

CATALYTIC HYDROTHERMAL DEPOLYMERIZATION AND KINETICS OF NYLON 6

Jinyang Chen*,¹ Guiyang Liu,¹ Lujiang Jin,¹ Pei Ni,² Zhi Li,¹ Yi Xu,¹ Jianqiu Zhang,¹
Haibo He,³ Junping Dong³

¹ School of Environmental and Chemical Engineering, Shanghai University,
Shanghai 200444, China

² State Key Laboratory for Mineral Deposit Research, Institute of Geo-Fluid, School of Earth
Science and Engineering, Nanjing University, Nanjing 210093, China

³ School of Sciences, Shanghai University, Shanghai 200444, China

E-mail: chenjy@shu.edu.cn

Abstract: Depolymerization of nylon6 to ϵ -caprolactam with environmental-friendly heteropolyacid catalyst at temperatures between 553K and 603K, under different pressures of 6.4-12.8 MPa in water medium. The products of depolymerization were analysed qualitatively and quantitatively by means of FT-IR, LC/MS and HPLC. The results indicated that the main depolymerized product was ϵ -caprolactam. Remnants solid product was undepolymerized nylon6 and the liquid products contained a little 6-aminocaproic acid and oligomer. The highest yield of ϵ -caprolactam was 77.96% at 573K under 85min. Compared with no catalyst, the depolymerization rate and yield of ϵ -caprolactam was high under catalytic condition. Temperature and time also had important effect on depolymerization reaction. Catalytic depolymerization kinetic at different reaction conditions was studied, where the reaction activation energy was evaluated to be 77.38kJ/mol.

Keywords: nylon6; heteropolyacid catalyst; depolymerization reaction; ϵ -caprolactam; kinetics

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 is batch, 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.[1-7] Pyrolysis of waste plastic

in high temperature and pressure water can avoid disadvantage of direct pyrolysis and shows good prospect for recycling waste polymer to produce chemicals.[8]

Nylon 6 (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 caprolactam ultimately in high temperature and pressure water.[9,10] With increasing temperature, although hydrolysis rate of PA 6 increases, but product of caprolactam also decomposes quickly. Therefore, we study phosphotungstic heteropoly acid (HPA) as catalyzer to accelerate hydrolysis of PA6 and increase yield of caprolactam in comparatively mild hydrothermal condition. HPA as an acid catalyzer presents strong acidity, high hydrothermal stability, and low acid corrosion to most metal owing to passivation layer forming.[11,12]

The hydrothermal vessel used is a volume of 18ml and heated with electric salt bath of mix of NaNO₃ and KNO₃. The samples of nylon:water:catalyzer is about 1:15:0.03 (Wt/Wt/Wt) and total volume of all samples put in vessel is 12 ml. After reaction, the hydrothermal vessel was put in ice water to cool to room temperature, and then opened to take product for analysis. Liquid products are neutralized by 0.1mol/L NaOH dissolution before measurement and were analyzed by MS and HPLC. The MS instrument is Hybrid Quadrupole-TOF system, Applied Biosystems Co. of USA made. The measurement uses ESI of 4.5kV and 300°C, GS1 of 45.00, GS2 of 30.00, CUR of 10.00μA, and range (m/z)90-1000. The HPLC is Aglient 1100 system, Aglient Co. of USA. The measurement uses chromatographic column of Zorbax SB- C18 (5μm, 250 mm ×4.6 mm), UV-Vis detector of 225nm, temperature of column 30°C, mobile phase water: acetonitrile=80:20+0.1% (V/V) acetic acid, velocity of flow 0.1ml/min, sample size 5μl.

Typical MS spectrum of liquid products is shown in Fig. 1 and corresponding compounds of main peaks is given in Tab. 1. The result clearly shows that the main product is caprolactam, and in addition, there are some 6- aminocaproic acid, dimer, trimer, tetramer, pentamer and other oligomer of caprolactam and 6- aminocaproic acid.

Fig. 2 and 3 give degradation rate of PA 6 and yield of caprolactam of different temperature 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 degraded, whereas, the time for 553, 573, and 583K are 100, 70, and 55 min, respectively. The result shows that high temperature benefits the degradation of PA 6.

At comparatively short time, yield of caprolactam present same change with degradation, that is it also increases with increasing time. Whereas, with increasing time to some comparatively long time, yield of caprolactam presents transition point. For example, as for the highest temperature of 603 K, the highest yield of 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 indicates that caprolactam will decompose with time at high temperature. Therefore, as for the process of hydrothermal degradation of PA 6 to produce caprolactam, temperature and time

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are both important effect to yield of caprolactam and determination of appropriate time and temperature is very important. According to the relation of yield of caprolactam with temperature and time, the optimum condition of 3% HPA as catalyzer is the temperature of 573K, time of 85 min, and caprolactam can attain highest yield of 77.96%.

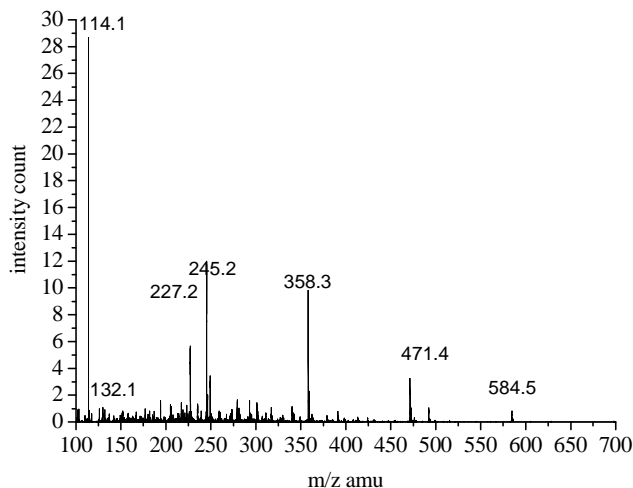


Fig. 1 Typical MS spectrum of liquid products (573K and 40min).

Tab. 1 Corresponding compounds shown in MS spectrum

m/z	compound
114.1	caprolactam
132.1	6- aminocaproic acid
227.1	caprolactam dimer
245.2	6- aminocaproic acid dimer
340.2	caprolactam trimer
358.0	6- aminocaproic acid trimer
471.4	6- aminocaproic acid tetramer
584.5	6- aminocaproic acid pentamer

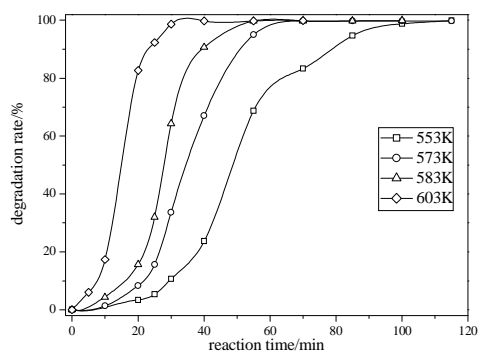


Fig. 2 Degradation rate with reaction time

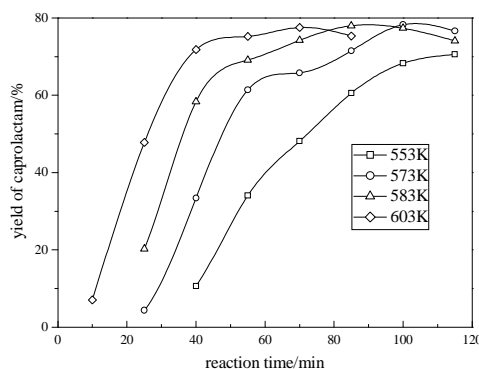


Fig. 3 Yield of caprolactam with reaction time

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 1 as pseudo first order reaction.

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

Owing to excess of water and constant of HPW, then the equation 1 can be simplified as equation 2.

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

If the initial content of PA 6 is expressed as $[\text{nylon6}]_0$, and the content of some time is expressed as $[\text{nylon6}]_t$, then, integral of equation 2 can be expressed as following equation 3.

$$\ln [\text{nylon6}]_0/[\text{nylon}]_t= K't \quad (3)$$

As for PA 6, it is solid, thus its content can be expressed as weight. Therefore, the expression of $[\text{nylon6}]_0/[\text{nylon6}]_t$ can be replaced as M_0/M_t . M_0 and M_t are weights initial and some time, respectively. Then the equation 3 can be changed as $\ln(M_0/M_t)= K't$. Fig. 4 shows relation between $\ln(M_0/M_t)$ and reaction time and the line fitting rate constant K' of different temperature is given in Tab. 2.

Tab. 2 Constant of catalytic degradation at different temperature

Temperature/K	553K	573K	583K	603K
K'/min^{-1}	0.0485	0.0965	0.1142	0.2003

The relation of rate constant K' and temperature is linearly fitted is shown in Fig. 5. According to Arrhenius equation, the line fitting relation of $\ln K'$ and $1000/T$ gives that reaction activation energy and pre-exponential factor A are 77.38 kJ/mol and 1.05×10^6 , respectively.

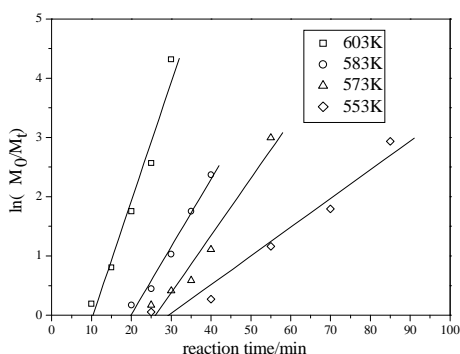


Fig. 4 Relation of $\ln(M_0/M_t)$ with reaction time

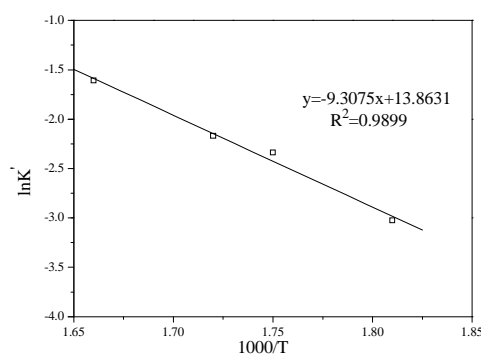


Fig. 5 Relation of rate constants with temperature

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