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Study on the Synthesis of CPAM Paper Reinforcing Agent in Aqueous Two-Phase System

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In this paper, low molecular weight CPAM paper reinforcing agent was synthesized in aqueous two-phase system by using acrylamide (AM) and methacryloyloxy ethyl trimethyl ammonium chloride (DMC) as the main raw material and the effects of monomer concentration, monomers mole ratio, initiator concentration, dispersant concentration, reaction temperature and reaction time on the CPAM paper reinforcing agent performance were mainly discussed by single factor experiments. Moreover, the molecular structure of CPAM was also identified by IR and NMR analysis. The results showed that the optimum process of the CPAM synthesized with AM and DMC in aqueous two-phase system are as follows: monomer concentration 25 %, the mole ratio of AM and DMC 1:3, PEG concentration 1 %, initiator concentration 0.15 % (the mass ratio of ammonium persulfate and urea 1:1), reaction of initial temperature for 35 ºC, reaction time 6 h, NaCl concentration 10 % and stirring speed 180 r/min.

Key Words: Aqueous two-phase, CPAM, Paper reinforcing agent.

INTRODUCTION

Cationic polyacrylamide can increases paper tensile index, bursting index, tearing index and folding index, *etc*. by enhanced hydrogen bonding between the fibers, which is an excellent paper reinforcing agent and widely used in the paper industry[1]. There are several ways to synthesize CPAM, in which, solution polymerization is more investigated and is the applicable way, while aqueous two-phase system is new synthetic methods developed in recent years. The polymerization requires the monomer to adsorb the free radicals generated by the initiator to initiate the polymerization because the aqueous two-phase system appeared homogeneous state. With the polymerization reaction, polymerization products interacted with the added dispersant phase because of different polarity. Reaction occurred in the dispersed phase. More monomer distributed in the dispersed phase can not only improves the conversion rate of monomer, but also can be beneficial for the preparation of high solid content polymerization products[2-6]. Therefore, these types of polymerization require more and more attention. The synthetic CPAM has an unique advantage applied in paper industry, lies in its side chain structure with a high density of charge. In aqueous solution, it forms cationic polymers and easily attracts each other with pulp. Moreover, the CPAM can be used directly in salted solution in absence of any organic solvent[7]. Therefore, it is especially suitable for paper reinforcing agent and is friendly to environments.

In this paper, low molecular weight CPAM paper reinforcing agent was synthesized in aqueous two-phase system in dispersant polyethylene glycol 4000 solution by using acrylamide (AM) and methacryloyloxy ethyl trimethyl ammonium chloride (DMC) as the main raw materials and the effects of monomer concentration, mole ratio of monomers, initiator concentration, dispersant concentration, reaction temperature and reaction time on the CPAM paper reinforcing agent performance were mainly discussed. Moreover, the molecular structure of CPAM was also identified by IR and NMR analysis.

EXPERIMENTAL

Acrylamide,industrial pure,was provided by Tianjin Kermel Chemical Reagent Development Center; methacryloyloxy ethyl trimethyl ammonium chloride (DMC), industrial pure,was provided by Wuxi Xinyu Chemical Plant; PEG 4000, Ammonium persulfate, potassium bromide, potassium bromate, potassium iodide, urea, soluble starch, methanol, ethanol, acetone, isopropyl alcohol, sodium chloride, epichlorohydrin, silver nitrate were all analytically pure.

DC-KZ300C Computer monitoring tensile tester; YQ-Z-20 paper tearing tester; DC-ZNP1600B computer monitoring bursting tester; DC-MET135A computer monitoring folding tester; Spectrum One-B Fourier transform infrared spectrometer, PE company, USA; INOVA400 superconducting NMR spectrometer, USA.

Synthesis of CPAM paper reinforcing agent in aqueous two-phase system: 10 g NaCl was dissolved in water and then a certain amount of PEG added to the aqueous solution of NaCl. After that, DMC and acrylamide monomer were added in the beaker and fully dissolved. The reaction system maintained the total mass of 100 g. Then the above-mentioned reaction solution was added in the four flasks with thermometer and constant speed stirrer. The four outlets flask was placed in water bath to control the reaction temperature and initiator was added after blowing nitrogen for 0.5 h. Under the protecting of nitrogen, the reaction solution became turbid after stirring for a certain time, which main the reaction system changed into a multiphase system from the uniform phase and the PEG solution was in continuous phase and resulting copolymer in dispersed phase. After reaction, the final product was colourless transparent liquid, which was stored in the bottle.

Handsheets make and determination of the paper properties: The bleached baggass pulp was fluffed by using fluffer for 2 min after diluted to a certain concentration and then the CPAM paper reinforcing agent synthesized in different processes were added in the pulp suspension and left for a certain time. After that, the handsheets were firstly made by using circular handsheet paper making apparatus and then drying on the electric fast dryer for 10 min, controlling the temperature at 105 ºC. The properties of dried handsheets were detected after constant temperature and humidity treatment for 24 h in constant temperature and humidity laboratory.

Characterization of molecular structure of the CPAM reinforcing agent

The CPAM were firstly washed with acetone and methanol and then with deionized water repeatedly. The washed CPAM samples were crushed into powder after dried in drying box after that, The molecular structure were characterized by using IR. The CPAM samples were dissolved in D_2O solvent and analyzed by INOVA-400 nuclear magnetic resonance spectroscopy for 1H NMR spectrum.

RESULTS AND DISCUSSION

Effect of monomer concentration on the performance of reinforcing agent: The reinforcing effect of cationic polyacrylamide (CPAM) on papers depends on the functional groups in the CPAM molecules. The concentration of monomer not only determines the molecular weight of the final product and the conversion rate of the monomers, but also has an impact on the viscosity of the agents during the polymerization process. Because the reactions between the monomers are radical polymerization, when the concentration of the monomers in the solution is low, the chances that the monomers collide with each other are low as well, which would have tremendous impacts on the reaction rate, reaction time and the properties of the final products, such as the molecular weight and diagnostic viscosity. In contrast, when the concentration of the monomers is high, the reaction rate will rise. Because this reaction is exothermic, the heat generated during the reaction can not dissipate resulting in a high temperature in the system, which would accelerate the reaction rate and affect the quality of the products enormously. Hence, the concentration of monomers is the key factor which can affect the equilibrium of the reactions. Therefore, in this study, we uses different concentrations of monomers when synthesizing CPAM paper reinforcing agents and investigate how this could affect the strength of papers. In the experiments, the mole ratio of DMC and AM monomers is 1:3, the initiator dosage is 0.18 g (the mass ratio of ammonium peroxydisulfate and urea is 1:1). 1 g of dispersant, 7.5 h of reaction time, 10 g of sodium chloride were used in the experiments. Deionized water was added into the reacting system until the mass reached 100 g. Table-1 shows the impact of monomer concentration on the performance of paper reinforcing agents.

In Table-1, when the concentration of monomers rises, the strength parameters of papers increase at first, then decrease. When the monomer concentration is 25 %, the zero-span tensile index, tearing index, bursting index and folding index of papers reach the maximum. This is because as the monomer concentration increases, the reaction becomes more intense and at the same time the chances that monomers collide with each other rise significantly, which will lead to longer molecule chains and faster reaction rates. However, this polymerization reaction is exothermic, if there is too much heat generated in the system, it is difficult for it to dissipate. When the monomer concentration is low, the reaction takes place easily and rapidly because the reaction heat diffuses quickly. However, when the monomer concentration reaches higher than 25 %, more cross-linking reactions may happen because abundant heat is generated during the reaction and temperature in the system raises fast, which results in products of lower quality and worsen the effects of the reinforcing agents. Besides, higher monomer concentrations result in higher specific viscosity in the system and products with larger molecular weights. When the monomer concentration is 25 %, the viscosity of reinforcing agents is ideal, the conversion percentage of AM monomers reaches 99 %. Taken all of these into account, when the monomer concentration is 25 %, the reactions proceed mildly, the reinforcing effect is the best. Hence, the optimal monomer concentration is 25 %.

TABLE-1
DIFFERENT PREPARATION MONOMER CONCENTRATION ON PAPER ENHANCER

Concentration (%)	Basis weight (g/m^2)	Tensile index (N m/g)	Tearing index (mN m^2/g)	Bursting index (Kpa m^2/g)	Folding index/number of times
Blank	67.2	47.3	5.36	2.82	34
10	68.1	50.2	5.68	3.16	45
15	67.3	53.5	5.78	3.28	98
20	67.8	55.6	5.81	3.33	101
25	66.9	57.8	5.88	3.48	108
30	67.5	54.2	5.69	3.24	78

*1. Bagasse pulp, beating degree 39ºSR; 2. Dosage of reinforcing agents: 2 % (absolute dry pulp).

Effect of mole ratio of DMC and AM on the reinforcing agent properties: The mole ratio of DMC and AM is also an important indicator on the reinforcing agent properties. CPAM enhances the strength properties of papers through increasing the binding chances between fibers and reinforcing agent, since there are repelling force between the cations of reinforcing agent and the anions of fiber surface. Therefore, the number of positive charge on the synthetic CPAM was an important indicator on the paper properties. As the mole ratio of DMC and AM reflects the effects of amount of monomer DMC on the cationic group of distribution uniformity on the synthesis CPAM, thereby affecting the strengthen effects. In the experiment, monomer dosage of 25 g, initiator dosage of 0.18 g (mass ratio of ammonium persulfate and urea is 1:1), dispersant dosage of 1 g, the reaction time 7.5 h, the amount of sodium chloride 10 g were used in the experiments. Deioned water was added into the reacting system until the mass reached 100 g. Table-2 shows the effect of mole ratio of DMC and AM on physical properties of the paper.

As can be seen in Table-2, with the DMC dosage increasing, both the tensile index and bursting index increased at first, then decrease and both of them reaches the maximum when the mole ratio of DMC and AM was 1/3. Tearing index reached the maximum when the mole ratio of DMC and AM was *ca.* 1/4. Folding index reached the maximum when the mole ratio of DMC and AM was 1/2. In aqueous two-phase system, the mole ratio of DMC and AM affected the cationic degree of reaction products. As the electrostatic interaction between the slurry and the reinforcing agent, the hydrophilic properties of CPAM was impacted, thereby the uniformity of fiber dispersion was affected. With the increased dosage of DMC, the steric effect and the role of chain growth will be increased. When the mole ratio of DMC and AM was *ca.* 1/3, the increasing intrinsic viscosity of the reaction products become flatten, these were because the effects balance of the steric effect of cationic monomer and concentration. When the mole ratio of DMC and AM was higher than 1/4, the effects of chain growth is greater than the steric. Therefore, the intrinsic viscosity of reaction products increases Therefore, the amount of cationic monomer is not the bigger the better.

As the increasing of tensile index was mainly focused on and both of the tensile index and tearing index increased larger, therefore, the mole ratio of DMC and AM of 1/3 was preferred.

Effect of concentration of dispersant PEG on the reinforcing agent properties: Dispersant is the key for aqueous two-phase polymerization system to stability. The selected dispersing agent should be dissolved in the reaction system and form large surface area of colloidal particles, therefore, the formed particles was easy to adsorb on the polymer surface, since the main mechanisms of dispersants were the charge repulsion and steric hindrance effects. In this paper, the effects of CPAM synthesized from different concentration of dispersant PEG on the physical properties were explored. In the experiment, mole ratio of DMC and AM of 1:3,initiator dosage of 0.18 g (mass ratio of ammonium persulfate and urea is 1:1), the reaction time 7.5 h, the amount of sodium chloride of 10 g were used in the experiments. Deionzed water was added into the reacting system until the mass reached 100 g. The effects of concentration of dispersant PEG on physical properties of the paper are shown in Figs. 1 and 2.

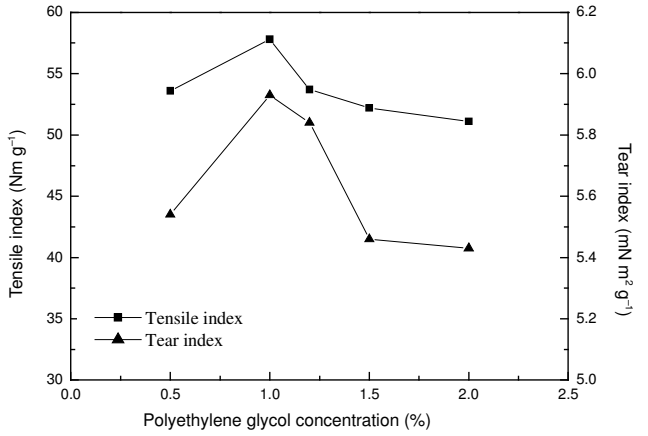

Fig. 1. Effect of PEG concentration on paper tensile index and tear strength

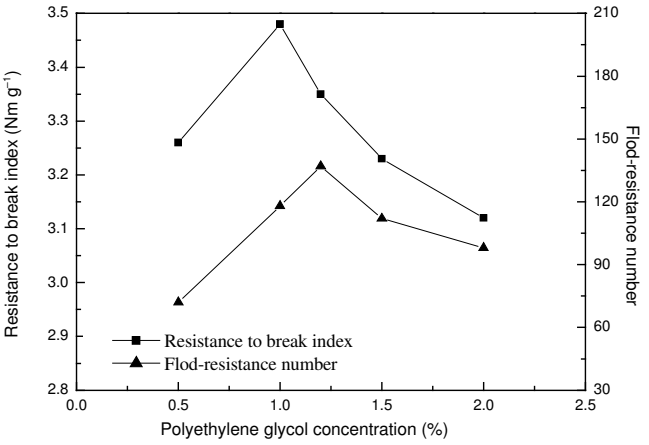

Fig. 2. Effect of PEG concentration on paper bursting and folding index. *1. Bagasse pulp, beating degree 39ºSR; 2. monomer concentration of 25 %, mole ratio of DMC and AM is 1:3, dosage of reinforcing agents: 2 % (absolute dry pulp)

The effect of dispersant polyethylene glycol concentration on the paper tensile index and tearing index are shown in Fig. 1 and the paper breaking and folding index are shown in Fig. 2. It can be seen from the figures, with increasing concentration

TABLE-2
DIFFERENT MOLE RATIO OF DMC AND AM ON PHYSICAL PROPERTIES OF THE PAPER

Mole ratio of DMC and AM	Basis weight (g/m^2)	Tensile index (N m/g)	Tearing index (mN m^2/g)	Bursting index (Kpa m^2/g)	Folding index/number of times
1/5	67.9	51.3	5.63	3.06	55
1/4	68.6	53.6	5.93	3.18	65
1/3	67.5	56.8	5.86	3.34	112
1/2	68.2	54.3	5.75	3.21	130

*1. Bagasse pulp, beating degree 39ºSR; 2. Dosage of reinforcing agents: 2 % (absolute dry pulp).

of polyethylene glycol, paper tensile index, tearing index, bursting index and folding index all increased in begining and then decreased, while paper tensile index, bursting index and tearing index all reached their maximum in the dispersant concentration of 1 % and the paper folding index in the dispersant concentration of 1.2 %. This is mainly because of the apparent viscosity of the copolymer increases with dispersant concentration gradually increased. Due to the increase of PEG concentration, the system reduces the concentration of the critical phase, so that more of the monomers polymerize in the dispersed phase ; the resulting polymer particles are more easily to adsorb stabilizer molecules and copolymer particles are more susceptible to coalescence, resulting in the increase of apparent viscosity of the polymer and the viscosity of the system; in the concentration of 1.5 % for the dispersant, the apparent viscosity of polymer was too large to stir with polymer stuck in the mixing shaft. Polyethylene glycol dispersant major impacted on the polymerization reaction in the generation of the colloidal particles' formation and the growth stage. When the dispersant concentration of PEG increased, the viscosity of the reaction system increased, leading to the resistance between the polymer particles being larger; the increasing of the concentration of dispersant also increased the collision risk between the polymer particles and dispersant; so dispersants particle had enough dispersant molecular to adsorb when it had lager surface area.

From the above analysis, the amount of dispersant was not the bigger the better. When the dispersant concentration reached 1 %, the paper tensile index, break index and tear index all reached the maximum and fold-resistance index was also significantly improved compared with the blank sample. At the same time, when the dispersant concentration was 1 %, the viscosity of the strengthening agent was the most appropriate and AM monomer conversion rate reached 99 %. Thus, when dispersant concentration was 1 %, the reaction had more moderate response; better enhancement effect. So in the selected single-factor experiment dispersant concentration is adopted to be 1 %.

Effect of initiator on the reinforcing agent properties: In aqueous two-phase system of DMC-AM polymerization, the initial state was similar to all states of the aqueous solution reaction system (polyethylene glycol, DMC, AM and water),which requested DMC and AM adsorbing initiator and producing free radicals after joining in the initiator, caused grafted polymerization reaction and make the reaction occur more in the dispersed phase.

In the experiments, ammonium persulfate and urea for initiator were used as the redox system. Ammonium persulfate was the oxidant, producing the free radicals; Free radicals were the activity center of polymerization reaction, the more free radicals, more active centers and the higher the molecular weight polymer accordingly will be; urea was reducing agent, which can accelerate the reaction speed and make the reaction more completely. So the dosage of oxidant, reducing agents determined the amount of free radicals in the polymerization system and then further influenced the structure and the properties of the polymerization.

Aqueous two-phase polymerization reaction is exothermic reaction. High system temperature would result in fast polymerization of monomer and the high viscosity of product, so the initiator concentration related to the success or failure of reaction. In the experiment, different initiator concentration was chosen to synthesize a series of cationic polyacrylamide strengthening agent. The results are shown in Figs. 3 and 4.

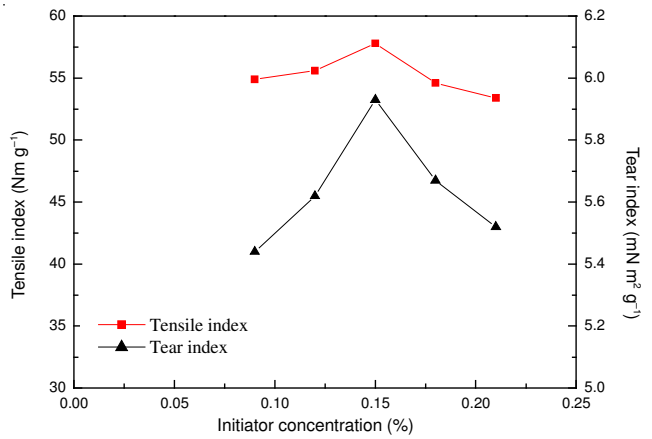

Fig. 3. Effect of initiator concentration on paper tensile and tear index

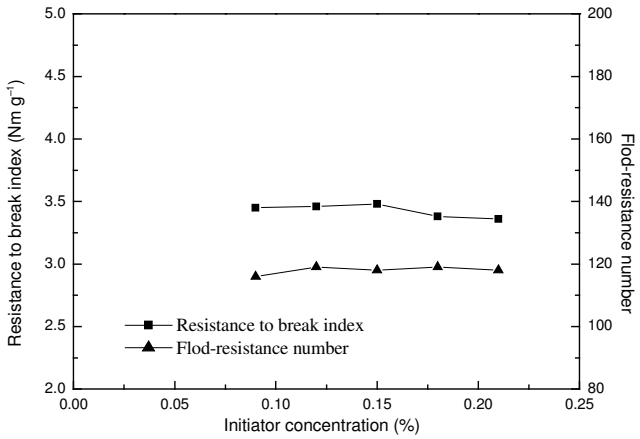

Fig. 4. The effect of initiator concentration on paper bursting and fold index. *: 1. Beating degree39ºSR; 2. Monomer concentration of 25 %, mole ratio of AM and DMC 1:3, PEG concentration 1 %

Figs. 3 and 4 show, the initiator concentration have a great impact on strength index of paper, especially on the tensile index, tearing index of the paper, while the little impact on the bursting index and fold strength. That is, the reaction initiator concentration of 0.15 % is appropriate. This is mainly because the concentration of initiator affects the amount of free radicals in the polymerization system. The number of free radicals affects the molecular weight and then influences the structure and the properties of the polymerization.

From the above analysis, the amount of initiator was not the bigger for the better polymerization. When the initiator concentration reached 0.15 %, the paper tensile index, tearing index reached the maximum, but paper bursting index and folding index did not change significantly. Thus, when initiator concentration was 0.15 %, the reaction product had a better reinforcing agent performance. So the initiator concentration of 0.15 % was preferred.

Effect of temperature on the reinforcing agent synthesis: The effect of reaction temperature on the reinforcing agent synthesis is shown in Fig. 5. As the temperature increased

within a certain range, the conversion rate of monomer first increased and then decreased. High temperature will cause the auto polymerization, so the reaction temperature was generally no more than 50 ºC. When the reaction temperature was at 35 ºC, the reaction was easier and the viscosity moderate increase, chemical reaction was smooth and monomer conversion rate and intrinsic viscosity reached the maximum, as shown in Fig. 5.

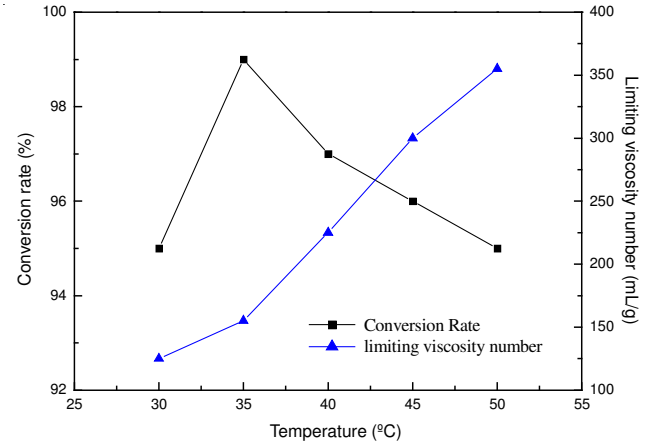

Fig. 5. Effect of temperature on monomer conversion rate and limiting viscosity number

Effect of reaction time on the reinforcing agent synthesis: The effect of reaction time on the reinforcing agent synthesis is shown in Fig. 6.

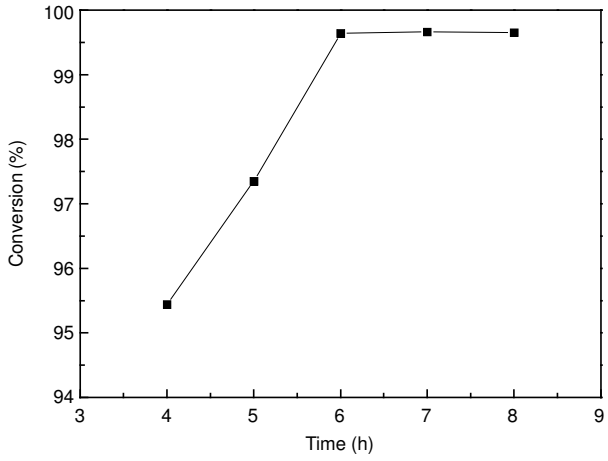

Fig. 6. Effect of reaction time on monomer conversion

When the reaction time was less than 6 h, the monomer conversion rate increased rapidly, when the time were more than 6 h, the reaction rate the reached its maximum and no longer significant increase, indicating that polymerization of DMC and AM completed basically at 6 h.

Process optimization of aqueous two-phase system synthesizing CPAM strengthening agent: Through the above single-factor experiments, the optimum process of the CPAM synthesized with AM and DMC in aqueous two-phase system are as following: monomer concentration 25 %, the mole ratio of AM and DMC 1:3, PEG concentration 1 %, initiator concentration 0.15 % (the mass ratio of ammonium persulfate and urea 1:1), reaction of initial temperature for 35 ºC, reaction time 6 h, NaCl concentration 10 % and stirring speed 180 rpm.

In the experiment, the CPAM was synthesized with optimum process and the physical properties of the product were determined according with national standards. The results were shown in Table-3.

TABLE-3
PHYSICAL PROPERTIES OF CPAM REINFORCING AGENT PHYSICAL WITH OPTIMUM PROCESS

The properties	Determination results
Appearance quality	Colourless liquid glue
Solid content	38.0 %
Solubility	Stir in the water < 10 min dissolved
Zeta potential	32.3-37.0 mV
Average particle size	150 d nm
Acrylamide surplus quantity	*ca.* 1 %
stability	No stratification for 4 months
pH value	6.5
Molecular weight	90-100 million
Centrifugal stability	30.7 %
Cationic poly-acryl degrees	30 %

Structural characterization of CPAM reinforcing agent: In order to characterize the structure of CPAM strengthening agent, IR and NMR were used to analyze the synthetic CPAM. Fig. 7 shows the IR spectrogram of the CPAM sample. The strong absorption peak of 1658.23 cm^{-1} was the amide carbonyl characteristic absorption peak, the wide absorption peak of 3433.75 cm^{-1} was -NH_2 stretching vibration absorption peaks and the 2900-2800 cm^{-1} was -CH_3 and -CH_2 stretching vibration absorption peak and the sharp absorption peak of 1415.98 cm^{-1} is the cationic monomer-CH_2-N^+ methylene bending vibration absorption peaks.

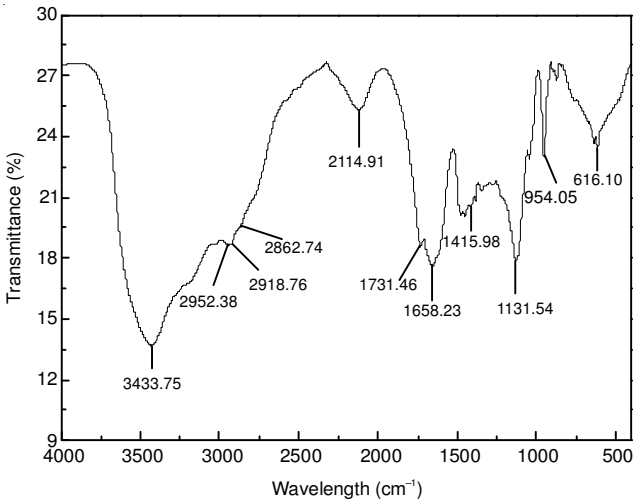

Fig. 7. IR spectrogram of the CPAM sample

Fig. 8 shows the ^1H NMR spectrogram of the CPAM sample. The attribution of the peaks are interpreted as follows: 2.0-2.25 was the chemical displacement for hydrogen on the acrylamide methylene (first hydrogen) and the methylene hydrogen connected to the double bond of cationic monomer (first hydrogen), number near 1.5 is the chemical displacement for second hydrogen, 3.2-3.35 is the chemical displacement for hydrogen connected with quarter ammonia nitrogen (fourth

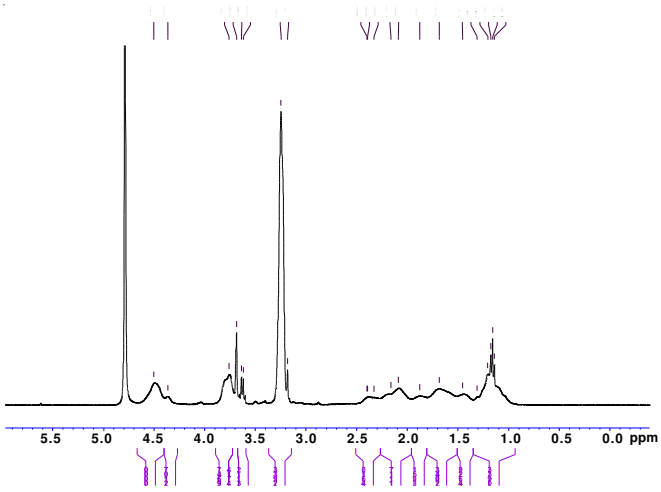

Fig. 8. ^{1}H NMR spectrogram of CPAM

hydrogen), 3.6 is the chemical displacement for the methyl hydrogen (third hydrogen).

The analysis of the IR and the NMR shows that the polymer molecular structure has the characteristic functional groups of AM and DMC. This means the synthesis polymer is the target product cationic polyacrylamide. The molecular structure unit of CPAM is shown in Fig. 9.

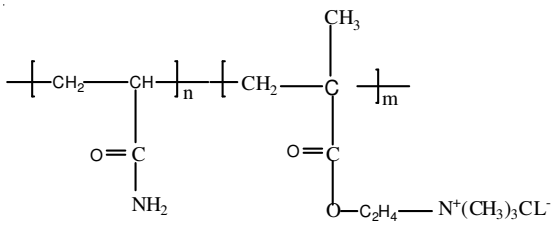

Fig. 9. Molecular structure of target product CPAM

Conclusion

The optimum process of the CPAM synthesized with AM and DMC in aqueous two-phase system are as following: monomer concentration 25 %, the mole ratio of AM and DMC 1:3, PEG concentration 1 %, initiator concentration 0.15 % (the mass ratio of ammonium persulfate and urea 1:1), reaction of initial temperature for 35 ºC, reaction time 6 h, NaCl concentration 10 % and stirring speed 180 r/min. Through FTIR and ^{1}H NMR analysis, the results show that, the molecular structure of target product contain AM and DMC chain section, which may determine the target product is CPAM.

ACKNOWLEDGEMENTS

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REFERENCES

1. Y.D. Shen, Preparation of Paper Chemicals and Mechanism, China Light Industry Press, Beijing, p. 318 (1999).
2. Zhu Yongqiang, Paper Strength Aid and the Mechanism of Strengthening, *Shanghai Paper Making*, **3**(4) (2004).
3. G.X. Wu, Y. Qiang and X.X. Ling, *J. Appl. Polym. Sci*., **67**, 1005 (1998).
4. X.H. Peng and J.R. Shen, *Polym. Mater. Sci. Eng.*, **14**, 63 (1999).
5. H.F. Ni and D. Hunkeler, *Polymer*, **38**, 667 (1997).
6. H.J. Zhang, F.S. Chen and H.R. Hu, *China Pulp Paper*, **22**, 15 (2003).
7. X. Peng and J. Zhao, *J. Appl. Polym. Sci*., **106**, 3468 (2007).