

Dispersion Polymerization of Acrylamide with Water-Soluble Chitosan as the Stabilizer

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ABSTRACT: A cationic polyelectrolyte of P (CMTC-AM-DMC) was synthesized by dispersion polymerization in aqueous solution of ammonium chloride, with acrylamide and dimethylaminoethyl methacrylate methyl chloride as main raw materials. *N*-carboxymethylthioureidochitosan was used as both the reactant and the stabilizer, and 2,2'-azobis (2-amidinopropane) dihydrochloride (V-50) as the initiator. The effects of the major reaction variables such as the concentration of inorganic salt and initiator, temperature, reaction time, and pH on the polymerization were discussed in this article. The optimal conditions of the polymerization were determined by orthogonal tests. The results showed that an increase in salt concentration resulted in an increase of molecular weight and particle size and a decrease of apparent viscosity, while when salt concentration was up to 23.9%, apparent viscosity was slightly higher than others. Molecular weight, particle size, and apparent

viscosity all decreased with the increase of initiator. The apparent viscosity, molecular weight, and particle size would decrease with pH, and the product would be coagulated when pH > 7. Temperature influenced the characteristic a lot. Overall conversion was less dependent on these factors except for the temperature. Molecular weight and overall conversion increased gradually with the time, and the monomers could react completely at about 5–7 h. Flocculation occurred with 13% of salt concentration, 0.005% of initiator, and pH > 7. The optimal reaction conditions for obtaining a stable aqueous dispersion were 22.3% for ammonium chloride, 0.007% for initiator, react under 55 °C for 5 h at pH = 4. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: polyelectrolytes; chitosan; acrylamide; dispersion polymerization; stabilization

INTRODUCTION

Acrylamide-based polymers and copolymers have found significant commercial applications. For example, they are used as flocculants in industries like ore processing, paper making, waste water treatment, etc. Polyacrylamide (PAM) has been prepared by four polymerization methods as below: (1) solution polymerization,^{1–3} (2) microemulsion polymerization,⁴ (3) inverse microemulsion polymerization,⁵ and (4) dispersion polymerization.⁶ Dispersion polymerization is a novel method put forward in 1970s. Comparing with other polymerization methods, it has attracted more attention because of its low toxicity, reasonably low cost, and environmentally benign nature. Another advantage is that the polymer can be easily dissolved in aqueous medium, making the polymer to be easily used in the industry. The dispersion polymerization is carried out in a reaction medium that dissolves monomers but does not dis-

solve the polymer. The polymerization proceeds in the reaction medium until a critical molecular weight for the solubility of the polymer chain, and then the precipitated primary particles are stabilized by a polymeric stabilizer to form stable particle nuclei. Once particles have been formed, they absorbed monomer from the continuous phase and the reaction mainly took place within the particles.^{6–9} It has been well reported about dispersion polymerization of cationic PAM with poly(dimethylaminoethyl methacrylate methyl chloride), poly(acryloyl-oxyethyl trimethyl ammonium chloride), poly(2-acrylamido-2-methylpropanesulfonic acid) etc, as the stabilizer.^{10–14}

Presently, we developed a method for preparing cationic PAM dispersion using acrylamide (AM) as the mainly raw material and dimethylaminoethyl methacrylate methyl chloride (DMC) as the cation comonomer in ammonium chloride (AC) medium. 2,2'-Azobis (2-amidino-propane) dihydrochloride (V-50) was used as the initiator and *N*-carboxymethyl-thioureidochitosan (CMTC) as both the steric stabilizer and one of the reactants. CMTC was a composite reacted among chitosan, ammonium thiocyanate, and chloroacetic acid.¹⁵ Chitosan was a partially *N*-deacetylated derivative of Chitin, commonly found

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in shells of insects and crustaceans, as well as cell walls of some fungi,^{16–18} which has been well documented with highly reactive hydroxyl and amino groups on its backbone for various chemical or physical means, enable various properties such as adsorption and grafting-polymerization. It has been reported that chitosan can be grafted onto the PAM chains by solution polymerization^{19,20} by which the product is less soluble and the reaction process is hard to be controlled, whereas dispersion polymerization of PAM in the presence of chitosan is little reported. According to the grafting-polymerization mechanism of stabilizer,²¹ chitosan and its derivative can be expected to act as a better stabilizer in the dispersion polymerization.

The factors such as concentration of monomers, stabilizer, inorganic salt and initiator, the proportion of monomers, temperature, reaction time, and pH can all influence the polymerization process. Stabilizer plays a crucial role. In the absence of a colloidal stabilizer, flocculation occurs, making it difficult to polymerize to high conversion.²² Inorganic salts can help the oligomers to precipitate by salting-out effect, and initiator can decompose into free radicals and react with monomers to form oligomer radicals. The effects of concentration of monomers, the proportion among monomers, and dosage of stabilizer were discussed previously.²³ In this work, effects of the concentration of inorganic salt and initiator, temperature, reaction time, and pH on the molecular weight, apparent viscosity, morphologies of particle, particle size and distribution, and the overall conversion of monomers were researched, and orthogonal tests have been worked out to determine the optimal conditions.

EXPERIMENTAL

Materials

Acrylamide (AM, 99%, Dia-Nitrix., Tokyo, Japan) and dimethylaminoethyl methacrylate methyl chloride (DMC, aqueous solution with concentration of 76%, Befar Group, Binzhou, China) are both industrial grade, used without further purification. Because of the impurity in the raw materials, the aqueous solution of ethylene diamine tetraacetic acid with concentration of 4 g/L is used to eliminate the side-effect of heavy metals from the materials. Ammonium Chloride (AC, NH₄Cl, Sinopharm Chemical Reagent, Shanghai, China), and 2,2'-azobis (2-amidino-propane)- dihydrochloride (V-50, Wako Pure Chemical Industries, Osaka, Japan) are of analytical grade, used as received. Deionized water was ternary distilled by Milli-Q Biocel system. Other reagents used in this work are all chemical grade. CMTC was prepared through the reaction among chitosan (CTS) [DD% (degree of deacetylation) =

90%, purchased from Yuhuan Ocean Biochemical, Zhejiang, China], ammonium thiocyanate, and chloroacetic acid in hydrochloric acid aqueous solution, which has been finished previously.¹⁵

Preparation of the dispersion polymer

About 3.8% of AM, 3.8% of DMC, 0.5% of CMTC were dissolved into 100 mL deionized water in a 250-mL glass reactor equipped with a stirrer, a reflux condenser, a thermometer, and attached a nitrogen (N₂) inlet. After purging with N₂ for half an hour and adjusting temperature at 60°C, added 22% of NH₄Cl into the mixture and then the polymerization reaction was initiated by injecting the V-50 initiator into the system. Maintained the temperature at 60°C ± 1°C with the protection of N₂ atmosphere, the polymerization was allowed to proceed for 5 h. The mixture was then cooled at room temperature to yield a fine, white dispersion system with well liquidity. The product was named P (CMTC-AM-DMC).

Viscosity-average molecular weight of the polymer

The viscosity-average molecular weight (M_V) can be calculated with the Mark-Houwink relationship:^{24–25}

$$M_V = \left\{ 10,000 \times \frac{[\eta]}{3.73} \right\}^{\frac{1}{0.66}} \quad (1)$$

where $[\eta]$ is intrinsic viscosity of the copolymer which can be determined in 1M NaNO₃ aqueous solution with an Ubbelode capillary viscometer at 30°C.

The total monomer conversion

The total monomer conversion could be obtained by determining the residual contents of AM and DMC with bromating method. About 4.0–5.0 g of copolymer dispersion was weighed out in a weighing bottle and resolved in 100 mL of deionized water. Excessive KBrO₃-KBr was added into the sample solution. In the existence of H⁺, KBrO₃ reacted with KBr to produce Br₂, and then Br₂ could react with residual double bonds from AM and DMC in the sample solution. Excessive KI was used to react with the residual Br₂ to produce I₂. By titrating I₂ with the standard solution of Na₂S₂O₃ and calculating the consumption of Na₂S₂O₃, the total residual contents of AM and DMC could be determined by means of the interrelationships of these ingredients.

Micrograph of the dispersion system

Drops of the colloidal polymer dispersion systems were coated on glass slides; the morphologies of the polymer particles could be observed under an optics

TABLE I
Influence of the Salt Concentration on the Reaction

AC (%)	Apparent viscosity (mPa s)	Viscosity-average molecular weight (10^4 g/mol)	Overall conversion (%)	Particle size (nm)
13.0	1523.0	132.6	97.4	57 (26–104)
15.2	1165.9	145.8	98.7	290 (107–370)
17.1	852.9	155.9	98.8	497 (316–566)
18.9	805.9	175.2	98.7	678 (537–715)
20.6	776.0	176.9	98.7	749 (641–646)
22.3	737.0	178.3	96.9	764 (673–845)
23.9	928.0	176.9	98.6	802 (704–836)

microscope by 160 times (XSZ-HS7, Chongqing Optical Instrument, China).

Purification of the samples

The samples were precipitated in ethanol, purified three times by repeated dissolving-precipitating treatment, washed by Soxhlet extraction using ethanol-water (7 : 3 by volume) as solvent further, and finally dried at 50°C in a vacuum oven for 48 h.

The apparent viscosity of samples

The apparent viscosity of the dispersion systems was measured with Programmable LVDV-II+ viscometer (Brookfield Engineering Laboratories) at room temperature in the salt solution ($v : v = 1 : 1$) in which concentration of AC kept equal with that of the original dispersion system.

The particle size and size distribution

The particle size and size distribution were measured using a laser particle size analyzer (LS230; Coulter). The samples were diluted into the same concentration of salt solution with the original dispersions.

Orthogonal tests

Orthogonal tests with four factors and three levels were designed to determine the integrated influences of important factors on the polymerization. These factors included dosage of inorganic salt, dosage of initiator, temperature, and pH value of the system. The factors and levels were listed in the Table V. According to statistics, orthogonal tests with three factors and four levels should include nine items of experiment, which were arranged in the Table VI. The results were evaluated with the M_v .

RESULTS AND DISCUSSION

The effect of concentration of inorganic salt on the dispersion polymerization

The polymerization experiments were carried out with varying AC concentration from 13.0 to 23.9%.

Other condition such as the concentrations of monomers, stabilizer, and initiator as well as the mass ratio of AM:DMC were kept constantly at 7.6%, 0.5%, 0.007%, and 1 : 1, respectively. The effects of AC concentration on M_v , apparent viscosity, particle size of the products, and overall conversion were shown in the Table I.

With an increase in salt concentration, an increase in the M_v , particle size and a decrease in apparent viscosity of the products were observed. The overall conversion was less dependent on the salt concentration, and the value varied from 96.6 to 98.8%. The characteristic of the products was quite different with the salt concentration. When AC concentration was 13.0%, particles coagulated each other and formed some large flocs. The morphology of the dispersion under this condition was shown in the Figure 1(a). The dispersion would become more fluidity with no flocs and fine and narrow distribution particles as the concentration of AC increased up to 22.3% of AC concentration [Fig. 1(b)].

According to the Electrical Double Layer Thesis of Colloids, AC was added into the reaction system as an electrolyte with a lower concentration, and it would reduce the thickness of diffusion electrical double layer of the copolymer molecules and particles. As a result, the ζ -potential of molecules decreased.^{9,24} On the one hand, the electrostatic repulsion between molecules was weakened. On the other hand, the stabilizer CMTC might be more easily adsorbed on particles and could act as a flocculant by adsorption-bridging mechanism, so a few flocs appeared. The system was so unstable that slightly congregated when cooled, and the fluidity decreased greatly, the apparent viscosity was 1523.0 mPa s after diluted by the same volume AC solution.

The particle size and M_v increased with an increase of AC concentration, but when the AC concentration was too high, high yield of the coagulum was obtained in the form of agglomerated lumps possibly due to limited solubility of CMTC. AC would be crystal and separated out from the solution when the AC concentration was over 23.9%. The salt concentration probably had two effects on

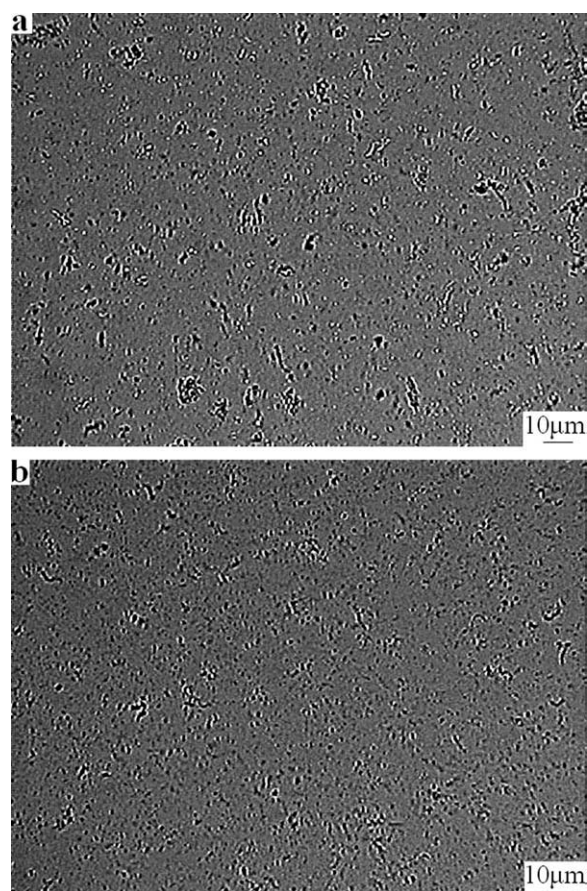


Figure 1 The morphology of the dispersion under (a) 13% of salt concentration and (b) 22.3% of salt concentration.

the dispersion polymerization. First, the salting-out effect, which would promote the oligomers to precipitate from the reaction media, might become stronger,²⁵ as AC concentration increased resulting in the critical molecular chain length of oligomers decreased which promoted the forming of more little particles. Then the particles would adsorb the monomers, and the polymerization would take place on the interphase of the particles. Therefore, the particles size and M_v increased, and at the same time, the apparent viscosity decreased gradually.

However, when AC concentration was much higher, the salting-out effect would be possibly so strong that over many particles appeared and Cl^- might neutralize the surface charge of the particles, resulting in the congregation among particles, and the apparent viscosity was increased to 928.0 mPa s. Second, AC could probably retard the stretch of the stabilizer molecules. The molecular chain of CMTC would be stretch largely under a proper salt concentration and have stronger stabilization, but that would be curled with higher AC concentration, and would be impossible to form a stable dispersion system. The proper interval for AC concentration was 18.9–22.3%.

The effect of concentration of initiator on the dispersion polymerization

The effects of initiator (V-50) concentration on apparent viscosity, particle size, M_v , and overall conversion were studied in the range from 0.003 to 0.020%. The concentrations of monomers, stabilizer, and the mass ratio of AM:DMC were kept constantly at 7.6%, 0.5%, and 1 : 1, respectively, and reacted under 55°C for 5 h in 22.3% salt medium. As seen in Table II, with increasing dosage of V-50 concentration, the M_v decreased from 186.5×10^{-4} to 100.5×10^{-4} g/mol, and the overall conversion changed from 91.0 to 96.9%, which seemed to be less influenced by initiator. The apparent viscosity decreased greatly from 1480.0 to 114.0 mPa s, and the average particle size decreased from 781.3 to 315.6 nm.

A greater initiator concentration might lead to form shorter oligomer chains, which had greater solubility in the reaction medium. The adsorption and polymerization of the monomers on the particles would, therefore, be retarded, leading to lower M_v , and the product took on less viscous and more translucent. The apparent viscosity was only 114 mPa s with 0.020% of initiator concentration. On the other hand, it was reported in the literature²⁶ that the length of radical chains of polymer was

TABLE II
Influence of V-50 Concentration on the Reaction

Initiator (%)	Apparent viscosity (mPa s)	Viscosity-average molecular weight (10^4 g/mol)	Overall conversion (%)	Particle size (nm)
0.003	1480.0	186.5	95.3	781 (675–841)
0.005	1284.0	184.2	94.1	779 (671–840)
0.007	737.0	178.3	96.9	764 (673–846)
0.009	542.9	171.6	93.5	760 (637–816)
0.012	489.9	160.5	91.5	755 (633–817)
0.014	431.9	143.8	96.2	699 (600–790)
0.016	365.9	125.8	95.6	588 (456–672)
0.018	281.9	112.9	91.0	460 (315–526)
0.020	114.0	100.5	92.3	316 (207–402)

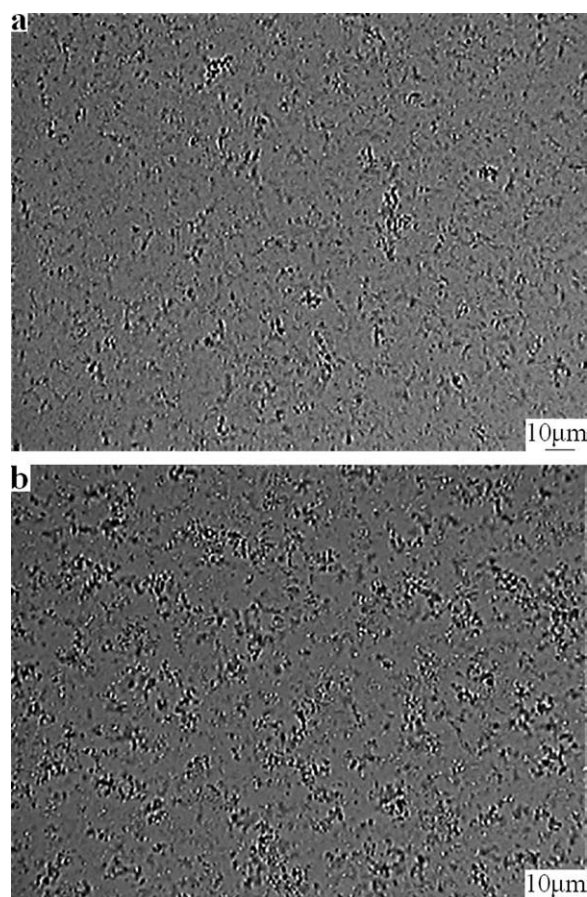


Figure 2 The morphology of the dispersion under (a) 0.005% of initiator concentration and (b) 0.003% of initiator concentration.

determined by the average number of monomers consumed per each radical, which initiated a polymer chain, and was proportional to the radical concentration. Therefore, the increase of V-50 concentration resulted in a lower polymer M_v .

However, when initiator concentration decreased to 0.005%, flocculation occurred and a few flocs appeared in the dispersion system [Fig. 2(a)]. The most probable explanation might be that with poorer initiator concentration, adsorption rate of CMTC stabilizer on oligomer would be much faster than the generation rate of the oligomeric radicals. Under this condition, a few particles would be conglomerated by

CMTC because of electrostatic adsorption, and then flocs formed. The amount of flocs increased as initiator concentration continuously decreased to 0.003% [Fig. 2(b)]. The proper initiator concentration is 0.007–0.012%.

The effect of temperature on the dispersion polymerization

Dispersion polymerization was conducted at 50, 55, 60, 65, and 70°C, respectively. Other conditions were that: 7.6% of monomers, 0.007% of initiator, 0.5% of stabilizer, and 22.3% salt, as well as the mass ratio of AM:DMC were kept at 1 : 1. The results were shown in the Table III. The M_v increased from 175.5×10^4 to 183.2×10^4 g/mol when temperature increased from 50 to 55°C, while it would decrease from 183.2×10^4 to 129.6×10^4 g/mol when temperature increased continuously to 70°C. The overall conversion increased from 85.5 to 98.9% with the increase of temperature. The apparent viscosity decreased greatly with the increase of temperature, while the particle size increased firstly and then decreased.

An increase of temperature in the polymerization system would probably lead to following effects: (1) an increase in the decomposition rate of the initiator and the propagation rate of oligomer radical which would help to form more active reaction areas and would greatly increase the possibility of chain-transfer and chain-terminate, but when it was 50°C, decomposition of the initiator was so tardy that the overall conversion was only 85.5%, and particle size and M_v were both lower than that of other conditions; (2) an increase in the solubility of the stabilizer and monomers adsorbed on the growing particle's surface, which would make it hardly to polymerize further,^{27,28} so particle size and apparent viscosity both decreased. In addition, there were other possible reasons. (1) Increase of temperature might result in an increase of chain-transfer constant, thus M_v decreased. (2) Monomers and stabilizer were both hydrophilic compounds. At lower temperature, it was more easily for water film to adsorb on the surface of active groups, the opportunity of chain-terminate reaction might decrease, accordingly.

TABLE III
Effect of Temperature on the Dispersion Polymerization

Temperature (°C)	Apparent viscosity (mPa s)	Viscosity-average molecular weight (10^4 g/mol)	Overall conversion (%)	Particle size (nm)
50	1593.9	175.5	85.8	700 (549–802)
55	962.9	183.2	92.5	753 (593–895)
60	737.0	178.3	96.9	788 (633–956)
65	514.9	140.5	98.2	626 (506–785)
70	370.9	129.6	98.9	413 (320–566)

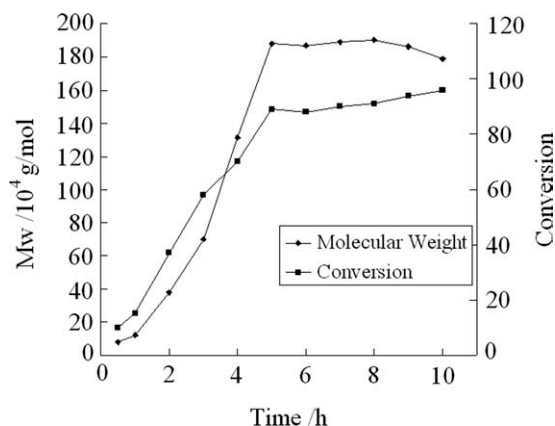


Figure 3 Effects of reaction time on the molecular weight and overall conversion.

(3) Higher temperature led to an increase in the critical phase separation concentration of the oligomers resulting from the increase of the solvency in the continuous phase. However, the dispersion system aggregated when the reaction temperature decreased to 50°C. It was possible because of the crosslink occurred among longer polymer chains under this condition.

The effect of reaction time on the dispersion polymerization

The monomer conversion and M_v as functions of reaction time were conducted with 7.6% of monomers, 0.007% of initiator, 0.5% of stabilizer, and 22.3% of salt, as well as the mass ratio of AM:DMC were kept at 1 : 1, and polymerized at 55°C.

The results were depicted in the Figure 3. The particle size and distribution with the time were shown in the Figure 4(a–i). The curve of conversion versus time was typically S-shaped. After a brief inhibition period, the reaction conversion increased quickly to about 89% within 5 h. The rate of monomers consumption decreased as the reaction progressed to higher conversion, which was readily attributed to growing PAM chains encountering lower monomer concentration at progressively higher conversion. Therefore, there was less probability for monomer radical to adsorb on the molecule chains, and the reaction was near completion on this condition. The M_v slightly decreased after 7 h that might be caused by an increase in the population of lower M_v PAM fractions, which was attributed to the greater probability of chain-transfer events occurring as the monomer supply exhausted at higher conversion.^{28,29} In

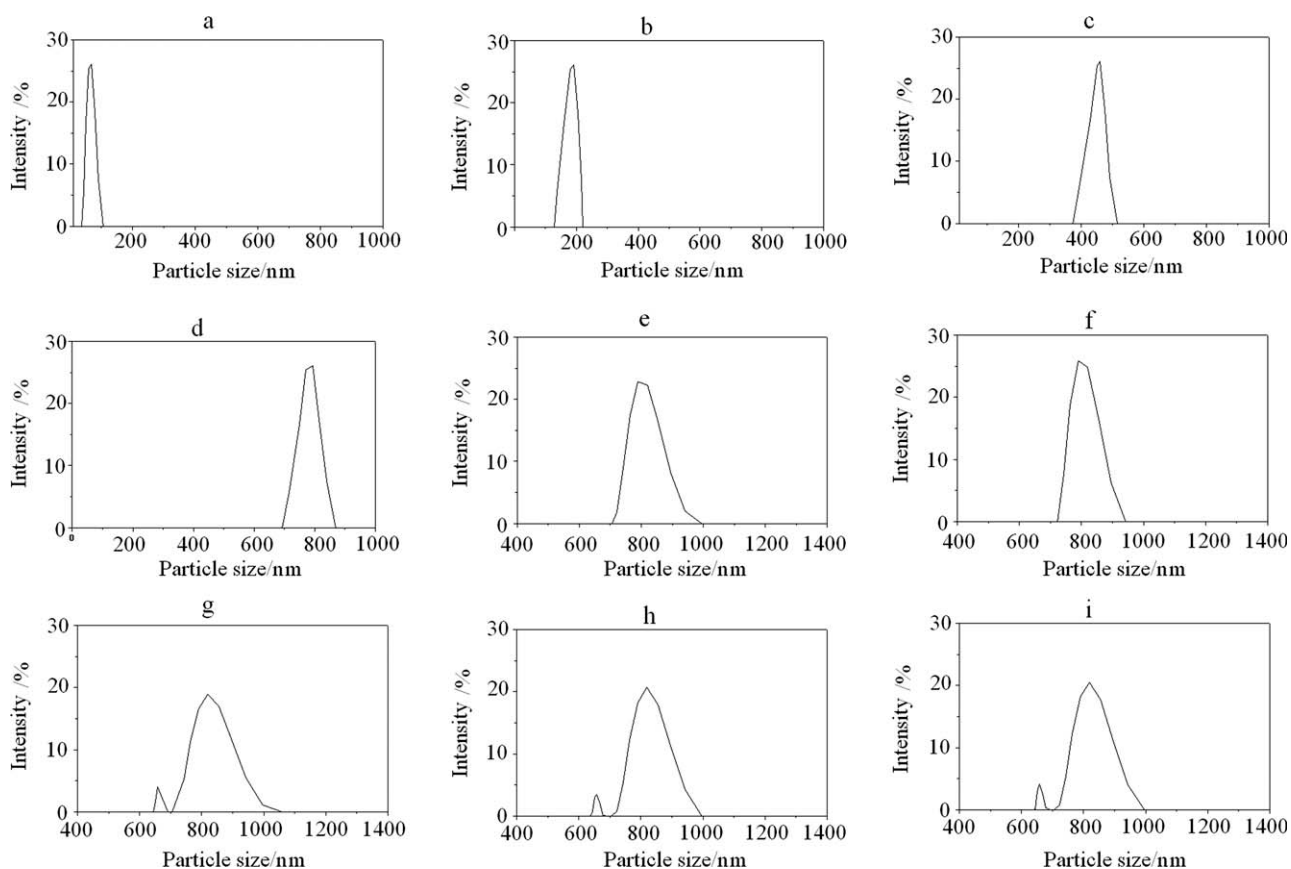


Figure 4 Particle size and distribution of the dispersion with time (a: 2 h after injecting initiator; b: 3 h; c: 4 h; d: 5 h; e: 6 h; f: 7 h; g: 8 h; h: 9 h; and i: 10 h).

TABLE IV
Effect of pH on the dispersion polymerization

pH	Apparent viscosity (mPa s)	Viscosity-average molecular weight (10^4 g/mol)	Overall conversion (%)	Particle size (nm)
2	220.9	118.6	92.0	261 (201–356)
3	437.9	130.4	95.1	316 (227–396)
4	521.0	158.8	93.5	612 (496–705)
5	673.9	170.5	95.1	786 (601–871)
6	737.0	178.3	96.9	796 (656–882)
7	–	–	–	–
8	–	–	–	–

addition, it could also be observed from Figure 4(a–f) that mean particle size increased from 65.22 nm to 806.48 nm with the reaction time was from 2 to 7 h after injecting the initiator. However, after 7 hours' reaction some short PAM fraction appeared [Fig. 4(a–f)], resulted in the mean particle size and M_v decreased slightly. The mean particle size was 761.51 nm and the M_v was 182.8×10^4 g/mol when reacted 8 h. The proper reaction time was 5–7 h.

The effect of pH on the dispersion polymerization

pH-Dependence of the dispersion polymerization was researched with 7.6% of monomers, 0.007% of initiator, and 0.5% of stabilizer in 22.3% of salt medium, as well as the mass ratio of AM:DMC were kept at 1 : 1 and polymerized at 55°C for 5 h, as shown in the Table IV. The apparent viscosity, M_v , and particle size were all increased with the increase of pH, but the product would be nonhomogeneous block-like gel with some flocs when $\text{pH} > 7$. There were greatly probability that (1) CMTC was a kind of pH-sensitive compound, and when $\text{pH} > 7$ it would separate out from the solution and form lots of floc-shape suspending, followed by the weakened adsorption of CMTC on polymer particles and slight aggregation. (2) Hydrolyzation of $-\text{OCNH}_2$ groups in AM occurred at higher pH and negatively charged on the surface of the polymer, resulting in an increase of electrostatic repulsion, and then it was hard for monomer radicals to enter into the active centers. However, when $\text{pH} < 3$, $-\text{NH}_2$ groups in AM and DMC could easily be protonized to be $-\text{NH}_3^+$, besides, quaternary ammonium from DMC was also positively

TABLE V
Factors and Levels of the Orthogonal Test for the Dispersion Polymerization

Levels	Factors			
	A	B	C	D
1	20.6	0.007	55	4
2	22.3	0.009	60	6
3	23.9	0.012	65	8

charged, which greatly enhanced the electrostatic repulsion between the monomers, and directly resulted in lower M_v , apparent viscosity, and particle size. The optimal pH was between 4 and 7.

Orthogonal tests

Orthogonal tests were used to examine the general influences of some important factors on the dispersion polymerization. Table V described the factors and levels in the orthogonal tests, with four factors marked *A*, *B*, *C* and *D*, respectively, and three levels for each factor in which *A* was dosage of inorganic salt, *B* was dosage of initiator, *C* was temperature, and *D* was pH value of the system.

Table VI showed the results of the orthogonal tests, containing nine items of experiment. M_v was used to evaluate the effects of each condition. K_1 , K_2 , and K_3 were the mean values of the products' M_v polymerized with the level 1, 2, 3 of each factor shown in the Table V, respectively. *R* was the extreme difference of each factor which can be calculated by subtraction between the maximum and minimum among K_1 , K_2 , and K_3 . The significance of factors was in proportion to the *R* value of factors.

TABLE VI
Results of the Orthogonal Tests for the Dispersion Polymerization

Run	A (%)	B (%)	C (°C)	D	Molecular weight (10^4 g/mol)
1	20.6	0.007	55	4	150.91
2	20.6	0.009	60	6	122.65
3	20.6	0.012	65	8	79.54
4	22.3	0.007	65	6	102.89
5	22.3	0.009	55	8	138.96
6	22.3	0.012	60	4	160.59
7	23.9	0.007	60	8	146.12
8	23.9	0.009	65	4	105.68
9	23.9	0.012	55	6	143.65
K_1	117.70	133.31	144.51	139.06	Influences:
K_2	134.15	122.43	143.12	123.06	$C > D > A > B$
K_3	131.82	127.93	96.04	121.54	Conclusion:
<i>R</i>	16.45	10.88	48.47	17.52	$A_2B_1C_1D_1$

As shown in the Table VI, the R value of temperature was 47.94, and it was the most important factor in the polymerization process, followed by pH, dosage of inorganic salt, and dosage of initiator, respectively. The optimal preparation conditions were as follows: 22.3% of inorganic salt, 0.007% of initiator, 55°C of temperature, and 4 of pH. This conclusion was further confirmed by the reappearance tests, so the test conditions were feasible.

CONCLUSIONS

P(CMTC-AM-DMC) was synthesized by dispersion polymerization in aqueous AC solution under suitable conditions. The effects of the concentration of inorganic salt and initiator, temperature, react time, and pH on the apparent viscosity, M_v , overall conversion of monomers and particle size and distribution were researched which were in conformity with those previously reported.^{12-14,25,28}

The M_v , particle size would increase and the apparent viscosity would decrease with the increase of salt concentration. An increase in initiator would result in decrease in apparent viscosity, M_v , and particle size. The M_v increased when temperature increased from 50 to 55°C, while it would decrease when temperature increased continuously to 70°C. The apparent viscosity and particle size decreased with the rise of temperature. When pH was regulated from 2 to 6, M_v , apparent viscosity, and particle size increased accordingly, while the product would be coagulated to form a block-like gel with a few flocs when pH > 7. Time effects M_v and overall conversion a lot. The monomers could react completely within 5–7 h. In addition, the results also show that the overall conversion would less dependent on these conditions, which could be higher 95%. However, when temperature was 50°C, the overall conversion was only 85.8%. Flocs would appear under a certain condition, such as lower salt concentration and lower initiator, and when pH > 7 a few flocs also appeared in the system.

The optimal condition is determined by orthogonal tests. Among these factors, temperature is most significant to polymerization process, followed by pH, dosage of inorganic salt, and dosage of initiator, respectively. For obtaining a stable aqueous dispersion of copolymer, the variables are controlled as fol-

lows: 22.3% for AC, 0.007% for initiator, react under 55°C for 5 h at pH = 4.

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