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Synthesis of N-vinyl caprolactam

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ABSTRACT

The synthesis of N-vinyl caprolactam (NVCL), with acetylene as alkylene agent, was studied in a stirred reactor system. With potassium hydroxide (KOH) being used as catalyst and 18-crown-6 ether as cocatalyst, NVCL was synthesized by the reaction of acetylene with caprolactam (CL). Crude products were purified by vacuum distillation. The addition of 18-crown-6 ether accelerates the reaction rate of the nucleophilic addition much greatly. The initial explanation suggests that the hole radius of 18-crown-6 ether is close to the one of K^+. A complex is formed between 18-crown-6 ether and K^+ ion on the formed intermediate of potassium caprolactam, so the addition reaction between acetylene and caprolactam was accelerated greatly. In the stirred tank reactor (500 mL four flask bottle), the CL conversion is 30.5% and the product selectivity is up to 73.4%. The experimental data indicate that the product mixture is a non-ideal liquid mixture. A single process of distillation is difficult to obtain a high purity NVCL product. The combination of extraction and distillation is an ideal separation process for producing high purity NVCL.

1. Introduction

N-vinylcaprolactam (NVCL) is one of an important group of vinyl compounds. NVCL is mainly used to synthesise polyvinylcaprolactam (PNVCL) or other water-soluble copolymers. PNVCL contains hydrophilic carboxylic and amide groups, where the amide group is directly connected to the hydrophobic carbon–carbon backbone chain so that its hydrolysis will not produce small amide compounds which are often bad for biomedical applications. NVCL finds wide applications in some biomedical fields. PNVCL of lower critical solution temperature (LCST) at the physiological temperature range 30–40 °C, is characteristic of water-soluble, non-adhesive, thermally sensitive and biocompatible and can be used as a new biomedical material, such as binding and release of medicines [1] and a liquid embolic material to cure cerebral arteriovenous malformation (AVM) endovascular [2]. PNVCL is also used in the fields of the UV-curable adhesive, synthetic resin in stereotypes, hair and skin caring products, agent for control of formation of natural gas-hydrate, intermediate for preparing some organic compounds [3–11].

The synthesis of NVCL was reported in the literature [12–17]. But due to the patent situation, the relevant details were not disclosed. In most cases acetylene and caprolactam are adopted as raw materials, KOH or alkali metal or potassium tert-butanol as a catalyst. The synthesis reaction was carried out at high pressure. This paper introduced an atmospheric synthesis of N-vinyl caprolactam, with acetylene as alkylene agent in a laboratory four flask stirred reactor system.

2. Experimental

2.1. Apparatus and materials

FT-IR: FTS-135, United States BIO-RAD; GC–MS: Agilent, 6890/5973 MSD.

Caprolactam (CL), polymerization grade, 99.9%; nitrogen, high purity, 99.9%; alkylene, high purity, 99.9%; KOH (>82%), AR grade; 18-crown-6 ether, AR grade.

2.2. Preparation of potassium caprolactam

Preliminary experimental results indicate that water may deactivate potassium caprolactam, which catalyzes the nucleophilic addition reaction, by its hydrolysis. So, potassium caprolactam was prepared separately in order to inhibit or reduce the hydrolysis of feedstock or potassium caprolactam

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resulting from water formed by the reaction of CL and KOH. The procedure is like this. 100 g CL and 15 g KOH are put into a four flask bottle. Under vacuum conditions, the temperature is increased to 140 °C, potassium caprolactam is formed, and the water produced is eliminated from the reaction system at the same time. Preparation of potassium salt is a critical step in preparing NVCL. If the water produced in the potassium salt is not completely removed, water will lead to the splitting of raw material CL and the potassium salt molecule ring, and then the activity of the catalyst is lost. The removal of water using vacuum distillation can avoid the hydrolysis and condensation of potassium CL and CL resulting from high temperature. Experiments show that the dehydration of potassium caprolactam preparation requires a high vacuum of 0.098 MPa, a temperature of 140 °C, and 2 h dehydration time. In this way, the water that is produced from raw material is completely removed. A mixture containing potassium caprolactam and CL is produced.

2.3. Synthesis of NVCL

Add CL, the mixture containing potassium caprolactam and co-catalyst into a four flask bottle (500 mL) heated by an electrical heater, reaction feedstock mixture is agitated by a mechanical stirrer. Nitrogen and alkylene are measured by a mass flow-meter and mixed together in a mixer. When the feedstock temperature rises to ca. 80–130 °C depending on reaction temperature, pass the mixture of nitrogen and alkylene into reactor, and keep for 2–8 h. The resulted reaction mixture goes through a simple distillation and further extraction and distillation, then a high purity NVCL is obtained.

3. Results and discussions

3.1. Investigation of the reaction process and product characterization

Based on the fundamentals of nucleophilic addition reactions, a catalyst system composed of potassium caprolactam and 18-crown-6 is used. The experimental results in a stirred four flask bottle reactor show that NVCL selectivity is up to 73.4% when CL conversion is 30.5%. Suitable reaction conditions are as follows: temperature 130 °C, reaction time 6 h, gas phase pressure 0.16 MPa, molar ratio $n(C_2H_2):n(CL) = 1.5/1$(mol/mol), adding amount of co-catalyst crown ether 0.5 wt%. The distillation of the obtained crude products under a vacuum of 0.098 MPa and a distillation temperature of 120–130 °C results in a mixture of NVCL and CL. GC–MS analysis is given in Figs. 1–3. Two main peaks and other minor peaks appear in Fig. 1, indicating that the mixture is composed of two main components and a small impurity.

The mass spectra of the component corresponding to the residence time 17.12 min in the gas chromatograph is shown in Fig. 2 and analyzed as follows. The peak of mass/charge 113 at the right is the peak of largest mass number. The ion is an odd electron ion and the mass number is in agreement with the nitrogen rule, so the ion peak of mass/charge ratio of 113 is a molecule ion peak. This is in accordance with the molecular weight of CL, and it is determined that the peak is CL.

The mass spectra of the component corresponding to the residence time of 14.38 min in the gas chromatograph is shown in Fig. 3 and analyzed as follows. The ion peak of $m/z = 139$ is a molecule ion peak. In accordance with the molecular weight of

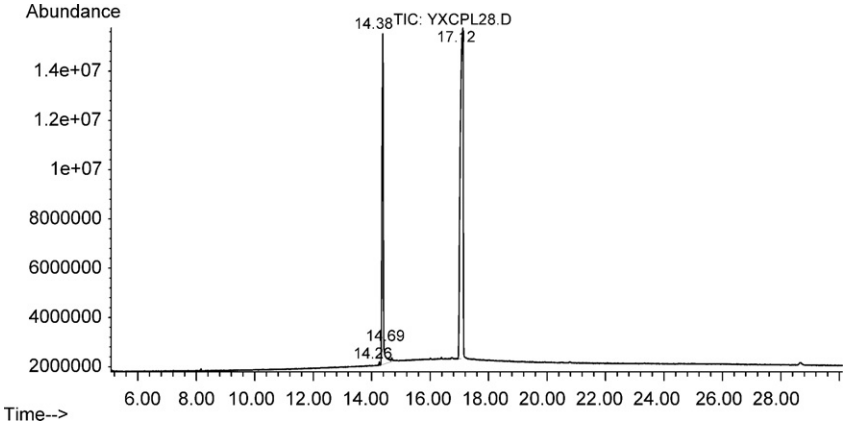


Fig. 1. Gas chromatograph of products.

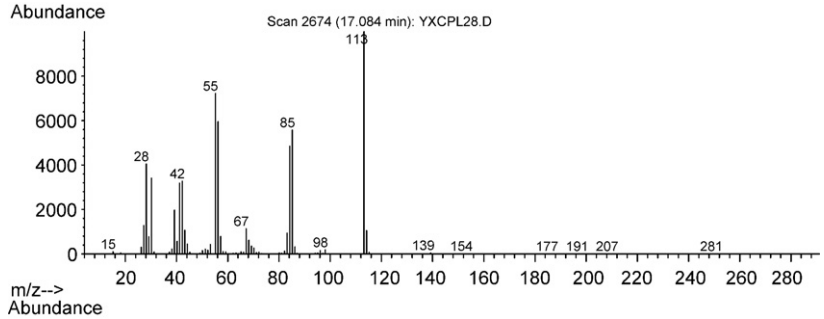


Fig. 2. Mass spectra of peak two.

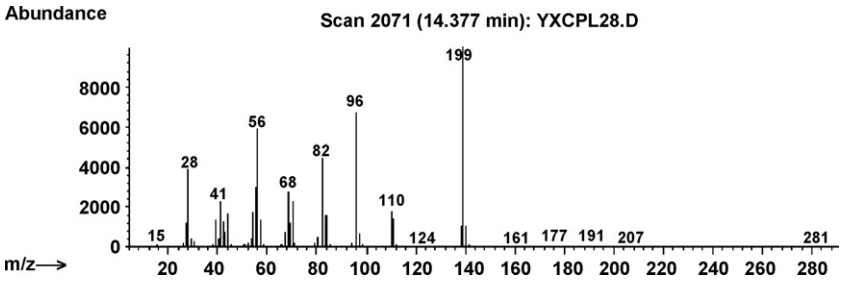


Fig. 3. Mass spectra of peak one.

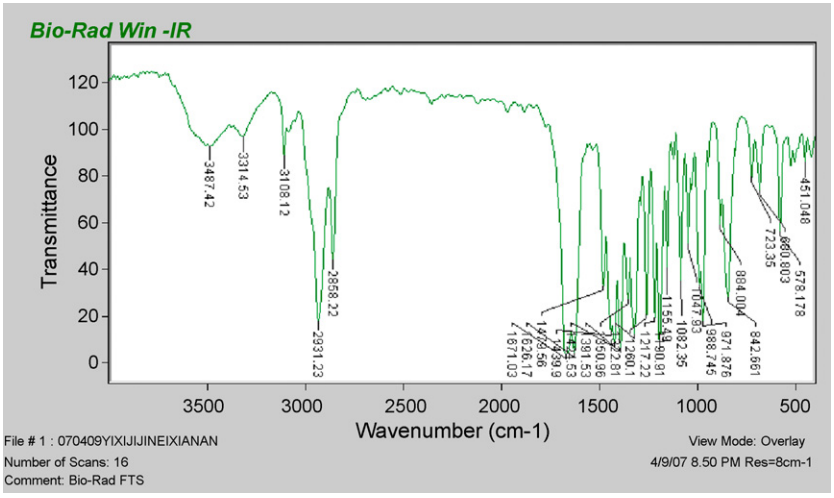
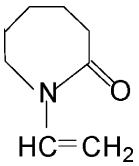


Fig. 4. Infrared spectra of the product NVCL.

NVCL, M = 139. Based on FT-IR spectra analysis of various groups, the molecule structure is determined as:

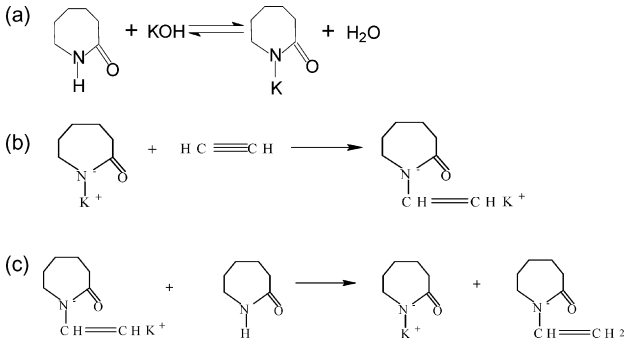


FT-IR spectra of a high purity NVCL is given in Fig. 4.

Compared to FT-IR spectra of CL, adsorption peaks at 2858.07 cm^{-1} and 2931.01 cm^{-1} of no change is a $-CH_2-C-H$ stretching vibration adsorption peak; 1479.88 cm^{-1} bands is a saturated C–H deformation vibration adsorption peak; 1190.91 cm^{-1} is a C–N stretching vibration adsorption peak; 1082.86 cm^{-1} is a C–N stretching vibration adsorption peak; 3314.53 cm^{-1}, 2858.07 cm^{-1} and 2931.01 cm^{-1} are N–H stretching vibration adsorption peaks; 1671.03 cm^{-1} is a C=O stretching vibration adsorb peak. The 1626.67 cm^{-1} peak is compared to FT-IR spectra of caprolactam, and is assigned to the C=C bond stretching vibration adsorption peak. The 971.876 cm^{-1} peak is the CH=CH–H swing plane bending vibration peak. These data showed that terminal olefinic groups have been formed. IR spectra suggest the successful synthesis of a vinyl caprolactam product.

3.2. Effect of the reaction process parameters on selectivity and yield

The synthesis of NVCL is a complex reaction system composed of parallel and consecutive reactions. Based on experimental results, following reaction mechanism is proposed. It can be seen that potassium caprolactam plays a role of transferring reaction cycle.



The product, feedstock, and catalyst will further go through a secondary reaction with the increasing time so that the utilization of feedstock is decreased. When the conversion of feedstock is higher than 30%, the selectivity begins to decrease. The effects of temperature and reaction time on the reaction process were investigated. The optimization of process conditions improves the product yield. When conversion is 30.4%, the selectivity is up to 73.4%. Typical addition reaction results are given in Figs. 5 and 6.

The effect of reaction temperatures on the selectivity and yield was investigated at the following conditions. The added amount of potassium hydroxide, the precursor of potassium CL, is 4 g/100 g feedstock CL. Reaction time is 6 h. $n(C_2H_2)$:n(CL) is 1.5/1(mol/mol). The added amount of polymerization-inhibiting agent is 0.5 g/100 g CL. The added amount of the co catalyst, 18-crown-6 ether, is

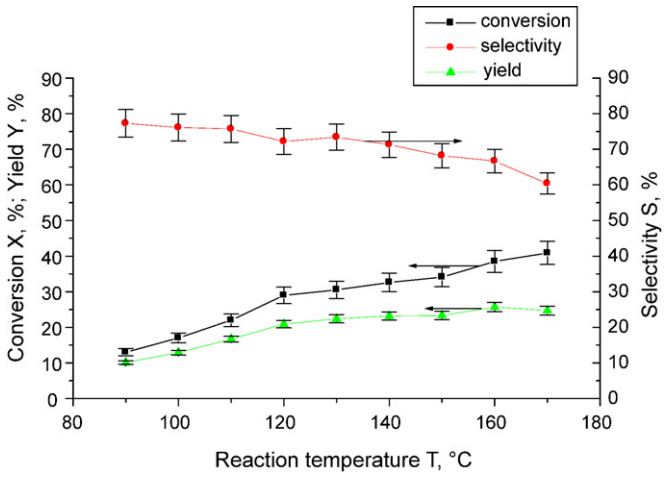


Fig. 5. Effect of temperatures on yield and selectivity.

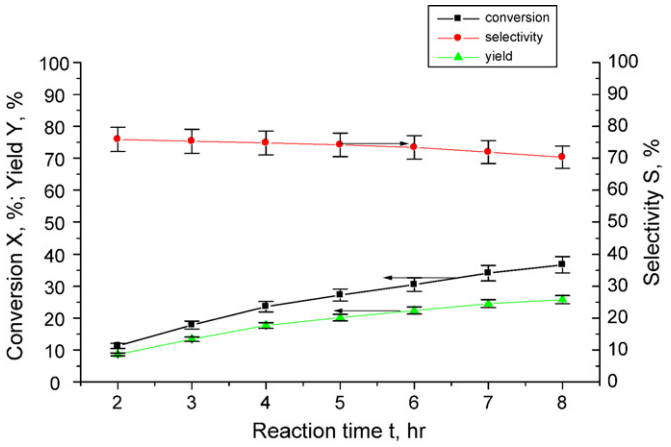


Fig. 6. Effect of reaction time on yield and selectivity.

1 g/100 g CL. The conversion of CL increases gradually as the temperature is increased, the yield of NVCL increases and then decreases. At the temperature of 160 °C, the selectivity of NVCL decreases with the increasing temperature, indicating secondary reactions occur and resin compounds were being gradually formed.

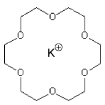
The effect of reaction time on the selectivity and yield was investigated under the following conditions. The added amount of potassium hydroxide, the precursor of potassium CL, is 4 g/100 g. Reaction temperature is 130 °C. $n(C_2H_2)$:n(CL) is 1.5/1 (mol/mol). The added amount of polymerization-inhibiting agent is 0.5 g/100 g CL. The added amount of the co-catalyst, 18-crown-6 ether, is 1 g/100 g CL. Similar regularity can be seen from the figure that the conversion of CL and the yield of NVCL increase gradually as the temperature is increased. The selectivity of NVCL decreases with increasing temperature, indicating secondary reactions occur and resin compounds were being gradually formed.

3.3. Purification of the product mixtures

The results of the distillation of product mixtures suggested that the liquid of caprolactam and N-vinyl caprolactam is a non-ideal liquid mixture. A single distillation column is difficult to separate these materials. To this end, an extraction-distillation complex separation process is proposed. Distilled water was used as an extraction agent. Caprolactam (80%) in the product mixture is extracted from the mixture in the extraction process. The extracted mixture is distilled and a high purity NVCL is obtained.

3.4. Reaction mechanism analysis of the addition reaction

An initial explanation of the reaction process is that the reaction rate of producing NVCL depends on the extent of separation N^- and K^+ in the potassium caprolactam molecule. The greater the distance between K^+ and N^- with a negative charge, nitrogen atoms are exposed to the greater extent. N atoms will have a more negative charge, resulting in the ease of the addition reaction with C_2H_2. Instead, the closer the distance between K^+ and N^-, the fewer negative charge which N atoms have, resulting in the difficulty of the nucleophilic addition between C_2H_2 molecule and nitrogen atoms on the potassium caprolactam molecule. The addition of a suitable amount of co-catalyst, 18-crown-6 ether, enhances the reaction rate and selectivity by promoting the separation of N^- and K^+. The 18-crown-6 ether ring has six oxygen atoms and the negative charge of oxygen atom is higher than the N atom, so oxygen atom behaves as a strong binding force with K^+. The 18-crown-6 ether attracts K^+ to form a cage complex, making K^+ almost removed the from potassium CL molecule ring, to form a bare N atom, thus greatly accelerating the addition reaction of caprolactam and acetylene and enhancing conversion and product yield. It was reported that the relationship between 18-crown-6 ether and a complex ion is called a host–guest relationship. 18-Crown-6 ether is a host, the ion is a guest. Only when the hole radius of crown ethers is similar to the ion radius, can the ion can form a complex with the host–guest relationship. The hole radius of 18-crown-6 ether is 0.26–0.32 nm, near to that of K^+ (0.266 nm), indicating that a complex can be formed. In this paper, potassium salt is used as a catalyst, and the radius of potassium ions is close to the one of 18-crown-6. The complex of 18-crown-6 with potassium ion enhances the negative charge density of N atoms in potassium caprolactam molecule so that the nucleophilic addition between caprolactam and acetylene goes more easily.



4. Conclusions

On a stirred reactor system, NVCL was prepared, acetylene as an alkylene agent; the selectivity of NVCL is up to 73.4% in the case of CL conversion 30.5%.

(1) A suitable process condition is as follows: temperature 130 °C, reaction time 6 h, gas phase pressure 0.16 MPa, molar ratio of $n(C_2H_2)$:n(CL) = 1.5/1(mol/mol), adding amount of co-catalyst 18-crown-6 ether is 0.5 wt%; GC/MS and FT-IR investigation indicates that a sample obtained from a simple distillation contains 40% of NVCL.
(2) The co-catalyst 18-crown-6 is a key factor in synthesizing NVCL.
(3) Another conclusion is that the liquid mixture of caprolactam and N-vinyl caprolactam is a non-ideal liquid mixture. It is difficult to separate them with a single distillation column. NVCL of 98% purity can be obtained by the combination of extraction and distillation.

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