



Catalytic hydrolysis of waste nylon 6 to produce ϵ -caprolactam in sub-critical water

Jinyang Chen^{a,*}, Guiyang Liu^a, Lujiang Jin^a, Pei Ni^b, Zhi Li^a, Haibo He^c, Yi Xu^a, Jianqiu Zhang^a, Junping Dong^c

^a School of Environmental and Chemical Engineering, Shanghai University, 333 Nanchen Rd., Baoshan, Shanghai 200444, China

^b State Key Laboratory for Mineral Deposit Research, Institute of Geo-Fluid, School of Earth Science and Engineering, Nanjing University, Nanjing 210093, China

^c School of Sciences, Shanghai University, Shanghai 200444, China

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ABSTRACT

The wide use of nylon 6 (PA 6) resulting in the resource recovery of waste PA 6 is urgent and its hydrolysis in sub-critical water to produce ϵ -caprolactam is a very important method. Hydrothermal diamond anvil cell (HDAC) was used to in situ observe transformation of PA 6 in water up to 513 K. The result shows that PA 6 melts at 488 K, and then hydrolyzes to produce low molecular dissoluble compounds such as 6-aminocaproic acid and ϵ -caprolactam from cleavage of acyl-amido bond. Different from the microreactor (about 0.075 μ l) of HDAC, degradation of PA 6 in hydrothermal vessel of 18 ml is far slow, so the higher temperatures of 553, 573, 583, and 603 K are tried. As for hydrothermal vessel runs, liquid products after degradation are mainly composed of ϵ -caprolactam. Phosphotungstic heteropoly acid (HPA) as catalyst can improve hydrolysis rate and yield of ϵ -caprolactam, and 3% HPA can attain preferable effect. The optimum hydrolysis conditions for ϵ -caprolactam are as follows: HPA amount is 3%, reaction temperature is 573 K and reaction time is 85 min, and the yield of ϵ -caprolactam is 77.96%. In the temperature range of 553–603 K, the non-catalytic and catalytic degradation kinetics are studied as pseudo-first-order reaction and apparent activation energy is 86.64 and 77.38 kJ/mol for no catalyst and 3% HPA, respectively.

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1. Introduction

Plastic products are widely used in human life and waste plastics have caused serious pollution. Recently, feedstock recycling is becoming a promising route for the management of waste plastic, and the pyrolysis to convert waste plastic into chemical intermediates gets more and more attention. Direct pyrolysis in inert atmospheric conditions has many disadvantages such as batch production, low yield, poor quality, long time, second pollution of dust, exhaust air, sewage, and solid waste, and high carbonization to block tubing, thus, its industrial application is very discommodious. Now it is known that high temperature and pressure water presents some unique properties such as dissolution of non-polar organic, low dielectric properties and high diffusibility, and high concentrations of H^+ and OH^- ions from dissociation of water [1–10]. From in situ visualization of polystyrene pyrolysis in sub- and super-critical water, it shows that products of pyrolysis can dissolve in water owing to the decrease of polarity of water at high temperature; therefore, it can

obtain higher yield of low molecule to avoid further condensation reaction and carbonization. In addition, after reaction, when the temperature decreases to the ambient temperature, some non-polar organic products can autosegregate from water [11]. Therefore, pyrolysis of waste plastic in high temperature and pressure water can avoid disadvantages of direct pyrolysis and shows good prospect for recycling waste polymer to produce chemicals [12].

PA 6 is an important engineering plastic and widely used, so treatment of waste PA 6 becomes more and more urgent. As a polymer of acyl and amido link, it is found that PA 6 can hydrolyze at acyl-amido bond to produce ϵ -caprolactam ultimately in high temperature and pressure water [13,14]. As a monomer to synthesize PA 6, ϵ -caprolactam is synthesized with cyclohexanone-oxime and rearrangement of Beckmann from benzene or toluene. The method is very complex, corrosive, pollutant and has byproduct, and thus, pyrolysis of waste PA 6 in sub- and super-critical water to obtain ϵ -caprolactam is very important. With increasing temperature, although hydrolysis rate of PA 6 increases, the product of ϵ -caprolactam decomposes quickly to cause low yield. In addition, with increasing temperature, corrosion is a very serious problem and high temperature makes it very difficult to industrial application. Whereas, at low temperature of sub-critical

* Corresponding author. Tel.: +86 21 6613 7729; fax: +86 21 6613 7725.

E-mail address: chenjy@shu.edu.cn (J. Chen).

water, although decomposition of ϵ -caprolactam is slow, hydrolysis of PA 6 is also slow and this is a disadvantage for industrial application [15]. Therefore, we study HPA ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) as catalyst to accelerate hydrolysis of PA 6 and increase yield of ϵ -caprolactam in comparatively mild sub-critical water. HPA as an acid catalyst presents strong acidity, high hydrothermal stability, and low acid corrosion to most metal owing to formation of passivation layer [16,17].

2. Experimental

The samples of PA 6 and HPA were obtained from Taizhou Luqiaosijia Biochemical Plastic Plant (Zhejiang, China) and Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). PA 6 was cleaned with distilled water and heated at 330 K for 24 h before use. The water used is distilled water.

The in situ observation method is adopted HDAC shown in Fig. 1 and it is the same described in the former paper [10] except for replacing of corundum with diamond. The culets of diamond anvils are about 1000 μm in diameter. The rhenium gasket of 260 μm in thickness was drilled a hole of 400 μm in diameter as sample chamber. Initially sample chamber remained some air bubbles in order not to cause pressure to increase too high after heating.

The hydrothermal vessel shown in Fig. 2 is a volume of 18 ml and heated with electric salt bath of mix of 1:1 (wt/wt) NaNO_3 and KNO_3 . The samples of nylon:water is about 1:15 (wt/wt) and total volume of all samples put in vessel is 12 ml to maintain appropriate pressure and keep relatively smooth reaction [10]. After reaction, the hydrothermal vessel was put in ice water to cool to room temperature and then opened to take product for analysis.

Liquid phase products were analyzed by MS and HPLC. The MS instrument is Hybrid Quadrupole-TOF system, made by Applied Biosystems Co., USA. The measurement uses ESI of 4.5 kV and 300 $^\circ\text{C}$, GS1 of 45.00, GS2 of 30.00, CUR of 10.00 μA , and range (m/z) 90–1000. The HPLC is Agilent 1100 system, made by Agilent Co., USA. The measurement uses chromatographic column of Zorbax SB-C18 (5 μm , 250 mm \times 4.6 mm), UV-vis detector of 225 nm, temperature of column 303 K, mobile phase water:acetonitrile = 80:20 + 0.1% (v/v) acetic acid, velocity flow of 0.1 ml/min, sample size 5 μl . Production after HPA catalysis is neutralized by 0.1 mol/L NaOH solution before measurement.

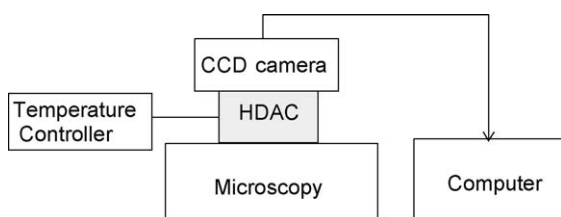


Fig. 1. Schematic diagram of the visualization system.

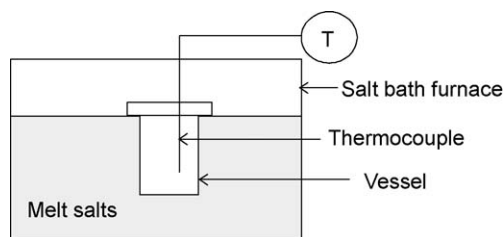


Fig. 2. Schematic diagram of hydrothermal vessel system.

3. Results and discussion

3.1. In situ visualization of transformation of PA 6 in water with increasing temperature

PA 6 is a plastic whose melting point and pyrolysis are about 488 and higher than 573 K, respectively. Fig. 3 gives some micro-photographs of observational transformations of PA 6 with increasing temperature in water. With increasing temperature, air bubbles disappear at the temperature of 386 K. PA 6 starts to metamorphose and melt at the temperature of 488 K and the solid powder PA 6 totally melts to non-soluble liquid phase at the temperature 504 K. Concomitant with melting process, the liquid phase PA 6 decreases. When temperature increases to 513 K and remains at that temperature, the liquid phase PA 6 decreases with increasing time, but at the time of 35 min, the residue becomes very small and remain steady with increasing time.

During cooling, the cell remains with no obvious change till ambient temperature. The in situ visualization indicates that disappearance of PA 6 results from degradation to low molecular dissoluble compounds even at ambient temperature. From the result, it indicates that the compounds should be polar compounds and it can be inferred that they stand a good chance to be 6-aminocaproic acid and ϵ -caprolactam from hydrolysis of acyl-amido bond. And from the micro-photograph (b) of residues of the lower anvil diamond after unlied upper diamond, they are oil phase drops and clearly different from solid PA 6, thus it should be non-dissoluble oligomer of degradation of PA 6. The result shows that the PA 6 almost totally decomposes at the 513 K of 35 min and produces mainly low molecular dissoluble compounds and non-dissoluble oligomer. Owing to that this is a very small volume (about 0.075 μl), the macroscopic effect of reaction such as diffusion cannot be considered, and so the reaction rate will be fast. But as for large volume of 18 ml hydrothermal vessel experiment, it is found at the same condition that the degradation rate of PA 6 is far slower than the HDAC experiment, i.e., at the temperature of 513 K, even at the time of 120 min, there is very little degradation of PA 6. The result indicates that microreactor will improve reaction condition [18]. Therefore, the temperature of hydrothermal vessel experiment is higher than 513 K to obtain appropriate result.

3.2. Hydrolysis products

Typical MS spectrum of products in liquid phase is shown in Fig. 4 and corresponding compounds of main peaks are given in Table 1. The result clearly shows that the main product is ϵ -caprolactam; and in addition, there are some 6-aminocaproic acid, dimer, trimer, tetramer, pentamer and other oligomer of ϵ -caprolactam and 6-aminocaproic acid, which is the same as former studies of non-catalytic process [13–15].

Typical HPLC spectrum is shown in Fig. 5 and the liquid phase product presents a main peak at around 5 similar to standard ϵ -caprolactam sample. The result indicates the main product of PA 6 degradation is indeed ϵ -caprolactam. The weak peaks ranged from 2 to 4 in the spectrum of liquid products should be some other products.

3.3. Appropriate amount of HPA as catalyst

As for the determination of optimum condition of PA 6 hydrolysis to produce ϵ -caprolactam, the degradation rate of PA 6 and yield of ϵ -caprolactam will be discussed. Degradation rate of PA 6 is expressed as $(m_0 - m_t)/m_0 \times 100\%$, and m_0 and m_t are weight of PA 6 and residual solid after reaction, respectively. Yield

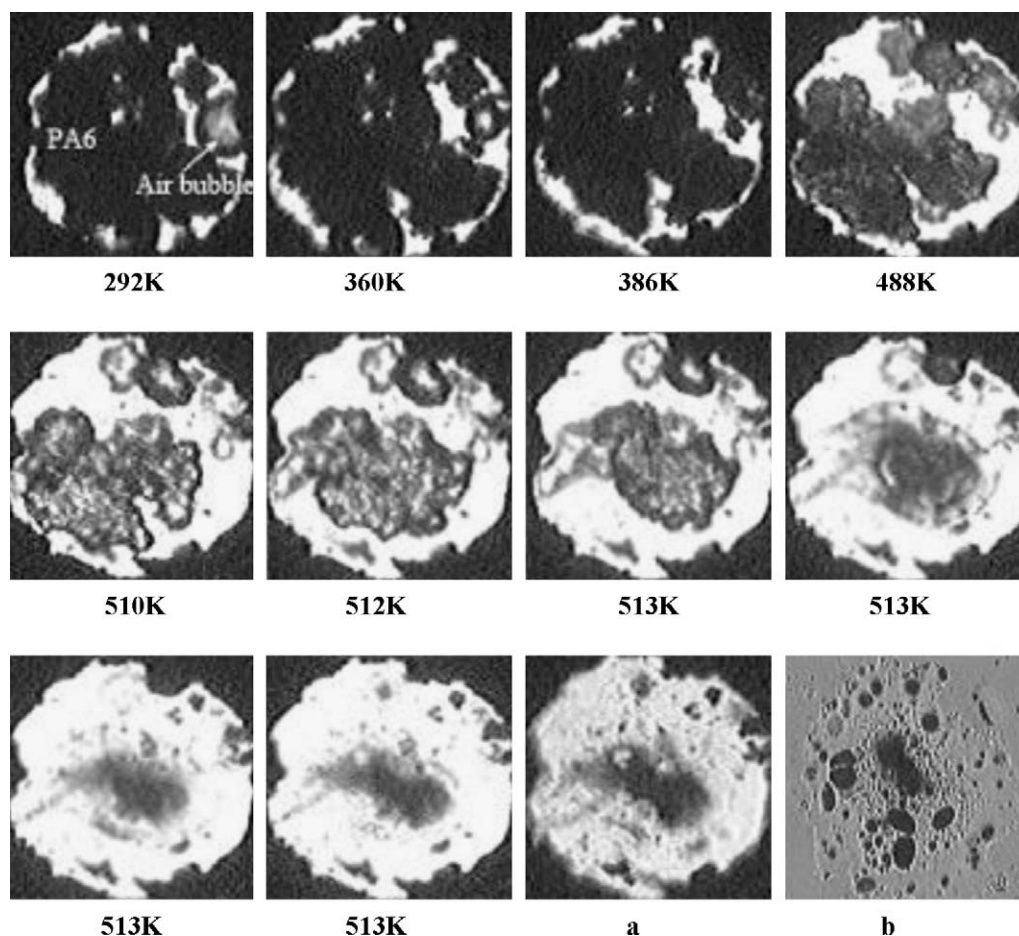


Fig. 3. Selected micro-photographs showing the observation transforms with increasing temperature of PA 6 in water: (a) ambient temperature after reaction; (b) residues on the culet of the lower anvil diamond after unlid upper diamond.

of ϵ -caprolactam is expressed as $M_t/m_0 \times 100\%$, and M_t and m_0 are weight of ϵ -caprolactam and initiative PA 6, respectively.

Fig. 6 gives the effect of different amounts of HPA on degradation rate of PA 6 and yield of ϵ -caprolactam at 573 K. It shows that the addition of HPA can accelerate the degradation rate and improve yield of ϵ -caprolactam. As for the hydrolysis of PA 6 at high temperature and pressure water, water participates in reaction with acid catalysis. Thus, HPA addition increases acidity

to accelerate reaction. With increasing amount of HPA, degradation rate and yield of ϵ -caprolactam will increase at comparatively short time, but comparing 3% with 5% HPA, it shows that the differences are not obvious. Especially at 55 min, the degradation of PA 6 is both almost 100%, and yield of ϵ -caprolactam is 59.32% and 60.87% for 3% and 5% HPA, respectively. Based on the results and considering the cost and after-treatment of HPA, it can be inferred that appropriate amount of HPA is 3%. Thus, the following study of effect of temperature, time and kinetics adopts 3% HPA.

3.4. Degradation of PA 6 and yield of ϵ -caprolactam in dependency on temperature and time

Fig. 7 gives degradation rate of PA 6 and yield of ϵ -caprolactam at different temperatures with time. With increasing temperature, the time of total degradation of PA 6 decreases. For the 603 K, it is only 25 min that almost all PA 6 is decomposed; whereas, the time

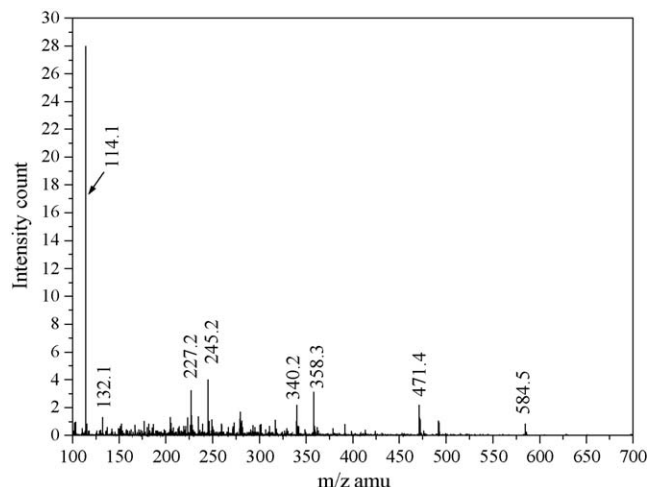


Fig. 4. Typical MS spectrum of liquid products (573 K, 40 min and 3%HPA).

Table 1

Compounds of main peaks shown in MS spectrum.

m/z	Compounds
114.1	ϵ -Caprolactam
132.1	6-Aminocaproic acid
227.1	ϵ -Caprolactam dimer
245.2	6-Aminocaproic acid dimer
340.2	ϵ -Caprolactam trimer
358.0	6-Aminocaproic acid trimer
471.4	6-Aminocaproic acid tetramer
584.5	6-Aminocaproic acid pentamer

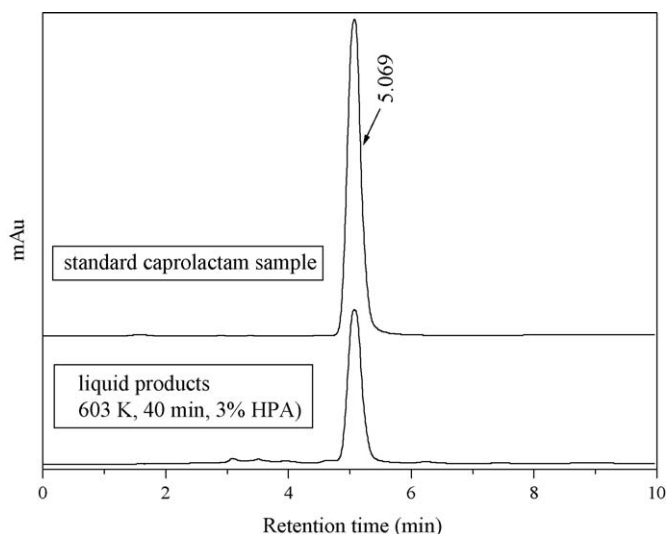


Fig. 5. Typical HPLC spectrum of standard ϵ -caprolactam and liquid products (603 K, 40 min and 3%HPA).

for 553, 573, and 583 K increases to 100, 70, and 55 min, respectively. The result shows that high temperature benefits the degradation of PA 6 owing to two effects, the first is decrease of water viscosity and increase of reacting substance diffusion to improve contact of PA 6 and catalyst, the second is dissociation of water to give more H^+ and OH^- to participate reaction.

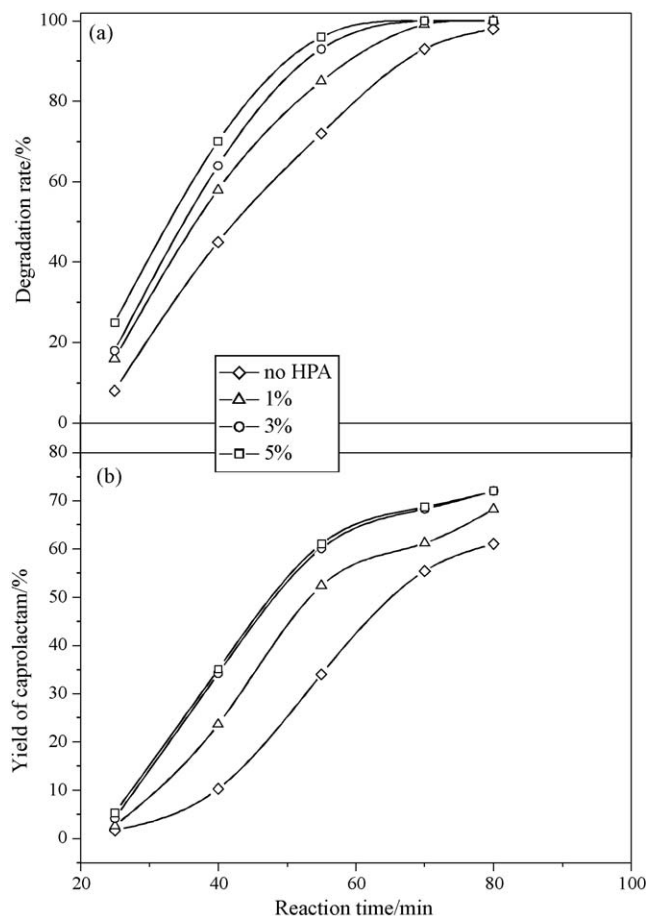


Fig. 6. Effect of catalyst on degradation rate of PA 6 and yield of ϵ -caprolactam at 573 K: (a) degradation rate of PA 6; (b) yield of ϵ -caprolactam.

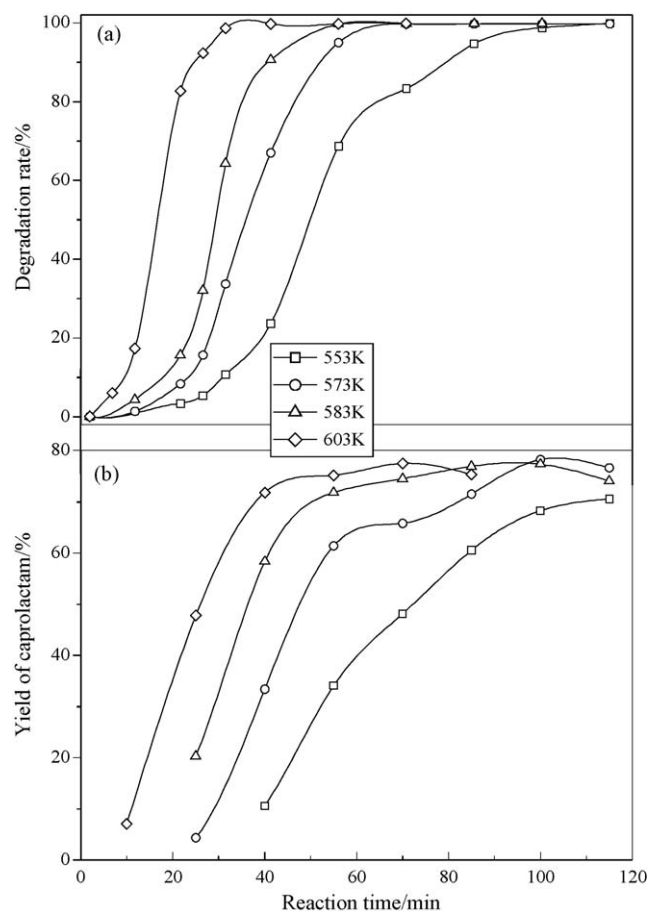


Fig. 7. Change of degradation rate of PA 6 and yield of ϵ -caprolactam with reaction time at different temperature (3% HPA): (a) degradation rate of PA 6 and (b) yield of ϵ -caprolactam.

At comparatively short time, yield of ϵ -caprolactam presents same change with degradation rate, that is it also increases with increasing time. But with increasing time further, the yield of ϵ -caprolactam presents transition change at some comparatively long time. For example, as for the highest temperature of 603 K, the highest yield of ϵ -caprolactam is 77.52% at 70 min, and with increasing time, at 85 min the yield decreases to 75.32% on the contrary. The result is owing to that product of ϵ -caprolactam cannot separate from the close reaction system and it will decompose with time at high temperature. Therefore, as for the process of hydrothermal degradation of PA 6 to produce ϵ -caprolactam, temperature and time are both important effect to yield of ϵ -caprolactam and determination of appropriate time and temperature is very important. According to the relation of yield of ϵ -caprolactam with temperature and time, the optimum condition of 3% HPA as catalyst is the temperature of 573 K, time of 85 min, and ϵ -caprolactam can attain highest yield of 77.96%.

3.5. Mechanism and kinetic

PA 6 is condensation polymerization from ring-opening reaction of ϵ -caprolactam and it is easy for degradation reaction at acyl-amido bond. The reaction mechanism can be shown in Fig. 8. As for sub-critical water, it dissociates to give H^+ and two H^+ attack acyl-amido bond to cause more positive electricity to C in carbonyl group. Then H_2O attacks carbonyl groups to take place nucleophilic addition reaction. Subsequently, the addition bond eliminates two H^+ to produce one 6-aminocaproic acid. The 6-aminocaproic acid quickly dehydrates and takes place cyclization

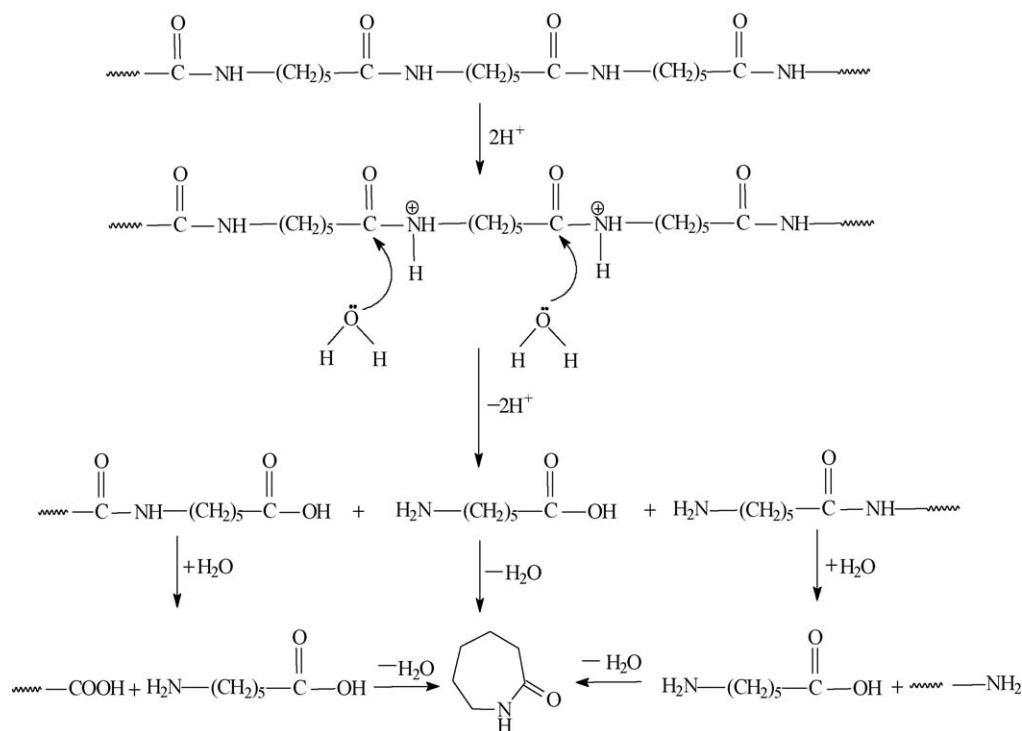
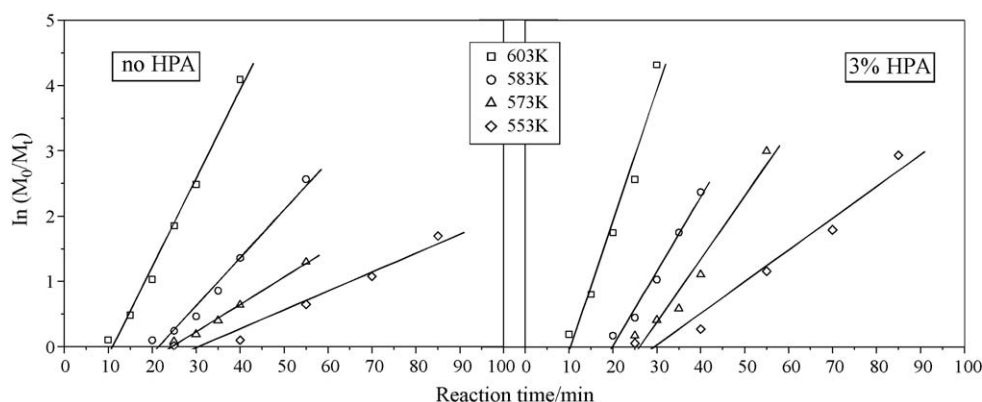


Fig. 8. Mechanism of catalytic hydrothermal degradation PA 6.

Fig. 9. Relationship between $\ln(M_0/M_t)$ and reaction time.

to produce ϵ -caprolactam. The corresponding oligomer will take analogous reaction step by step till total degradation. Whereas, as for thermal decomposition of PA 6, it has two reaction processes of an intramolecular back-biting process and a hydrogen transfer reaction leading to scission of the C–N bond β to the amide group, and thus, the products are more complex [15,19,20].

According to the study of Iwaya et al. [15] that the activation energy of degradation of PA 6 to aminocaproic acid should be greater than its cyclodehydration to caprolactam at comparatively low temperature sub-critical water, it indicates that the degradation of PA 6 is a key step; therefore, the kinetics of PA 6 degradation is discussed. As for the kinetics of polymer degradation, it can be treated as pseudo-first-order reaction. Thus, the equation of PA 6 degradation kinetics can be expressed as following Eq. (1) as pseudo-first-order reaction:

$$-\frac{d[\text{PA 6}]}{dt} = K[\text{PA 6}][\text{H}_2\text{O}]^n \quad (1)$$

Owing to excess of water, then Eq. (1) can be simplified as Eq. (2):

$$-\frac{d[\text{PA 6}]}{dt} = k'[\text{PA 6}] \quad (2)$$

If the initial content of PA 6 is expressed as $[\text{PA 6}]_0$, and the content of some time is expressed as $[\text{PA 6}]_t$, then, integral of Eq. (2) can be expressed as following Eq. (3):

$$\ln \frac{[\text{PA 6}]_0}{[\text{PA 6}]_t} = k't \quad (3)$$

Table 2

Degradation constants at different temperatures.

T (K)	553	573	583	603
k' min ⁻¹ (no HPA)	0.0289	0.0418	0.0733	0.1355
k' min ⁻¹ (3% HPA)	0.0485	0.0965	0.1142	0.2003

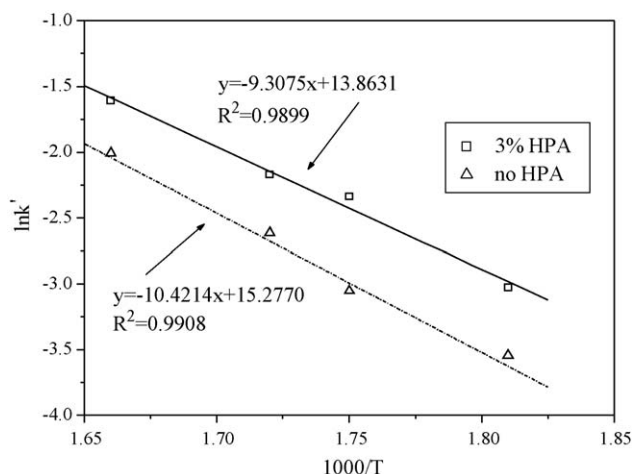
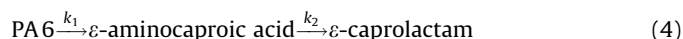


Fig. 10. Relationship between degradation constants and temperature.

As for PA 6, it is solid, thus its content can be expressed as weight. Therefore, the expression of $[PA\ 6]_0/[PA\ 6]_t$ can be replaced as M_0/M_t . Then Eq. (3) can be changed as $\ln(M_0/M_t) = k't$. Fig. 9 shows relation between $\ln(M_0/M_t)$ and reaction time and the line fitting rate constant k' of different temperature is given in Table 2.

The relation of rate constant k' and temperature is linearly fitted as shown in Fig. 10. According to Arrhenius equation, the line fitting relation of $\ln k'$ and $1000/T$ gives that reaction apparent activation energy (E_a) are 77.38 and 86.64 kJ/mol for 3% HPA catalyst and no catalyst, and corresponding pre-exponential factor A are 1.05×10^6 and 4.31×10^6 , respectively. The decrease of reaction apparent E_a with 3% HPA indicates that addition of HPA indeed can accelerate degradation rate of PA 6. It is reported that if the hydrolysis of PA 6 is described by following Eq. (4), the E_{a1} was 97.1 kJ/mol at 573–633 K and 5.4 kJ/mol at 633–673 K [15].



The non-catalytic degradation E_a of PA 6 at 553–603 K is less than the E_{a1} and the paradoxical result indicates that the residual solid after hydrolysis should have some oligomer other than ε -aminocaproic acid, especially at comparatively low temperature, thus, the production rate of ε -aminocaproic acid should be slow than degradation rate of PA 6 and then the corresponding fitted E_a decreases. In addition, comparing with E_a of thermal decomposition of 40–220 kJ/mol, it is obvious that the method of hydrolysis in sub-critical water to produce ε -caprolactam is more feasible.

4. Conclusions

Hydrolysis of PA 6 in sub-critical water can obtain main product of ε -caprolactam. This method is very important not only for the treatment of waste PA 6 but also for the resource recovery of ε -

caprolactam. In situ visualization shows that after melting of PA 6, it can fast hydrolyze to produce low molecular compounds which can dissolve in water forming homogeneous phase even cooling to ambient temperature. As for main compounds of ε -caprolactam, it decomposes quickly at high temperature of super-critical water to lower its yield. Appropriate amount of HPA addition can improve PA 6 hydrolysis to obtain high yield ε -caprolactam in comparatively low temperature sub-critical water, and the kinetics shows that decrease of apparent activation energy with 3% HPA indicates that addition of HPA can indeed accelerate degradation rate of PA 6. As for the separation of ε -caprolactam from HPA solution, it can adopt new method of pervaporation through crosslinked PVA membranes [21,22], and then residual HPA solution can be recycled again.

According to the great difference between microreactor of HDAC and hydrothermal vessel, it obviously shows advantage of microreactor which can far lower reaction temperature and shorten reaction time. The microreactor should be a trend of development for industrial application of high temperature hydrothermal reaction which can avoid main obstacles such as unsafety and corrosion.

Acknowledgements

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References

- [1] N. Akiya, P.E. Savage, Chem. Rev. 102 (8) (2002) 2725–2750.
- [2] A. Kruse, E. Dinjus, J. Supercrit. Fluids 39 (3) (2007) 362–380.
- [3] A. Kruse, E. Dinjus, J. Supercrit. Fluids 41 (3) (2007) 361–379.
- [4] G. Brunner, J. Supercrit. Fluids 47 (3) (2009) 373–381.
- [5] T. Sato, E. Haryu, T. Adschiri, K. Arai, Chem. Eng. Sci. 59 (6) (2004) 1247–1253.
- [6] T. Arita, K. Nakahara, K. Nagami, O. Kajimoto, Tetrahedron Lett. 44 (5) (2003) 1083–1086.
- [7] H. Weingärtner, E.U. Franck, Angew. Chem. Int. Ed. 44 (2005) 2672–2692.
- [8] W. He, G. Li, L. Kong, H. Wang, J. Huang, J. Xu, Resour. Conserv. Recycl. 52 (5) (2008) 691–699.
- [9] K. Arai, R.L. Smith Jr., T.M. Aida, J. Supercrit. Fluids 47 (3) (2009) 628–636.
- [10] H. Cheng, X. Zhu, C. Zhu, J. Qian, N. Zhu, L. Zhao, J. Chen, Bioresour. Technol. 99 (9) (2008) 3337–3341.
- [11] J. Chen, H. Zhang, H. Zheng, X. Zhu, Y. Zeng, J. Anal. Appl. Pyrolysis 76 (1–2) (2006) 260–264.
- [12] M. Goto, J. Supercrit. Fluids 47 (3) (2009) 500–507.
- [13] O. Sato, Y. Ikushima, Kobunshi Ronbunshu 58 (10) (2001) 533–540.
- [14] M. Goto, M. Umeda, A. Kodama, T. Hirose, S. Nagaoka, Kobunshi Ronbunshu 58 (10) (2001) 548–551.
- [15] T. Iwaya, M. Sasaki, M. Goto, Polym. Degrad. Stabil. 91 (9) (2006) 1989–1995.
- [16] I. Arslan-Alaton, J.L. Ferry, Appl. Catal. B: Environ. 38 (4) (2002) 283–293.
- [17] N. Mizuno, M. Misono, Chem. Rev. 98 (1) (1998) 199–217.
- [18] W. Ehrfeld, V. Hessel, H. Löwe, Microreactors: New Technology for Modern Chemistry, Wiley-VCH Verlag GmbH, Weinheim, Germany, 2000, pp. 1–14.
- [19] S.V. Levchik, E.D. Weil, M. Lewin, Polym. Int. 48 (7) (1999) 532–557.
- [20] B.J. Holland, J.N. Hay, Polym. Int. 49 (9) (2000) 943–948.
- [21] L. Zhang, P. Yu, Y. Luo, J. Membr. Sci. 306 (1–2) (2007) 93–102.
- [22] L. Zhang, P. Yu, Y. Luo, Sep. Purif. Technol. 52 (1) (2006) 77–83.