

Preparation and Characterization of Poly(dimethyldiallylammonium chloride) with High Molar Mass Using High Purity Industrial Monomer

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ABSTRACT: A preparation method for high molar mass poly(dimethyldiallylammonium chloride) (PDMDAAC) is reported in this article. PDMDAAC was prepared by using the high purity industrial grade dimethyldiallylammonium chloride (DMDAAC) monomer from one-step method and ammonium persulphate (APS) as the initiator. The initiator was added all at once and the reaction temperature was increased stepwise to complete the polymerization gradually. The effects of several polymerization condition variables on the intrinsic viscosity value ($[\eta]$) and monomer conversion rate (Conv.) of product PDMDAAC were investigated, respectively. The variables included: T_1 (42.0 to 52.0°C), T_2 (47.5 to 57.5°C), T_3 (55.0 to 75.0°C), $m(\text{DMDAAC})$ (60.0 to 70.0%), $m(\text{APS}) : m(\text{DMDAAC})$ (0.25 to 0.45%), $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC})$ (0 to 0.0071%).

Under an optimum condition of $T_1 = 46.0^\circ\text{C}$, $T_2 = 52.5^\circ\text{C}$, $T_3 = 65.0^\circ\text{C}$, $m(\text{DMDAAC}) = 65.0\%$, $m(\text{APS}) : m(\text{DMDAAC}) = 0.35\%$, $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC}) = 0.0035\%$, the maximum $[\eta]$ of obtained product PDMDAAC reached 3.43 dL/g, at a Conv. of 100.00%. The M_w of the product measured with GPC-MALLS was 1.034×10^6 , polydispersity M_w/M_n was 2.421, and the R_g was 60.3 nm. The structure and properties of products were characterized by FTIR and NMR. Thermal decomposition was determined by TGA-DSC. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1152–1159, 2010

Key words: poly(dimethyldiallylammonium chloride); dimethyldiallylammonium chloride; polyelectrolytes; water-soluble polymers; radical polymerization

INTRODUCTION

Poly(dimethyldiallylammonium chloride) (PDMDAAC) was successfully synthesized by George Butler, after its homologues Poly(dimethyldiallylammonium bromide) was made in 1957.¹ Thereafter, the interests in research on this polymer have never diminished because of its important applications in the fields of paper making, coal mineral beneficiation, dyeing, petroleum, domestic chemicals, pharmaceuticals, water treatment, and so on.^{2,3} It is especially useful in municipal engineering where it is used as a coagulant and flocculant in raw and waste water treatment.^{4,5}

Therefore, new developments on its preparation,^{6,7} application,^{8,9} reaction mechanism,^{10–12} and the relationships between structure and properties^{13–16} have being hot topics all the time.

Figure 1(a,b) shows the main structural units of the linear polymer PDMDAAC reported in the literature; Figure 1(c) shows a segment of a pendant double bond that occurs in a low percentage (<3%).^{1,2}

Concerning the preparation processes, the most interesting thing for the researchers is how to obtain product PDMDAAC with high molar mass (measured as intrinsic viscosity $[\eta]$) through a simple, economic, and effective method, as higher molar mass of the product means an extended range of application is possible.^{2,3} Generally, the monomer dimethyldiallylammonium chloride (DMDAAC) prepared in laboratory or purchased commercially is used as the raw material for synthesizing PDMDAAC.² Therefore, the commercial preparation processes for high-molecular-weight PDMDAAC are happened by the difficulty supplying adequate amounts of high purity monomer, as there are a lot of impurities in commercially available monomer. As a result, the production of high molar mass PDMDAAC on a

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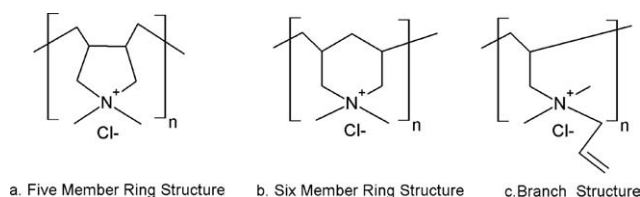


Figure 1 The structure units of PDMDAAC.^{1,2}

large scale is not achievable, and its application are limited in practical.²

Until now, the highest reported intrinsic viscosity values of PDMDAAC were 3.28 dL/g (measurement method was not indicated) prepared with laboratory-made monomer and ammonium persulphate (APS),¹⁷ 1.71 dL/g prepared with industrial grade monomer (1.0 mol/L NaCl as solvent, measured by using Ubbelohde Viscometer in 30.0°C ± 0.1°C water bath, with conditions the same as below),¹⁸ and 3.17 dL/g prepared with the purified industrial monomer before polymerization.¹⁹ Obviously, it is difficult to prepare PDMDAAC with high molar mass using industrial grade monomer because of its higher content of impurities. It is also well known from literatures cited above that high molar mass PDMDAAC could be realized in industry not only needs high purity industrial monomer but also should be based on a proper polymerization method.

In this article, a polymerization method of using APS as an initiator, adding the initiator all at once and rising the temperature stepwise to complete the polymerization gradually, was researched for obtaining the high molar mass PDMDAAC by using the high purity industrial monomer from one-step method.^{20,21} Meanwhile, the effects of the polymerization conditions on intrinsic viscosity value ($[\eta]$) and monomer conversion rate (Conv.) of product PDMDAAC were investigated, to supply a basement for the industrialization of the method and the further researches of mechanism. Moreover, the structures, M_w , and thermal stability of the DMDAAC and PDMDAAC were investigated.

EXPERIMENTAL

Materials

Ammonium persulphate (APS) (AR grade, Degussa-AJ (Shanghai) Initiators Co., China), Na₄EDTA (AR grade, Sinopharm Chemical Reagent Co., China), NaCl (AR grade, Sinopharm Chemical Reagent Co., China).

High purity industrial monomer, DMDAAC in solution made from an industrial One-step method was produced according to a literature method^{20,21} (Industrial grade, Anhui Wuhu Aini Cosmetic Co., China). The impurities contained were as follows,

dimethylallyl amine ≤ 16 mg/kg, dimethylallyl amine hydrochloride ≤ 105 mg/kg, dimethyl amine hydrochloride ≤ 197 mg/kg, NaCl ≤ 8834 mg/kg, allyl alcohol was below 5 mg/kg, Fe and Cu were below 0.1 mg/L and 0.2 mg/L, respectively. The contents of other impurities such as allyl chloride, dimethylallyl amine, and allyl aldehyde were all below 1 mg/kg.

The determination of $[\eta]$ and Conv. of PDMDAAC products

The determination of $[\eta]$ was carried out according to a literature method (1.0 mol/L NaCl as solvent, measured by using Ubbelohde Viscometer in 30.0°C ± 0.1°C water bath).^{2,22}

One can calculate the reacted monomer amount, i.e., monomer conversion rate (Conv.), from the amount of unreacted double bond, i.e., the residual double bond amount, using the following equation by assuming that only a tiny amount of terminal double bonds exist.

The residual double bonds were measured by the Bromate-Bromide Titration Method (Chinese National Standard GB12005.3-89), and the corresponding calculation was made.

Conv. (%) = (1 - unreacted DMDAAC mole amount/total DMDAAC mole amount) × 100.00%

i.e., Conv. (%) = (1 - residual double bond mole amount/total double bond mole amount) × 100.00%.

The preparation of PDMDAAC

Placed a monomer solution with 28.0 g pure DMDAAC into a four neck flask equipped with a thermometer and a water bath. Added a certain amount of initiator APS, Na₄EDTA solution, and deionized water to adjust the $m(\text{DMDAAC})$ (the weight percent of DMDAAC), $m(\text{APS}) : m(\text{DMDAAC})$ (the mass ratio), and $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC})$ (the mass ratio) in the reaction mixture to the required values. Then stirred and purged the reaction mixture under a nitrogen atmosphere at a temperature below 40°C for 20 min. The solution temperature was increased in steps to T_1 , T_2 , T_3 . The solution temperature was maintained for 3 h at each temperature step. Then, we cooled down the temperature of the reaction mixture after the polymerization was completed. After a total of 9 h reaction time, a gel-like PDMDAAC product was obtained.

Based on the optimization experiments (orthogonal experiments), the obtained best condition is as follows: $T_1 = 46.0^\circ\text{C}$, $T_2 = 52.5^\circ\text{C}$, $T_3 = 65.0^\circ\text{C}$, $m(\text{DMDAAC}) = 65.0\%$, $m(\text{APS}) : m(\text{DMDAAC}) = 0.35\%$, $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC}) = 0.0035\%$, the corresponding product's $[\eta]$ and Conv. were 3.44 dL/g and 100.00%, respectively.

Furthermore, we were also monitoring the residual monomer present for each 1 h reaction time during the course of polymerization.

Meanwhile, the effects of polymerization condition variables on the products' $[\eta]$ and Conv. were investigated over a range of T_1 from 42.0 to 52.0°C, T_2 from 47.5 to 57.5°C, T_3 from 55.0 to 75.0°C, $m(\text{DMDAAC})$ from 60.0 to 70.0%, $m(\text{APS}) : m(\text{DMDAAC})$ from 0.25 to 0.45%, and $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC})$ from 0 to 0.0071%, respectively. Here, it should be pay attention to when one of variables changes within the range, the others keep unchanged values based on the optimum conditions.

Characterization

The DMDAAC solution was stripped under vacuum to a dried solid, and then kept in vacuum. Polymer sample was dried at 100°C for 6 h, then grinded into a powder.

FTIR spectra were measured by using a MB154S spectrophotometer (Bomem, Canada) and KBr pellets. In the FTIR spectra of the monomer DMDAAC and polymer PDMDAAC with $[\eta]$ 3.43 dL/g and Conv. 100.00%, the peaks in $\nu_{\text{C-H}}$ 3012 and 1477 cm^{-1} were the asymmetrical stretch vibration and bending vibration of methyl, respectively. The peaks in $\nu_{\text{C-H}}$ 2941 cm^{-1} and $\nu_{\text{C-H}}$ 2867 cm^{-1} were the asymmetrical stretch vibration and stretch vibration of methylene, respectively.

^1H - and ^{13}C -NMR spectra were recorded in D_2O on a NRX-300MH spectrometer using tetramethylsilane as an internal standard. In the ^{13}C -NMR spectrum of DMDAAC, the peaks $\delta = 49.5, 66.1, 124.4,$ and 129.1 ppm were the absorption of $-\text{CH}_3$, $-\text{CH}_2-$, $-\text{CH}=\text{}$, and $\text{CH}_2=\text{}$ in DMDAAC, respectively. In the ^{13}C -NMR spectrum of PDMDAAC, the peak $\delta = 26.6$ ppm was the absorption of $-\text{CH}_2-$ in polymer main chain, peaks $\delta = 38.7, 38.2$ and $\delta = 52.3, 54.8$ ppm were the absorption of $-\text{CH}-$ and $-\text{CH}_2-$ in the polymer five member ring. In the ^1H -NMR spectrum of DMDAAC, the peak $\delta = 2.88$ ppm was the absorption of $-\text{CH}_3$ linking with N, peak $\delta = 3.74$ ppm was the absorption of $-\text{CH}_2-$ ($J_{\text{CH}_2-\text{CH}=\text{}} = 0.02451$ ppm), peaks $\delta = 5.57$ and 5.89 ppm were the multiple absorption of $\text{CH}_2\text{CH}-$ ($J_{\text{CH}_2=\text{CH}-} = 0.03298$ and 0.05533 ppm). In the ^1H -NMR spectrum of PDMDAAC, the peak $\delta = 3.69$ ppm was the absorption of $-\text{CH}_2-$ linking with N, peak $\delta = 2.56$ ppm was the absorption of $-\text{CH}-$ in the polymer five member ring. Peak $\delta = 2.99$ ppm was the absorption of $-\text{CH}_3$ linking with N. Peak $\delta = 1.17$ and 1.40 ppm were the absorption of $-\text{CH}_2-$ in the main chain.

The weight-average molar mass (M_w) of polymers were determined with a DAWN HELEOS GPC-MALLS system (Wyatt, USA) by using 0.5 mol/L

NaCl solution as mobile phase. The polymer sample solution was filtered through a 0.45 μm membrane (Glass Microfiber filter, Whatman, USA). A value of $dn/dc = 0.170$ was used.²³

The thermal decomposition was recorded on DSC/DTA/TG (STA449C) Jupiter (Netzsch, Germany) by using a 0.3000 mg polymer sample in an Al_2O_3 pan. The scan was performed from 30 to 900°C at a heating rate of 10°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

The effects of reaction temperature

T_1

Figure 2 shows the effect of T_1 on products' $[\eta]$ and Conv. It was obvious that the $[\eta]$ and Conv. increased from 2.22 to 3.43 dL/g and 92.43 to 100.00%, respectively, when T_1 increased from 42.0 to 46.0°C. When T_1 increased to higher than 50.0°C, the $[\eta]$ and Conv. decreased rapidly because of an uncontrollable exothermic polymerization. $[\eta]$ and Conv. were only 0.93 dL/g and 82.31% when T_1 reached 52.0°C.

The main effect of T_1 is to promote the initiator decomposition rate for proper starting free radical concentration. If T_1 is too low, the effective polymerization for forming polymers could not be obtained because of the low concentration of free radicals. If T_1 is too high, high molecular PDMDAAC could not be formed either, because of the too high concentration of free radicals and rapid polymerization rate which easily leads to the fast termination rate. The both situations above would lead to a lower value of product's $[\eta]$ and Conv.²⁴

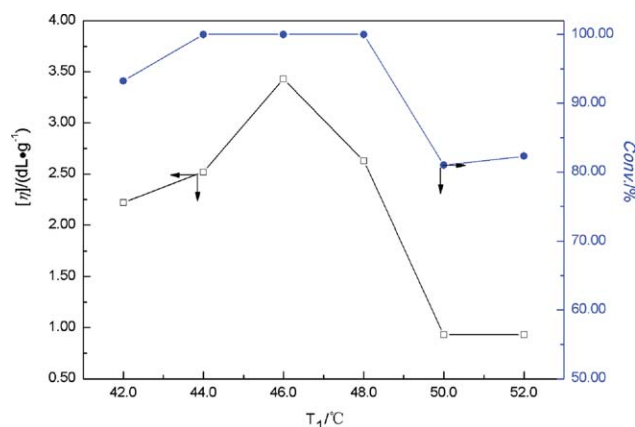


Figure 2 The effect of T_1 on $[\eta]$ and Conv. when $T_2 = 52.5^\circ\text{C}$, $T_3 = 65.0^\circ\text{C}$, $m(\text{DMDAAC}) = 65.0\%$, $m(\text{APS}) : m(\text{DMDAAC}) = 0.35\%$, $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC}) = 0.0035\%$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

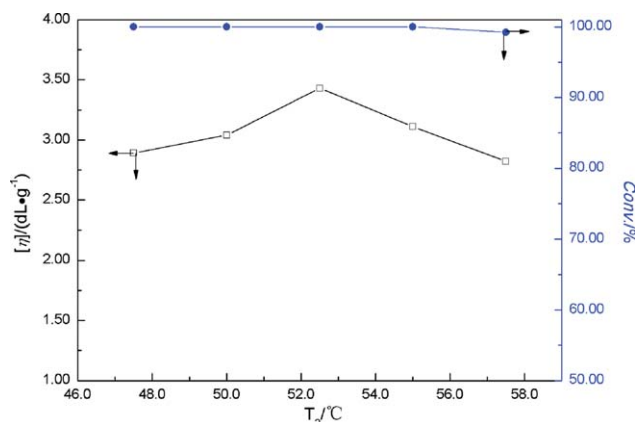


Figure 3 The effect of T_2 on $[\eta]$ and Conv. when $T_1 = 46.0^\circ\text{C}$, $T_3 = 65.0^\circ\text{C}$, $m(\text{DMDAAC}) = 65.0\%$, $m(\text{APS}) : m(\text{DMDAAC}) = 0.35\%$, $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC}) = 0.0035\%$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

T_2

Figure 3 shows the effect of T_2 on products' $[\eta]$ and Conv. It was evident that the $[\eta]$ increased from 2.89 to 3.43 dL/g as T_2 increased from 47.5 to 52.5°C. If T_2 increased further, the $[\eta]$ decreased rapidly and reached 2.82 dL/g when T_2 increased to 57.5°C; however, the Conv. was consistently higher than 99.22% over the entire set.

To promote the formation of polymer, the main effect of T_2 is to maintain the proper concentration of free radicals formed from APS decomposition for polymerization. T_2 needs to be greater than T_1 because of the lower concentration of APS at this stage. However, the effect of T_2 on $[\eta]$ is not so obviously as T_1 , as a certain amount of polymer has formed already, which means formation of glassy state and diffusion limitation of monomer and initiator. However, T_3 will burn out the residual monomer, so the Conv. is still high.

T_3

Figure 4 shows the effect of T_3 on products' $[\eta]$ and Conv. It was clear that the $[\eta]$ increased from 1.94 to 3.43 dL/g when T_3 increased from 55.0 to 65.0°C. If T_3 was increased further, $[\eta]$ decreased rapidly and reached 1.29 and 1.15 dL/g when T_3 increased to 70°C and 75°C, respectively, because of the cross-linking occurred in the product. However, the Conv. was consistently higher than 98.08% over the entire set.

The main effect of T_3 is to accelerate the decomposition of residual initiator APS to promote the polymerization of the residual monomer in the reaction system and increase the average molar mass M_w of product PDMDAAC. If T_3 is too low, the polymer-

ization reaction of the residual monomer cannot be completed, high molar mass and monomer conversion rate cannot be obtained. If T_3 is too high, the high temperature can overcome the activation energy allowing pendant double bonds to polymerize with each other, leading to a slight crosslinking and resulting in a crosslinked product, i.e., a low $[\eta]$ of product PDMDAAC with high Conv. As the measurements of $[\eta]$ and Conv. are carried out by testing dissolved PDMDAAC solutions, insoluble crosslink segment is filtered out before the measurement, which results in low $[\eta]$ values.

The coordination effects of T_1 – T_3

Conventionally, free radical polymerization process in aqueous solution is carried out by the dropwise addition of the initiator solution for maintaining a low free radical concentration in a reaction medium.¹⁷ This is necessary, so the PDMDAAC products have a high molar mass and monomer Conv. As the processing of synthesizing PDMDAAC is carried out in a high concentration of reactant, gel is formed in a short time after the beginning of the polymerization, which leads the diffusion limitation of the monomer and initiator, when the dropwise method of adding initiator was used.¹⁷ As a result, neither the $[\eta]$ nor Conv. is high because of the incomplete polymerization. However, the polymerization method of preparing PDMDAAC through adding the initiator all at once and rising the temperature stepwise to complete the polymerization gradually is used in our research to decompose the initiator stepwise both to form the macro molecules at the beginning of the reaction, i.e., T_1 and T_2 period, and to complete the residual monomer

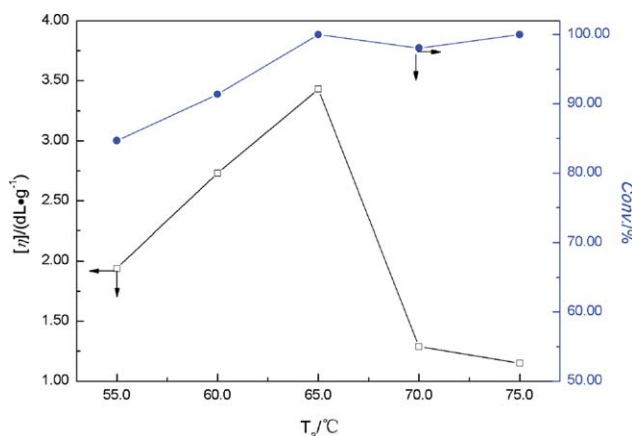


Figure 4 The effect of T_3 on $[\eta]$ and Conv. when $T_1 = 46.0^\circ\text{C}$, $T_2 = 52.5^\circ\text{C}$, $m(\text{DMDAAC}) = 65.0\%$, $m(\text{APS}) : m(\text{DMDAAC}) = 0.35\%$, $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC}) = 0.0035\%$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

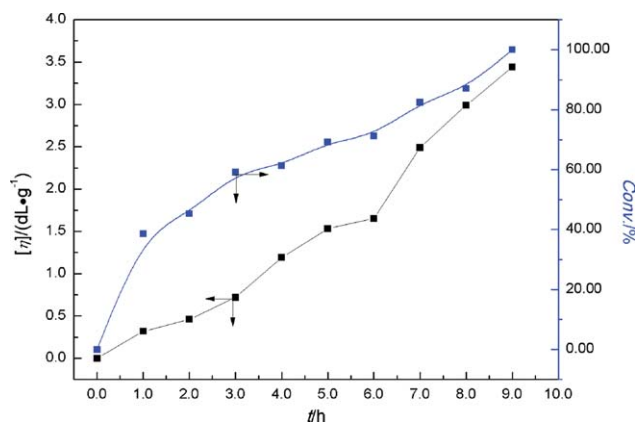


Figure 5 The effect of reaction time on $[\eta]$ and Conv. when $T_1 = 46.0^\circ\text{C}$, $T_2 = 52.5^\circ\text{C}$, $T_3 = 65.0^\circ\text{C}$, $m(\text{DMDAAC}) = 65.0\%$, $m(\text{APS}) : m(\text{DMDAAC}) = 0.35\%$, $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC}) = 0.0035\%$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymerization at the end of the reaction i.e., T_3 period. It means that this method functions the same as the stepwise method of adding initiator.

The contributions of T_1 – T_3 to the $[\eta]$ and Conv. are different. Further understanding of the effect of temperatures on the $[\eta]$ and Conv. could be obtained by tracing intermediates under the optimum condition for each 1 h (shown in Fig. 5).

Figure 5 shows that the $[\eta]$ increased from 0 to 0.72 dL/g accompanying with the increase of Conv. from 0 to 59.15%, during the T_1 reaction period. The $[\eta]$ increased from 0.72 to 1.65 dL/g accompanying with the increase of Conv. from 59.15 to 71.25%, during the T_2 reaction period. And $[\eta]$ increased from 1.65 to 3.44 dL/g accompanying with the increase of Conv. from 71.25 to 100.00%, during the T_3 reaction period. These results were well in accordance with expectation and successfully validated the rationality of the polymerization method of adding the initiator all at once and rising the temperature stepwise.

The effect of the $m(\text{DMDAAC})$

Figure 6 shows the effect of $m(\text{DMDAAC})$ on products' $[\eta]$ and Conv. It was clear that the $[\eta]$ increased from 1.69 to 3.43 dL/g and Conv. increased from 84.77 to 100.00%, when $m(\text{DMDAAC})$ increased from 60.0 to 65.0%. But $[\eta]$ gradually decreased to 3.00 dL/g when $m(\text{DMDAAC})$ reached 70.00%, meanwhile, the Conv. decreased to 91.39%.

The reason might be that the rate of polymerization increases with the monomer concentration, i.e., $m(\text{DMDAAC})$, and $[\eta]$ gradually reaches its maximum when $m(\text{DMDAAC})$ value is within a lower range. The rate of polymerization is accelerated as

the collision between monomer molecules increases significantly with an increase of $m(\text{DMDAAC})$ further, e.g., higher than 65.0%. Fast polymerization happens and the formation of macromolecules causes an increase of the systemic viscosity rapidly, which leads to a difficulty in heat transfer. Then, the temperature of the reaction system increases further which results in the polymerization becoming even more rapid and more difficult for heat dissipation, this is called a process of self-acceleration²⁴ in T_1 period, presenting as serious increase of the temperature and formation of the bubbles. As a result, the decomposition of the initiator is finished too early and premature autopolymerization occurs, which leads to incomplete polymerization presenting as low $[\eta]$ and Conv.

The effect of the $m(\text{APS}) : m(\text{DMDAAC})$

Figure 7 shows the effect of $m(\text{APS}) : m(\text{DMDAAC})$ on products' $[\eta]$ and Conv. It was clear that the $[\eta]$ increased from 3.05 to 3.43 dL/g, Conv. increased from 93.47 to 100.00%, when $m(\text{APS}) : m(\text{DMDAAC})$ increased from 0.25 to 0.35%. But the $[\eta]$ and Conv. swiftly decreased when $m(\text{APS}) : m(\text{DMDAAC})$ was more than 0.40% because of formation of crosslinked products. The $[\eta]$ fell to 1.34 dL/g when $m(\text{APS}) : m(\text{DMDAAC})$ reached 0.45%, the corresponding Conv. decreased to 81.73%.

The main reason for these might be: if the initiator concentration, i.e., $m(\text{APS}) : m(\text{DMDAAC})$ is low, a low initiator efficiency due to cage effect causes the polymerization reaction incompletely and results in the high amount of residual monomer, i.e., low Conv. If the $m(\text{APS}) : m(\text{DMDAAC})$ is higher, the products' $[\eta]$ increases, because formed enough free

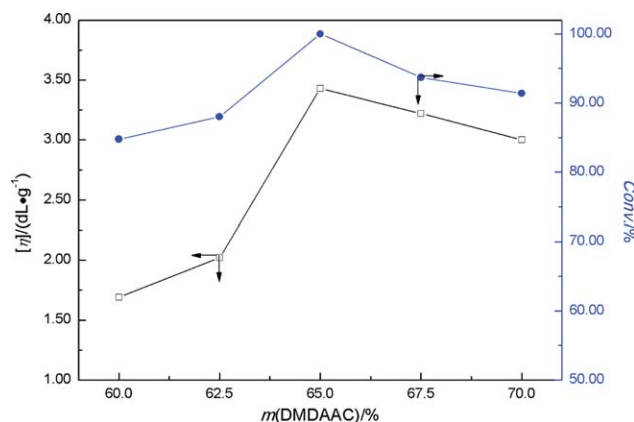


Figure 6 The effect of $m(\text{DMDAAC})$ on $[\eta]$ and Conv. when $T_1 = 46.0^\circ\text{C}$, $T_2 = 52.5^\circ\text{C}$, $T_3 = 65.0^\circ\text{C}$, $m(\text{APS}) : m(\text{DMDAAC}) = 0.35\%$, $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC}) = 0.0035\%$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

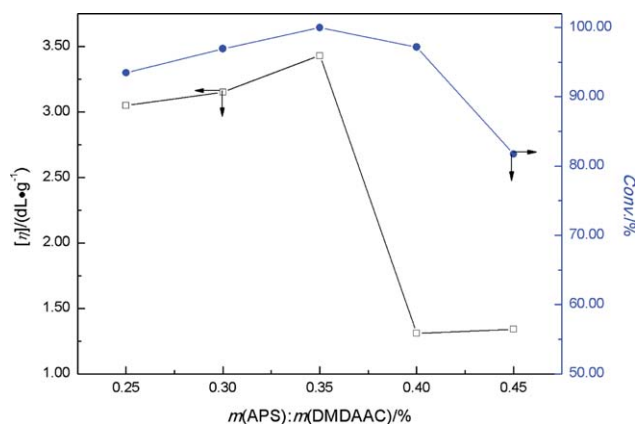


Figure 7 The effect of $m(\text{APS}) : m(\text{DMDAAC})$ on $[\eta]$ and Conv. when $T_1 = 46.0^\circ\text{C}$, $T_2 = 52.5^\circ\text{C}$, $T_3 = 65.0^\circ\text{C}$, $m(\text{DMDAAC}) = 65.0\%$, $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC}) = 0.0035\%$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

radicals could replenish the loss due to the cage effect and meet the needs of the polymerization. When the $m(\text{APS}) : m(\text{DMDAAC})$ is too high, there would be a superabundance of initiator,² which results in formation of crosslinked molecules and the product's $[\eta]$ is small.

The effect of the $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC})$

Figure 8 shows the effect of $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC})$ on products' $[\eta]$ and Conv. It was clear that the $[\eta]$ and Conv. increased from 2.26 to 3.43 dL/g and 86.91 to 100.00% respectively, when $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC})$ increased from 0 to 0.0035%. Then, the change of $[\eta]$ was within the range of 3.20–3.43 dL/g, the corresponding Conv. kept the values higher than 96.74%, when $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC})$ increased further from 0.0035%.

A possible reason for the significant increase of $[\eta]$ is when the low amount of Na_4EDTA is enough to chelate the tiny amount of metal ions which would inhibit polymerization, it would contribute to

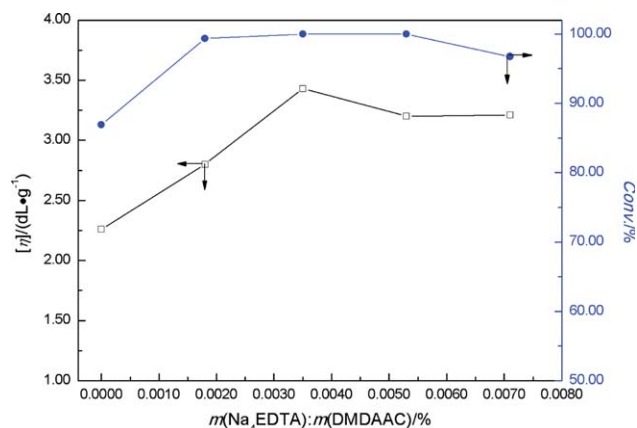


Figure 8 The effect of $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC})$ on $[\eta]$ and Conv. when $T_1 = 46.0^\circ\text{C}$, $T_2 = 52.5^\circ\text{C}$, $T_3 = 65.0^\circ\text{C}$, $m(\text{DMDAAC}) = 65.0\%$, $m(\text{APS}) : m(\text{DMDAAC}) = 0.35\%$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the polymerization.²² Meanwhile, it can also play the role of a buffer to keep pH value in constant range for restraining the APS self-accelerated decomposition. Then, the initiator efficiency could be improved and $[\eta]$ of product could be increased. However, there would be no significant changes of the $[\eta]$ and Conv. keeping in a range of high values, when the $m(\text{Na}_4\text{EDTA}) : m(\text{DMDAAC})$ increased more.

Characterization

FTIR

The spectrum exhibited strengths of characteristic absorbance peaks (the reciprocal of transmittance) of functional groups in monomer $\nu_{\text{C-H}}$ 3025, 3080, 1929, 1424 cm^{-1} and $\nu_{\text{C-H}}$ 849–880 cm^{-1} . They were all weakened or disappeared in product PDMDAAC, which showed that the monomer was polymerized completely. As the peaks of $\nu_{\text{C=C}}$ and H_2O both existed at 1640 cm^{-1} , they could not be used as a proof of the double bond presence.

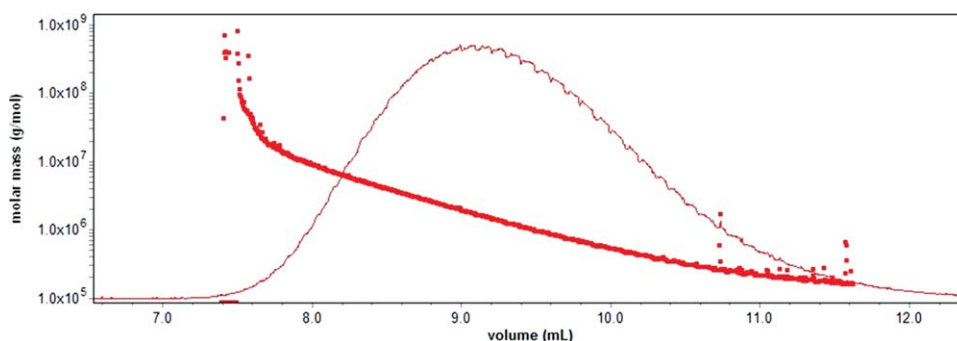


Figure 9 The chromatogram curve of PDMDAAC molecular weight versus elution volume (GPC-MALLS) ($[\eta] = 3.44$ dL/g, Conv. = 100.00%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

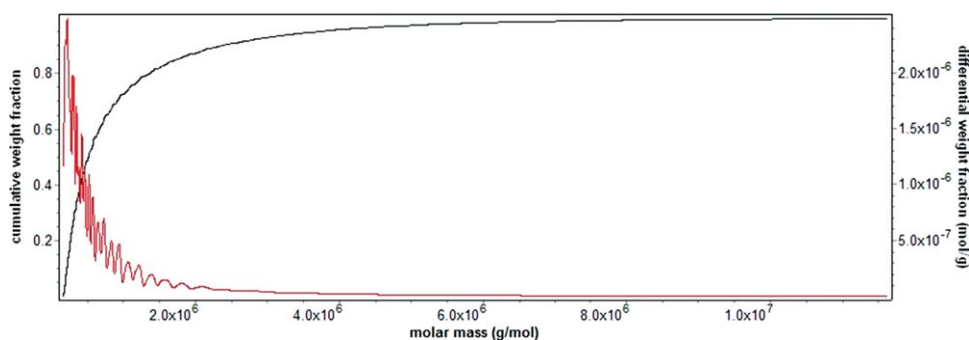


Figure 10 The molecular weight distribution of PDMDAAC ($[\eta] = 3.44$ dL/g, Conv. = 100.00%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

NMR

The peaks $\delta = 124.4$ and 129.1 ppm relating to the double bond disappeared in polymer's ^{13}C -NMR spectrum, which meant the polymerization of DMDAAC were complete. The peaks $\delta = 5.5$ and 5.9 ppm disappeared in PDMDAACs ^1H -NMR spectrum, which could also be a proof of the complete polymerization of DMDAAC.

GPC-MALLS

Figures 9 and 10 shows the calibration curve of molar mass (the corresponding RI and one of the MALLS signals at 90°) and the molar mass distribution of the product ($[\eta] = 3.44$ dL/g, Conv. = 100.00%), respectively.

The result from GPC-MALLS measurement demonstrated that, the M_w of PDMDAAC was 1.034×10^6 , polydispersity M_w/M_n was 2.421, and the R_g was 60.3 nm.

TGA-DSC

Figure 11 shows the thermal stability of PDMDAAC via the measurement of its decomposition process.

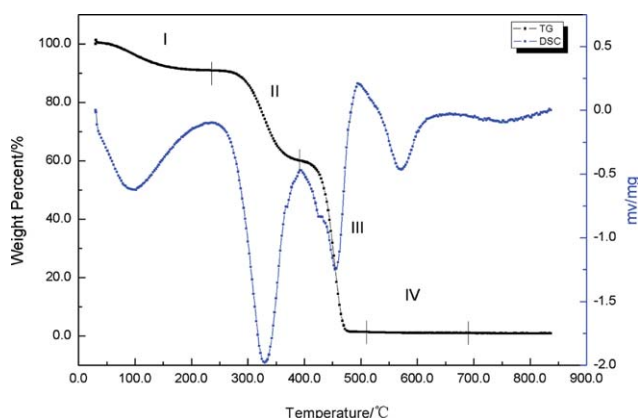


Figure 11 The TGA-DSC thermography of PDMDAAC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The PDMDAAC lost weight in three stages. The first stage I was from 30 to 234°C with a weight lost 9.14% and the corresponding enthalpy change ΔH_I was 362.8 J/g. The second stage II was from 234 to 389°C with a weight lost 30.85% and the corresponding enthalpy change ΔH_{II} 576 J/g. The third stage III was from 389 to 509.6°C with a weight lost 58.6% and the corresponding enthalpy change ΔH_{III} was 314.6 J/g. The fourth stage IV was from 509.6 to 830°C without significant weight lost, but with enthalpy change ΔH_{IV} was 314.6 J/g.

CONCLUSIONS

The polymerization method of using APS as the initiator, adding the initiator all at once and rising the temperature stepwise to complete polymerization gradually had been applied for obtaining high molecular PDMDAAC, by using the high purity industrial monomer from one-step method. A product with $[\eta]$ 3.43 dL/g and Conv. 100.00% were obtained. The FTIR and NMR spectra showed that the monomers were well polymerized to PDMDAAC. The M_w of PDMDAAC was 1.034×10^6 , polydispersity M_w/M_n was 2.421, and the R_g was 60.3 nm. The PDMDAAC thermal decomposition process divided mainly in two stages. One was from 234 to 389°C with a weight lost 30.85%, and the corresponding enthalpy change ΔH_{II} was 576 J/g. The other one was from 389 to 509.6°C with a weight lost 58.6%, and the corresponding enthalpy change ΔH_{III} was 314.6 J/g. Meanwhile, the effects of the polymerization condition variables on products' $[\eta]$ and Conv. have been investigated.

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