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A cleaner two-step synthesis of high purity diallyldimethylammonium chloride monomers for flocculant preparation

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Abstract: In order to improve the flocculation efficiency of polydiallyldimethylammonium chloride (PDADMAC), high molecular weight PDADMAC should be prepared from high purity diallyldimethylammonium chloride (DADMAC) monomers. In this paper, a cleaner method with microwave irradiation and alkali solidification was proposed for preparing high pure DADMAC by selective heating under low temperature, and the prepared high purity DADMAC is characterized using FTIR and atomic absorption spectrometry. The new method provides a solution to the key technical problem of PDADMAC synthesis. Comparing with the conventional methods, the results showed that the advantages of the novel synthesis include: (a) high purity DADMAC is improved from 57% to 71%; (b) reaction time of tertiary amine preparation is shortened from 6 h to 7 min; (c) water instead of acetone was used as reaction medium; (d) toxic by-products, wastewater and waste gas are eliminated. Flocculant made from the synthesized high purity DADMAC monomers was proved more efficient in flocculation tests.

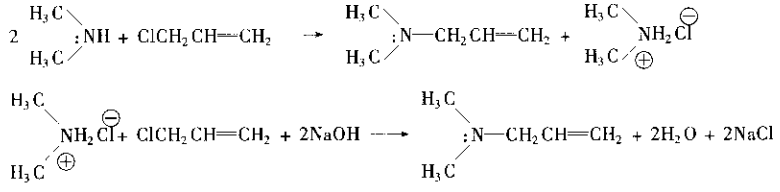
Keywords: diallyldimethylammonium chloride; microwave irradiation; flocculant; cleaner process

Introduction

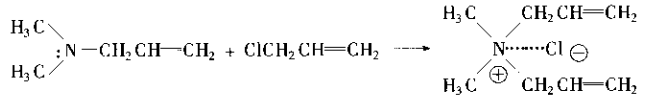
Flocculation is one of the most important decontamination processes in drinking and wastewater treatment. Flocculant is undoubtedly the most important factor in this process. Cationic, quaternary ammonium polyelectrolytes have the subject of increased research efforts in recent years because of their diverse commercial applications. Polymers of diallyldimethyl ammonium chloride (PDADMAC) are the most prominent water-soluble cationic ammonium polymers (Chang, 2000; Ren, 2001). They have been widely used as primary flocculants or flocculant aids in destabilization of colloidal suspensions, clarification of industrial wastewaters, separation of solid-liquid systems, treatment of sewages (Zhao, 2002; Wandrey, 1999). However, comparing with other polymer flocculants, PDADMAC is difficult to have high molecular weight because of the allyl monomers chain transfer reaction and low purity of the DADMAC monomer prepared using the conventional processes. This will make against adsorption bridging performance of PDADMAC when it is used as a flocculant in water treatment. Many studies have been carried out on the synthesis of high purity monomer (diallyldimethylammonium chloride, DADMAC), which is a key step for producing higher molecular weight or higher intrinsic viscosity PDADMAC flocculants (Wandrey, 1999; Brain, 1995; Matsumoto, 2001).

By far, DADMAC is mostly synthesized in one-pot processes (Butler, 1949; 1958; Hunter, 1979; Boothe, 1969). Such one-pot processes suffer from several drawbacks: lots of toxic byproducts, long reaction time, high energy consummation, as well as too many undesirable impurities in the produced DADMAC to prepare high molecule weight PDADMAC. In order to gain high purity DADMAC, the two-step synthesis (Scheme 1) was developed (Chang, 2000; Negi, 1967). The reported two-step synthesis process also has some limitations such as low product yields, long reaction time, using acetone as reaction medium, and lots of wastewater and waster gas.

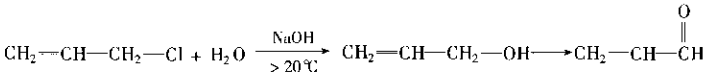
The first step (preparation of allyl dimethylamine)



The second step (preparation of DADMAC)



Side reaction



Scheme 1 Synthesis of diallyldimethylammonium chloride

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In recent years, microwave assisted organic synthesis has been reported as one of the promising approaches that is in the development of environmentally benign processes based on enhanced reaction rates, higher yields and the associated ease of manipulation, because of selective absorption of microwave irradiation (MI) energy by polar molecules, nonpolar molecules being inert to the MI dielectric loss (Caddick, 1994; Huang, 1996; Varma, 2001; Cherng, 2002).

In this paper, a novel two-step synthesis using MI was developed to prepare high purity DADMAC monomers. The obtained high purity DADMAC was characterized using FTIR and atomic absorption spectrometry, and performance of the flocculant made from the high purity DADMAC monomers was proved in flocculation test. The effect of MI on the cleaner synthesis process was discussed.

1 Materials and methods

1.1 Apparatus

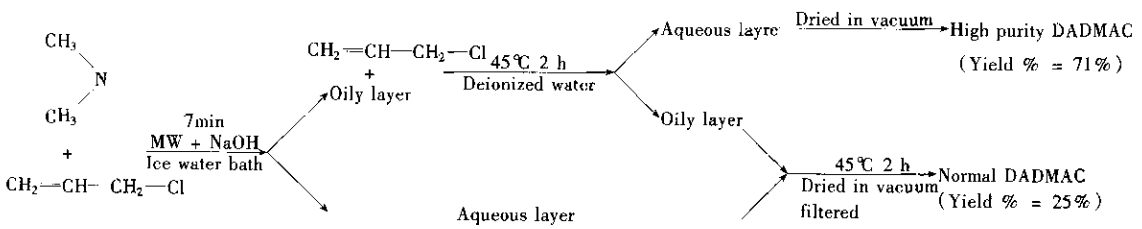
The self-improved domestic microwave oven (LG Korea), was used. Its irradiation power is 75—750 W. Inside the modified microwave oven, a 50 ml flask was placed into a beaker containing 500 ml ice-water (8 : 2) mixture. The flask was used as reactor and attached to a four-way tube connected with a reflux condenser, stirring apparatus and a feeding tube. This system allowed for different adding methods of NaOH (solution or solid) under microwave irradiation at low temperature.

1.2 Materials

Allyl chloride, dimethylamine and sodium hydroxide (Beijing Chemical Reagent Agent, China) were of chemical purity and were used without further purification. Distilled water was used for preparing all solutions.

1.3 DADMAC synthesis steps

Routes of DADMAC synthesis were shown in Scheme 2. In the first step: (1) 14.5 ml, 0.1 mol dimethyl amine of 33% aqueous solution, and 8 ml, 0.1 mol allyl chloride, was fed into the flask, stirred, and cooled to 5℃; (2) 4.1 g, 0.1 mol solid sodium hydroxide was added into the flask; (3) the microwave(MW) oven was started and lasted for 7—15 min at power of 75—450 W, with the mixtures being stirred; (4) after the reaction, the oily layer was repeatedly separated and washed using 3.6 ml, 0.2 mol deionized water; the obtained oily matter was added into a flask (Flask Ⅰ), while the obtained aqueous solutions were added into another flask (Flask Ⅱ). In the second step: (1) another 8 ml, 0.1 mol allyl chloride and 3.6 ml, 0.2 mol deionized water were added into Flask Ⅰ; (2) pH value of the mixture was adjusted to 6.0 with 0.1 mol/L HCl; (3) the mixtures were heated and refluxed for 3 h at 45℃; (4) after being cooled, the aqueous solution was separated from the oily phase, then it was dried in vacuum for getting the target high purity DADMAC; (5) the obtained oily matter was fed into Flask Ⅱ, heated and refluxed for 3 h at 45℃; (6) after being cooled and dried in vacuum, the mixture was filtrated and removed sodium chloride, and the obtained filtrate was the normal purity DADMAC. NaCl contents of the both kind of the obtained DADMAC monomers were determined by atomic absorption spectrometry (Hitachi model Z-6100), and their IR spectrums were obtained using a Nicolet model FTIR 170SX. All spectra were measured with a resolution of 4 cm^{-1} and accumulating 100 scans. The solid samples were prepared in the form of pressed wafers (ca. 2 wt.% sample in KBr).



Scheme 2 The novel two-step the synthesis of high purity DADMAC under MI

DADMAC monomers were also synthesized for comparing with conventional routes as depicted in the literature (Chang, 2000; Hunter, 1979). The traditional synthesis was carried out in magnetic mixer (YY 90-3, China) under ice water bath. The other conditions and processes were similar to those of the synthesis under MI.

Conversion of dimethyl amine and yield of tertiary were determined by the following methods as described in the previous studies (Chang, 2000; Butler, 1949; 1950; Hunter, 1979). Concentration of produced DADMAC aqueous solution was measured by the precipitation titration using sodium tetrephenylboron, while the yield of tertiary amine was calculated according to high purity DADMAC yield.

Homopolymer of DADMAC was prepared through radical polymerization under the same conditions in aqueous solution (Chang, 2000; Butler, 1949; 1950; Hunter, 1979; Boothe, 1969). Intrinsic viscosity of PDADMAC was determined in aqueous 1 mol/L NaCl solution at 30 ℃ using an Ubbelohde type viscometer.

1.4 Flocculation test

A total of 1 L water was transferred to a beaker. Under rapid stirring conditions, 1.5 ml of the stock kaolin suspension (100 g/L) was added, giving a clay concentration of 150 mg/L. The flocculation experiments were conducted at room temperature (20—23℃). Prior to the addition of flocculants, the target pH was adjusted by adding a predetermined amount of NaOH or HCl into the kaolin suspension. After being dosed, 1 min of rapid mixing at 300 r/min was applied, followed by 10 min of slow stirring at 40 r/min. The flocs were allowed to settle for 30 min, and the residual turbidity (RT) was measured using a HACH 2100N Tubidimeter (Hach, Loveland, Co).

2 Results and discussion

2.1 Cleaner two-step the synthesis of high purity DADMAC under MI

A cleaner two-step synthesis of high purity DADMAC under MI was developed, as schematically shown in Scheme 2. It is different from the conventional two-step methods and one-pot methods reported in the previous literature. Details were depicted in the experiment part. In the novel process, the reaction of tertiary amine formation was carried out under MI, and further, it was in water instead of acetone medium that the reaction of DADMAC synthesis was carried out.

As shown in Table 1, comparing with those of the conventional processes, yield of high purity DADMAC was increased to 71%, and reaction times were markedly shortened.

Table 1 Experimental data of the cleaner process

Methods	Yields of high purity DADMAC, %	Yields of normal DADMAC, %	Total yields of DADMAC, %	Reaction time of the first step, min	Reaction time of the second step, h	Waste water and waste gas	The toxic solvents
One-pot method[a]	-	96	96	> 360	6	much	-
Two-step method[b]	57	-	57	> 360	48	more	Acetone
A cleaner process	71	25	96	7	2	less	-

Notes: [a] The data of one-pot method cited from the literature(Butler, 1949; 1958; Hunter, 1979; Boothe, 1969); [b] the data of two-step method cited from the literature (Chang, 2000; Negi, 1967)

The products prepared in the cleaner two-step process were characterized, and the results were shown in Table 2. Comparing with the color of normal DADMAC(light yellow), high purity DADMAC is water-white aqueous solution. The content of NaCl in the prepared products was determined by atomic absorption spectrometry. The content of NaCl in high purity DADMAC was 43 mg/L and was lower than the value of 1000 mg/L in normal DADMAC. Moreover, the products prepared by the cleaner process were characterized using FTIR and the results were shown in Fig.1. Fig.1a shows that the absorptions at 3087 cm^{-1} and 1680 cm^{-1} come from stretching vibrations for bond C—H and C=C, respectively. The absorption at 1400 cm^{-1} and, 1015 cm^{-1} is for N—H and C—N stretching, respectively. C—H absorption occurs at 990 cm^{-1} and 877 cm^{-1}. Fig.1b shows that the IR spectra of normal DADNAC seem to be slightly different in that of high purity DADMAC: more small peeks of impurities such as O—H, C—OH and C=O being shown in Fig.1b. The reason is that most byproducts such as sodium chloride, allyl alcohol and allyl aldehyde are water soluble and they can be removed through the oil-water separation during the novel synthesis process.

Table 2 Characteristics of high purity DADMAC and normal DADMAC

Products	Color	Contents of NaCl, mg/L	Intrinsic viscosity(η) of homopolymers, g/dl	FTIR	The effects of flocculation
High purity DADMAC	Water-white	43	2.7	See Fig.1	See Fig.2
Normal DADMAC	Light yellow	> 1000	1.1		

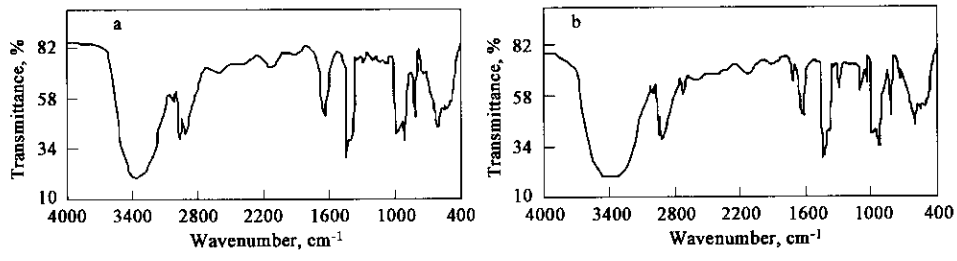


Fig.1 Infrared spectra of (a) high purity DADMAC and (b) normal DADMAC

Intrinsic viscosity of the homopolymer prepared from high purity DADMAC obtained in the cleaner two-step synthesis was 2.7. This value is far higher than that of homopolymer (Florage, SNF, France) prepared by conventional method, whose intrinsic viscosity is about 0.7. Both kinds of the homopolymers were tested as flocculants, and the flocculation experiments were carried out by the jar test. The results are shown in Fig.2. It can be seen that either the optimum dose or the optimum residual turbidity of PDADMAC prepared with the cleaner two-step synthesis is smaller than those with the conventional process. This indicates that the high intrinsic viscosity PDADMAC prepared from high purity DADMAC is more efficient in flocculation. It can be suggested by the "bridging action" of flocculants: higher the molecule weight is, stronger the "bridging action" is.

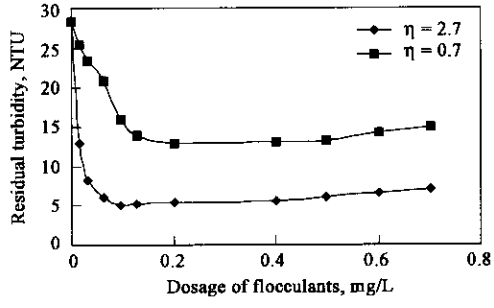


Fig.2 Effect of different molecular weight PDADMAC on the flocculation of kaolin suspensions

2.2 Effect of MI on the first step of synthesis of DADMAC

When the reaction of the first step of synthesis of DADMAC was carried out in the presence of MI, allyl

dimethylamine was produced as a main product. Most byproducts such as quaternary ammonium salt, sodium chloride, water soluble allyl alcohol and allyl aldehyde can be removed through oil-water separation. Table 3 illustrates the effect of MI on yields of tertiary amine in the first step.

It can be seen in Table 3 that MI has a significant effect upon yields of tertiary amine. The optimum yield and reaction time appeared at the power of 150 W, and respectively as 71.0% and 7 min. Too high power or too much reacting time was found unbeneficial as shown in Table 3.

Table 3 Yields of tertiary amine in Step 1 of the novel process

Powers of microwave irradiation, W	Yields of tertiary amine, %			
	3 min	7 min	11 min	15 min
0	16.3	28.2	41.5	46.5
75	34.6	65.1	67.0	67.1
150	37.0	71.0	70.2	70.5
300[a]	42.4	66.1	63.6	64.3
450[a]	47.3	65.8	65.1	63.8

Notes: [a] When the power of MI was higher than 300 W, it was necessary to continuously add the ice-water into ice water bath to maintain low temperature

In order to better understand the reaction mechanism of forming tertiary amine under MI, kinetic experiments were carried out in the presence and absence of MI. The results are shown in Fig. 3. MI has significant effect upon the conversion of dimethyl amine, especially in the region where conversion of dimethyl amine is higher than 40%. It is inferred that synthesis of tertiary amine occurs at the oily-aqueous interface in the heterogeneous reaction. At low temperature, quaterisation carried out in the oil phase and hydrolyzing side reaction of allyl chloride may be inhibited. By using microwave irradiation, the aqueous phase with high dielectric constant may be rapidly heated; whereas the oily phase with low dielectric constant does not couple and therefore can hardly be heated by microwave irradiation. Thus by selectively heating, microwave irradiation can accelerate reaction rates of allyl tertiary amine formation at the oily-aqueous interface and quickening the diffusion rate of dimethyl amine in the aqueous phase.

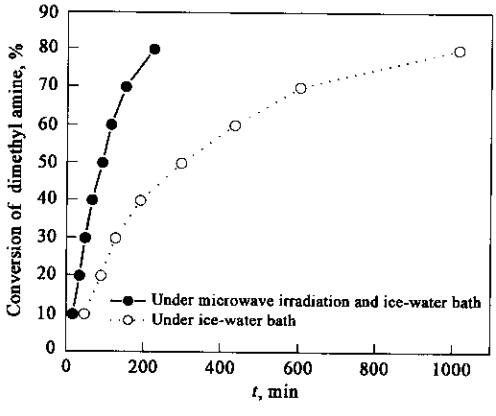


Fig.3 Variations of dimethyl amine conversion with reaction time in the presence and absence of MI(MI power is of 150 W)

3 Conclusions

A cleaner two-step synthesis of high purity DADMAC monomers for flocculant preparation is developed. Comparing with the conventional methods, the novel synthesis method is cleaner: (1) yield of high purity DADMAC was increased from 57% to 71%; (2) reaction time of tertiary amine formation was shortened from 6 h to 7 min; (3) the preparation of high purity DADMAC was carried out in water instead of acetone; (4) toxic by-products, wastewater and waste gas were eliminated. Flocculation efficiency of PDADMAC prepared from high purity DADMAC was obviously enhanced.

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