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## Crystal Structure Analysis for Polyurea

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**Abstract:** We focused on crystal structure and crystallization process of polyurea with differential scanning calorimetry and in-situ polarized optical microscopy and small and wide angle X-ray scattering (SAXS and WAXS) measurements with BL40B2 at SPring-8, Nishiharima, JAPAN and BL6A at PF, KEK, Tsukuba, Japan. We performed X-ray scattering measurements in a wide range of scattering vector  $Q = 4\pi/\sin\theta$ ; 0.2~ 2.0 nm<sup>-1</sup> for SAXS and 5.0 ~ 25 nm<sup>-1</sup> for WAXS measurements during heating and cooling processes of glassy and molten polyurea samples, respectively. We observed the melting and crystallization processes of polyurea. In the case of cooling down from molten state, we could observe crystalline transform, that is  $\delta$ -form to  $\alpha$ -form at 140 °C. This tendency is very similar to the so-called Brill-transition of polyamide. Heating up from the glassy state, we could observe crystal growth of  $\delta$ -form from 70 °C, above the glass transition temperature, 40 °C.

**Keywords:** Crystallization; Polyurea, in-situ X-ray scattering measurements

### 1. Introduction

Crystalline polyurea is one of crystalline polymers, and the properties are very similar to polyamides. Polyurea has “urea” functional group, then the inter-chain strong hydrogen bonding exists between urea functional groups. Especially as polyamides and polyurethanes, the melting point becomes much high and the mechanical properties become improved because of strong inter-chain hydrobondings. Furthermore, crystalline polyurea is one of thermoplastic resins and good property of molding process.

However, there are a few data of polymer properties and structural analysis for polyurea.

One of the reasons is that polyurea is too hard and brittle to make fibers by melt spinning, then a little studies were carried out about polyureas [1]. However, polyurea is one of bio-plastics made from carbon dioxide and bio-diamine then polyurea is expected to new type engineering plastics. Nowadays, it is quite important to research crystalline polyureas for improving properties and developing new uses.

In order to clarify structure formation processes of polyurea, we carried out differential scanning calorimetry and in-situ polarized optical microscopy and small and wide angle X-ray scattering (SAXS and WAXS) measurements.

### 2. Experimentals

## 2.1 Samples

Samples of polyurea were provided by Unitika Ltd (Osaka, Japan). The chemical structure and hydrogen bonding of polyamide [2] and polyurea are shown in Figure 1. The crystalline polyurea powders were melted in a vacuum oven at 270 °C for 3 min and then quenched to 0 °C with a cooling gas to obtain amorphous films. Subsequently, the amorphous films were dried for 1 day in a vacuum oven at the room temperature to remove water. In order to clarify heat resistance, we carried out thermo gravimetry analysis (TGA) with Q-50 instruments by TA-Instruments (New Castle, DE, USA). On heat up from room temperature, the reduction of mass began at 220 °C and onset temperature is 290 °C. Table 1 shows that annealing temperature dependence of weight loss rate (dm/dTmax). From this result, the oxidation could be accelerated above 260 °C.

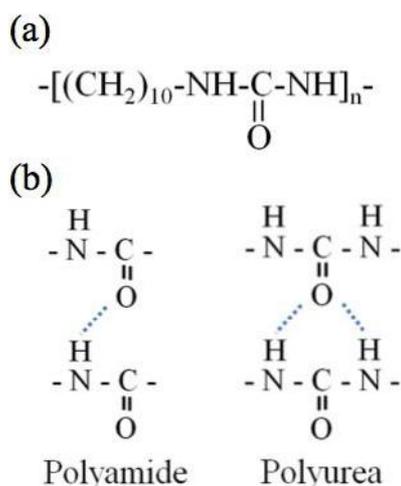


Figure 1 (a) Molecular structure of polyurea. (b) Hydrogen bonding of polyamide (left) and polyurea (right).

Table 1. Annealing temperature dependence of weight

loss rate.	
Annealing Temperature [°C]	Weight Loss Rate [%/min]
240	-0.020
250	-0.031
260	-0.077
270	-0.112

## 2.2 DSC Measurements

The thermal analysis data were measured with a Q-200 system differential scanning calorimeter (TA Instruments, New Castle, DE, USA). For analysis of crystallization and melting behaviors of polyurea film, we discussed about heating scan from glass state and crystalline state, 1st cooling scan from molten state. The scanning rate is 5 °C/min under nitrogen atmosphere.

## 2.3 In-situ SAXS and WAXS Measurements

Simultaneous small-angle and wide-angle x-ray scattering (SAXS/WAXS) measurements were carried out at the beam-line BL-6A, Photon Factory, KEK, Tsukuba, Japan [3] and at beam-line BL-40B2, SPring-8, Nishiharima, Japan [4]. The camera length was 2.1 m and 75 mm for SAXS and WAXS, and x-ray wavelength was 1.5 Å, and 1.0 Å, respectively. A CCD camera (C7330) for SAXS with an image intensifier and a flat panel CCD camera (C9252DK-14) for WAXS (Hamamatsu Photonics K.K.) were used as a detector system. The q range was 8 x 10<sup>-2</sup> and 1.5 nm<sup>-1</sup> for SAXS and 5.0 and 25 nm<sup>-1</sup> for WAXS. The exposure time was 0.5 s for SAXS/WAXS measurements.

## 2.4 Sample Conditions

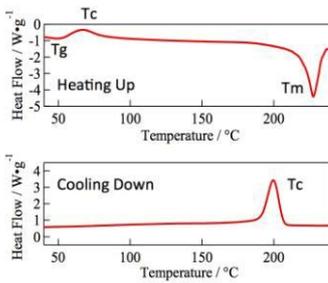
down of the molten sample from 250 to 40 °C. The rate is 5 °C/min. The aim is to clarify the crystal growth process during heating and cooling,

melting process from crystals for improvement of mechanical and thermal properties.

### 3. Results and Discussion

#### 3.1 DSC results

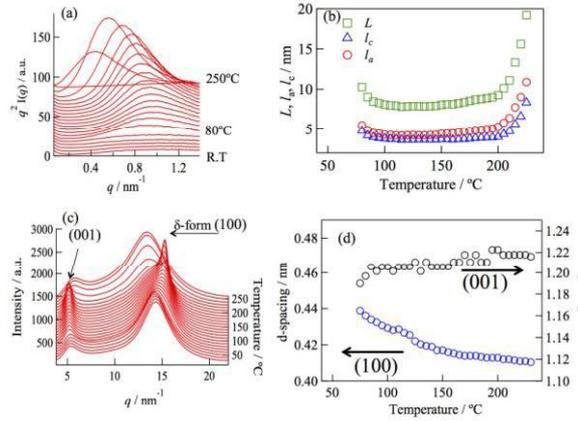
From DSC profiles in Figure 2, we could determine the glass transition temperature, 45 °C, crystallization temperature, 80 °C and the melting temperature, 235 °C. From the molten state, the crystallization temperature was 200 °C.



**Figure 2** DSC profiles of polyurea during heating up (up) and cooling down (below).

#### 3.2 Heating of the glassy sample

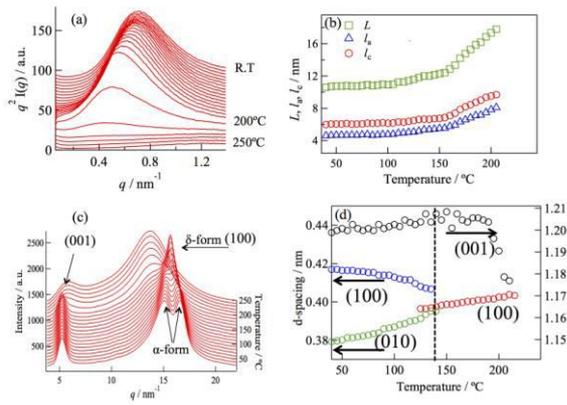
Figure 3(a) shows temperature dependence of SAXS profiles. At 80 °C, the peak at 0.6 nm<sup>-1</sup> emerged and moved to low q region. We evaluated the thickness of lamellar crystal ( $l_c$ ) and inter-lamellar amorphous region ( $l_a$ ) in Figure 3(b). Below 100 °C, the crystal nucleation began then lamellar crystals might grow all over the sample and have higher density fluctuation between lamellar crystal and amorphous. On further heating up, the peak position decreases with temperature. This is one of features of lamellar crystal growth during heating up. The WAXS patterns showed in Figure 3(c). Just two peaks were observed at  $q = 5 \text{ nm}^{-1}$ , (001) and  $15 \text{ nm}^{-1}$  (010) for  $\delta$ -form crystal. From temperature dependence, the (001) peak is almost independent



**Figure 3** (a) SAXS profiles during heating up of the glassy sample. (b) The long spacing period ( $L$ ), the thickness of lamellar crystal ( $l_c$ ) and amorphous ( $l_a$ ) from SAXS measurements. (c) WAXS profiles and (d) the d-spacing, (001) and (100).

#### 3.3 Cooling down of the molten sample

Figure 4(a) shows temperature dependence of SAXS profiles. At 225 °C, the peak at 0.45 nm<sup>-1</sup> emerged and moved to high q region. The lamellar crystals grow gradually into the inter-lamellar crystal region from the thickness of lamellar crystal ( $l_c$ ) and inter-lamellar amorphous region ( $l_a$ ) in Figure 4(b). The lamellar thickness and inter-lamellar amorphous thickness monotonically decreased with cooling down. Figure 4(c) shows the WAXD profiles of cooling down of the molten sample. At 225 °C, we could observe the single crystalline diffraction peak. This peak was assigned as (100) of  $\delta$ -form crystal. During cooling down, the peak was divided into two  $\alpha$ -form peaks (110) and (010) at 130 °C. The (001) peak does not change during cooling down process. This phenomena are very similar to the so-called Brill-transition as polyamides.



**Figure 4 (a) SAXS profiles during cooling down of the molten sample. (b) The long spacing period ( $L$ ), the thickness of lamellar crystal ( $l_c$ ) and amorphous ( $l_a$ ) from SAXS measurements. (c) WAXS profiles and (d) the d-spacing, (001) and (100).**

#### 4. Conclusion

We have studied precise crystal structure and temperature dependence of crystallization process of crystalline polyurea. On heating up of the glassy sample, we could observe only  $\delta$  form crystals. The lamellar structure grows up during heating up. On the other hand, during cooling down of the molten sample, we could observe the Brill-transition type crystal form transition.

#### 4. Acknowledgments

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