Optimizing of ultraviolet initiated template polymerization of cationic polyacrylamide by response surface methodology

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ABSTRACT

Cationic polyacrylamide (CPAM) is a commonly used flocculant for water treatment. The main factors affecting its flocculation performance are cationic degree and intrinsic viscosity. This study was to improve the intrinsic viscosity and cationic degree of CPAM, sodium polyacrylate was selected as the template (T), and dimethyldiallylammonium chloride (DMD) and acrylamide (AM) were used as monomers to prepare a Novel cationic polyacrylamide (TPDA) with ultraviolet (UV)-initiated template polymerization. First, single-factor tests were conducted to screen the factors that had significant effects on TPDA intrinsic viscosity, and then response surface methodology (RSM) tests were conducted using the selected factors to obtain the optimal polymerization conditions. The results showed that the addition of template increased the cationic degree of TPDA, and decreased its intrinsic viscosity. there were three factors that significantly affected TPDA intrinsic viscosity, and the order of significance was the initiator concentration, monomer mass fraction and pH. A model that could guide the TPDA polymerization was obtained by RSM tests. The results of model optimization showed that the optimal conditions for TPDA polymerization were as follows: the monomer mass fraction, pH value, concentration of photoinitiator (V-50), mass fraction of urea and $n(T):n(DMD):n(AM)$ in the polymerization solution were 27.1%, 7.2, 0.47‰, 0.3%, 3:3:7, respectively, and the ultraviolet irradiation time of 70 min, and the intrinsic viscosity of the obtained TPDA was.10.98 dL/g.

Keywords: Template polymerization; Acrylamide; Allyl trimethyl ammonium chloride; Intrinsic viscosity; Cationic polyacrylamide; Response surface methodology

1. Introduction

Cationic polyacrylamide, synthesized with cationic monomer and acrylamide, is an organic flocculant. It is extensively applied to sewage treatment because most sewage has the property of negatively charged colloid [1].

The common cationic monomers are dimethyldiallylammonium chloride, acryloyloxy ethyl trimethyl ammonium chloride and methacryloyloxyethyl trimethyl ammonium chloride, etc. Among them, dimethyldiallylammonium chloride (DMD) is more widely used because of its low toxicity, especially in the field of drinking water production

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[2]. Cationic polyacrylamide (CPAM) has the long molecular chain and cationic unit, so its main flocculation methods are adsorption bridging and electrical neutralization. In general, when the molecular weight of CPAM is larger, the longer its molecular chain is, the stronger its bridging adsorption is, and the better its flocculation performance is; when the cationic degree of CPAM is higher, the stronger its electrical neutralization [3]. The molecular weight of a polymer is generally proportional to its intrinsic viscosity [4]. Therefore, it is very important to improve the intrinsic viscosity and cationic degree of CPAM.

Up to now, there have been amounts of researches about template or UV-initiated polymerization of organic flocculant. For example, Zhang et al. [5] successfully synthesized anionic polyacrylamide through template polymerization, and studied the reaction kinetics of template polymerization. Sun et al. [6] prepared the terpolymer of AM, DAC, butyl-acrylate by UV-initiated polymerization, and researched its molecular structure and sludge dewatering performance. Zheng et al.'s [7] research proved that CPAM by using UV-initiated template polymerization had a cationic microblock structure in its molecular chain, which contributes to improve the flocculation performance of CPAM. However, the study on how to improve the intrinsic viscosity and cationic degree of CPAM by template polymerization has been rarely reported. To make up for the defect of present researches, this paper tried to synthesize TPDA with UV-initiated template polymerization, sodium polyacrylate (PAAS) was selected as the template because of its good linear structure. First, preliminary studies, namely, single-factor experiments, were conducted to obtain better levels of influence factors, Then, response surface methodology (RSM) experiments were performed to accurately determine the optimal conditions of CPAM polymerization. The goal of overall study was to improve the intrinsic viscosity and cationic degree of CPAM. Meanwhile, the common polymer (CPDA) of DMD and AM was also prepared with UV-initiated polymerization, the necessary controlled trials were also done, and the results were compared with those of TPDA to research the template impact on polymer.

2. Experimental set-up

2.1. Materials

The monomer AM (>99%) was supplied by Chongqing Lanjie Tap Water Company (Chongqing, China). The cationic monomer DMD (60% in water) was obtained from Jinan Yifan Chemical Co., Ltd., (Jinan, China). The template PAAS (30% in water, the molecular weight is approximately 3000) was offered as a gift from Shandong Xintai Water Treatment Co., Ltd., (Zaozhuang, China). The photoinitiator 2,2'-azobis (2-methylpropionamide) dihydrochloride (V-50) was purchased from Ruihong Biological Technology Co., Ltd., (Shanghai, China). Urea [$CO(NH_2)_2$] was obtained from Tianjing Kaitong Chemical Reagent Co., Ltd., (Tianjing, China). DMD, AM and PAAS were of technical grade, and other reagents, including ethanol, V-50, urea, hydrochloric acid (HCl) and sodium hydroxide (NaOH), were of analytical grade. All aqueous and standard solutions were prepared with homemade deionized water. The purity of nitrogen gas was higher than 99.99%.

2.2. Polymers preparation

The preparation process of CPAM is as follows. When the predetermined dosages of monomers (AM, 57.0 mmol; DMD, 24.4 mmol) were put in a glass reaction vessel, the predetermined dosages of distilled water was immediately added into the vessel, the urea (4.0 wt.‰ of total mass) was added to increase solubility, and then the pH was adjusted to the predetermined value by adding HCl or NaOH solution. After that, the solution was purged with nitrogen bubbling for 20 min to remove oxygen. In addition, the prearranged dosage of V-50 initiator was added into the solution. After another 10-min purge with nitrogen, the reaction vessel was sealed, and the solution was irradiated for 80 min with a UV lamp (main wavelength 365 nm, Shanghai Jiguang Special Lighting Electric Factory, China) to ensure that the monomer in the reaction vessel could be polymerized as fully as possible. Then, the reaction bottle was placed at room temperature to cool and develop the polymer for 60 min. Then, the prepared polymer was completely dissolved in deionized water, and the polymer solution was adjusted to pH less than 2 and then purified with ethanol to obtain the CPAM product. During polymerization, the dosage of photoinitiator and the molar ratio of monomer raw materials were changed to obtain a series of CPAM products with different intrinsic viscosities or cationic degrees. The possible synthesis reaction during polymerization is shown in Fig. 1.

2.3. Detection of polymers

The intrinsic viscosities of polymers were measured with an Ubbelohde capillary viscometer (Shanghai Shenyi Glass Instrument Co., Ltd., China) [8]. The cationic degrees of copolymers were determined by colloid titration [9].

3. Single factor tests and its results and discussion

3.1. Single factor tests

To study the influences of the template dosage, monomer mass ratio, total monomer mass fraction, dosage of initiator, polymerization solution pH, ultraviolet illumination time on the intrinsic viscosities and cationic degrees of polymers, the single factor tests were carried out to explore
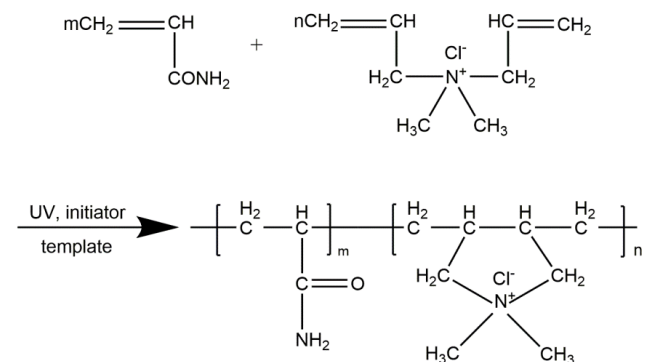

Fig. 1. Possible synthesis reaction of TPDA.

the optimum level of each factor, and provide data for the follow-up design of RSM test.

3.2. Results and discussion

3.2.1. Effect of template dosage on polymer

A set of gradient tests, was conducted to study the effect of template, dosage on the intrinsic viscosities and cationic degrees of polymers. and the conditions of flocculation treatment were as follows: the total monomer mass fraction, $n(DMD):n(AM)$ (the mole ratio of DMD to AM), mass fraction of urea, UV irradiation time, polymerization solution pH, V-50 concentration were 40%, 3: 7, 0.3%, 70 min, 5, and 0.03%, respectively, the corresponding dosage of template was added to the polymerization solution according to the preset of the mole ratio of DMD to AM ($n(T)$: $n(DMD)$). Eight TPDA products were obtained through the above polymerization test. and their intrinsic viscosities and cationic degrees were detected and shown in Fig. 2.

Fig. 2 shows that the intrinsic viscosity of TPDA continued to decrease with the increase of template dosage, which might be due to the inhibition effect of PAAS on the polymerization of AM and DMD [6]. The cationic degree of TPDA first increased and then decreased with the increase of template; when $n(T)/n(DMD)$ was 1, the cationic degree reached the maximum value of 20.6%. This phenomenon proved that the addition of template improved the cationic degree of the polymer, the reason for this was that some DMD monomers were continuously adsorbed on the molecular chain of PAAS under the action of electrostatic attraction, when one DMD monomer was attacked by free radicals and formed the new monomer free radical, it was easier to polymerize with the adjacent DMD monomer, thus, more DMD monomers were encouraged to participate in the polymerization reaction [10]. When $n(T):n(DMD)$ was less than 1, the adsorption and assembly space of template for DMD was insufficient, and only limited cationic monomers could be adsorbed and assembled on the molecular chain of PAAS under the action of electrostatic attraction, therefore the increasing of template dosage in th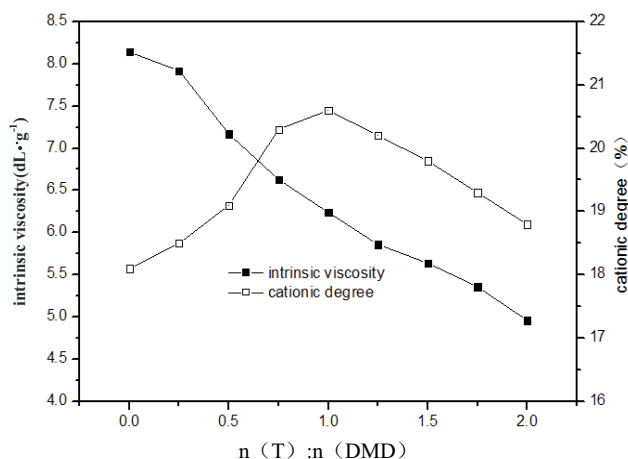is range could enable more DMD to be adsorbed and assembled on the template, which promoted DMD participation in polymerization, and improved the cationic degree of TPDA [11]. However, when $n(T):n(DMD)$ was greater than 1, the adsorption space on the template gradually became loose, and the arrangement of DMD on the template molecular chain became relatively dispersed, so that the probability of DMD monomer participating in the polymerization reaction was reduced, which resulted in the decrease of the cationic degree of TPDA.

3.3.2. Effect of monomer mass fraction on polymer

It follows from the mechanism of free radical polymerization that the mass fraction of monomer in the polymerization largely determines the number of free radicals, which in turn affects the polymerization rate, monomer conversion rate, the intrinsic viscosity and cationic degree of copolymer, etc., so it is necessary to study the influence of the mass fraction of monomer on polymer properties. The polymerization conditions for TPDA were identical to those in 3.2.1 except that $n(T):n(DMD):n(AM)$, was 3:7:7, and PAAS, AM and DMD were added to the polymerization solution according to the predetermined gradient dosages. In addition, the controlled trials of CPDA were also done. The intrinsic viscosities and cationic degrees of the obtained polymers were detected and analyzed, and the results are shown in Fig. 3.

As shown in Fig. 3, the intrinsic viscosities of TPDA products first increased and then decreased with the increase of monomer mass fraction. when the total monomer mass fraction increased to 25%, the TPDA intrinsic viscosity reached a maximum of 6.87 dL/g. According to the kinetic principle of polymerization reaction, the intrinsic viscosity of polymer is generally positively correlated with the concentration of monomer, that is, the higher the monomer mass fraction, the greater the intrinsic viscosity of polymer [12]. However, when the mass fraction of polymerized monomer exceeded 25% and continued to increase in this study, the intrinsic viscosity of the polymer decreased instead. which might be the reason that a large amount of heat released and couldn't be diffused out of the polymerization solution

Fig. 2. Effect of template dosage on the intrinsic viscosity and cationic degree of polymer.
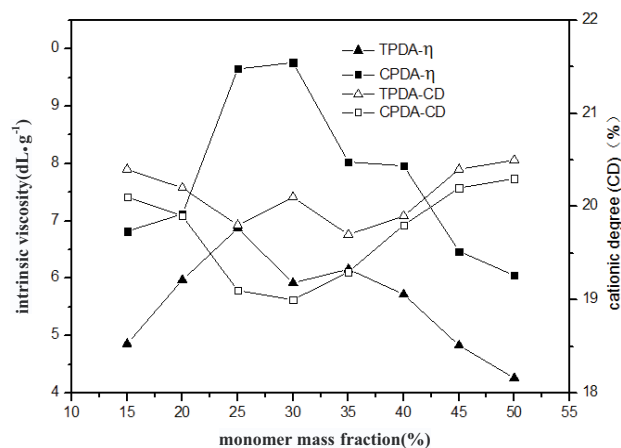

Fig. 3. Effect of monomers fraction on the intrinsic viscosity and cationic degree of polymer.

in time, and accelerated polymerization reaction, which caused that the molecular chain of the polymer broke and its intrinsic viscosity decreased [13]. Under the same test conditions, the change trend of CPDA intrinsic viscosity was similar to that of TPDA, and the difference was that its maximum value reached 9.76 dL/g, and the corresponding monomer mass fraction is 30%. Obviously, the intrinsic viscosity of CPDA was greater than that of TPDA. The reason might still be that the template inhibited the polymerization of monomers and the diffusion of reaction heat

Fig. 3 also shows that the influence of the monomer mass fraction on the cationic degree of the polymer was not obvious, and the cationic degrees of TPDA products were slightly higher than those of CPDA products, the reason for this was still that the addition of template increased the reaction activity of DMD, thus increasing the content of DMD units in the polymer molecule [10]. Further observing the change rules of cationic degree and intrinsic viscosity in the figure, it was found that the cationic degrees of TPDA and CPDA were both negatively correlated with their intrinsic viscosities, which indicated that the intrinsic viscosity of the polymer was positively correlated with the ratio of AM to DMD units, which might be because AM has higher reactivity than that of DMD and is more conducive to the formation of macromolecular polymers.

3.3.3. Effect of polymerization solution pH on polymer

The pH value of polymerization solution has a serious impact on the monomer reaction activity and the dissociation of PAAS in the solution, and then affect the kinetic process of the polymerization reaction [14]. To study the effect of polymerization solution pH on copolymer properties, the following polymerization experiments were performed, and the polymerization conditions were identical to those in 3.2.2 except that the polymerization solution pH was adjusted to the predetermined gradient values by adding NaOH or HCl solution. The intrinsic viscosities and cationic degrees of the obtained polymers were detected and analyzed, and the results are shown in Fig. 4.

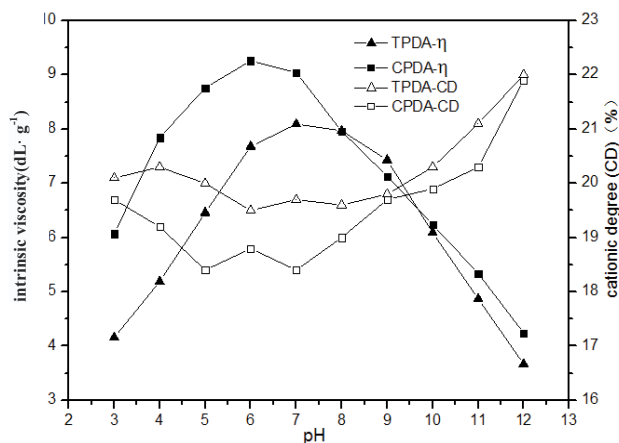As shown in Fig. 4, with the pH increase of the polymerization solution, the intrinsic viscosities of TPDA products increased rapidly at first, reached the maximum of 8.09 dL/g at the pH of 7, and then decreased gradually, which indicated that the too high or low pH of the polymerization solution was not conducive to the formation of TPDA with high intrinsic viscosity. When the pH of the polymerization solution was less than 7, the amide group in the acrylamide occurred amidation reaction, and generated a certain amount of branched or crosslinked polymers, which resulted in the decrease of intrinsic viscosities of TPDA products; When the pH of the polymerization solution exceeded 7, the acrylamide was easy to occur hydrolysis reaction to generate the nitro acrylamide, which has the function of chain transfer agent and can inhibit the generation of polymers with long molecular chains [3]. The change trend of the intrinsic viscosity of CPDA is similar to that of TPDA, except that the maximum intrinsic viscosity of CPDA was 9.26 dL/g, which was significantly higher than that of TPDA.

It can also be seen from Fig. 4 that that the cationic degrees of TPDA and CPDA both decreased first and then increased with the increase of pH, the cationic degree of TPDA was slightly higher than that of CPDA, which proved that the template could improve the reaction activity of cationic monomer DMD again.

3.3.4. Effect of monomer ratio on polymerization

To study the effect of molar ratio of n(DMD):n(AM) on polymers, the following polymerization experiments were performed, and the polymerization conditions were identical to those in 3.2.3 except that the corresponding dosage of monomers were added to the polymerization solution according to the preset of n(DMD):n(AM). The intrinsic viscosities and cationic degrees of the obtained polymers were detected and analyzed, and the results are shown in Fig. 5.

Fig. 5 shows the relationship between the intrinsic viscosity and cationic degree of polymer with molar percentage of DMD. On one hand, the intrinsic viscosities of both TPDA and CPDA continuously decreased with the increase of DMD mole percentage. The reason for this phenomenon was that the reactive activity of AM was greater than that of DMD, and the former was more helpful to generate
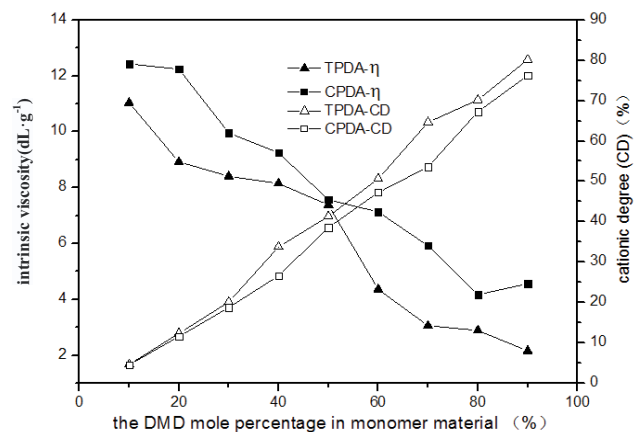

Fig. 4. Effect of pH on the intrinsic viscosity and cationic degree of polymer.

Fig. 5. Effect of dimethyldiallylammonium chloride mole percentage on the intrinsic viscosity and cationic degree of polymer.

polymers with higher molecular weight [4]. With the increase of DMD and the decrease of AM in the polymerization system, the polymerization condition was not conducive to the production of polymers with high intrinsic viscosity. In addition, the cationic degrees of TPDA and TPDA both increased with the increase of the molar percentage of DMD, this was due to that more DMD monomers participated in the polymerization reaction.

3.3.5. Effect of photoinitiator dosage on polymerization

To study the effect of photoinitiator dosage on polymers, the following polymerization experiments were performed, and the polymerization conditions were identical to those in 3.2.4 except that the corresponding dosages of V-50 were added to the polymerization solution according to the predetermined concentration. The intrinsic viscosities and cationic degrees of the obtained polymers were detected and analyzed, and the results are shown in Fig. 6.

As shown in Fig. 6, with the increasing of initiator concentration, the intrinsic viscosities of TPDA products generally showed a trend of increasing first and then decreasing. When the initiator concentration was 0.05%, the intrinsic viscosity reached the maximum value of 9.66 dL/g. According to the principle of free radical polymerization, too many initiators can produce more active centers and accelerate the polymerization reaction rate, but it is not conducive to the formation of polymers with long molecular chains, the reason for this was that the heat released by the polymerization reaction cannot be diffused in time, which leaded to polymer molecular chain fracture [15]. However, if the initiator concentration in the polymerization solution is too low, it is not conducive to the initiation of the polymerization reaction, and the molecular weight of the generated polymer will be small [16]. The influence of initiator concentration on CPDA was similar to that on TPDA, but the initiator concentration corresponding to the maximum intrinsic viscosity of CPDA was 0.03%, which was lower than that of TPDA. The reason might be that PAAS was added to the TPDA polymerization system, which inhibited the polymerization reaction, and more initiators needed to be added to make up for it.
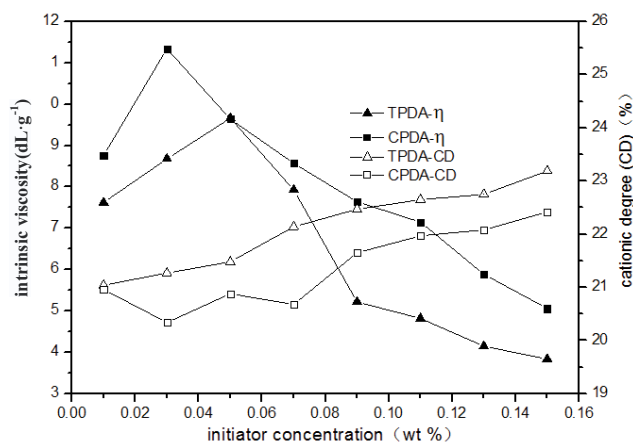
Fig. 6 also shows that with the increase of initiator concentration, the cationic degrees of TPDA and CPDA both presented a continuous increasing trend, this was because the high concentration of initiator produce more free radicals, which improved the probability of DMD and AM reaction. However, if the concentration of initiator was too high, it would lead to too many free radicals colliding with each other, urging the termination of polymerization reaction, and might also lead to the decrease of polymer cationic degree [16].

3.3.6. Effect of illumination time on polymerization

This test is to study the effect of the illumination time on polymers, the following polymerization experiments were performed, and the polymerization conditions were identical to those in 3.2.5 except that the UV irradiation times were set according to the predetermined values. The intrinsic viscosities and cationic degrees of the obtained polymers were detected and analyzed, and the results are shown in Fig. 7.

As shown in Fig. 7, with the extension of UV irradiation time, the intrinsic viscosity of TPDA increased rapidly at first, reached the maximum of 10.65 dL/g when the irradiation time was 80 min, then decreases slowly, and finally tended to be stable. Within the first 80 min, the amount of active free radical increased gradually, and there are many unreacted monomers in the solution, which was conducive to the formation of polymers with high intrinsic viscosity. After the 80th min, the intrinsic viscosity of TPDA decreased, which might be caused by two factors, one reason was that the number of active free radicals and unreacted monomers in the polymerization system gradually decreased, and the other is that the heat released by the polymerization reaction couldn't be diffused in time, which resulted in disproportionation and chain transfer reaction. The effect of UV irradiation time on CPDA was similar to that of TPDA, and the UV irradiation time corresponding to the maximum intrinsic viscosity was 70 min.

Fig. 7 shows that with the increase of illumination time, the cationic degrees of TPDA and CPDA both presented a

Fig. 6. Effect of initiator concentration on the intrinsic viscosity and cationic degree of polymer.
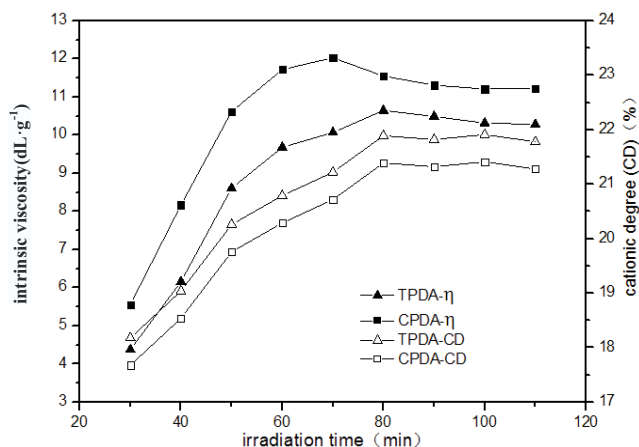

Fig. 7. Effect of irradiation time on the intrinsic viscosity and cationic degree of polymer.

trend of rising first and then maintaining stable. This phenomenon was in accordance with the characteristics of free radical polymerization that the reaction has a slow start, fast rate and timely termination. At the initial stage of the polymerization reaction, because the relative activity of AM is higher than that of DMD, more AM monomers participated in polymerization. As the reaction continued, the number of unreacted AM gradually reduced and was less than that of DMD, the probability of DMD participating in the reaction increased, thus the cationic degree of polymer also gradually increased. However, as the reaction continued for a certain time, the free radicals in the polymerization system were gradually consumed, the polymerization reaction slowed down and finally stopped, and the cationic degree of the polymer gradually tended to be stable.

4. RSM test and its results and discussion

4.1. RSM test

Single factor test generally has the following two shortcomings: one is that the test ignores the influence of the interaction between variable factors on the test results; the other is that the span of the variable value is too large to accurately capture the optimal value of the variable [17]. To obtain the best variable level and test result, further optimization of test design, should be carried out according to the single factor test results. RSM is an excellent method for optimizing and verifying scientific research and industrial studies. It uses the multivariate quadratic regression equation to fit the relationship between the index and influencing factors through regression equation analysis. This method aims to find the best process parameters and has the ability to provide maximum information with minimum experiments [18]. The Box–Behnken design (BBD), a kind of RSM design, is the most frequently used design in pioneering studies because of it is more scientific compared with other designs in RSM [19].

The results of single-factor tests showed that the variables including the monomer mass fraction, photoinitiator concentration and polymerization solution pH all had significant effects on the intrinsic viscosity of TPDA, and the optimums of these variables would be obtained through further RSM test. The influence of all factors on the cationic degree of TPDA was relatively simple, and their optimal values could be obtained only by single factor test, so it was of little significance to conduct RSM tests. Hence, on the basis of the single-factor test results, a BBD test was designed and conducted. The BBD test took improving the intrinsic viscosity of TPDA as the optimization goal,

and the factors including monomer mass fraction, polymerization solution pH and photoinitiator concentration as variables, The BBD test was designed with Design–Expert 8.0.6 software, and each influence factor was set at three experimental levels, namely, high (+1), low (–1), and central point (basic level 0) [20]. The experimental levels and corresponding values of independent variables were determined and are listed in Table 1. The other factor values were kept unchanged, including the mass fraction of urea in the polymerization solution of 0.3%, the molar ratio of monomers of $n(T)$: $n(DMD)$:$n(AM)$ of 3:3:7, and the ultraviolet irradiation time of 70 min.

A total of 17 groups of TPDA polymerization tests were carried out, including 12 factorial tests and 5 central tests for inspection errors. The variable values of each test and the measured values of the intrinsic viscosities of TPDA obtained from the tests are shown in Table 2.

According to the scheme of the BBD test, a total of 17 groups of TPDA polymerization tests were carried out, including 12 factorial tests and 5 central tests for inspection errors. The variable values and the corresponding intrinsic viscosity of each test are listed in Table 2. The results showed that the intrinsic viscosities of the 5 central tests were significantly lower than those of the others, which was consistent with the results of the single factor test and proved that the central point values of the influencing factors of the RSM tests were reasonable but not necessarily the optimal values, which could be obtained through further RSM analysis [21].

In terms of linear, quadratic, and cross terms, the quadratic equation model (Y) was constructed according to Eq. (1) as follows:

$$Y = A_0 + A_1 Z_1 + A_2 Z_2 + A_3 Z_3 + A_{12} Z_{12} + A_{13} Z_{13} + A_{23} Z_{23} + A_{11} Z_1^2 + A_{22} Z_2^2 + A_{33} Z_3^2 \qquad (1)$$

Eq. (1) reflects the relationship between variables and response. In this study, Y referred to the response to be modeled, that is, the intrinsic viscosity of TPDA; Z_1, Z_2 and Z_3 refer to the first-order terms of variables, that is, monomer mass fraction (%), polymerization solution pH value and photoinitiator concentration (%), respectively; Z_1^2, Z_2^2 and Z_3^2 refer to their quadratic terms; and Z_{12}, Z_{13} and Z_{23} refer to the corresponding terms of interaction effects between two variables, respectively. A_0 is a constant term, A_1, A_2 and A_3 refer to the primary linear coefficients of the monomer mass fraction (%), the pH value of the polymerization solution and the photoinitiator concentration (%), respectively; A_{11}, A_{22} and A_{33} represent their secondary term coefficients,

Table 1
Experimental levels of independent variables

Variables code	Variables	Variable levels and corresponding values		
		–1	0	1
Z_1	Total monomer mass fraction (%)	15	25	35
Z_2	Polymerization solution pH	5	7	9
Z_3	Dosage of initiator (%)	0.3	0.5	0.7

Table 2
Actual response values of BBD tests

Run	Monomer mass fraction (%)	Polymerization solution pH	Dosage of initiator (%)	Measured value of TPDA intrinsic viscosity (dL/g)
1	35	7	0.7	6.92
2	15	7	0.3	7.16
3	15	9	0.5	7.55
4	25	9	0.7	6.56
5	25	7	0.5	11.06
6	35	9	0.5	8.77
7	25	5	0.3	7.35
8	15	7	0.7	4.96
9	25	7	0.5	10.96
10	25	5	0.7	6.09
11	25	7	0.5	10.91
12	25	7	0.5	10.93
13	35	7	0.3	8.08
14	25	9	0.3	8.52
15	15	5	0.5	6.58
16	35	5	0.5	8.79
17	25	7	0.5	10.16

respectively; and A_{12}, A_{13} and A_{23} refer to the interaction term coefficients among variables, respectively [22].

According to the response results of the model, analysis of variance (ANOVA) was applied to analyze the feasibility of establishing the quadratic equation model between the variables and the responses [23]. To check the statistical significance of the quadratic equation model and test variables, F-tests and p-values at 95% confidence level were used. The modeling quality of the model was tested based on the coefficient of determination R^2 and adjusted R^2. Additionally, the interaction effect of the factors (Z_1Z_2, Z_1Z_3, Z_2Z_3) on the response value were analyzed using three-dimensional plots and two-dimensional contour [24].

4.2. Results and discussion

4.2.1. Model fitting

Using the data in Table 2, regression simulation was conducted according to Eq. (1), the ternary quadratic polynomial regression model between response and variables was obtained, and the final equation in terms of actual factors is shown in Eq. (2) as follows [25]:

$$Y = -33.020 + 0.953Z_1 + 5.4351Z_2 + 58.156Z_3 - 0.012Z_{12}$$
$$+ 0.13Z_{13} - 0.438Z_{23} - 0.017Z_1^2 - 0.339Z_2^2 - 62.456Z_3^2 \quad (2)$$

4.2.2. Significance analysis of variable influence

The ANOVA for response surface quadratic model, that is, Eq. (2), was conducted, the significance of the influence of each variable was tested, and the results are listed in Table 3. Generally, "p-values Prob. > F" less than 0.0500 indicate that the model terms are significant [26].

In this case, Z_1, Z_2, Z_2, Z_{12}, Z_{13}, Z_{23}, Z_1^2, Z_2^2, and Z_3^2 were all significant model terms and had significant impacts on the intrinsic viscosity. The "p-values Prob. > F" of the model were less than 0.0500, which implied that the model was significant. The "Lack of fit F-value" of 0.0513 implied that the lack of fit was not significant relative to the pure error and indicated that the equation was reliable [8]. The "Pred. R-Squared" of 0.9981 was in reasonable agreement with the "Adj. R-squared" of 0.9957, which indicated that Eq. (2) was well fitted and could be used to predict the intrinsic viscosity of TPDA [27]. the predicted values of all flocculating tests are listed in Table 2.

#### 4.2.3. Response surface analysis

The ANOVA result shows that the interaction between any two factors had an insignificant impact on the intrinsic viscosity of TPDA, Therefore, it is necessary to conduct response surface analysis. The design expert 8.0.6 software was used to draw the response surface diagrams which are shown in Fig. 8a–c. The influence of each factor on TPDA intrinsic viscosity could be judged by the steepness of the three-dimensional response surface. The steeper the slope of the response surface, the more significant the influence of this factor on the test results; On the contrary, the impact is smaller [27]. The influence of the interaction between factors on the TPDA intrinsic viscosity could be judged by the shape of the two-dimensional contour graph. If the contour graph was oval, it indicated that the interaction effect of the corresponding factors had a significant influence on the TPDA intrinsic viscosity, while when the contour tended to be circular, it indicated that the influence is small [28]. One of the factors was fixed, and the influences of the other two factors on the response value were investigated. Fig. 8a shows

Table 3
Variance analysis of regression equation

| Source	Sum of squares	df	Mean squares	F-value	p-value Prob. > F	Remark
Model	63.09	9	7.01	407.94	<0.0001	Significant
Z_1-monomer mass fraction (%)	4.98	1	4.98	289.61	<0.0001	–
Z_2-pH value of polymerization solution	0.84	1	0.84	48.79	0.0002	–
Z_3-photoinitiator concentration (%)	5.41	1	5.41	314.93	<0.0001	–
Z_1Z_2	0.25	1	0.25	14.26	0.0069	–
Z_1Z_3	0.27	1	0.27	15.73	0.0054	–
Z_2Z_3	0.12	1	0.12	7.13	0.0320	–
Z_1^2	12.25	1	12.25	712.88	<0.0001	–
Z_2^2	7.74	1	7.74	450.35	<0.0001	–
Z_3^2	26.28	1	26.28	1,529.18	<0.0001	–
Residual	0.12	7	0.017	–	–	–
Lack of fit	0.100	3	0.033	6.48	0.0513	Not significant
Pure error	0.021	4	0.13	–	–	–
Cor. total	63.21	16	–	–	–	–
R^2	0.9981	–	–	–	–	–
R^2_{adj}	0.9957	–	–	–	–	–
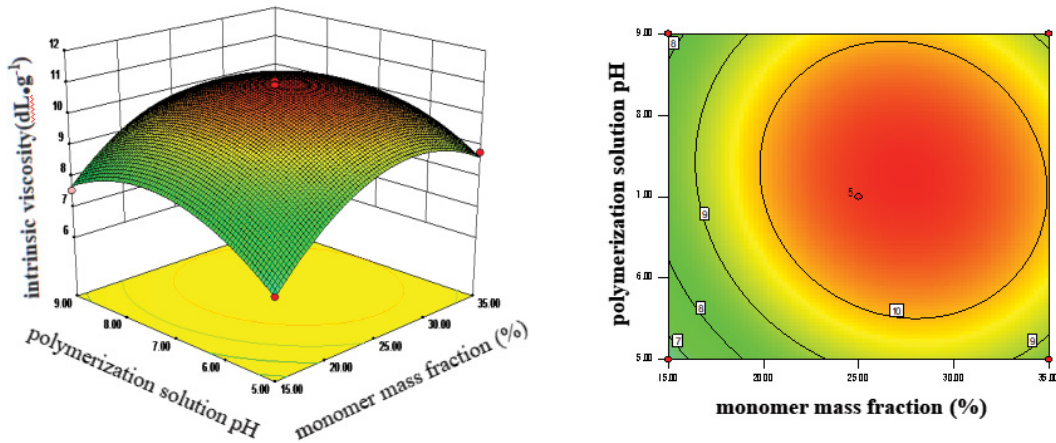
(a) the interaction between monomer mass fraction and polymerization solution pH
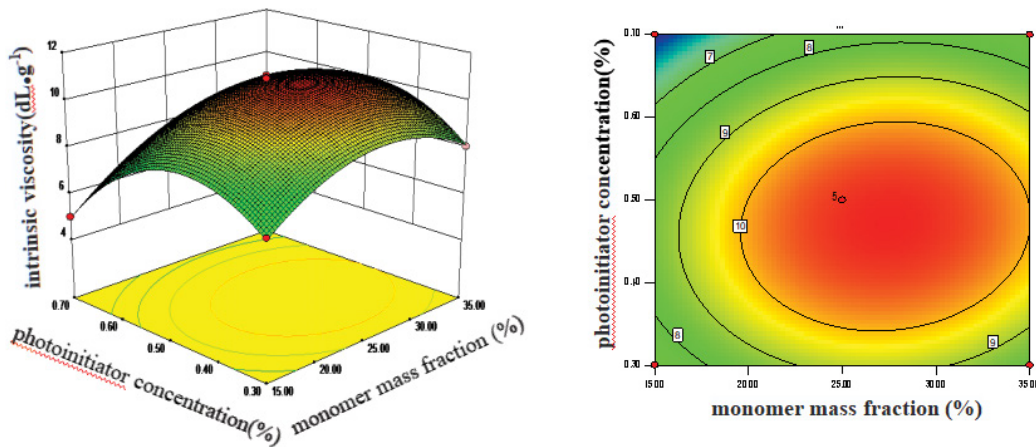
(b) the interaction between monomer mass fraction and photoinitiator concentration

Fig. 8. (Continued)
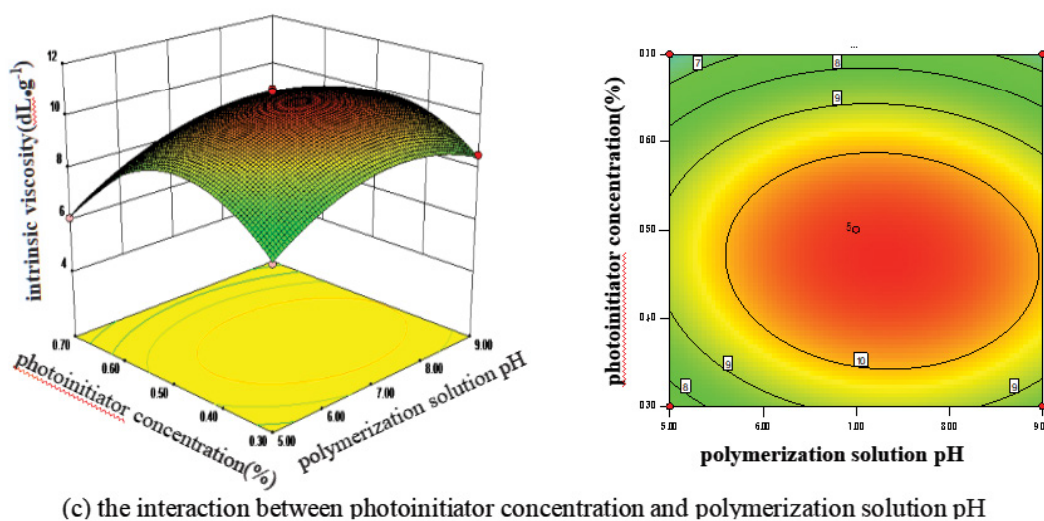
(c) the interaction between photoinitiator concentration and polymerization solution pH

Fig. 8. Response surface diagrams and contour chart of plot of interaction of various factors on TPDA intrinsic viscosity.

Table 4
Measured and predicted values of intrinsic viscosity

Polymerization conditions					Intrinsic viscosity (dL/g)	
Monomer mass fraction (%)	pH value of polymerization solution	Photoinitiator concentration	$n(T){:}n(DMD){:}n(AM)$	Ultraviolet irradiation time (min)	Average of measured value	Predicted value
27.1%	7.2	0.47‰	3:3:7	70	10.98	11.15

that with increasing of monomer mass fraction and pH, the TPDA intrinsic viscosity first increased and then decreased under the condition of fixed photoinitiator concentration. and the monomer mass fraction and pH value were in the range of 25 to 30% and 7 to 8, respectively, the TPDA intrinsic viscosity was at the maximum value. Similarly, as shown in Fig. 8b, when the polymerization solution pH was fixed, with increasing of photoinitiator concentration and the monomer mass fraction, the TPDA intrinsic viscosity showed a trend of first increasing and then decreasing. when photoinitiator concentration and the monomer mass fraction were in the range of 25% to 30% and 0.4% to 0.5%, respectively, the intrinsic viscosity of TPDA had a maximum value; as shown in Fig. 8c, when the monomer mass fraction was fixed, with increasing of photoinitiator concentration and polymerization solution pH, the TPDA intrinsic viscosity increased first and then decreased. When photoinitiator concentration and polymerization solution pH were in the range of 0.4% to 0.5% and 7 to 8, respectively, the TPDA intrinsic viscosity had a maximum value.

4.2.4. Model validation

In Eq. (2), the first-order partial derivative was obtained and solved by being set to zero, and the optimal conditions for the synthesis of TPDA with high intrinsic viscosity were obtained as follows: the monomer mass fraction, pH and concentration of photoinitiator (V-50) were 27.11%, 7.22 and 0.47‰, respectively, the predicted intrinsic viscosity of

TPDA was 11.15 dL/g [21]. To confirm the reliability of the prediction model, two runs of additional experiments were conducted under the polymerization conditions obtained from the model optimization, and the settings of other factors were that $n(T){:}n(DMD){:}n(AM)$ and the ultraviolet irradiation time were 3:3:7, and 70 min, respectively. The experimental results are listed in Table 4 and show that the average of the measured intrinsic viscosity was 10.98 dL/g, and the relative error with the predicted value was only 1.52%. which indicated that the prediction model could be used to guide the polymerization of TPDA [29].

5. Conclusions

To improve the intrinsic viscosity and cationic degree of CPAM. PAAS was selected as the template, DMD and AM were used as monomers to prepare TPDA with ultraviolet-initiated template polymerization. First, single-factor tests were conducted to preliminarily explore the optimal range of influencing factors of polymerization, and then RSM tests were performed to accurately determine the optimums of influencing factors. The single-factor test results showed that the addition of templates increased the cationic degree of CPAM, but decreased its intrinsic viscosity. The monomer mass fraction, polymerization solution pH and photoinitiator concentration all had significant impacts on the intrinsic viscosity of TPDA, and were screened to conduct RSM experiment. A model that could guide CPAM flocculation was obtained by RSM tests. The results of model

optimization showed that the optimal conditions for TPDA polymerization were as follows: the monomer mass fraction, pH value, concentration of photoinitiator (V-50), mass fraction of urea and $n(T):n(DMD):n(AM)$ in the polymerization solution were 27.1%, 7.2, 0.47‰,0.3%, 3:3:7, respectively, and the ultraviolet irradiation time of 70 min, and the intrinsic viscosity of the obtained TPDA was 10.98 dL/g.

Conflict of interest

The authors confirm that this article content has no conflict of interest.

Acknowledgements

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