Asian Journal of Chemistry; Vol. 26, No. 15 (2014), 4691-4694

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16171

Synthesis and Characterization of UV-Initiated Anionic Polyacrylamide

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Received: 9 August 2013; *Accepted*: 7 January 2014; *Published online*: 16 July 2014; AJC-15552

Assisted by ultraviolet initiation, an anionic polyacrylamide (APAM) was synthesized by acrylamide (AM), acrylic acid (AA) and sodium hydroxide. Through the single factor experiment, the optimum condition of preparing anionic polyacrylamide was investigated by using molecular weight as a indicator. Infrared radiation spectrum and scanning electron microscope were used to analyze the characterization of anionic polyacrylamide. The results show that anionic polyacrylamide with molecular weight of 16 million Da was prepared in the following optimum condition: M_{AM}:M_{AA}:M_{NaOH} was 7.0:2.0:1.0, the total monomer concentration was 35 %, the initiator concentration was 0.15 %, the UV initiation time was 50 min, the urea concentration was 0.10 % and the EDTA concentration was 0.10 %. The active groups and net structure of anionic polyacrylamide were represented.

Keywords: Anionic polyacrylamide, UV irradiation, Molecular weight, EDTA.

INTRODUCTION

The water-soluble anionic polyacrylamide (APAM) was synthesized by acrylamide (AM), acrylic acid (AA), which contained strong charge neutrality, hydrophilic and adsorption capacity[1-3]. There were some techniques to prepare anionic polyacrylamide, such as aqueous solution polymerization, inverse emulsion polymerization, dispersion polymerization, *etc.*[4-7]. However, these polymerization techniques had the disadvantage of slow polymerization rate, the unstable flocculating capacity of products and the secondary pollution of solvent. Now, a new polymerization technology of ultraviolet (UV) initiation was extensively studied for its efficiency and the quality of the production[8-10].

In this study, an anionic polyacrylamide was synthesized by acrylamide, acrylic acid and sodium hydroxide with the assistance of UV irradiation and azo-initiator. The synthesis condition was optimized. The related influencing factors such as the proportion of three monomers, the total monomer concentration, the initiator concentration, the illumination, the urea concentration and the EDTA concentration were studied. Infrared radiation spectrum and scanning electron microscope were used to describe the characterization of anionic polyacrylamide.

EXPERIMENTAL

The monomer acrylic acid was analytical grade and the monomer acrylamide was technical grade which was sourced from Lanjie Water Supply Company (China). The sodium hydroxide, hydrochloric acid, sodium chloride, 2,2'-Azodiisobutyramidine Dihydrochloride (V50) initiator and ethanol were analytical grade. EDTA (ethylene diamine tetraacetic acid) and carbamide as the additives were added in to the process of polymerization reaction (Chuandong Chemical Co., Ltd, China).

The 85-2A magnetic stirrer was from Yuanbo Experimental Analysis Instrument Co., Ltd (China). The GY-500 ultraviolet high-pressure mercury lamp was provided by the Tianyuanhuiteng Co., Ltd (China). The DK2-2B bathing constant temperature vibrator was supplied by the Jinghong Experimental Facility Co., Ltd (China). The Ubbelohde viscometer was from Shanghai SRD Scientific Instrument Co., Ltd (China). The vacuum drying apparatus was applied by the Keelrein Instrument Co., Ltd (China). The 550 Series II infrared spectrometer was provided by the Mettler Toledo Instrument (Switzerland). The VEGA II LMU scanning electron microscope (SEM) was supplied by the TES-CAN Company (Czech).

Preparation of flocculants: To prepare the anionic polyacrylamide, the monomer of 7.0 g acrylamide, 2.0 g acrylic

acid and 1 g sodium hydroxide were added into a 100 mL of reactor with moderate deionized water. The mixture was being stirred until it completely dissolved. Then the nitrogen gas was used to drive the oxygen out of the reactor and the initiator was added into before sealing. At last, the mixture was placed under the ultraviolet high-pressure mercury lamp for 50 min. After cooling down and aging 24 h, the high quality anionic polyacrylamide was obtained.

The main factors and their initial values of preparation condition in this experiment were room temperature, the monomer mass ratio of 7.0:2.0:1.0, the total monomer concentration of 35 %, initiator concentration of 0.15 %, the concentration of EDTA of 0.10 % the concentration of urea of 0.10 % and the time of UV irradiation of 50 min.

Molecular weight of anionic polyacrylamide: Dissolve 0.1 g anionic polyacrylamide into 100 mL deionized water to form a solution. Then add 100 mL sodium chloride (2.0 mol L^{-1}). After that, get the mixed solution through the filter paper funnel. Finally, the molecular weight of anionic polyacrylamide was measured through the Ubbelohde viscometer.

Characterization of anionic polyacrylamide: Purified anionic polyacrylamide was analyzed through infrared spectrum to study the active group. The scanning electron microscope was used to analyze the surface character of anionic polyacrylamide.

RESULTS AND DISCUSSION

IR spectra: Fig. 1 presents IR spectra of anionic polyacrylamide synthesized by acrylic acid and acrylamide. The peaks at 1179 and 1121 cm^{-1} are attributed to the C-O-C group. And The peak at 1326 cm^{-1} is assigned to connection of -COOH group. Moreover the -CH group is observed at the 1407 cm^{-1}. And the stretching vibration of -C=O group in -COONa is observed at the 1453 cm^{-1}. In addition, the peaks at 1561 and 1665 cm^{-1} are attributed to the stretching vibrations of -C=O group in -CO-NH_2. And the absorption band at 2943 cm^{-1} was ascribed to the -CH_2 group. The IR spectra of anionic polyacrylamide confirms that some active groups are produced by the polymerization.

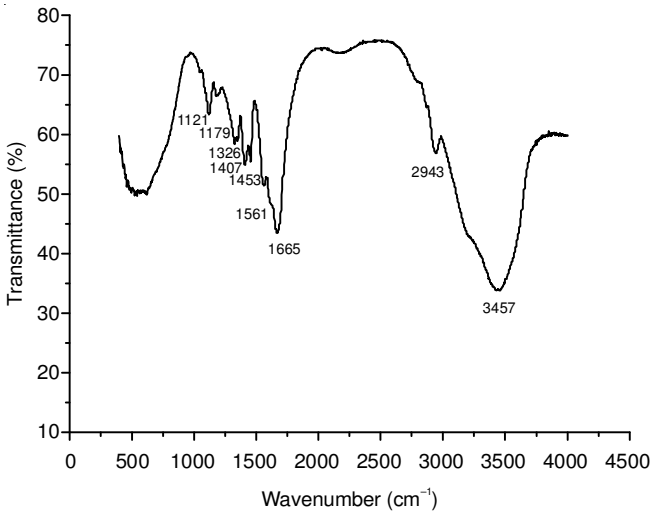

Fig.1. Infrared spectrogram of APAM

SEM: Fig. 2 is the SEM images of anionic polyacrylamide which was amplified three thousand times and five thousand times. It shows that the surface of anionic polyacrylamide represents the net structure. And the lamellar cellular structure of anionic polyacrylamide increases its specific surface area. So the surface structure of anionic polyacrylamide makes it more effectively flocculating the colloidal and suspended particle from the waste water through the processes of compressing the charge neutrality, double electrode layer and adsorption bridge.

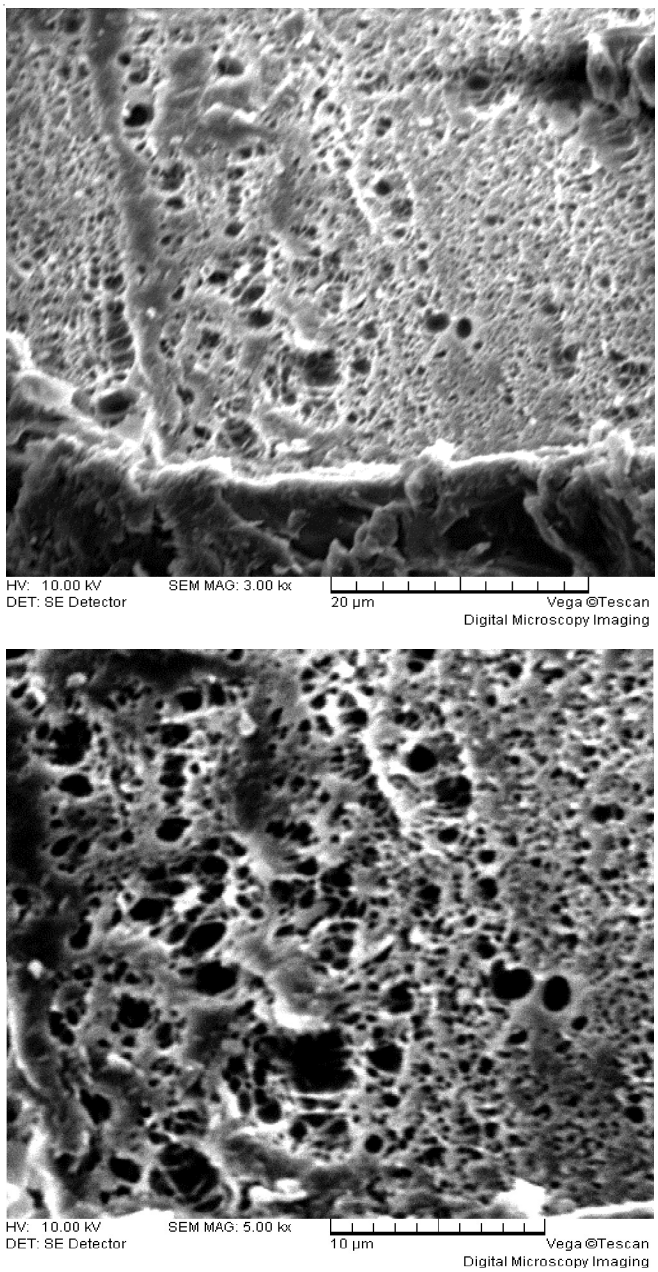

Fig. 2. SEM picture of APAM

Effect of monomer mass ratio: The monomer mass ratio is the main factor that influences the copolymer synthesis, especially influencing the polymer molecular weight. When the initial condition are invariable, we only studied the effect of the monomer mass ratio on polymer molecular weight and the results are shown on Table-1.

TABLE-1
EFFECT OF PROPORTION BETWEEN MONOMERS ON MOLECULAR WEIGHT OF APAM

Num.	AM:AA:NaOH	Polymer molecular weight (1×10^4 Da)
1	6.0:3.5:0.5	501
2	6.0:3.0:1.0	618
3	6.0:2.5:1.5	872
4	7.0:2.5:0.5	622
5	7.0:2.0:1.0	1523
6	7.0:1.5:1.5	693
7	8.0:1.5:0.5	1092
8	8.0:1.0:1.0	1319
9	8.0:0.5:1.5	212

As showed in Table-1, when the concentration of acrylamide is low, the molecular weight of prepared anionic polyacrylamide increases with the increasing of the concentration of acrylamide. However, when the acrylamide concentration exceeds 70 %, the polymer molecular weight decreases obviously for the system temperature rise which is caused by excessive heat producing during the polymerization process. Furthermore, when the concentration of acrylamide is too high, it's easy to cause intermolecular cross linking which will reduce the solubility of product. The proportion of acrylic acid and sodium hydroxide which would affect the pH value of solution could not be too high or too low. In the condition of extreme acidity or alkalinity, the molecular weight of APAM is always low.

Effect of total monomer concentration: As showed in Fig. 3, in the case of low concentration, molecular weight of polymer anionic polyacrylamide increased with the increasing of concentration increases. And when the total monomer concentration reaches 35 %, the molecular weight of anionic polyacrylamide gets the maximum. It is due to the increasing of the total monomer concentration which greatly increased the collision frequency among the monomer and active chain. However, after reaching the peak, the polymer molecular weight decrease gradually with the increasing of the total monomer concentration. This attributed to the abundance insoluble substance of cross linking produced when the total monomer concentration is too high. The transfer rate of the polymer chain is slower than the growth rate of the polymer chain, it is also not conducive to the synthesis of anionic polyacrylamide.

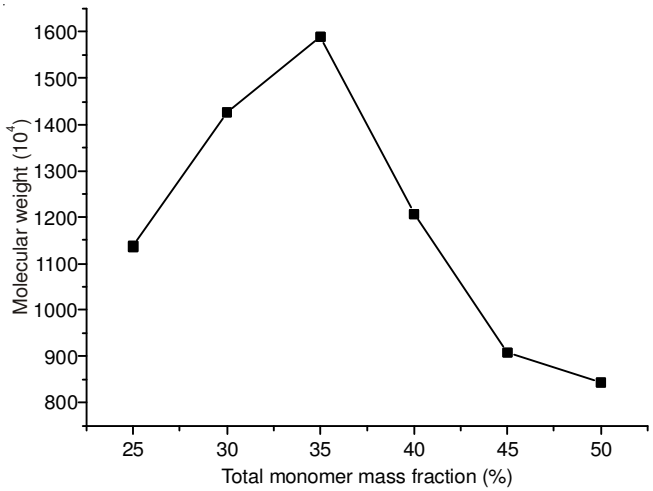

Fig. 3. Effect of the total monomer concentration

Effect of initiator concentration: As showed in Fig. 4, with the increase of initiator dosage, the polymer molecular weight increases firstly and then decreases. When the dosage of initiator is too low, the reaction is hard to react and react incompletely. Moreover, a large number of residue monomer is found. However, when the dosage of initiator is too high, it's easy to make a rapid reaction which contains too many free radicals and active centers. That will shorten the length of the main chain and lead to the decreasing of the polymer molecular weight. As a result, the optimal value of the dosage of initiator is 0.15 %.

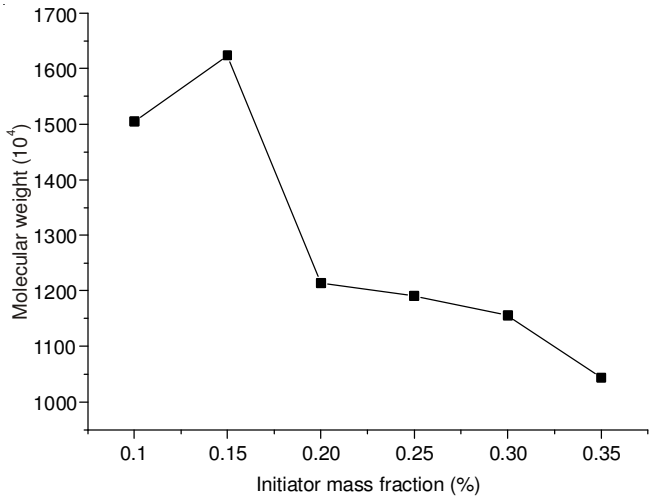

Fig. 4. Effect of the initiator concentration

Effect of time of UV irradiation: As showed in Fig. 5, the polymer molecular weight increases firstly and then decreases with the extension of the irradiation time. It is due to the transfer rate of monomer increase gradually when the time of UV irradiation is moderate. However, when the irradiation time is too long, the reaction temperature will increase gradually which causes the cross linking reaction and decreases the polymer molecular weight.

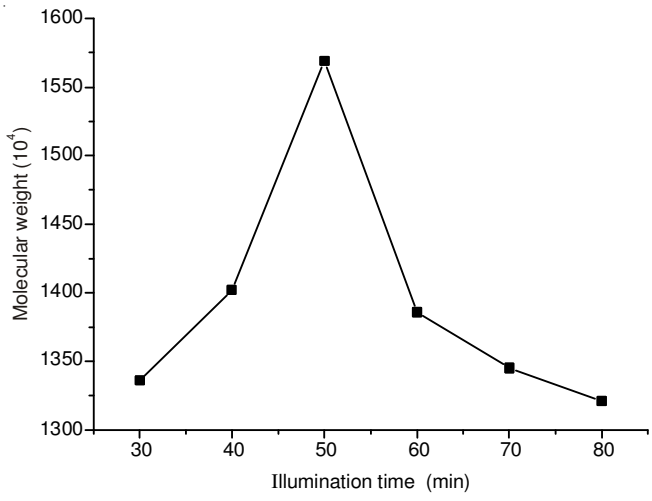

Fig. 5. Effect of the irradiation time

Effect of concentration of EDTA: There are some trace heavy metals that has an impact on free radicals in a polymerization reaction system. EDTA is a chelating agent which is

frequently used to remove the trace heavy metals. Thus, it's advantageous to the polymerization reaction if some EDTA was added into the reaction system. As showed in Fig. 6, the molecular weight of anionic polyacrylamide increases with the increasing of the concentration of EDTA. when the concentration of EDTA reaches 0.1 %, the molecular weight of anionic polyacrylamide gets the maximum. However, when the concentration of EDTA exceeds 0.1 %, the molecular weight of anionic polyacrylamide decreases. That is because too much EDTA would present the polymerization reaction.

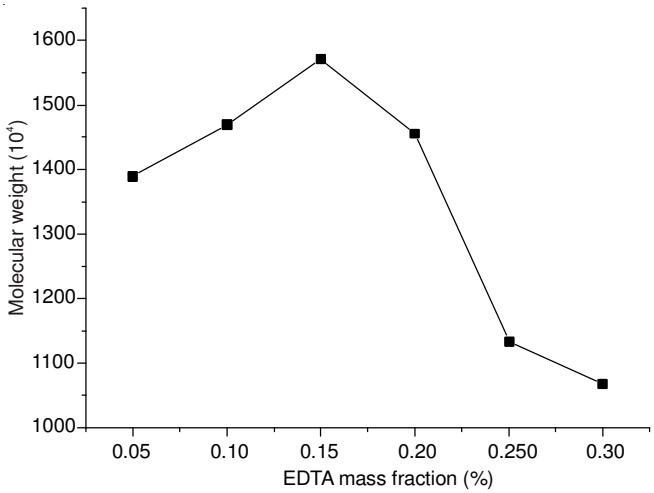

Fig. 6. Effect of the EDTA concentration

Conclusion

Assisted by UV irradiation, an anionic polyacrylamide was synthesized by acrylamide, acrylic acid and sodium hydroxide. The optimal synthesis conditions is M_{AM}:M_{AA}:M_{NaOH} of 7.0:2.0:1.0, the total monomer concentration of 35 %, the initiator concentration of 0.15 %, the concentration of EDTA of 0.10 % the concentration of urea of 0.10 % and the time of UV irradiation of 50 min. The molecular weight of the prepared anionic polyacrylamide is 16 million Da. The characteristic analysis of anionic polyacrylamide shows that it contains some active groups such as -C=O, C-O-C and its surface structure is lamellar cellular and net through Infrared radiation spectrum and scanning electron microscope.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support provided by the National Natural Science Foundation of China (Project No. 21177164).

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