazolyl)-2,4-hexadiyne) (poly(DCH)) multilayer structure and found that bromination of poly(DCH) assembly of a nanocrystal thin film converts it to a mixed polyacetylene structure with absorption spectrum maxima at 540 nm and 479 nm (17). But when the reprecipitation method is used for urethane-substituted DAs, such as ETCD, they aggregate and form visible precipitates, which are larger than 1  $\mu\text{m}$ . The reason is that there are strong hydrogen bonds in this kind of DA monomer crystal, so it is difficult to separate the molecules in the solution. Thus other methods are explored for preparing ETCD micron-sized and nano-sized crystals. Our approaches used to fabricate these poly(ETCD) crystals include ultrasonication, surfactant addition and vapor phase processing techniques.

## Experimental

### *Ultrasonication Method*

In this experiment, ETCD monomer in acetone solution with concentrations of 10 mM and 20 mM was used. 100  $\mu\text{l}$  of either of these solutions were injected jet like to 10 ml of deionized Milli-Q water while vigorously stirring over 1 min. (If irradiated with UV light (254 nm) at this moment, the poly(ETCD) microcrystals were formed, but they were not stable and exhibited visible precipitates.) Ultrasonic irradiation (42 kHz) was carried out within VWR ultrasonic cleaner (1.9 L). After ultrasonication of the solution for 15 min, the suspension formed and became cloudy. Then polymerization was immediately conducted by UV irradiation (254 nm) for 30 min. The initially cloudy solution became blue without any visible particles and precipitates.

### *Surfactant Addition Method*

In this experiment, 100  $\mu\text{l}$  ETCD monomer in acetone solution (5 mM) was injected into 10 ml of vigorously stirred deionized Milli-Q water in the presence series of different concentrations ( $10^{-5}\text{ M} \sim 9 \times 10^{-3}\text{ M}$ ) of sodium dodecyl sulfate (SDS). After different retention time which is defined as an interval from the injection of ETCD acetone solution into water until UV-irradiation for polymerization (18), UV light (254 nm) was used to polymerize ETCD microcrystals suspended in water by irradiation over a period of 30 min.

### Vapor Phase Processing Method Using Inert Gas

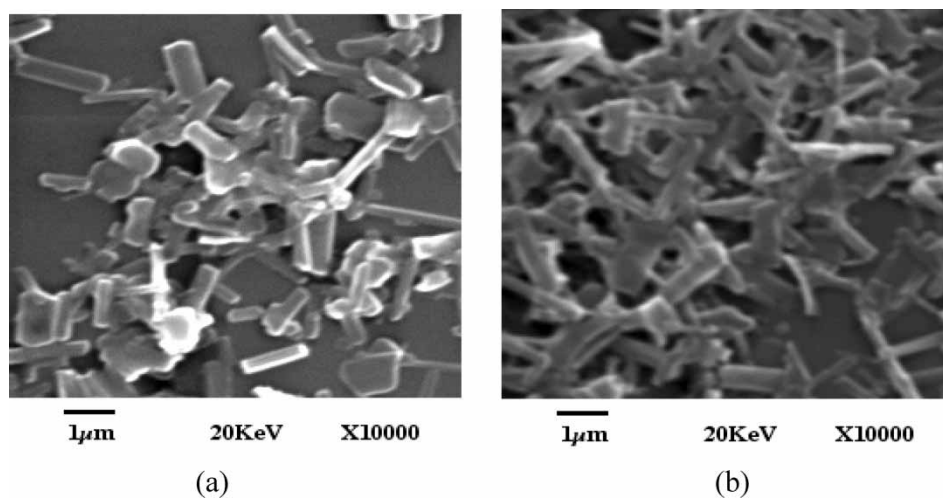
In this experiment, ETCD monomer was ground thoroughly with a mortar and pestle for 10 min. Then the ETCD powders were put into the tungsten crucible. Pumps were turned on and the chamber was evacuated. After the chamber vacuum reached  $10^{-6}$  torr, the argon gas flowed in and the chamber pressure was slowly increased to 2–3 torr and this pressure was kept for 10 min. Then the input of the argon gas was shut down and powder samples were gradually heated. The samples were evaporated and condensed on the substrates and copper grids for UV/Vis spectroscopy and TEM characterization, respectively. Under this situation, the blue thin films with nanoscale poly(ETCD) crystals were formed after being irradiated by UV light (254 nm) for 10 or 20 min.

Among the above methods, the poly(ETCD) microcrystal suspension in water was dropped on the glass substrates and the water was evaporated in the hood. Then, an ultrathin film of conductive Palladium-Gold alloy was coated on these samples for SEM study. SEM (Amray 1400 SEM with EDXS analysis), TEM (Philips EM-400T), DLS (Brookhaven Instruments Corporation, BI-9000AT) and UV/Vis/NIR spectrometer (Perkin-Elmer Corporation) were used to characterize and probe the particles' shape, size, size distribution and optical absorption.

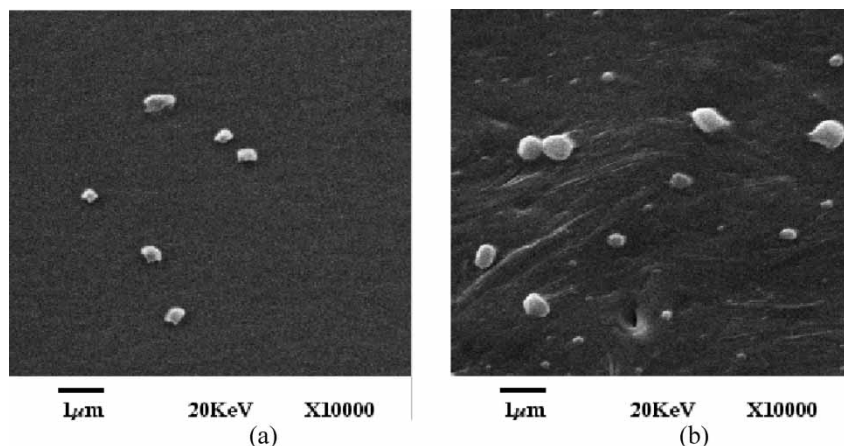
### Results and Discussion

Ultrasound (42 kHz) was used to fabricate micron-sized ETCD monomer crystals. Figure 1 shows the size and morphology of UV-polymerized ETCD micronscale crystals obtained by SEM. It was noticed that the shape of most of micron-sized crystals is that of rectangular prism, and the size distribution is polydisperse. Thus, it is not easy to obtain a monodisperse distribution in size with ultrasonication approach. Their average size is roughly 1–2  $\mu\text{m}$  using two different concentrations in acetone.

Figure 2 shows SEM images of poly(ETCD) submicron-sized crystals prepared from different concentrations of surfactant SDS followed by UV polymerization. The average



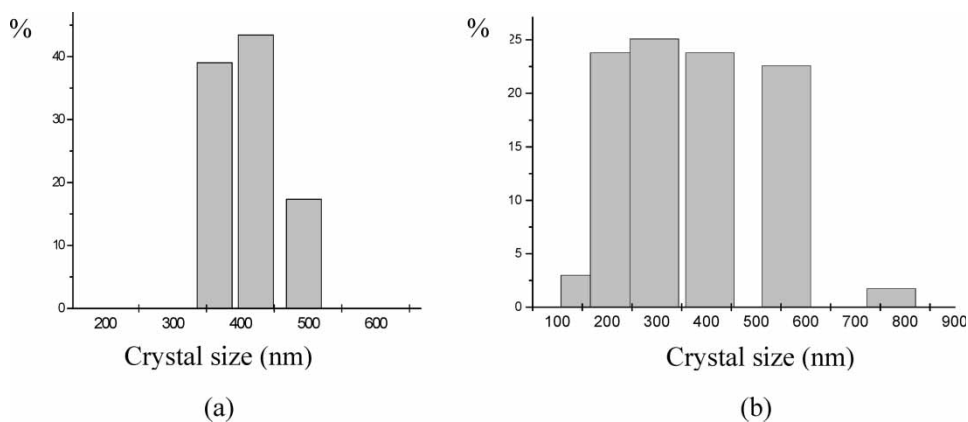
**Figure 1.** SEM images of UV-polymerized ETCD micronscale crystals prepared from different concentrations in acetone solution by ultrasonication. (a) 10 mM, (b) 20 mM.



**Figure 2.** SEM images of poly(ETCD) submicron-sized crystals fabricated from the monomer acetone solution (5 mM) in the presence of different concentrations of surfactant SDS (a)  $10^{-3}$  M, (b)  $5 \times 10^{-3}$  M.

size of poly(ETCD) submicron crystals prepared from different concentrations of surfactant SDS (a)  $10^{-3}$  M, (b)  $5 \times 10^{-3}$  M was around 450 nm and 400 nm respectively, which is in agreement with the results obtained from DLS measurement shown in Figure 3. The DLS method is a useful and quick technique to estimate in situ crystal size distribution. The average size of poly(ETCD) crystals is 410 nm (a) with the size range from 360 to 500 nm and the average size of poly(ETCD) crystals is 370 nm (b) with the size range from 150 to 770 nm prepared from SDS with concentrations of (a)  $10^{-3}$  M, (b)  $5 \times 10^{-3}$  M, respectively.

Matlab software was used to plot and analyze the electronic absorption spectra of the poly(ETCD) submicron-sized crystal solutions fabricated by surfactant addition method. It is found that all of the spectra maximum absorbance  $\lambda_{\max}$  is in the visible range and the absorption intensity increases with increasing the concentration of SDS from  $10^{-5}$  M,  $10^{-4}$  M,  $10^{-3}$  M, to  $5 \times 10^{-3}$  M, but the absorption intensity begins to decrease with

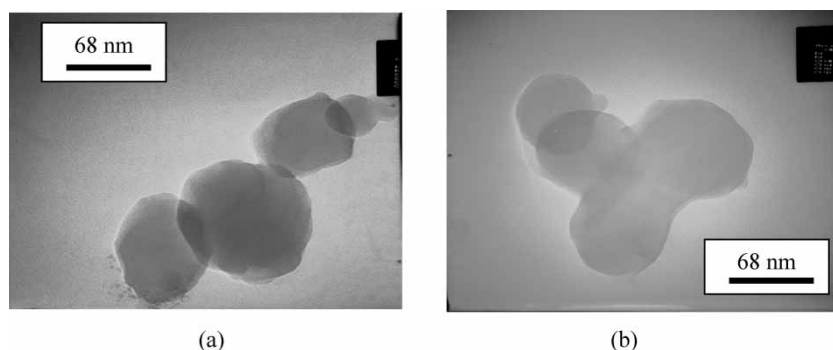


**Figure 3.** Size distribution obtained by DLS method for poly(ETCD) submicron-sized crystals formed from different concentrations of surfactant SDS (a)  $10^{-3}$  M, (b)  $5 \times 10^{-3}$  M.

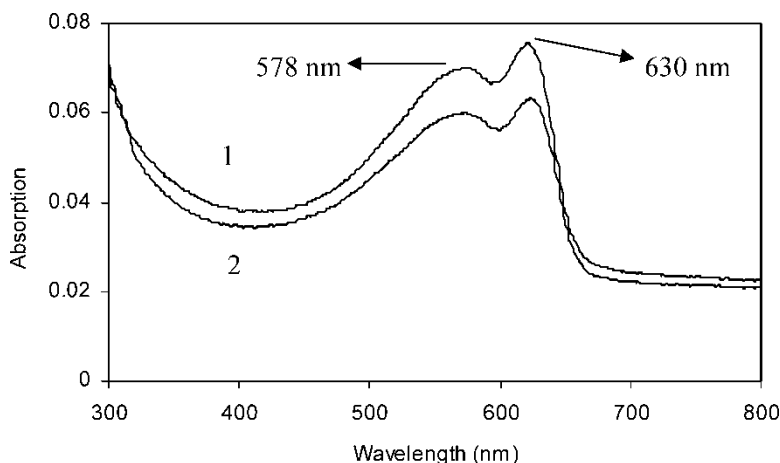
increasing the concentration of SDS from  $6 \times 10^{-3}$  M,  $7 \times 10^{-3}$  M,  $8 \times 10^{-3}$  M, to  $9 \times 10^{-3}$  M under keeping same retention time condition, among which the absorption intensity reaches maximum when concentration of SDS is  $5 \times 10^{-3}$  M. Meanwhile, absorption intensity increases with increasing retention time from 1.0, 10, to 30 min under keeping the same concentration of SDS. By combining these two results and the relationship between absorption intensity and concentration of suspension, we conclude that the concentration of poly(ETCD) submicron-sized crystals reaches maximum value when concentration of surfactant SDS is  $5 \times 10^{-3}$  M and retention time is 30 min.

We have selected two representatives of the above different poly(ETCD) submicron-sized crystal suspensions fabricated by surfactant SDS with concentration of  $10^{-3}$  M and  $5 \times 10^{-3}$  M and SEM was used to characterize their size and shape (shown in Figure 2). Their average size is roughly around 0.4–0.5  $\mu\text{m}$ . It is known that dynamic light scattering measurements revealed an average hydrodynamic radius of 20 Å for the SDS micelles. Thus, the diameter of SDS micelles is roughly 4 nm, which is much smaller than that of the fabricated poly(ETCD) submicron-sized crystals. So, we conclude that ETCD monomers do not go into SDS micelles, but SDS molecules help stabilize the ETCD monomer crystals before they are polymerized in this experiment. These surfactants can adsorb on the surfaces or even form envelopes around ETCD particles to provide either electrostatic or steric repulsion, and the attractive interaction for particles in suspension is normally a van der Waals force. The net attractive or repulsive force between the ETCD particles in a suspension is the sum of the electrostatic repulsion and the attractive van der Waals forces. When these two forces reach equilibrium, relatively stable poly(ETCD) submicron-sized crystal suspension was formed after UV light (254 nm) irradiation.

Figure 4 shows the size and shape of two different poly(ETCD) nano-sized crystals fabricated by the vapor phase processing method obtained by TEM. It is noticed that the shape of nanoscale crystals is spherical or elliptical and their diameter size range is roughly 50–80 nm. Compared with micron- or submicron-sized poly(ETCD) crystals which have a rectangular prismatic shape prepared by ultrasonication and surfactant addition approaches, the reason that the geometry of nano-sized crystals fabricated by vapor phase technique became round is due to the monomer crystals undergoing many collisions with inert gas atoms or molecules (e.g. Ar, N<sub>2</sub>) before they condensed onto the substrate during transport. Figure 5 shows electronic absorption spectra of nano-sized



**Figure 4.** TEM images of UV-polymerized nanoscale poly(ETCD) crystals—(a), (b) fabricated by vapor phase processing method in stationary argon gas ambient (Pressure = 2~3 torr) with different nanocrystal aggregation geometric shapes. (a) linear cluster; (b) triangular cluster.



**Figure 5.** Electronic absorption spectra of nano-sized poly(ETCD) crystals with diameter range of 50–80 nm under different UV irradiation time, 1 (10 min) and 2 (20 min).

poly(ETCD) crystals with diameter range of 50–80 nm under different UV irradiation time 10 and 20 min, respectively. In both of these spectra, the wave number separation between peaks at 578 nm and 630 nm is approximately  $1420\text{ cm}^{-1}$ , which corresponds to a carbon-carbon double bond vibration in the excitonic state.

After micron-sized, submicron-sized and nano-sized poly(ETCD) crystals were fabricated, we prepared samples by depositing each one of such crystals on glass slides, respectively. Each sample slide was put on a small round platform, which can be heated, and a thermometer was inserted closely underneath the platform in order to measure the temperature. Every one of the samples was slowly heated from room temperature until sample's blue color became red. In the meanwhile the temperature was recorded and regarded as thermochromic transition temperature. Then the samples color turned back to the blue color after they cooled down. The thermochromic transition temperature is around  $128\text{--}130^\circ\text{C}$ , comparable to bulk crystals (5).

## Conclusions

Micron-sized and submicron-sized poly(ETCD) crystals were successfully prepared and their shapes are that of a rectangular prism. Nano-sized poly(ETCD) crystals with spherical or elliptical shape and diameter range between 50 nm and 80 nm were also successfully fabricated by vapor phase processing technique using inert gas (argon). Thermochromic phenomena still exist for urethane-substituted poly(ETCD) crystals even though their sizes are decreased down to nanoscale ( $<100\text{ nm}$ ).

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