

The Effects of Alkali and Temperature on the Hydrolysis Rate of N-methylpyrrolidone

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Abstract: By studying the hydrolysis of N-methylpyrrolidone, it was found that the effects of NaOH concentration and temperature on N-methylpyrrolidone's hydrolysis were remarkable. Fourier transform infrared (FTIR) and Gel Permeation Chromatography (GPC) detected that the mainly hydrolyzate was 4-(methylamino)butyric acid, and the hydrolyzate can generate polymers, which of molecular weight increases with temperature rising. The results of Gas Chromatography (GC) and moisture meter test showed that adding alkaline and raising temperature can aggravate hydrolysis of NMP. This study provide theoretical basis for recycling solvent (NMP) in the production of polyphenylene sulfide (PPS).

1. Introduction

N-methylpyrrolidone (henceforth referred to as NMP), molecular formula is C_5H_9ON , molecular weight is 99.13, colorless transparent oily substance and slightly with ammonia. It can mix with water at any percentage and can completely mixed with almost all solvents. NMP has many advantages, for example: strong polarity, low toxicity, strong solubility, no corrosion, low volatility, strong biodegradability, low volatility, etc[1,2]. NMP is widely used in lithium batteries, high-grade paint, insulating material, petrochemical solvent, medicine and other fields[3-5] as a chemical materials. Polyphenylene sulfide (PPS) is known as the plastic gold, which combination property become more excellent after modification, and is widely used in electrical, automotive, aerospace and military industry and other fields[6-8]. NMP, which dosage is very large, is used as a solvent in the process of PPS synthesis. With the usage amount increasing of PPS, a large quantity of NMP is used in the process of PPS synthesis. If we can effectively recover NMP, we can greatly reduce the production costs of PPS. So recycle of NMP has great economic value in the production of PPS. NMP is stable under neutral conditions, but it is easy to open loop under acidic or alkaline conditions to form acid and other products, and both alkali and temperature have effects on the hydrolysis of NMP[9]. Now the main technology of the production of PPS is sodium sulfide method[10-12]. Raw material Na_2S need to dehydrate in the production process, and in the process of dehydration need to add NaOH to prevent the hydrolysis of Na_2S and the reaction system is alkaline. NMP will open the ring at high temperature, and finally will affect the quality of PPS. So it is important to study the hydrolysis of NMP in alkaline environment and high temperature.

In this work the effects of temperature and alkali on the hydrolysis rate of NMP was studied, which provided the theoretical basis for the recovery of NMP.

2. Experiment

2.1. Materials



The following chemicals were used in this study without further purification: NMP (AR, purity over 99.9%) was provided by Tianjin Damao Chemical Reagent Factory, China. Sodium hydroxide (NaOH) (AR, Solid) was purchased from Tianjin Kedi Chemical Reagent co., Ltd., China.

2.2. Preparation of hydrolyzate in room temperature

A solution was prepared using 200 g NMP and 22.22 g water and then added 7-8g NaOH. After the NaOH was completely dissolved, the mixed solution was poured into a separatory funnel. As shown in Figure 2, the solution divided three layers in separatory funnel, and the middle layer and the lower layer of oil are extracted, respectively. Finally, the composition of hydrolyzate was detected by IR spectra and the molecular weight of hydrolyzate was detected by GPC.

2.3. Preparation of hydrolyzate in 200°C

A solution that was prepared using 2.5g NaOH, 11.11 g water and 200 g NMP was distilled using a beaker exposure and a round bottom flask in an oil bath, respectively, and then cooling after up to 200°C. The raffinate of the round-bottomed flask and beaker was separated by high-speed centrifuge that could get light yellow precipitate. Finally, the composition of the light yellow precipitate was detected by IR spectra and the molecular weight of the light yellow precipitate was detected by GPC.

2.4. Preparation of solution in different temperature

A solution that was prepared using 0.5g NaOH, 10g water and 90g NMP, the temperature of oil bath was raised to 80 °C, 100 °C, 120 °C, 140 °C, 160 °C, 180 °C, 190 °C, respectively. After cooling to room temperature, small amount of precipitation will appear at the bottom of beaker. The mixture was processed by high-speed centrifugation. The mass of supernatant and precipitate were weighed and the content of supernatant was detected by GC, thereby the hydrolysis rate of NMP was calculated.

2.5. Preparation of solution contain different amounts of NaOH

A solution that was prepared using 10g water, 90g NMP and NaOH, which is 0.5g, 1g, 2g, 4g, 6g, 8g, 10g, respectively, will be divided into supernatant and hydrolyzate. The solution will be divided into supernatant and hydrolyzate by separatory funnel after storing for a month, and then the mass of supernatant and hydrolyzate that is initial and storing for a month later were weighed. Finally, the content of supernatant was detected by GC and the rate of hydrolysis of NMP was calculated.

3. Results and discussion

3.1. The detection and characterization of the hydrolyzate in room temperature and 200°C

The solution, which contained NaOH, NMP and water, was prepared and a portion of the oil appeared and stratified on the bottom of the beaker at room temperature. The solution, which was prepared at room temperature can get light yellow hydrolyzate when the solution heated up to 200°C. Figure 1 presents the FTIR of samples that were dried under air and under vacuum and were oil and light yellow hydrolyzate, which were hydrolyzate of NMP in room temperature and 200°C. The hydrogen bonding area of oil material was particularly wide in front of the heating and the hydrogen bond area of light yellow hydrolyzate was narrow, the absorption peaks that was secondary amine, methylene and sodium carboxylate appeared. The results indicated that a large amount of monomer of N-methyl-4-aminobutyric acid was present in the oil and the monomer of N-methyl-4-aminobutyric acid was produced in a light yellow hydrolyzate by polymerization. From Table 1, it was found that the oil and light yellow hydrolyzate contained a polymer, which had a high molecular weight in the case of sufficient contact with air and heating. It was shown that the hydrolyzate of NMP could produce polymer at room temperature. The presence of oxygen in the mixed solution of NMP is not only beneficial to the decomposition of NMP, but also to the polymerization of decomposition products. The data in Table 1 explains the phenomenon, which was divided into three layers that the supernatant is unhydrolyzed NMP and the middle layer and the lower are the hydrolyzate of NMP

(Figure 2), water, NaOH and NMP solution at room temperature. The molecular weight of the middle layer and the lower layer of oil is quite different. The decomposition of NMP in OH radicals was mentioned in the literature[13-15], and three possible decomposition routes of NMP was presented, the formation of N-methyl-4-aminobutyric acid is the least likely, and the literature referred to the oligomer, which possibly were NMP or the oligomers of N-methyl succinimide (NMS) of the decomposition products of NMP. DAN W.REYNOLDS et al. [12] proposed that the solutions of NMP and water could be first oxidized to N-methyl succinimide, and hydrolyzed to form N-methyl-4-aminobutyric acid, which further hydrolyzed to form succinic acid and also might be further generated succinic anhydride at 60°C.

The Fig. 1 and Table 1 illustrated that the biggest possibility was that the NMP hydrolysis to produce N-methyl-4-aminobutyric acid in the alkaline environment, and it is most likely to form a polymer.

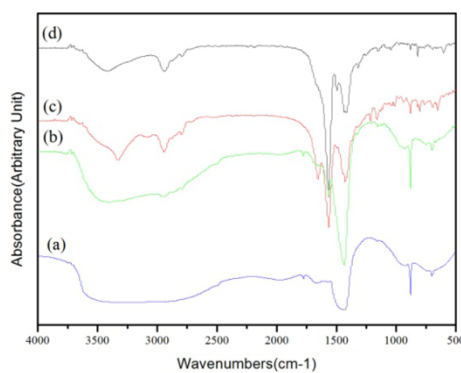


Figure 1. FTIR spectra of (a) the fluid hydrolyzate of the lower layer at room temperature, was dried in non-vacuum, (b) the fluid hydrolyzate of the intermediate layer at room temperature, was dried in non-vacuum, (c) the light yellow hydrolyzate was dried in vacuum, (d) the light yellow hydrolyzate was dried in non-vacuum

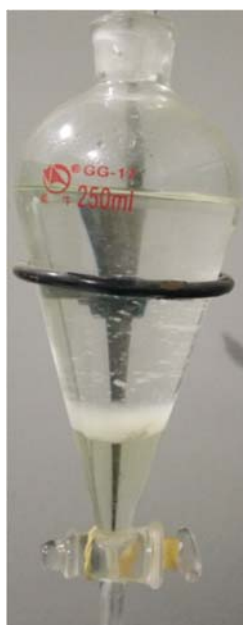


Figure 2. The solution of contain 7-8g NaOH, 22.22g water and 100g NMP

Table 1. The molecular weight of hydrolyzate at different conditions

Elution time (min.)	Molecular weight of fluid hydrolyzate of intermediate layer	Molecular weight of fluid hydrolyzate of lower layer	Molecular weight of yellow hydrolyzate at beaker	Molecular weight of yellow hydrolyzate at round-bottomed flask
11.87			64609	
13.233		6907		
15.233				66161
15.417	13083			
18.533			1524	
18.583		1306		
19.350				1197
19.681		1056		
20.033	1996			
20.042			1044	

3.2. Effects of temperature (*T*) on hydrolysis of NMP

As shown in Figure 3, it can be observed that precipitate were obtained by centrifugation, and the amount of precipitate was gradually increased and the supernatant was gradually reduced with increasing temperature. Finally it found that a small amount of the fluid hydrolyzate still remained at the bottom of solution on $T \leq 140^\circ\text{C}$, a white precipitation was appeared at $T \geq 160^\circ\text{C}$, and the weight of white precipitation was equal roughly. As shown in Figure 4, it found that the rate of hydrolysis increases dramatically, when the temperature exceeds 120°C . So above-mentioned phenomenon was summarized, it can be found that the rise of temperature can exacerbate hydrolysis of NMP, combining literature and the evidence of Figure 1, though exist polymer at room temperature, the mainly product of hydrolyzate is 4-(methylamino)butyric acid, and 4-(methylamino)butyric acid react with NaOH for corresponding organic sodium salt. As the temperature gradually elevated, and exacerbate the degree of 4-(methylamino)butyric acid to hydrolyze. So the rise of temperature can help polymerization of hydrolyzate of NMP, which explains the reasons that molecular weight become large with rising temperature, as shown in Table 1. At the same time, there will be separated out some white precipitate that is NaOH by detect at $T \geq 160^\circ\text{C}$, it was explained that there will be some unreacted NaOH which dissolved in the solution before the water has evaporated when the temperature rises. NaOH was gradually precipitated with water evaporated. The weight of NaOH that were precipitated is substantially equal. This phenomenon could indicate that the solubility of NaOH is constant under certain conditions in components of NMP and water. The conformation of hydrogen bond that water with NMP can form hydrogen bond²⁰ could reduce the solubility of NaOH and a part of NaOH can't cause ionization. Finally, this part of NaOH could precipitate when water evaporates completely. This also shows that the hydrolyzate of NMP only can react with the part of ionizable NaOH after the temperature rising, the product is 4-(methylamino)butyrate sodium. Because the amount of ionizable NaOH is certain, when the ionizable NaOH with 4-(methylamino)butyric acid react completely, the remaining hydrolyzate can not react with NaOH, but the polymerization reaction will easy occur at case of high temperature, so that the molecular weight is increased, as shown in equation (1) to equation (5). This process is similar to the process of emulsion polymerization, i.e., the first step is pre-emulsification, then generate the seed emulsion, and further polymerized. It was

further explained the causes that the molecular weight of NMP's hydrolyzate increased with elevated temperature.

In summary, the temperature has significant effect on hydrolysis of NMP, it is the chief causes that NMP's hydrolyzate polymerized, so the temperature needs to be as low as possible in the course of NMP to contact with air.

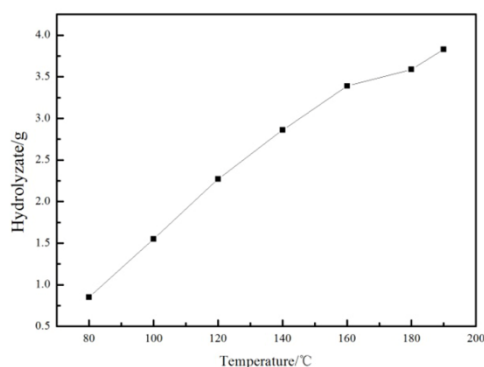
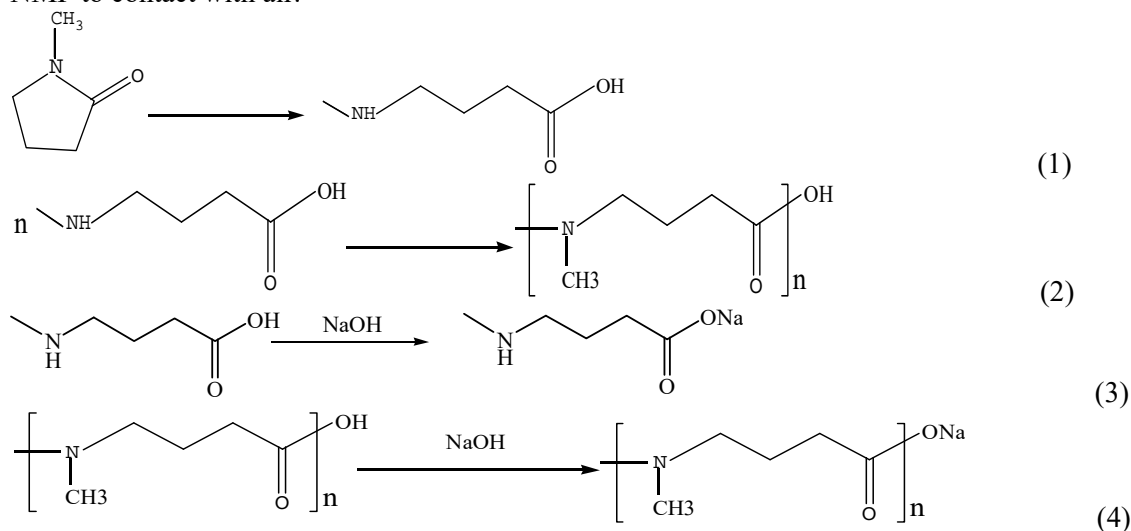


Figure 3. Effect of temperature on hydrolyzate of NMP

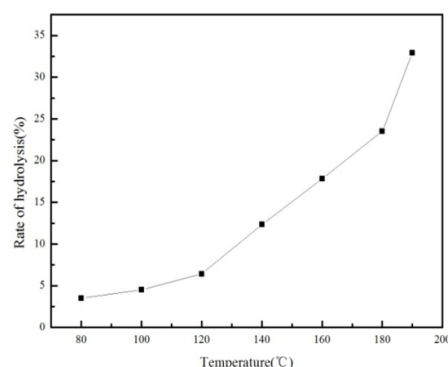


Figure 4. Effect of temperature on rate of hydrolysis of NMP

3.3. Effects of Alkali content on hydrolysis of NMP

As shown in Figure 5, it can be observed that the mass of fluid hydrolyzate have increased with increasing amount of NaOH before and after storing, but the difference mass between before and after storing was gradually widening. This phenomenon indicate that the alkaline of solution was enhanced with increasing the amount of NaOH and the hydrolysis of NMP became even more serious and NaOH reacted with 4-(methylamino)butyric acid, but the molar weight of NMP more than NaOH and the NaOH was ionized partially. So there are residual 4-(methylamino)butyric acid and this hydrolyzate can be dissolved in NMP, this case cause the difference mass of liquid hydrolyzate between before and after storing. The degree of hydrolysis is the most serious when the concentration of NaOH reaches saturation, as result, hydrolyzate of the 4-(methylamino)butyric acid disappearing, NMP and water were miscible. As shown in Figure 6, it is found that the hydrolysis rate of NMP changed little and floated between 6% and 8% when the content of NaOH is less than 3.51% and the hydrolysis rate of NMP increased dramatically when the content of NaOH is more than 3.51%. The NaOH solution is capable to disrupt hydrogen bonds, so hydrogen bonds of NMP and water was reduced and the amount of free water increased. The alkaline of solution is also enhanced with the

more NaOH dissolved. At last the hydrolysis of NMP was exacerbated. As shown in Figure 2, the infrared spectra indicated that the polymer is amide which can be seen from Table 1. The molecular weight of polymer can reach 13000, but the probability is small that the 4-(methylamino)butyric acid occurs olymerization forming amide. So these indicate alkaline environment not only make the NMP hydrolysis but also cause polymerization of hydrolyzate of NMP.

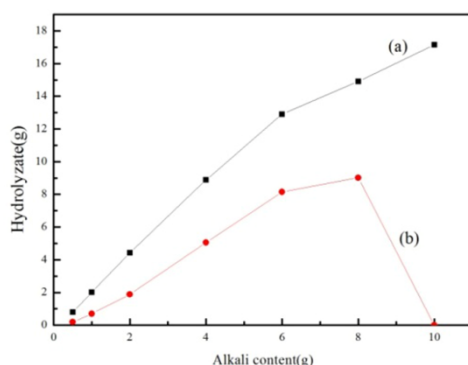


Figure 5. Effect of alkali content on hydrolyzate of NMP, (a) before storing; (b) after storing for one month

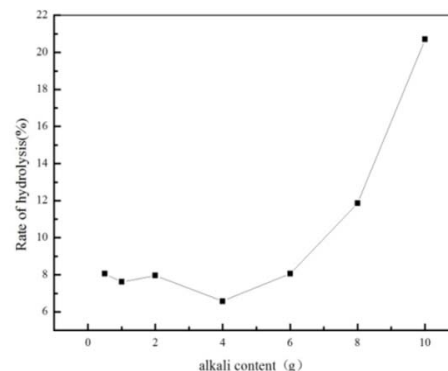


Figure 6. Effect of alkali content on rate of hydrolysis of NMP

4. Conclusions

This article study the effects of temperature and content of alkali on hydrolysis of NMP. It was found that:

(1) The content of NaOH and temperature have huge impact on the hydrolysis of NMP. In alkaline environment, decomposition route of NMP is one of the smallest possibility route that was mentioned by investigators which the monomer of polymerization reaction were not NMP or NMS and the monomer was 4-(methylamino)butyric acid that was the hydrilyzate of NMP;

(2) It was confirmed the phenomenon of literature mentioned that partial decomposition of NMP will be re-dissolved in NMP after storing and the hydrolyzate of NMP was 4-(methylamino)butyric which was re-discovery of substance dissolved in NMP;

(3) The temperature was higher, NMP was easier to hydrolyze and the high temperature was the main cause of hydrolysis product to polymerized;

(4) The more hydrogen bonds of NMP and water were damaged with the amount of NaOH increasing and solubility of NaOH becomes large due to more free water was generated, so a stronger alkaline of solution was formed and increased the hydrolysis of NMP;

In short, the raising of the temperature and the amount of alkali will intensify hydrolysis of NMP, so the process of recovery of NMP should avoid high temperature and high concentration of NaOH.

Acknowledgments

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