# Hydrolytic degradation of monomer casting nylon in subcritical water

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## ARTICLE INFO

## ABSTRACT

In contrast with the conventional physical methods, sub- and supercritical hydrolysis is not only a more environmentally friendly method to recycle the monomer casting nylon (MC nylon) wastes, but also a more feasible way to produce the corresponding monomer. In subcritical water, MC nylon was decomposed completely into water-soluble oligomers within 45 min at 345 °C and 9 MPa. Fourier transform infrared spectroscopy and X-ray diffraction were employed to characterize the chemical composition and crystalline form changes of the solid products obtained within 30 min of the degradation. Qualitative and quantitative analyses of liquid phase product were performed by liquid chromatography mass spectrometry and high performance liquid chromatography. The yield of the main degradation product $\varepsilon$-caprolactam largely depended on the hydrolysis temperature and reaction time. The maximum yield value reached 89.0% when the reaction time was 75 min. A hydrolytic degradation mechanism of MC nylon in subcritical water is proposed as well.

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## 1. Introduction

Generally, polyamide materials can be recycled as normal thermoplastics by grinding, granulation or other mechanical methods without the decrease of the excellent performance [1]. It was reported that after 7 cycles of injection molding, the properties of nylon 6 essentially remained the same and the performance had not declined until the 10th injection cycles [2]. Thus the recycled polyamide wastes are mainly used to mix with new resins or directly reused as raw material to produce auto parts or other engineering parts.

As a special kind of nylon 6, the monomer casting nylon (MC nylon) is synthetized by casting method through the anionic ring-opening polymerization of $\varepsilon$-caprolactam. Plenty of unique performances such as the high strength, insulation, anticorrosive capacity and oil-resistance etc., make MC nylon having a wide range of applications as an engineering plastic [3]. However, the conventional physical recycling methods are not suitable for recycling MC nylon in some degree, because the molecular mass of MC nylon is up to $0.5$–$1.0 \times 10^5$ g/mol which leads to an entanglement between the molecules in the melting state and a particularly high melt viscosity.

Moreover, it is hardly possible to find any researches devoted to the decomposition of MC nylon, but some chemical methods for recycling regular nylon 6 have been developed which could provide some technical support [4–9]. The corresponding monomer $\varepsilon$-caprolactam is able to be recovered from the pyrolysis of nylon 6, in spite of that the energy consumption and the cost of the multi-component separation systems are relatively high. Other methods such as bio-degradation, photo-degradation and radiation degradation are time-consuming and incapable to obtain the valuable monomer. In comparison, catalytic hydrolysis or supercritical hydrolysis of nylon 6 is much more environment-friendly, and the monomer could be easily extracted from water after the hydrolytic reaction [10,11]. As a solvent and reaction medium, sub- and supercritical water has been found with increasingly wide utilization in the fields of catalysis, degradation, extraction and separation etc. [12–14]. Goto et al. [15] applied reactions in sub- and supercritical water to convert nylon 6 into its monomers. It was reported that the total yields of $\varepsilon$-caprolactam and the other monomer aminocaproic acid were about 100% for reactions at 300 °C in 60 min or at 330 °C in 30 min. Tomoko Iwaya et al. [16] discussed the influences of reaction temperature, time and water density on the degradation of nylon 6 in sub- and supercritical water; the reaction rate and the scheme were also investigated.

As compared with supercritical water, the reaction condition of subcritical water is much more moderate. Thus we selected the subcritical water to investigate the hydrolytic degradation of MC nylon wastes. The chemical composition of hydrolysis products,

including the solid and liquid phases, and the influences of condition parameters on the product yields are examined. The discussion regarding the degradation of MC nylon in subcritical water is provided and a mechanism is proposed.

## 2. Experimental

### 2.1. Materials

MC nylon samples for this study were ivory MC nylon which was unmodified and collected as processing wastes. The samples were cleaned and crushed into small pieces. The water used in hydrolysis experiments was distilled water. Chromatographically pure ε-caprolactam and ε-aminocaproic acid were obtained from J & K (Beijing, China).

### 2.2. Decomposition in subcritical water

The reaction apparatus is shown in Fig. 1. The 90 cm$^3$ batch-type autoclave made of stainless steel was equipped with a pressure gauge and heated by an electric heating salt bath furnace with the mix of 0.45:0.55 (wt./wt.) NaNO$_2$ and KNO$_3$.

For the reaction, 1.0 g MC nylon sample was placed into the reactor, and then the water was added in a certain weight ratio. The liquid phase in the reactor was transformed into gas–liquid phase as the temperature rose and further raised the inside pressure. In this experiment, the pressure in the reactor with added water began to grow about 3 min after putting the sealed autoclave into the preheated salt bath and this time was defined to be start.

After the specified time at desired conditions, the reaction was quenched by placing the autoclave in an ice water bath quickly, cooling it to room temperature, then the pressure in the reactor dropped to ambient pressure. The products in the first 40 min of the reaction could be separated into solid phase and liquid phase while only liquid phase product existed after 45 min. After filtering and washing, the solid product was dried at 80 °C for 12 h. The liquid product was diluted and then filtered with 0.45 μm filter membrane for further analysis.

### 2.3. Analyses and characterization

The obtained solid products were examined by Fourier transform infrared spectroscopy (FTIR, NICOLET-Nexus 670, USA). The mass ratio of dried KBr and dried solid sample was about 100:1.0–1.5. The mixture powder was ground and compressed into a disk under the infrared lamp. The FTIR spectra were acquired in the wave number range of 400–4000 cm$^{-1}$ with the optical resolution of 2 cm$^{-1}$. Each sample was prepared and tested with 3 repetitions.

Wide-angle X-ray diffraction (WAXD, Empyrean) was employed to reveal the crystalline form changes of the solid products. Diffractograms were obtained from $2\theta = 10°–80°$ with a step size of 0.0131°.

Liquid chromatography mass spectrometry (LC-MS) and high performance liquid chromatography (HPLC) with gradient elution were used to analyze the liquid phase products. The LC-MS instrument was Hybrid Finnigan LCQ DECA XP MAX system with chromatographic column ASB-C18 (5 μm, 150 mm × 4.6 mm). The mass spectrometry used electrospray ionization (ESI) of 5.0 kV, 350 °C and positive ion mode with $m/z$ range 50–1500. The mobile phase was water: acetonitrile = 90:10; the flow rate was 0.3 mL/min; sample size was 5 μL.

The HPLC apparatus was Agilent 1100 system with chromatographic column Zorbax SBC-18 (5 μm, 150 mm × 4.6 mm); UV detector read at 215 nm; the temperature of column was 30 °C. The mobile phase was the mixture of 0.1% acetic acid: acetonitrile = 90:10; velocity flow was 1.0 mL/min; injection volume was 5 μL.

## 3. Results and discussion

### 3.1. Analyses of solid phase products

In subcritical water, MC nylon decomposed completely into water-soluble oligomers without any gas phase product at 345 °C within 45 min, so the solid phase products existed only in the first 40 min of the hydrolytic reaction. The infrared spectra of unreacted MC nylon and the solid product obtained at 15 min of the degradation were investigated to study the chemical composition of solid hydrolytic product. The unreacted MC nylon gave the spectrum basically the same as typical nylon 6 (Fig. 2(a)). Fig. 2(b) obviously indicated that the solid phase product was the incompletely decomposed MC nylon. However a number of noticeable changes appeared in the intensity and area of some absorption bands.

Consequently, Figs.3 to 5 presents the specific infrared spectra of the solid residues obtained at 10, 20 and 30 min of the reaction to demonstrate the changes of solid phase products. The quantity of the solid product detected at 40 min was too small to be collected for further analysis.

The infrared absorption bands matched with CH$_2$ vibrations at 2861 cm$^{-1}$, 2933 cm$^{-1}$ (symmetric and asymmetric stretching
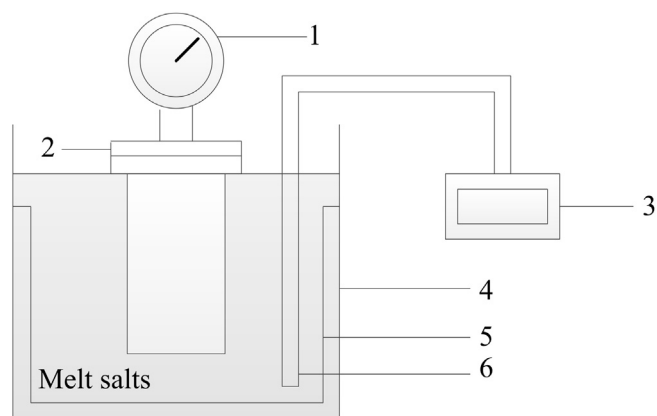


Fig. 1. Apparatus for the decomposition of MC nylon in subcritical water (1-pressure gauge; 2-autoclave; 3- thermometer; 4-salt bath furnace; 5-heater; 6-thermocouple).
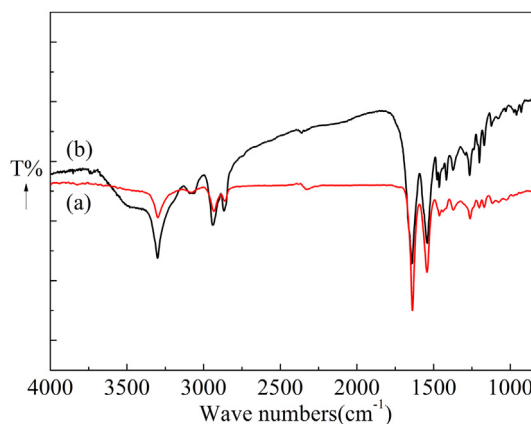


Fig. 2. FTIR spectra of (a) Unreacted MC nylon, (b) Solid product existed at 15 min of the hydrolysis reaction (345 °C, added water 30 g).
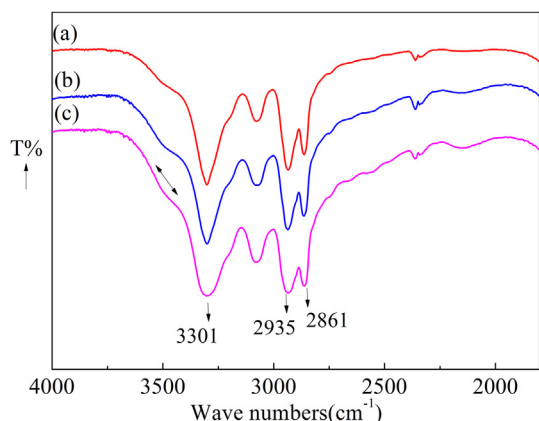
**Fig. 3.** FTIR spectra of solid residues existed at (a) 10 min, (b)20 min, (c) 30 min of the hydrolysis reaction (345 °C, added water 30 g) in the range of 4000–1800 cm$^{-1}$.

vibration of −CH$_2$) in Fig. 3 and 1373 cm$^{-1}$ in Fig. 4 became wider during the hydrolysis reaction, which suggested an enhancement of methylene activities and reflected the changing of the chain conformation.

Absorption band at 1122 cm$^{-1}$ in Fig. 4 belonged to C−CO stretching in the amorphous phase, and the band at 443 cm$^{-1}$ in Fig. 5 was due to the deformation vibrations of unsaturated alkene groups [17]. Changes of these two bands as the reaction time increased described a growth portion of amorphous phase in the solid products.

As shown in Fig. 3, the band at 3301 cm$^{-1}$ (Amide I) assigned to vibrations of hydrogen bonding N−H became wider and weaker during the course of the reaction. Meanwhile a broad band ranging from 3400 cm$^{-1}$ to 3550 cm$^{-1}$ belonging to free stretch N−H vibrations [18] appeared more and more clearly as the reaction time increased. In the FTIR spectra of polyamide, the bands related to the −NHCO− are mainly affected by the mutual arrangement of the hydrogen bonds which dominate the crystal structure of nylons. These results indicated that as the reaction carried on, the strength of hydrogen bond gradually weakened and partially dissociated into free amino group.

Other characteristic infrared absorption bands of amide such as the bands at 1641 cm$^{-1}$ (Amide I, C=O stretching vibration), 1542 cm$^{-1}$ (Amide II, N−H deformations and C−N stretching vibration), 1265 cm$^{-1}$ (Amide III, C−N−H vibration) and 692 cm$^{-1}$ (Amide V) [19] were all observed to change broader as the reaction

time increased (Figs. 4 and 5). This indicated that the number of hydrogen bonds had decreased and the crystal form of solid residue had changed.

Generally, nylon 6 exhibits two well-characterized crystalline forms, named α and γ forms [20,21]. According to Fig. 5, the characteristic infrared absorption bands of the crystalline γ form of MC nylon at 623 cm$^{-1}$, 711 cm$^{-1}$, 975 cm$^{-1}$ and 1170 cm$^{-1}$ became stronger and more clearly observable as the reaction proceeded. This phenomenon indicated the growth of γ form in the solid phase, and obviously suggested that the transformation of crystalline forms occurred during the process of degradation.

The transformation of crystalline forms of solid phase products could also be confirmed by the X-ray diffraction measurements. Fig. 6 shows the XRD patterns of the unreacted MC nylon and the solid residues obtained at different time of the reaction. The unreacted MC nylon showed two typical α crystalline diffraction peaks of nylon 6 at $2\theta = 21°$ and $24°$ which were indexed as 200 and 002 reflections, respectively. The peaks at $2\theta = 22°$ and $23°$ began to be observed in the residues existed at 10 min of the hydrolysis reaction, and the intensity increased obviously as the reaction time increased. These two peaks were indexed as 001 and 200 reflections of γ form respectively, and the 200 reflection always appeared as a shoulder to the 001 reflection [22].

The γ form in MC nylon is determined by the skew conformation of the CH$_2$ units adjacent to the amide group, so it is less ordered than the α form and also a less thermodynamically stable crystal
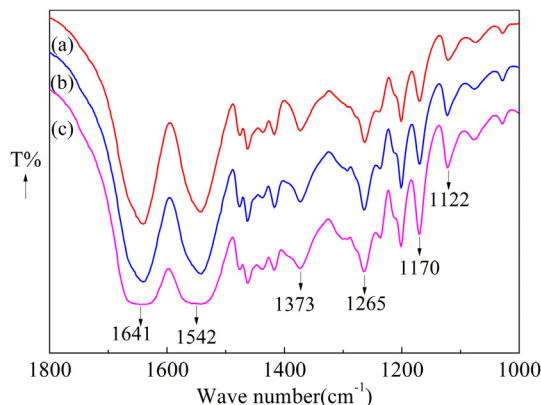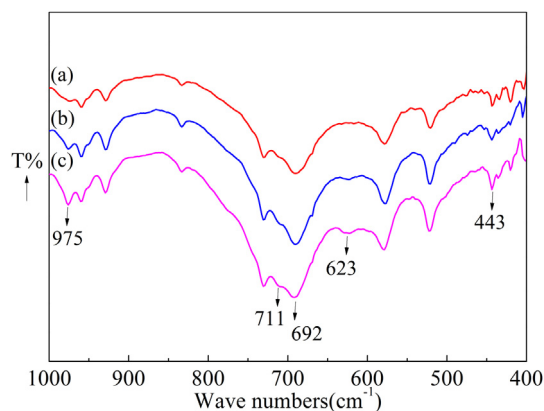


**Fig. 5.** FTIR spectra of solid residues existed at (a) 10 min, (b)20 min, (c) 30 min of the hydrolysis reaction (345 °C, added water 30 g) in the range of 1000–400 cm$^{-1}$.



**Fig. 4.** FTIR spectra of solid residues existed at (a) 10 min, (b)20 min, (c) 30 min of hydrolysis reaction (345 °C, added water 30 g) in the range of 1800–1000 cm$^{-1}$.
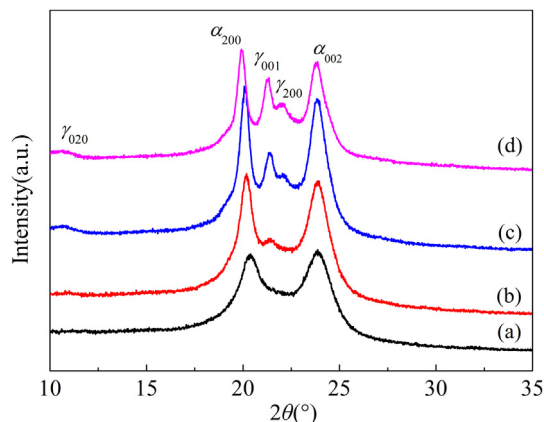


**Fig. 6.** XRD patterns of (a) Unreacted MC nylon and solid residues existed at (b) 10 min, (c)20 min, (d) 30 min of the hydrolysis reaction (345 °C, added water 30 g).

phase [23]. The generation of γ form in the solid residue represented a shorter chain-axis repeat and further reflected the chain scission of MC nylon in the subcritical water. The growth of the less stable crystal phase also revealed that the solid products of the hydrolytic degradation became more and more unstable under the same cooling conditions in the process of reaction.

## 3.2. Analyses of liquid phase products

LC-MS was used to analyze the liquid phase products of degradation reaction. The MS spectra of liquid phase are shown in Fig. 7, and the corresponding compounds of main peaks are given in Table 1. The components in liquid phase could be divided into two categories: the cyclic oligomers $C_n$ and linear oligomers $L_n$. The chemical structures of $C_n$ and $L_n$ are given in Scheme 1. The linear oligomers eluted out from the chromatographic column earlier than the cyclic oligomers because of the exposed amino and carboxyl groups.

According to Fig. 7, the principal product in liquid phase was the target monomer ε-caprolactam (C1). The $n$-value of oligomers dissolved in the reaction medium water was ranging from 1 up to 12, but the peaks attributed to the components with $n > 9$ were so weak that did not be exhibited. As only the oligomers with $n \leq 5$ were detected in the hydrolytic liquid phase of regular nylon 6 [24], the degradation products of MC nylon were much more complex due to the high molecular mass.
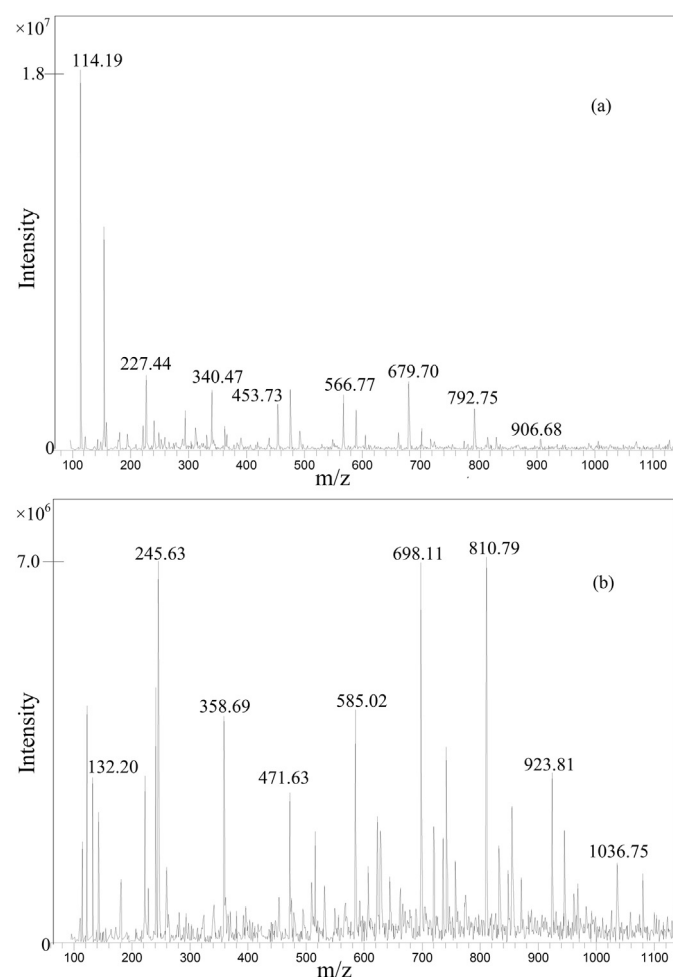


**Fig. 7.** MS spectrum of liquid product existed at 40 min of the hydrolysis reaction (a) cyclic oligomers (b) linear oligomers(345 °C, added water 30 g).
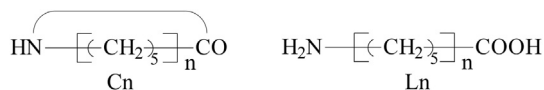
**Table 1**
The relative composition of MC nylon degradation liquid products under different reaction times (at 345 °C, added water 30 g) determined by LC-MS.

| Measured $m/z$ positive | Corresponding compounds | Retention time(min) | Relative peak area[a] (%) | | | |
|---|---|---|---|---|---|---|
| | | | L-10 | L-30 | L-50 | L-70 |
| 114.19 | C1 | 4.13 | 1.28 | 1.78 | 8.85 | 100 |
| 227.44 | C2 | 4.13 | 2.16 | 5.25 | 8.60 | 24.46 |
| 340.47 | C3 | 9.45 | 4.06 | 9.51 | 32.50 | 16.44 |
| 453.73 | C4 | 10.87 | 4.13 | 3.10 | 21.53 | 11.37 |
| 566.77 | C5 | 11.47 | 4.56 | 17.23 | 46.50 | 8.51 |
| 679.70 | C6 | 11.95 | 6.37 | 21.12 | 39.80 | 2.57 |
| 792.75 | C7 | 12.30 | 2.41 | 7.17 | 16.66 | 1.20 |
| 906.68 | C8 | – | – | – | – | – |
| 132.20 | L1 | 1.48 | – | – | – | 1.20 |
| 245.63 | L2 | 1.94 | – | – | 5.84 | 8.87 |
| 358.69 | L3 | 4.66 | – | 0.51 | 5.72 | 2.58 |
| 471.63 | L4 | 8.90 | 1.70 | 5.79 | 18.16 | 3.28 |
| 585.02 | L5 | 9.81 | 7.79 | 24.11 | 65.09 | 5.39 |
| 698.11 | L6 | 10.34 | 14.56 | 42.02 | 73.97 | 3.54 |
| 810.79 | L7 | 10.72 | 12.32 | 32.21 | 51.94 | 1.83 |
| 923.81 | L8 | 11.03 | 9.23 | 30.54 | 41.76 | 1.37 |
| 1036.75 | L9 | 11.33 | 4.46 | 6.07 | 12.12 | – |

[a] Reference compound is ε-caprolactam in L-70.

The liquid products at 10 min, 30 min, 50 min and 70 min of the reaction (hereinafter referred to as L-10, L-30, L-50 and L-70) were collected to examine the compositional changes of liquid phase during the hydrolytic degradation of MC nylon. Because the chromatographic peak area of the ε-caprolactam (C1) in L-70 was the largest among the detected components of different reaction time, the peak area ratio of other components to C1 in L70 was defined as relative area for convenience, which could directly reflected concentration of the components in the liquid phase. The relative peak area of the compositions is calculated and listed in Table 1, as well as the retention times and the corresponding identified degradation products. As it can be seen (Table 1), the concentration of the components with small $n$-value ($n \leq 2$) increased throughout the reaction as the reaction time increased, while the components with $n \geq 3$ increased in the first 50 min and then decreased rapidly. For cyclic oligomers, C5 and C6 were the dominant components within 30 min of the reaction. The data of L-50 and L-70 indicated that the relative area of C3 and C4 increased more rapidly in L-50 than other cyclic oligomers, and the main components of the liquid phase became C1 and C2 in L-70. For linear oligomers, the components L5-L8 had been the primary compositions until the reaction time was more than 50 min.



**Scheme 1.** The chemical structures of $C_n$ and $L_n$.

**Table 2**
The appearance of reaction products under different conditions.

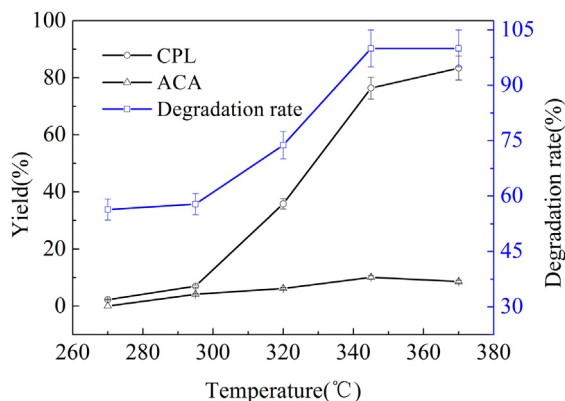| Product appearance | $m_{water}:m_{MC\ nylon}$ | T(°C) | t(min) |
|---|---|---|---|
| Dark yellow slurry, black solids | <20:1 | 320–380 | >15 |
| White hard solids | 20:1–50:1 | 280–320 | <20 |
| White slurry | 20:1–50:1 | 320–350 | 20–40 |
| Transparent colorless liquid, no solids | ≥30:1 | 320–350 | 40–55 |
| | | 350–380 | 25–40 |
| Transparent yellow liquid, no solids | ≥30:1 | 320–350 | >55 |
| | | 350–380 | >40 |

**Fig. 8.** Effect of temperature on the degradation of MC nylon (45 min, added water 30 g).

## 3.3. Effect of reaction parameters on hydrolytic degradation

The effects of temperature, reaction time and the water amounts on the degradation of MC nylon were examined respectively. Appearance of the hydrolysis products changed a lot under different reaction conditions how it is summarized in Table 2. The degradation rate and the yield of relevant monomers, namely ε-caprolactam (CPL) and ε-aminocaproic acid (ACA), are two important indicators to evaluate the effect of hydrolysis reaction that are defined as follows:

$$\text{Degradation rate } (\%) = \text{quantity of soluble parts} \times 100/ \text{quantity of MC nylon taken for hydrolysis}$$

$$\text{Yield } (\%) = \text{quantity of relevant monomer product} \times 100/ \text{quantity of MC nylon taken for hydrolysis}$$

As it can be seen in Fig. 8, the hydrolysis reaction was highly temperature sensitive. Below 300 °C the degradation rate was about 60% only. After rapid cooling the reactor, some white hard solids stuck to the bottom and detected as unreacted MC nylon were observed (Table 2). When the temperature increased to 345 °C, MC nylon decomposed completely into the oligomers dissolved in the water, meanwhile the yield of CPL increased rapidly from 6.9% (at 300 °C) to 76.4%.
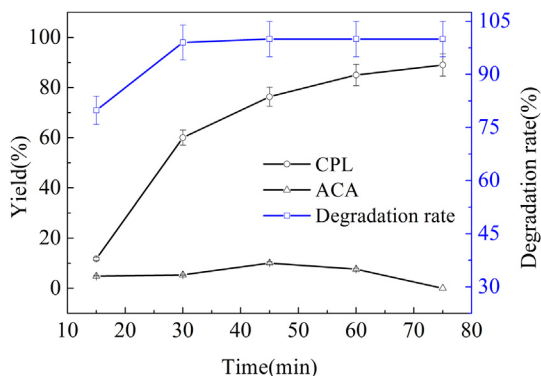
**Table 3**
The pressure in the reactor with different added water amounts.

| Amount of water (g) | Pressure (MPa) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 280 °C | 310 °C | 330 °C | 340 °C | 360 °C | 370 °C | 380 °C |
| 25 | 3.0 | 5.5 | 7.0 | 8.2 | 11.5 | 13.5 | 14.7 |
| 35 | 3.0 | 5.5 | 8.0 | 9.1 | 12.0 | 14.0 | 16.0 |
| 45 | 3.0 | 5.6 | 8.0 | 9.0 | 12.0 | 14.0 | 16.1 |

The yield of CPL increased drastically after 15 min reacting, and the degradation rate reached 100% at 45 min (Fig 9). When the reaction time was longer than 55 min, the color of water changed to be darker due to some side reactions (Table 2). It was obvious that the increasing reaction time had a basically similar effect on the degradation of MC nylon in subcritical water as the increasing temperature.

The pressure in the reactor with different quantities of water is listed in Table 3, and Fig. 10 shows the effect of water quantity on the degradation rate and the monomer yields. When the amount of added water was more than 30 g, the yield of CPL and the degradation rate were essentially unaffected due to the almost stable pressure in the reactor as shown in Table 3. However, the yield of CPL was only 48% when the quantity of water was less than 20 g and some black solids together with the dark yellow slurry were generated. We assume it was caused by some oxidation reaction along with carbonization reaction due to insufficient contact between the MC nylon and the water.

ACA was considered to be an intermediate hydrolytic product of nylon 6 in subcritical water [16]. The maximum yield of ACA reached about 12.1% as shown in Fig. 10. Similar with the case of CPL, the yield of ACA also maintained almost constant (about 10%) when the added water was more than 30 g with the fixed temperature and reaction time.

As Figs. 8 and 9 suggest, the yield of ACA tended to decrease when the hydrolysis temperature and time increased, this could be attributed to the further polymerization or cyclodehydration of ACA in subcritical water. However, the increasing time and temperature were preferred for obtaining more CPL. The maximum yield of CPL was 89% in this experiment when the reaction was carried out for 75 min at 345 °C.

## 3.4. Proposal of hydrolytic degradation scheme

A scheme proposed by the analyses of solid and liquid phase products of MC nylon in subcritical water is shown in Scheme 2. The hydrogen bonds between the molecules were destructed in the subcritical water, followed by the increasing concentration of free
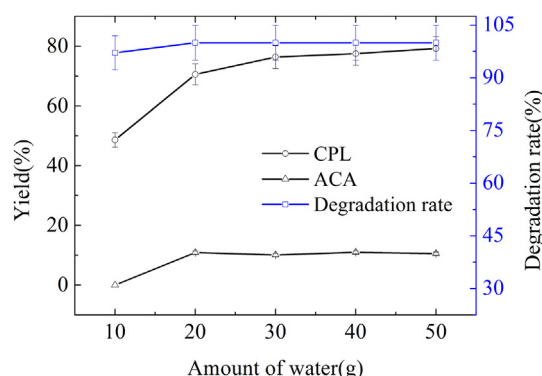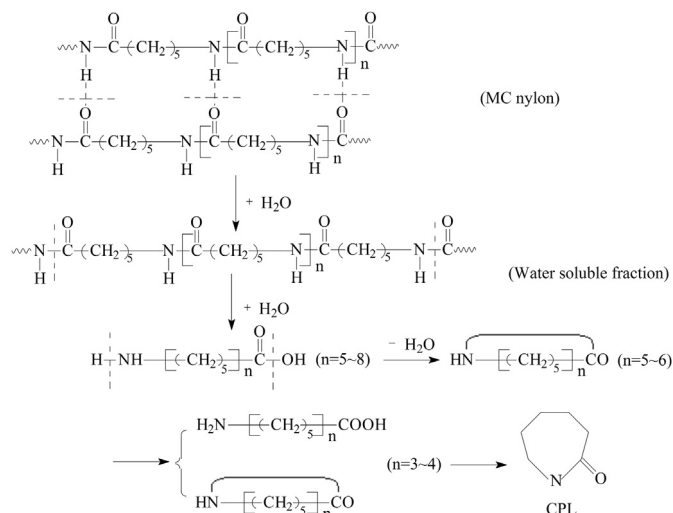


**Fig. 9.** Effect of reaction time on the degradation of MC nylon (345 °C, added water 30 g).



**Fig. 10.** Effect of water amounts added to the reactor on the degradation of MC nylon (345 °C, 45 min).

**Scheme 2.** A proposed mechanism for the degradation of MC nylon in subcritical water.

N–H, unsaturated species and the amorphous phase in the solid residues. At the same time, $H_2O$ attacked carbonyl groups to take place the nucleophilic substitution reaction. The chain scission caused by these hydrothermal effects generated the oligomers dissolved in water. LC-MS analysis indicated that the monomer CPL was produced gradually by the cyclization and dehydration of the cyclic and linear oligomers step by step till the complete degradation of MC nylon, but not excluding the possibility of some random scission.

## 4. Conclusions

MC nylon was subjected to hydrolytic degradation using the subcritical water in this work. The solid phase products observed in the first 40 min of the decomposition were unreacted MC nylon. However, the crystalline form of the solid products transformed from $\alpha$ to $\gamma$ form which was less thermodynamically stable as the reaction proceed. The components in the liquid phase were much more complex than that of regular nylon 6, involving the linear and cyclic oligomers according to the LC-MS measurement.

In subcritical water, MC nylon was completely decomposed to water-soluble monomers and oligomers after 45 min at 345 °C and 9 MPa. The goal product was $\varepsilon$-caprolactam and the maximum yield was up to 89% after hydrolysis reaction for 75 min. The researches on the reaction parameters proved that the temperature and the reaction time were two influential factors of the degradation, while the amount of water was less important due to the almost constant pressure in the subcritical state when the amount was more than 30 g.

The broken of hydrogen bonds and the molecular chain scission occurred during the degradation reaction of MC nylon, and then generated the oligomers dissolved in water. As the hydrolytic reaction went on, the yields of linear and cyclic oligomers with smaller $n$-value ($n \leq 2$) increased while the yields of oligomers with $n \geq 5$ decreased. The hydrolytic process of MC nylon in subcritical water was a typical nucleophilic substitution reaction which took place step by step till the complete degradation.

## Acknowledgment

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