Aqueous solution polymerization of acrylamide: a pilot-scale study

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Abstract. The polymerization of acrylamide was initiated by complex redox system in aqueous solution. Meanwhile, according to the best experimental craft, we conducted a pilot-scale polymerization of acrylamide. We studied the effects of different pilot experiment intrinsic viscosity of the polymer, dissolution time, solubility, and the conversion rate. And it determines the reaction based on the state polymerization time curve. By infrared spectroscopy the way we determine the desired final product.

Introduction

Polyacrylamide is one of the most widely used varieties of water soluble polymer compound. It was widely applied to the fields such as chemical industry,medicine, water treatment and so on[1]. The main synthetic methods of polyacrylamide are aqueous solution polymerization, inverse emulsion polymerization method and the method of suspension polymerization method and so on[2-4]. The water solution polymerization method is low cost, and small damage to the environment .But there are still some problems along with the polyacrylamide powder products. Its low relative molecular mass and bad solubility make it unable to meet the demand of industry and environment, and the low dissolution rate leads to inconvenient application and storage[5-7].Therefore, the research on the development of polyacrylamide with high molecular weight synthesized by aqueous exists great practical significance.

In this paper,according to the best experimental craft,we conducted a pilot-scale polymerization of acrylamide.Through the comparison of these experiments, we hope to study the problems of the polymer in practice.

Experimental

Materials.

Acrylamide (AM) was purchased from Changjiu Agrochemical Co.Ltd. (Jiangxi, China); Ammonium peroxydisulfate used as the oxidant was provided by Yongda (Tianjin, China);Ammonium iron(II) sulfate used as reducing agent was provided by Aladdin;2,2'-Azobis(2-methylpropionamidine)dihydrochloride was provided by Aladdin.

FTIR Spectrometer Two from Perkin Elmer.

Experimental method.

For this study, a series of steps were carried out as follows:The desired amount of acrylamide and other additive was weighed out and transferred to jars；The jar was sealed with nitrogen in addition to oxygen,A syringe was used to transfer the desired amount of initiator into the sealed jars containing the monomer；After the polymerization reaction was finished, the reaction jars was opened and the polymer was removed out into a beaker containing acetone then the mixture was standing for some time.The resulting products were dried and crushed.These pilot experiment are operating above.

Results and Discussion

The best optimum of these experiment.

The choice of the acrylamide concentration plays a vital role in polymerizing acrylamide. This paper studies the effect of different concentration. It is shown in Fig.1.

Azo initiators have a significant impact in acrylamide polymerization. The biggest advantage of azo initiators are sensitive to solvents and impurities, by introducing a polar group can increase its water solubility. Azo initiator concentration on viscosity is shown in Fig.2.

Polymer viscosity with increasing initiator concentration increased first and then decreased. We investigate the effect of initiator concentration on polymerization of acrylamide. The viscosity of polymer for the reactions performed at redox initiator concentration is shown in Fig.3.

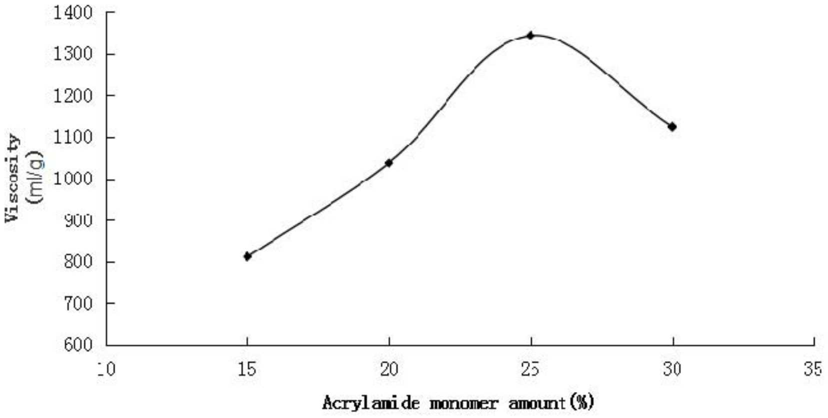

Fig.1 The influences of different concentration content on polymer viscosity

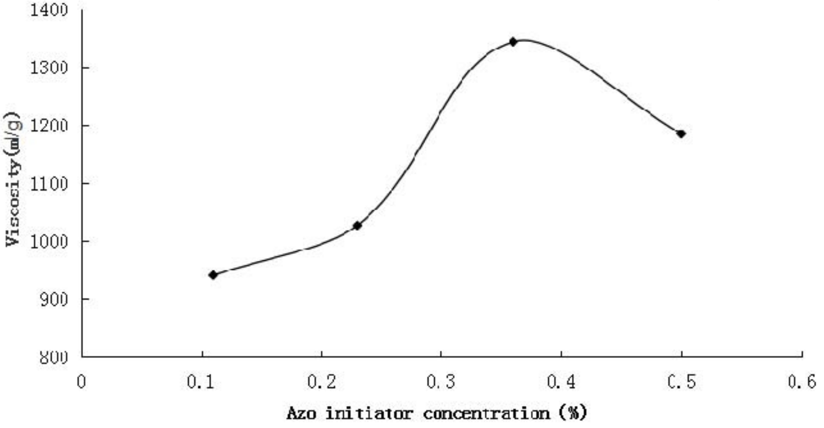

Fig.2 The influences of different Azo initiator on polymer viscosity

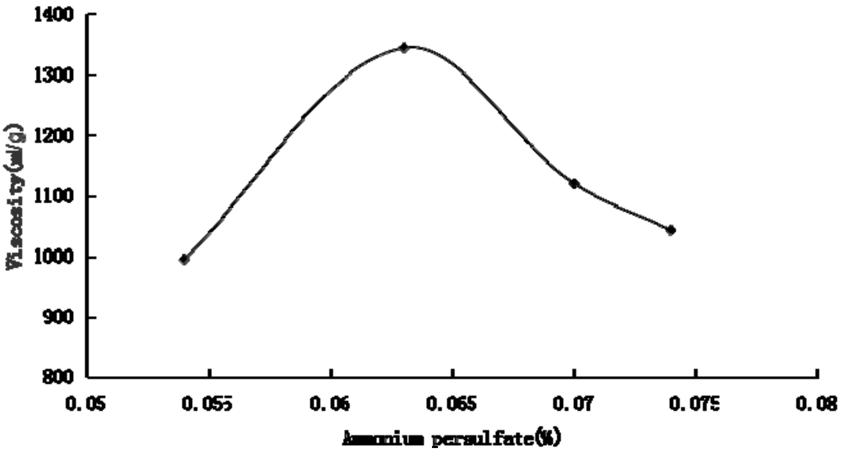

Fig.3 The influences of ammonium persulfate on polymerization viscosity

It is clear that,from Fig.1,polymerization viscosity increase with acrylamide concentration as a result of increase in the reaction constant. After reaching the maximum value, the polymerization viscosity was decreased with higher of acrylamide concentration. The polymer viscosity increased first and then decreased,, when the concentration of acrylamide was 25%, the viscosity of the polymer was maximum.From Fig.2,when the concentration of azo initiators was 0.4%, the viscosity of the polymer was maximum.From Fig.3,polymerization viscosity are increased with the increased of initiator when the concentration is lower than 0.062%, however it showed decreasing when the concentration higher than 0.062%. The main reason of this phenomenon: when the concentration of oxidant is small, with the increase of initiator concentration that reactive intermediates increased and polymerization reaction completely. So the increase of the molecular weight of polymer and showing the polymerization viscosity increase. But when the initiator concentration exceeds a certain amount, activity center is more. So that the reaction speed is quick. Eventually leading to the heating rate is too large and the heat of reaction is not easy to spread out. The molecular chain is easy to break. The molecular weight of the polyacrylamide decreases, which leads to the polymerization viscosity reducing.

In summary, the optimum synthetic conditions can be achieved according to the concentration of acrylamide is 25%, the best concentration of azo initiator concentration is 0.036%, the best concentration of redox concentration is 0.062%.

Impact on pilot experiments with different volume intrinsic viscosity of the polymer.

According to the optimum process, we conducted some pilot-scale polymerization of acrylamide.Then we measured their viscosity and conversion rate.As shown in Table.1.

Table.1 Effect of different volumes of polymer intrinsic viscosity

Volume(L)	The maximum temperature of reaction(℃)	The intrinsic viscosity（ml/g）	The conversion rate(%)
0.1	63	1344	94.8
5	78	1153	94.6
20	96	1017	94.5

It is clear that from Table 1, with the expansion of the experiment, the higher of the volume, the smaller the viscosity of the polymer, the conversion rate is also lower. It is because the larger the volume, the more intense the collision test molecule polymerization, since the reaction is exothermic, the greater the volume, the more heat, but heat can not be grooming out soon, resulting in the occurrence of crosslinking system section, so that the intrinsic viscosity is smaller, which also explains why, the greater the volume of the experiment, the intrinsic viscosity of even smaller.

Effect of different experiments on polymer solubility test.

According to the pilot-scale polymerization of acrylamide, We also measured the performance of their dissolution, As is shown in Table.2.

Table.2 Dissolution experiments with different volume

Volume(L)	Dissolution time(min)	Solubility(%)	Dissolved state
0.1	52	0.156	Completely dissolved
5	60	0.123	Completely dissolved
20	80	0.088	a few fragments

It is clear that from Table.2,In synthetic polymers, when volume increases, the solubility of the polymer becomes small, the dissolution time becomes longer. The reason is that the volume becomes large, the reaction was more intense, heat can not be output, so that crosslinking reaction occurred, resulting insolubles. Therefore, in order to further used in industry, we need to address in case of a large dose-response, the impact of crosslinked polymeric occur, so as to promote the process of industrialization.

Polymerization temperature and reaction time of the pilot-scale.

For the polymerization of acrylamide, it is strongly exothermic process, the reaction temperature, the direct relationship between the degree of crosslinking of the polymer and water-soluble. The relationship of polymerization temperature and reaction time is shown in Fig.4.

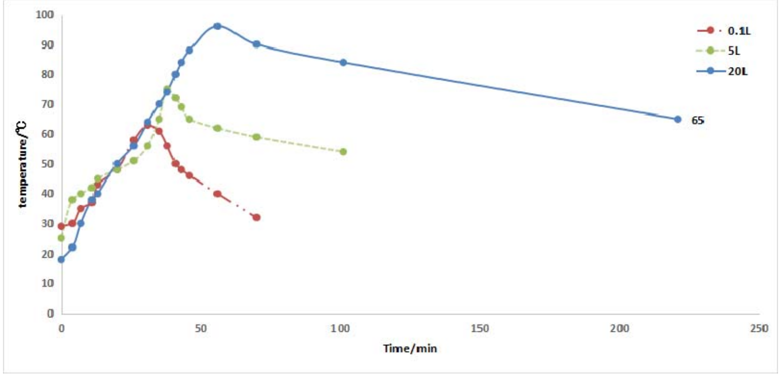

Fig.4 Relationship of polymerization temperature and reaction time

Different polymerization reactor during the polymerization reaction, the heating and cooling rate are different, the larger the reactor, the higher the maximum temperature,and the longer the cooling time.According to the literature, after the start of the polymerization initiator, the polymer maintaining the temperature at 50℃ of five hours, can be such that the monomer conversion rate of 99%.As it can be see from the chart, pilot reactor is designed such that the maximum temperature at around 96℃, to ensure that the conversion of the monomers. But the resulting polymer intrinsic viscosity reduced, so,the process recipe for further adjustments.

FTIR spectrum of PAM.

Structural spectrograms are shown in Fig.5.

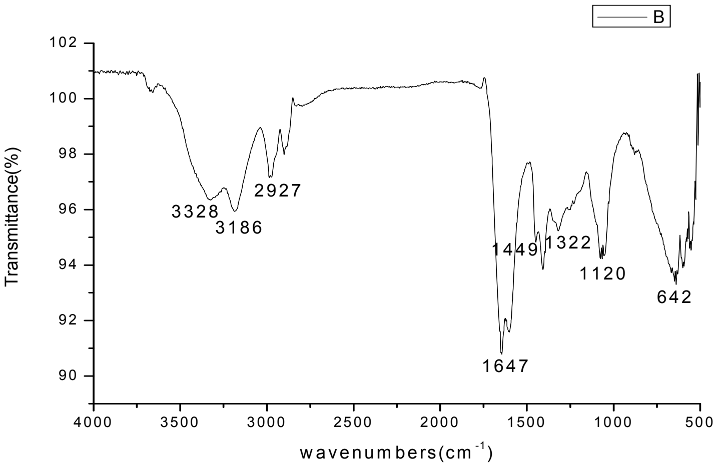

Fig.5 Infrered of PAM

Samples were characterized by FTIR spectrum (Fig.5). The FTIR spectrum of polymer showed strong stretching vibration peaks at 3186 cm^{-1} and 2927 cm^{-1} for amino group and methylene group of amide,respectively.C=O stretching vibration band characteristic the amide Ⅰ and —CONH$_2$ bending vibration band characteristic the amide Ⅱ respectively at 1569 cm^{-1} and 1647 cm^{-1}. The peak at 1449 cm^{-1} indicated methylene deformation bond.The peak at 1120 m^{-1} is evident in the cationic spectrum, it is associated with the C-N stretching vibration. According to the FTIR analysis, the results confirmed the polymer was synthesized.

Summary

Experimental results show that under the same conditions, with the magnification increases, the polymer heating and cooling rates are reduced, system maximum temperature increased slightly. Pilot-scale product intrinsic viscosity is also higher, slightly lower performance. Therefore, we need to continue to improve the polymerization process, so as to get better performance, viscosity of the product, for the further industrial production to provide an excellent process.

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