Synthesis Process of Amphoteric Polyacrylamide

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In this work, amphoteric polyacrylamide(AmPAM) was synthesized *via* copolymerization and homopolymerization cohydrolysis based on photoinitiator as initiator, respectively. The result indicates that monomer ratio, monomer concentration, the amount of the initiator and pH have effects on the intrinsic viscosity of polymer. It achieved the best inherent viscosity when monomer ratio of n(AM):n(NaAA): n(DMC) was 1: 0.65:0.16, the monomer concentration was 35 %, the amount of the initiator was 0.08 % and pH value was adjusted to 7 by using copolymerization. The best intrinsic viscosity of the product was 759 mL/g and acrylamide (AM) conversion rate was 99.97 %. In contrast, it achieved the best inherent viscosity when monomer ratio of n(AM): n(NaOH): n(DMC) was 1: 0.15: 0.18, the monomer concentration was 35 %, the amount of the initiator was 0.06 % and pH value was adjusted to 7 by using homopolymerization cohydrolysis. The result demonstrates that the best intrinsic viscosity of the product was 531 mL/g and acrylamide conversion rate was 99.94 %.

Keywords: Photo-initiation, AmPAM, Homopolymerization cohydrolysis, Copolymerization.

INTRODUCTION

A rapid increase in population, the rapid development of industry and many other factors lead to water shortage and water pollution. The water pollution has become more and more serious since the 20th century[1]. A kind of green water treatment agent, amphoteric polyacrylamide (AmPAM) has been proposed and synthesized. Amphoteric polyacrylamide is a class with a special structure of linear water soluble polymer compound[2], in the same polymer chain with cationic and anionic radicals[3], compared with cationic polyacrylamide (CPAM) and anionic polyacrylamide (APAM), it has advantages of the above mentioned polyacrylamide (PAM)[4-5]. Additionally, AmPAM has been used widely because of its less dosage, low toxicity and could be used in the fields of exploitation of the oil field, wastewater treatment and paper-making[6-9].

In general, the larger molecular weight the better the effect of flocculation, the main focus of the study focused on how to obtain high molecular weight polymers. Currently, research of AmPAM is relatively less, especially the light trigger a synthesis of AmPAM, most of the laboratory research stage[10,11].

To date, for the synthesis of AmPAM into copolymerization and molecular modification method[12,13], the preparation of AmPAM by aqueous dispersion polymerization process that it polymer particles fine and uniformly, easy to adjust the molecular weight and water solubility, the dissolution rate of

water fast, good application performance[14]. In this study, used photoinitiation polymerization methods by aqueous dispersion, through homopolymerization cohydrolysis and copolymerization method used to prepare AmPAM, respectively. Homopolymerization cohydrolysis use NaOH to provide an anionic group as a hydrolyzing agent and copolymerization use sodium acrylate (NaAA) as anionic donor, two synthetic methods were selected methacryloxyethyltrimethyl ammonium chloride (DMC) as cationic monomers. For nature of the product and two synthetic methods comparison, select the optimal synthesis conditions and synthesis methods. The results might be helpful for synthesis of high molecular weight product, so that anionic and cationic degree of controllable and improve the conversion rate of acrylamide.

EXPERIMENTAL

Photoinitiator was homemade in laboratory: Slime water provided by the coal preparation plant of Huainan Zhang Ji; acrylamide (AM, 98 %) and acrylic acid were purchased from Tianjin Bodi Chemical Co., Ltd.; sodium hydroxide were purchased from Shanghai Jianxin Chemical Co., Ltd., Reagent Factory; methacryloxyethyltrimethyl ammonium chloride (DMC, aqueous solution with concentration of 76 %) were purchased from Shandong ZiboYili New Chemical Materials Co., Ltd. All the reagents used were of analytical grade and

chemical pure. Industrial polyacrylamide were purchased from Bengbu city of Anhui Tianrun Chemical Industry Co., Ltd.

Synthesis of amphoteric polyacrylamide (AmPAM): Copolymerization procedure is as follows: the preparation of a certain concentration of sodium hydroxide solution and titrate acrylic acid solution to pH neutral to obtain an sodium acrylate. According to a certain molar ratio, weighed acrylamide, a cationic monomer *i.e.*, DMC, sodium acrylate solution and deionized water was added to dissolve a certain amount of diphenyl ketones initiator, the sealed oxygen by nitrogen chemotaxis nitrogen into the reactor for discharging oxygen. Seal the vessel and placed in the light, after completion of the reaction, the generated transparent colourless gum is AmPAM products.

Homopolymerization cohydrolysis procedure is as follows: a certain molar ratio AM, DMC and NaOH were dissolved in deionized water, then magnetic stirring for 2 h at room temperature. Subsequently small amount of photoinitiator was added dropwise into the solution, vigorous stirring was maintained throughout the entire process. After purging with nitrogen (N_2) for 10 min then sealed and placed it under the UV light irradiation, after completion of the reaction, the generated transparent colourless gum is AmPAM products.

Flocculation tests of AmPAM: The flocculation tests were investigated using slime water (60 g/m^3) of Huainan Zhang Ji coal preparation plant as a probe in a measuring cylinder (500 mL). The reaction system containing 400 mL of slime water solution and a certain amount of AmPAM was magnetically stirred at a constant speed of 180 rpm for 5 min to complete flocculation. After 0.5 h, the liquid on the upper layer is used for flocculation tests. The experiments were carried out by measuring absorbance at 340 nm wavelengths. At the same time selection of three kinds of industrial products of CPAM, APAM and PAM which intrinsic viscosity were similar with AmPAM were checked and compared with AmPAM .

Copolymerization of monomer ratio determined: In order to obtain the optimal AmPAM flocculant, the effect of copolymerization synthesis conditions on AmPAM was observed. Table-1 showed the monomer molar ratio influence to intrinsic viscosity of AmPAM, The mass fraction, the amount of the initiator, time and temperature of the mixed solution was 30 %, 0.08 % , 4 h and 30 °C, respectively. As can be seen from the diagram, the intrinsic viscosity of AmPAM first increased and then decreased. It indicated an appropriate proportion could improve the intrinsic viscosity of AmPAM. In the process of the copolymerization, with the increase of anionic monomer sodium acrylate (NaAA) that the probability of participating in the reaction becomes large and make the anion degree increasing. With the increase of cationic monomer DMC that the monomer free radical increase and the polymerization rate becomes larger and larger, polymerization degree increased and in a certain range of characteristic viscosity increases. But excessive anionic monomer and cationic monomer causes system generates a lot of heat and at the same time the increase in the viscosity of the system while the rate of diffusion decreases and reactivity decreased, resulting in decreased intrinsic viscosity. It is found that when the mixed ratio of AM, DMC and NaAA is 1:0.18:0.65, the intrinsic viscosity was optimal.

Determination of homopolymerization cohydrolysis of monomer ratio: In order to obtain the optimal AmPAM flocculant, we discussed the effect of homopolymerization cohydrolysis synthesis conditions on AmPAM. Table-2 showed the monomer molar ratio influence to intrinsic viscosity of AmPAM. The mass fraction,the amount of the initiator, time and temperature of the mixed solution was 30 %, 0.08 %, 4 h and 30 °C, respectively. It is found that with increase of the addition of DMC and NaOH, the viscosity of AmPAM has a maximum value and degree of anion, degree of cation increased continuously. A number of cationic groups and anionic groups

TABLE-1
EFFECT OF COPOLYMERIZATION SYNTHESIS CONDITIONS ON AmPAM

Monomer ratio			Intrinsic viscosity (mL/g)	AM Conversion rate (%)	Degree of anion (%)	Degree of cationic (%)
n(AM)	n(DMC)	n(NaAA)				
1	0.08	0.40	332	97.12	26.12	5.09
1	0.10	0.45	431	98.45	28.91	6.26
1	0.12	0.50	478	99.81	30.13	7.11
1	0.14	0.55	524	99.87	32.43	8.01
1	0.16	0.60	589	99.92	34.01	8.93
1	0.18	0.65	642	99.97	35.49	9.72
1	0.20	0.70	591	99.95	36.07	10.19

TABLE-2
EFFECT OF HOMOPOLYMERIZATION COHYDROLYSIS SYNTHESIS CONDITIONS ON AmPAM

Monomer ratio			Intrinsic viscosity (mL/g)	AM Conversion rate (%)	Degree of anion (%)	Degree of cationic (%)
n(AM)	n(DMC)	n(NaAA)				
1	0.10	0.11	212	97.3	9.71	9.01
1	0.12	0.12	231	98.2	10.11	10.71
1	0.14	0.13	326	99.61	11.20	12.09
1	0.16	0.14	398	99.95	11.92	13.63
1	0.18	0.15	423	99.97	11.31	15.07
1	0.20	0.16	386	99.82	12.85	16.54
1	0.22	0.17	348	99.34	13.47	17.29

produce the repulsion between groups make the chains extend and reduce the chance of crosslinking at the same time the molecular chain increase due to increase concentration of NaOH. At the same time in a certain range of DMC involved in the reaction probability becomes large and chain growth rate increased so as to product synthesis higher intrinsic viscosity. Nucleophilic substitution reaction of NaOH hydrolysis process that causes the chain structure of the carboxyl group in a certain range increased continuously and degree of anion increased. With the increase of DMC that increases the cationic monomer in the reaction leads to the increase of cationic degree. When excess NaOH causes high pH, AM as chain transfer agent and hinder the reaction, while the polymerization capacity of DMC itself is very small and with the increase the DMC at the same time the rate of diffusion decreases and reactivity decreased so as to resulting in decreased intrinsic viscosity. It is found that when the mixed ratio of acrylamide, DMC and NaOH is 1:0.18:0.15, the intrinsic viscosity was optimal.

Effect of monomer concentration on viscosity characteristics of the polymer: The constant monomer mass fraction is 30 %, light initiator is 0.08 %, the reaction time is 4 h, the room temperature is about 30 °C, copolymerization monomer ratio of n(AM): n(NaAA): n(DMC) = 1:0.65:0.16, homopolymerization cohydrolysis monomer ratio of n(AM): n(DMC): n(NaOH) = 1:0.18:0.15. As can be seen from Fig. 1, two methods of synthesis of AmPAM characteristic viscosity first increased and then decreased with the increase of monomer mass fraction. This is due to the low monomer concentration, concentration decreases accordingly reduces the collision frequency of monomer and active chain[15], meanwhile less radical generation is not conducive chain reaction. Along with the increase of monomer mass fraction that the product intrinsic viscosity increased. When the mass fraction of monomer is excessive, the viscosity increase and at the same time the excess monomer involved in the reaction. The heat generated is difficult to discharge the molecular chain cross-linking, thereby increasing the polymer relative molecular mass effect is not obvious, leading to the intrinsic viscosity decreases trend, the mass fraction of monomer exists an optimum dosage, selection in 35-40 %.
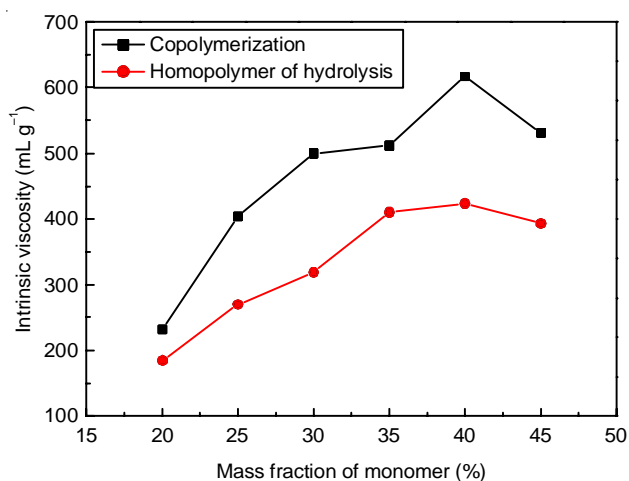
Effect of the amount of initiator on intrinsic viscosity of the polymer: In order to examine the effect of the amount of initiator intrinsic viscosity of AmPAM, two polymerization method mass fraction of monomer selection was 35 %, with other reaction conditions are similar as mentioned before. Fig. 2 indicated that with the increase of the number of the initiator, the intrinsic viscosity of two methods of synthesis of current increases and then decreases. When the initiator content is too small, the number of free radicals generated that can not be meet the chain growth. When the initiator content is too large, formation of a large number of unstable oligomer radicals or dead polymer, free radical grafting achieve stability and free radical production rate is high, so that the chain termination and chain transfer reaction rate increases, cause the product molecular weight decrease, Polymerization initiator dosage 0.08 %, homopoly-merization cohydrolysis initiator dosage is about 0.06 %.
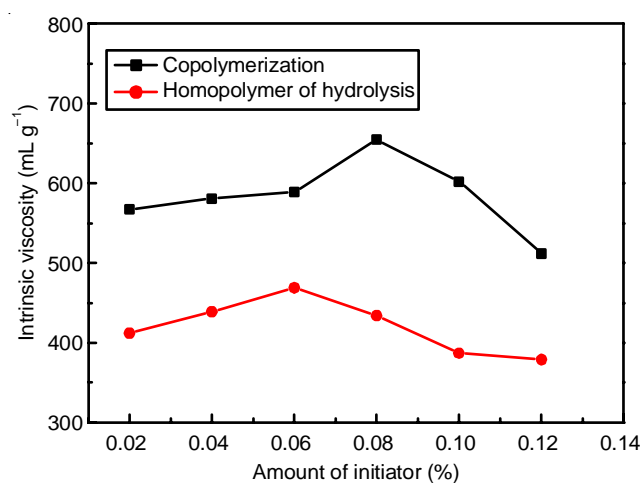

Fig. 2. Effect of the amount of initiator on intrinsic viscosity of the polymer

Effect of pH on characteristics of polymer adhesive: The value of pH is one of very important factors for intrinsic viscosity of AmPAM. Fig. 3 shows the effect of pH on intrinsic viscosity of AmPAM. It is found that the intrinsic viscosity of AmPAM with curve distribution with the increase of pH value from 4.5 to 9.5. When the pH value was lower, the molecular chain of the amide groups crosslinking reaction occurs imidization and the intrinsic viscosity of the product is less.
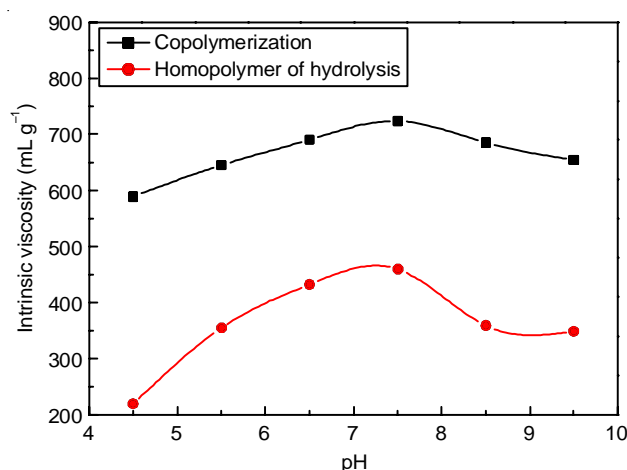

Fig. 1.   Effect of monomer concentration on viscosity characteristics of the polymer

Fig. 3. Effect of pH on intrinsic viscosity of AmPAM

When pH value is too high produce a large number of NH$_3$, at the same time, AM is easy to react with NH$_3$ to form a chain transfer agent three propylene amide[16-17], which not conducive to the growth of the chain. In a word, pH with about 7 is considered to be best in the present experiment.

Nature of the product under optimal experimental conditions: Table-3 observed that the optimum experimental conditions of two synthesis methods were determined by single factor experiment.

TABLE-3
NATURE OF THE PRODUCT UNDER OPTIMAL
EXPERIMENTAL CONDITIONS

Performance indicators	Copolymerization	Homopolymerization cohydrolysis
Intrinsic viscosity (mL/g)	531	759
Conversion rate of AM (%)	99.97	99.94
Anionic degree (%)	11.27	35.19
Cationic degree (%)	13.94	9.80

IR spectroscopy of AmPAM: The FT-IR spectra of the AmPAM prepared from copolymerization (Fig. 4A) and homopolymerization cohydrolysis (Fig. 4B) were as-shown. As observed in Fig. 4, two ways were prepared AmPAM that IR spectra functional groups peak position exactly the same. The peak at 3440 cm^{-1} corresponded to the N-H stretching mode of the amide. The peak at 1645 cm^{-1} corresponded to the C= O stretching mode of the amide. The peak at 1560 cm^{-1} corresponded to the N-H bending vibration of the amide. The peak at 1400 cm^{-1} corresponded to the symmetric stretching band of COO$^-$. The peak at 1460 cm^{-1} was assigned to the bending vibration absorption of the methylene -CH$_2$ group. The peak at 950 cm^{-1} was assigned to the absorption of quaternary ammonium-CH$_2$-N$^+$(CH$_3$)$_3$ group, namely DMC characteristic absorption peaks and AmPAM characteristic groups.
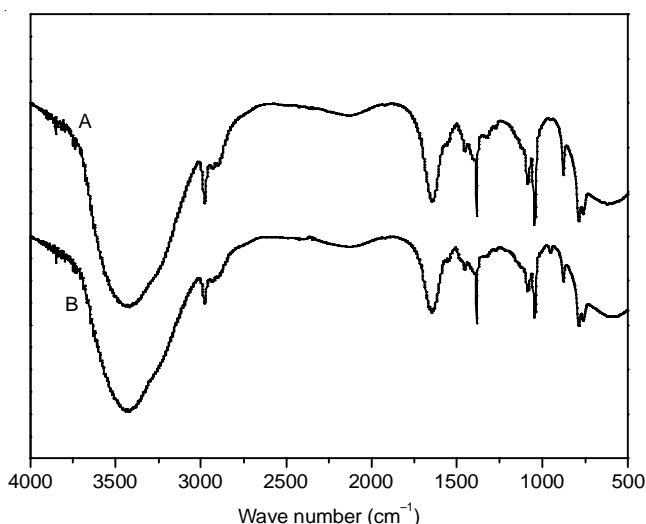

Fig. 4. FT-IR spectra of the the AmPAM

Conclusion

A novel AmPAM flocculant was successfully prepared *via* copolymerization and homopolymerization cohydrolysis based on photoinitiator as initiator, respectively. It was found that the optimum reaction conditions: the monomer ratio of n(AM):n(NaAA):n(DMC) was 1:0.65:0.16, the monomer concentration was 35 %, the amount of the initiator was 0.08 % and pH value was adjusted to 7, the reaction time was 4 h by used copolymerization. And the optimum reaction conditions: the monomer ratio of n(AM):n(NaOH):n(DMC) was 1: 0.15 :0.18, the monomer concentration was 35 %, the amount of the initiator was 0.06 % and pH value was adjusted to 7, the reaction time was 4 h by used homopolymerization cohydrolysis. The intrinsic viscosity of the AmPAM synthesized by copolymerization is far greater than the homopolymerization cohydrolysis synthesis products. Experiments shows that the flocculation effect is better than other industrial products. Therefore, this work not only demonstrated a facile route to the synthesis of AmPAM with improved performance, but also expected to be useful for domestic sewage treatment application.

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