

Hydrothermal Treatment of Polyamide 6 with Presence of Lanthanum Chloride^{*}

Zhi-liang Wang^a, Jia-li Xu^a, Qian Yuan^a, Mahmoud H.M.A. Shibraen^a,
Jian Xu^b and Shu-guang Yang^{a**}

^a State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 201620, China

^b Lab of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Abstract Hydrothermal processing of polyamide 6 (PA6) with the presence of lanthanum chloride (LaCl₃) was studied in the temperature region from 160 °C to 250 °C. PA6 will be dissolved in the superheated water when temperature is above 160 °C. And as PA6 is dissolved, hydrolysis will happen, which makes PA6 chains degrade. By adding LaCl₃ in the hydrothermal environment, the PA6 hydrolysis will intensify, especially when the hydrothermal temperature is higher than 200 °C. When the hydrothermal system cools down, the hydrolyzed PA6 segments will crystallize from the solution or remain dissolved in the solution depending on molecular weight. In addition, the hydrolyzed compound of LaCl₃ would affect the crystallization of PA6 segments with proper size, and γ phase would be presented.

Keywords: Nylon 6; Hydrolysis; Hydrothermal processing; Crystallization.

INTRODUCTION

Polyamide 6 (PA6) is a semi-crystalline polymer with good temperature-resistance and mechanical strength. Generally, PA6 is processed in melting state to prepare plastics or fibers. PA6 is seldom processed in solution state because PA6 is only dissolved in a few strong polar solvents, which have high-cost and environment pollution. Water is an environment-friendly solvent. Though PA6 does not dissolve in water at room temperature, it can dissolve in super-heated water under pressure^[1–3]. Recently, the idea using water as solvent to process polyamides is put forward^[4, 5].

Above 160 °C, PA6 dissolves in water under pressure^[6]. Once PA6 is dissolved in the super-heated water, hydrolysis of amide groups is hard to be avoided. Hydrolysis makes PA6 degrade, which is adverse to produce a product. However, hydrolysis reaction in the super-heated water can be utilized to recycle PA6^[7–15]. Iwaya *et al.* reported that PA6 hydrolyzed to form ϵ -caprolactam at temperatures between 575 and 673 K under the pressures estimated up to 35 MPa^[13]. In the presence of organic acid, the yield of ϵ -caprolactam production is nearly 100% under supercritical condition^[14, 15].

Although the physical and chemical behaviors in hydrothermal environment have been investigated, the

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^{**} Corresponding author: Shu-guang Yang (杨曙光), E-mail: shgyang@dhu.edu.cn

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hydrothermal processing of polyamides has not been fully explored. In this work, we study the hydrothermal processing of PA6 with presence of an inorganic salt, lanthanum (III) chloride. In the hydrothermal environment, lanthanum chloride also hydrolyzes, which generates protons. Protons are helpful for the PA6 hydrolysis. In addition, the hydrolyzed product of lanthanum chloride affects the crystallization behavior of PA6 segments from the aqueous solution and γ phase is presented.

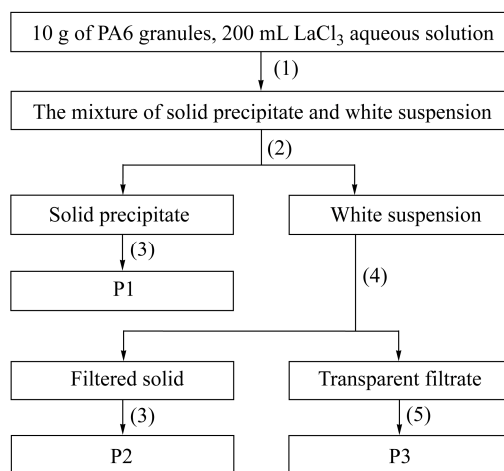
EXPERIMENTAL

Materials

PA6 granules (Grade M2400, melt index $2.6 \text{ g} \cdot \text{min}^{-1}$) were provided by Xinhui Meida Nylon Co., Ltd. Lanthanum chloride heptahydrate ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, AR) was purchased from Aladdin Industrial Corporation.

The Hydrothermal Processing of PA6

Hydrothermal processing of PA6 was carried in a 250 mL titanium autoclave (Weihai Chemical Machinery Co., Ltd. China). 10 g of virgin PA6 granules and 200 mL LaCl_3 aqueous solution with different concentrations were sealed in the autoclave. The mixed system was heated to the set temperature, resided for 1 h with 300 r/min stirring and cooled down to room temperature spontaneously. After cooling down the system, the precipitate, the suspension, or both are presented depending on the hydrothermal temperature and lanthanum chloride concentration. The products of hydrothermal processing were collected as shown in Scheme 1. The precipitate was labeled as P1. The solid sample filtered out from the suspension was labelled as P2. Both P1 and P2 were dried in vacuum at 40°C for 24 h. The transparent filtrate from the suspension solution was freeze-dried to get the solid sample which labeled as P3. The samples collected from the system without adding LaCl_3 were labelled as P1r, P2r and P3r accordingly.



Scheme 1 The process of hydrothermal treatment and samples collection: (1) hydrothermal treatment, (2) separate the mixture with 600 meshes copper net, (3) dry the product in a vacuum oven at 40°C for 24 h, (4) filter the white suspension by filter paper and (5) freeze-drying

Characterization

FTIR spectra were recorded with a Nicolet 8700 IR spectrometer (Thermo Scientific). PA6 samples were ground with KBr powder and then pressed into standard disc (sample content 1%) for IR characterization. Wide angle X-ray diffraction (WAXD) of the samples was carried out with a Bruker D2 desktop diffractometer ($\text{Cu-K}\alpha$ 0.15418 nm, 30 kV and 10 mA). The data were collected using a Ni-filtered Cu-target tube at room temperature in the 2θ range of $5^\circ - 90^\circ$ with a scan step width of 0.02° (0.1 s/step). The content of element lanthanum was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Prodigy, Leeman, US). Molecular weights of P1 and P2 were measured through the method of intrinsic viscosity, and the details were

mentioned in Ref. 6. Molecular weight of P3 was determined on an ABSciex Plus 4800 MALDI-TOF-Mass spectrometer. The scanning electron microscope (SEM) observations were performed on a Hitachi S-4800 apparatus equipped with a field emission gun.

RESULTS AND DISCUSSION

Previous study has demonstrated that PA6 can be dissolved in the superheated water above 160 °C^[6]. However, when PA6 is dissolved, the hydrolysis will happen, which makes polymer chains decompose into segments. When the hydrothermally processed system cools down, small PA6 segments will still be dissolved in the solution whereas large PA6 segments will crystallize and then precipitate out. After hydrothermal process, the weight of the precipitate can reflect the hydrolysis degree of PA6. Less precipitate means the higher degree of PA6 hydrolysis.

The weight of the precipitate (P1) and the weight of solid particles (P2) from the suspension were measured, as shown in Fig. 1. As the hydrothermal temperature (T_H) is elevated, the weight of P1 decreases, which declines dramatically when $T_H > 200$ °C. For the system without adding LaCl_3 , the weight of the precipitate (P1r) also decreases as T_H is elevated, but much slowly compared with that of the P1. With the presence of LaCl_3 , the hydrolysis of the PA6 in the hydrothermal environment intensifies.

If T_H is higher than 200 °C, the solution is very cloudy when the hydrothermal system cools down. Through filtration, the solid particles (P2) were collected from the suspension solution. The weight of P2 as a function of hydrothermal temperature is also shown in Fig. 1. Without adding LaCl_3 , it is hard to collect P2. With the presence of LaCl_3 , the weight of P2 is very low when $T_H < 200$ °C, but P2 collection becomes easy when $T_H > 200$ °C. At 220 °C, the weight of P2 gets a maximum value.

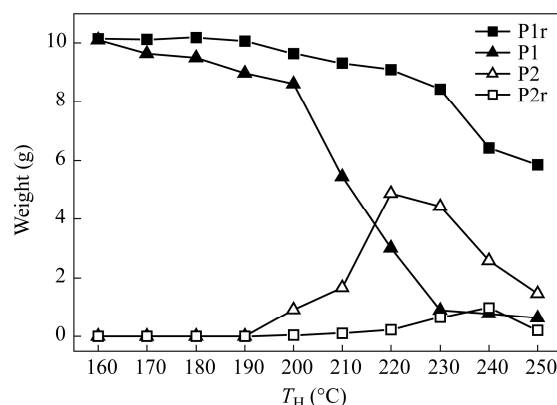


Fig. 1 Weights of hydrothermal processing products as a function of the hydrothermal temperature (P1 and P2 are obtained from the system containing 10.0 mmol/L LaCl_3 ; P1r and P2r are from the system without LaCl_3 , which are used as reference.)

Hydrolysis makes PA6 chains decompose into segments. When the temperature cools down, the large segments will crystallize and precipitate out from the solution (P1). The small segments can be dissolved in the solution (P3). The middle segments crystallize to form micro-particles which are dispersed in the solution (P2). The molecular weights of PA6 segments in P1, P2 and P3 were measured. PA6 molecular weights in P1 and P2 were determined through intrinsic viscosity, while that of P3 was measured with a MALDI-TOF-Mass spectrometer. The molecular weight of PA6 segments in P1 and P2 as a function of temperature is shown in Fig. 2. The molecular weight of PA6 in P1 is higher than 2000. The molecular weight of PA6 in P2 is ranged from 1000 to 2000. The MALDI-TOF-Mass indicates that the molecular weight of segments in P3 is less than 1000 (Fig. 3). P3 consists of linear PA6 oligomers and a small fraction of cyclic oligomers.

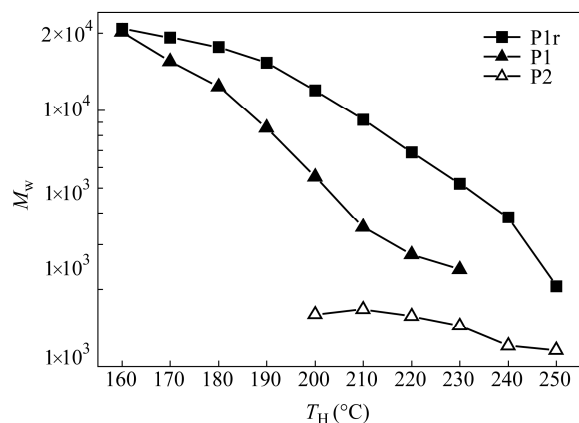


Fig. 2 Molecular weights of hydrothermal processing products as a function of the hydrothermal temperature (P1 and P2 are obtained from the system containing 10.0 mmol/L LaCl_3 .)

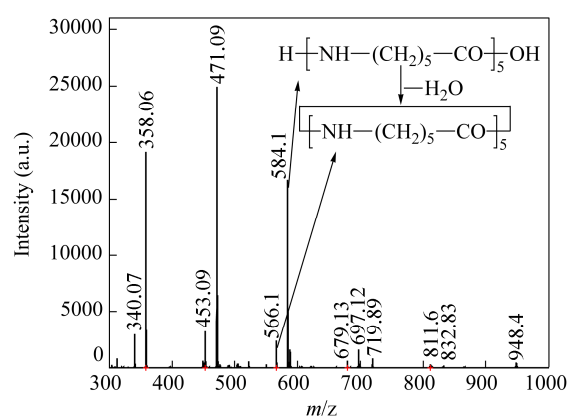


Fig. 3 The MALDI-TOF-Mass spectrum of P3 (T_H is 220 °C and LaCl_3 concentration is 10.0 mmol/L.)

P1 and P2 were characterized with XRD and elemental analysis, as shown in Fig. 4. In P1, the content of lanthanum element continuously increases as T_H is elevated. At T_H lower than 200 °C, P1 displays two characteristic diffraction peaks around $\sim 20^\circ$ and $\sim 24^\circ$, which are assigned to the α phase of PA6^[16–18]. At T_H higher than 200 °C, new diffraction peaks appear, which should be attributed to the hydrolyzed product of lanthanum chloride. Through retrieval in Inorganic Crystal Structure Database (ICSD), the hydrolyzed product of lanthanide chloride is $\text{La}(\text{OH})_2\text{Cl}$ (CCode: 6280). As T_H is elevated from 200 °C, the diffraction peaks of PA6 in P1 gradually disappear while the diffraction peaks of $\text{La}(\text{OH})_2\text{Cl}$ become prominent.

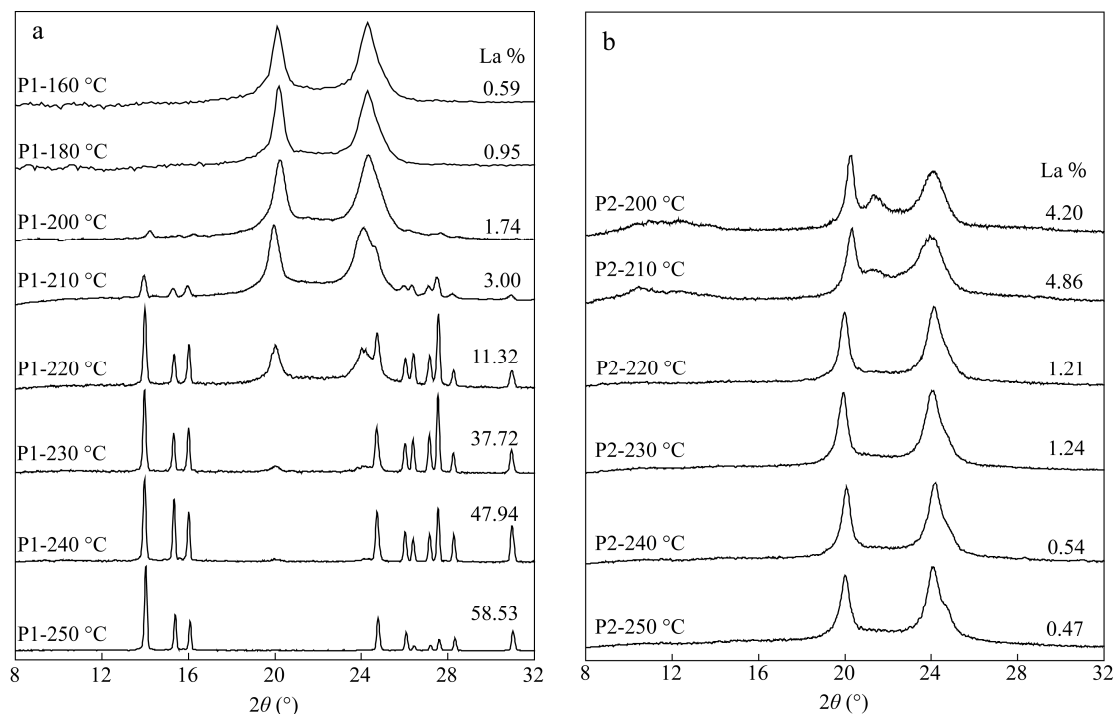


Fig. 4 The XRD curves of hydrolyzed samples: (a) P1 and (b) P2. P1 and P2 are obtained from the system containing 10.0 mmol/L LaCl_3 . The element content of La in the corresponding sample is also shown.

FTIR spectra of P1 samples are shown in Fig. 5. The peaks at 3300 cm^{-1} , 1639 cm^{-1} , 1543 cm^{-1} are assigned to N—H stretching vibration, amide I and amide II bands of PA6 respectively^[19]. At T_H higher than $200\text{ }^{\circ}\text{C}$, P1 exhibits the peaks at 3570 cm^{-1} and 3554 cm^{-1} , which are assigned to O—H stretching vibration of $\text{La}(\text{OH})_2\text{Cl}$ crystal^[20]. When $T_H > 220\text{ }^{\circ}\text{C}$, XRD curves show very weak signal of PA6 in P1 but IR spectra still display relatively strong signal of PA6. Inorganic crystals have high diffraction intensity compared with polymer crystals. At elevated T_H , the PA6 content in P1 greatly decreases, and the diffraction signal of PA6 is covered by the diffraction of $\text{La}(\text{OH})_2\text{Cl}$.

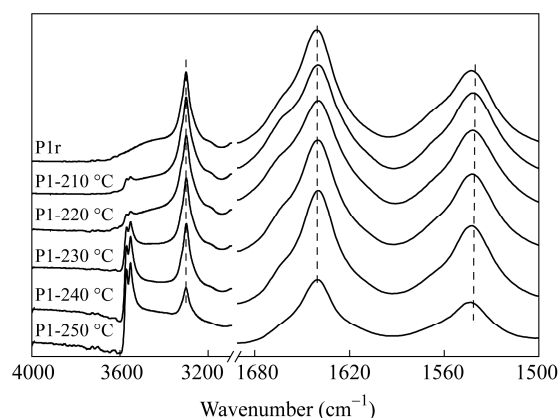
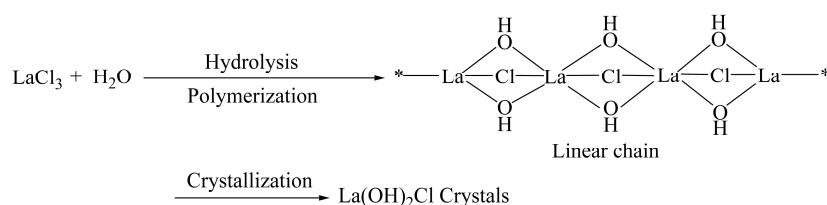


Fig. 5 FTIR spectra of P1 (T_H from $210\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ and LaCl_3 concentration 10.0 mmol/L) and P1r ($T_H = 210\text{ }^{\circ}\text{C}$, without LaCl_3)

Elemental analysis indicates that P2 samples contain lanthanum element too. When T_H is elevated, the lanthanum content in P2 decreases, which is reverse to that in P1. XRD curves only show the diffraction peaks of PA6 and no diffraction peaks of the hydrolyzed compound of LaCl_3 . The hydrolyzed compound, $\text{La}(\text{OH})_2\text{Cl}$, should be amorphous in P2.

It is interesting that when T_H is $200\text{ }^{\circ}\text{C}$ or $210\text{ }^{\circ}\text{C}$, P2 samples exhibit not only α phase of PA6 but also γ phase. γ phase shows two characteristic diffraction peaks around $\sim 10^{\circ}$ and $\sim 22^{\circ}$, which are assigned to the (020) and (001) planes respectively^[21–24]. However, when T_H increased to $220\text{ }^{\circ}\text{C}$ and up, γ phase disappears and P2 just shows α phase.

The hydrolysis of LaCl_3 and crystallization of the hydrolyzed compound are shown in Scheme 2. The hydrolysis of LaCl_3 produces protons which catalyze the hydrolysis of PA6. Figure 1 demonstrates that when $T_H < 200\text{ }^{\circ}\text{C}$, the hydrolysis of PA6 is relatively slow with the presence of LaCl_3 . Figure 4(a) shows when $T_H < 200\text{ }^{\circ}\text{C}$, there are no diffraction peaks of $\text{La}(\text{OH})_2\text{Cl}$ crystals. These results reflect that the hydrolysis of LaCl_3 is weak when $T_H < 200\text{ }^{\circ}\text{C}$. Prominent diffraction peaks of $\text{La}(\text{OH})_2\text{Cl}$ crystals indicate that the hydrolysis of LaCl_3 is fast and the hydrolyzed compound has strong crystallization ability when $T_H \geq 220\text{ }^{\circ}\text{C}$. In the T_H region from $200\text{ }^{\circ}\text{C}$ to $210\text{ }^{\circ}\text{C}$, the diffraction peaks of $\text{La}(\text{OH})_2\text{Cl}$ can be observed but are not strong, which reveals that LaCl_3 hydrolysis is relatively strong but the crystallization of the hydrolyzed compound is relatively weak.



Scheme 2 The hydrolysis of LaCl_3 and the crystallization of $\text{La}(\text{OH})_2\text{Cl}$ crystals

PA6 segments would crystallize when the hydrothermal system cooled down to 120 °C^[6]. When 160 °C < T_H < 200 °C, most PA6 segments crystallize and precipitate out from the solution as the hydrothermal system is cooling down. When $T_H \geq 220$ °C, the hydrolysis product of LaCl_3 , $\text{La(OH)}_2\text{Cl}$, almost crystallizes and precipitates out from the solution before the crystallization of PA6 segments. However, when 200 °C $\leq T_H \leq 210$ °C, there is enough non-crystallized $\text{La(OH)}_2\text{Cl}$ in the system. As shown in Scheme 2, the non-crystallized $\text{La(OH)}_2\text{Cl}$ in the solution is in the form of a rigid linear chain polymer. γ phase of PA6 in P2 is supposed to be related with the non-crystallized $\text{La(OH)}_2\text{Cl}$. The γ phase is only presented when the molecular weight of PA6 segments is ranged from 1000 to 2000 and does not appear when the molecular weights of PA6 segments are higher than 2000. So the sizes of PA6 segments ($1000 < M_w < 2000$) should match the chain length of the non-crystallized $\text{La(OH)}_2\text{Cl}$ in the system.

The concentration of the non-crystallized $\text{La(OH)}_2\text{Cl}$ in the solution is also very important. If the concentration is too low, γ phase will not form. The γ phase formation would consume the non-crystallized $\text{La(OH)}_2\text{Cl}$. When the non-crystallized $\text{La(OH)}_2\text{Cl}$ is consumed up, the γ phase will not be formed anymore and α phase will grow. So both γ phase and α phase are displayed in P2.

To further illustrate the effect of the non-crystallized $\text{La(OH)}_2\text{Cl}$ in the hydrothermal system on the formation of γ phase of PA6, PA6 was hydrothermally processed at 210 °C with different LaCl_3 concentrations. Figure 6 shows the XRD curves of P2 samples. All P2 samples show γ phase except the one that was prepared with 1.2 mmol/L LaCl_3 . γ phase formation is related with the concentration of non-crystallized $\text{La(OH)}_2\text{Cl}$ in the system. If the concentration of non-crystallized $\text{La(OH)}_2\text{Cl}$ is low, γ phase of PA6 will be very hard to form. Using 1.2 mmol/L LaCl_3 , the $\text{La(OH)}_2\text{Cl}$ concentration is very low and hence there is no γ phase presented.

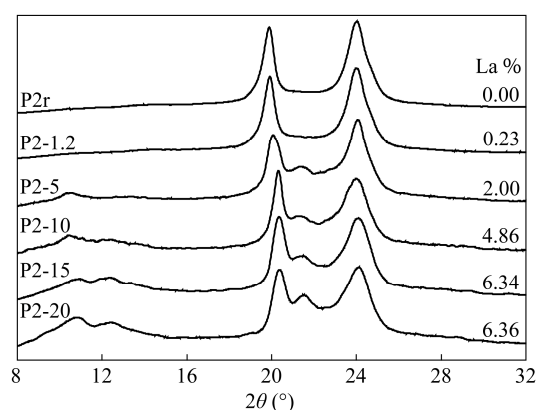


Fig. 6 The WAXD patterns of P2 and P2r
(Hydrothermal condition for P2r: pure water, $T_H = 240$ °C, 1 h; Hydrothermal condition for P2 series: $T_H = 210$ °C, LaCl_3 concentrations 1.2, 5.0, 10.0, 15.0 and 20.0 mmol/L.)

The FTIR spectra of P2 samples prepared at 210 °C with different LaCl_3 concentrations are shown in Fig. 7. As the content of the non-crystalline $\text{La(OH)}_2\text{Cl}$ in P2 increases, the amide I band (C=O stretch) and amide II band (C-N stretch + C(O)-N-H bend) both move to low wavenumber side while N-H stretching vibration shifts to high frequencies. The reason is that the OH groups on $\text{La(OH)}_2\text{Cl}$ chains can form hydrogen bonds with C=O in PA6, which weakens the hydrogen bond between C=O and N-H in PA6.

Figure 8 shows the SEM images of P2 and P2r particles. P2 particles exhibit different morphologies compared with P2r particles. P2r particles are fan-like originated from the chain-folded α phase crystals of PA6. While P2 particles show root-like morphology. The non-crystallized $\text{La(OH)}_2\text{Cl}$ has interaction with PA6, which will affect chain package and growth mode during the crystallization process. So the non-crystallized $\text{La(OH)}_2\text{Cl}$ induces the formation of γ phase and different crystallization morphologies.

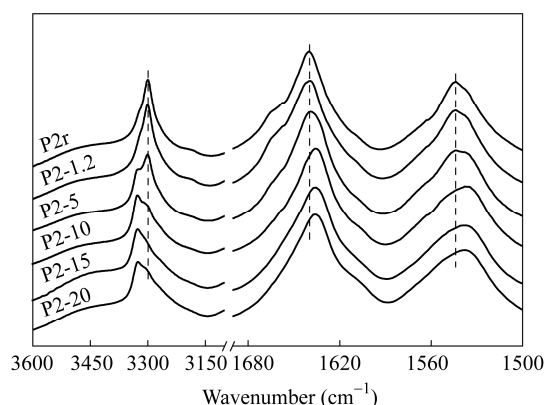


Fig. 7 FTIR spectra of P2 and P2r
(Hydrothermal condition for P2r: pure water, $T_H = 240\text{ }^{\circ}\text{C}$, 1 h; Hydrothermal condition for P2 series: $T_H = 210\text{ }^{\circ}\text{C}$, LaCl_3 concentration 1.2, 5.0, 10.0, 15.0 and 20.0 mmol/L.)

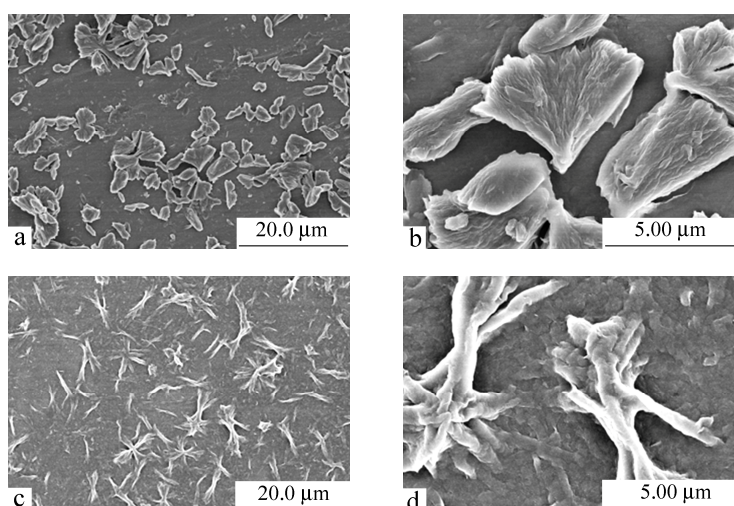


Fig. 8 The SEM micrographs of P2r (a, b: pure water, $240\text{ }^{\circ}\text{C}$, 1 h) and P2 (c, d: 10.0 mmol/L LaCl_3 solution, $210\text{ }^{\circ}\text{C}$, 1 h)

CONCLUSIONS

With the presence of LaCl_3 , the hydrolysis of PA6 in hydrothermal environment intensifies. In the hydrothermal environment, LaCl_3 hydrolyze to produce H^+ ions and $\text{La}(\text{OH})_2\text{Cl}$. H^+ ions can catalyze the hydrolysis of PA6. The hydrolysis makes PA6 chains decompose into segments. If the molecular weight is lower than 1000, the segments dissolve in the solution. If the molecular weight is higher than 2000, the segments will crystallize to form α phase and then precipitate out from the solution. When the molecular weight ranged from 1000 to 2000, the crystallization of PA6 segments will be affected by the non-crystallized hydrolysis product of LaCl_3 , $\text{La}(\text{OH})_2\text{Cl}$, and γ phase will be presented.

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