Effects of Maintaining Temperature and Time on Properties and Structures of Poly(dimethyldiallylammonium chloride)

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ABSTRACT: Effects of maintaining temperature (T_3) and time (t) on properties and structures of product poly(dimethyldiallylammonium chloride) (PDMDAAC) are researched in this article. The results showed that higher the T_3 shorter the time t needed for polymer products' intrinsic viscosity ($[\eta]$) and monomer conversion (Conv.) to reach their maximum values. The maximum $[\eta]$ was 4.69 dL g^{-1} and corresponding Conv. was 100.00%, when $t = 96$ h and $T_3 = 55°C$. The reaction phenomena and products' FTIR and NMR spectra indicated the possible reasons for the increase of $[\eta]$, the formation of branched and crosslinked products after the conversion was more than 100.00% in T_3 term were the results of polymerization happened among the residual monomers, hanging and terminal double bonds. Compared with solubility of products, it was found that the time needed for dissolving the linear, branched, and crosslinked PDMDAAC products increased in turn, whereas their dissolved amount decreased reversely. The linear product's M_w, M_w/M_n, and R_g measured by GPC-MALLS were 4.169×10^6, 5.109, and 127.7 nm, respectively. Meanwhile, the linear and crosslinked products were characterized by DTA-TG. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1–9, 2012

Key words: dimethyldiallylammonium chloride; poly(dimethyldiallylammonium chloride); maintaining temperature; reaction time; thermal stability; solubility, structure

INTRODUCTION

It is well known that poly(dimethyldiallylammonium chloride) (PDMDAAC) being a homopolymer of dimethyldiallylammonium chloride (DMDAAC) is widely used in many fields, because of its properties such as cationic quaternary ammonium structure, good water solubility, easily controlled molecular weight, and nontoxicity.[1,2] Especially, it's important role in municipal engineering, such as the coagulant in raw water treatment and flocculant in waste water treatment have been further developed in recent years.[3,4] Researches on the development of its new preparation[5,6] application,[7,8] reaction mechanism,[9–11] and relationships between structure and properties[12–15] are becoming new hot points. The main structures of linear PDMDAAC reported in literatures are as shown in Figure 1 with branched structure units.

It is noteworthy that the high-molecular weight of the product obtained indicates that more novel properties and much wider applications could be acquired. So, how to obtain the product with higher molecular weight (measured as intrinsic viscosity value $[\eta]$) by the simplest, most economic, and effective method has been focused in Refs. 1, 2. In recent several decades, there are many researches taking efforts to find a new way obtaining the PDMDAAC products with high-molecular weight. Unfortunately, there is no obvious progress occurred in this research area. It has been reported lately that the improvement of monomer purity[6,16] and preparation conditions[17,18] could help to reach the aim.

The reported polymerization method used purified commercial DMDAAC as monomer, ammonium persulfate (APS) as initiator, and the initiator was added all at once and temperature was raised stepwise to complete the polymerization gradually.[18] The highest intrinsic viscosity value of PDMDAAC is 3.43 dL g^{-1} and corresponding monomer conversion rate (Conv.) is 100.00%.[18] Meanwhile, the effects of the processing conditions on products' $[\eta]$ and Conv. are investigated. The results indicate that
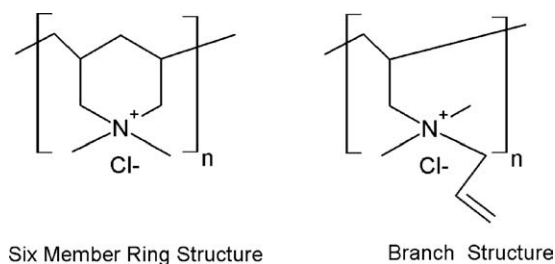
Figure 1 Structure of PDMDAAC.[1,2]

maintaining temperature, i.e., T_3 has a significant influence on the products' $[\eta]$ and Conv., i.e., they could be increased from 1.65 to 3.44 dL g^{-1}, 71.25 to 100.00%, respectively, within 3 h. On the other hand, the increase of $[\eta]$ and Conv. could only be realized effectively by rising the temperature in T_3 term under a limited reaction time within 9 h. Similarly, it has been believed that the highest $[\eta]$ value 4.07 dL g^{-1} of PDMDAAC product was prepared under a low-maintaining temperature of 40°C for a long reaction time of 48 h by aqueous solution polymerization (using AZO initiator).[19] Therefore, it is obvious that a good coordination of the temperature and reaction time might be available for the preparation of product with higher molecular weight.

In this article, the effects of maintaining temperature T_3 and corresponding reaction time t on the products' $[\eta]$ and Conv. were investigated in detail based on the reported polymerization method.[18,19] The effects of the two factors T_3 and t on the structures and properties of product and possible mechanism explanations were illustrated, respectively, by the analysis of the reaction phenomena, the characterization of FTIR, NMR, DTA-TG, and the solubility test of polymer product PDMDAAC.

EXPERIMENTAL

Materials

APS [AR grade, Degussa-AJ (Shanghai) Initiators, China], Na$_4$EDTA (AR grade, Sinopharm Chemical Reagent, China), NaCl (AR grade, Sinopharm Chemical Reagent), deionized water ($\kappa \leq 16.6$ MΩ cm), and nitrogen (purity $\geq$ 99.95%).

High-purity commercial monomer DMDAAC in solution made from an industrial one-step method was produced according to a method described in Refs. 20, 21 (Industrial grade, Anhui Wuhu Aini Cosmetic, China). The impurities contained were shown in Table I.

Preparation of PDMDAAC

A monomer solution with 28.0 g pure DMDAAC was placed into a four-necked flask equipped with a thermometer and water bath. A certain amount of initiator APS, Na$_4$EDTA solution, and deionized water were added to adjust the m(DMDAAC) = 65.0% (the weight percent of DMDAAC), m(APS):m(DMDAAC) = 0.35% (the mass ratio), and m(Na$_4$EDTA):m(DMDAAC) = 0.0071%(the mass ratio) in the reaction solution. Then, the reaction mixture was stirred and purged under a nitrogen atmosphere at a temperature below 40°C for 20 min. The solution temperature was increased in steps to the initiation temperature T_1 = 46°C, the polymerization temperature T_2 = 50°C, and maintained for 3 h, respectively,[18] and then increased to the maintaining temperature T_3 for t h. Then, we cooled down the temperature of the reaction solution after the polymerization was completed, and a gel-like PDMDAAC product was obtained.

The effects of polymerization conditions variables on the products' $[\eta]$ and Conv. were investigated in detail over a range of the maintaining time t from 0 to 240 h under each selected T_3 from 50 to 70°C.

Determination of $[\eta]$ and Conv. of PDMDAAC products

Because the intrinsic viscosity value $[\eta]$ have a relationship with the Mv, as indicated in the following formula $[\eta] = KM^{\alpha}$ (K and α are constants for certain testing condition), it can be used for representing the molecular weight.

The determination of the product's $[\eta]$ was carried out according to a literature method (1.00 mol/L NaCl as solvent, measured by using Ubbelohde viscometer in 30.0 $\pm$ 0.1°C water bath).[1,22]

The reacted monomer amount can be calculated, i.e., monomer conversion rate (Conv.), from the amount of residual double bond, using the following equation, assuming that only a small amount of terminal double bonds exist.

The residual double bonds were measured by the Bromate–Bromide Titration Method (Chinese National

TABLE I
Impurities Composition of Industrial Monomer DMDAAC

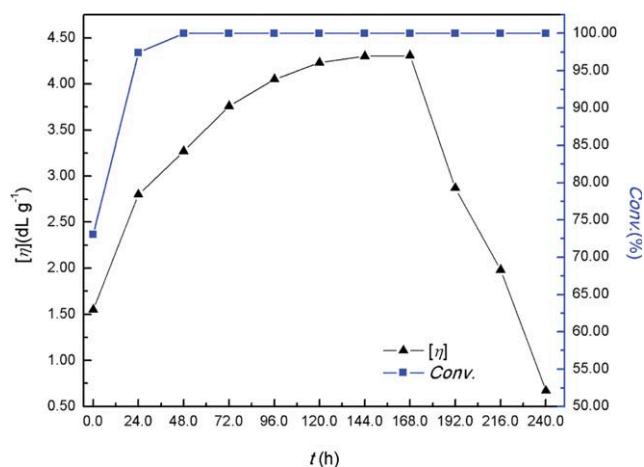| Dimethylallyl amine (mg kg^{-1})	Dimethylallyl amine hydrochloride (mg kg^{-1})	Dimethyl amine (mg kg^{-1})	Dimethyl amine hydrochloride (mg kg^{-1})	NaCl (mg kg^{-1})	Allyl alcohol (mg kg^{-1})	Allyl alderhyde (mg kg^{-1})	Allyl chloride (mg kg^{-1})	Fe (mg L^{-1})	Cu (mg L^{-1})
$\leq$19	$\leq$879	$\leq$1	$\leq$1049	$\leq$5588	$\leq$5 mg	$\leq$1	$\leq$1	$\leq$0.1	$\leq$0.2

Figure 2 The effects of t on the products' $[\eta]$ and Conv. when $T_3 = 50°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Standard GB12005.3-89), and the corresponding calculation was made.

$$\text{Conv. }(\%) = (1 - \frac{n_{\text{unreacted DMDAAC}}}{n_{\text{total DMDAAC}}}) \times 100.00\%$$

Here, $n_{\text{unreacted DMDAAC}}$ and $n_{\text{total DMDAAC}}$ is the mole amount of unreacted DMDAAC and total DMDAAC, respectively.[18]

Characterization

The linear PDMDAAC with low- or high-molecular weight and crosslinked PDMDAAC were selected to characterization. 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) using KBr pellets method. ^1H and ^{13}C NMR spectra were recorded in D_2O on a NRX-300MH spectrometer (Bruker, Ger-
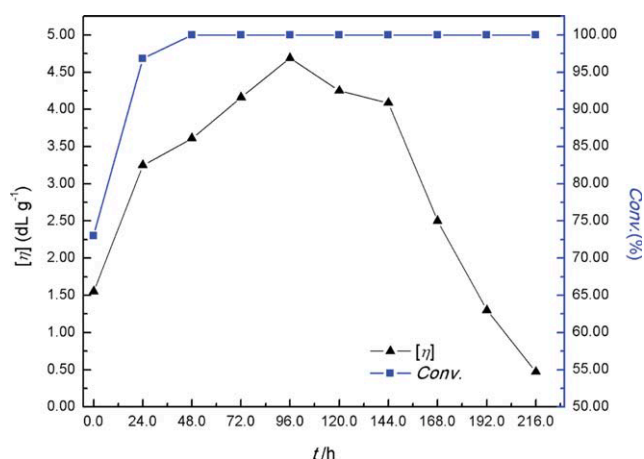

Figure 3 The effects of t on the products' $[\eta]$ and Conv. when $T_3 = 55°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
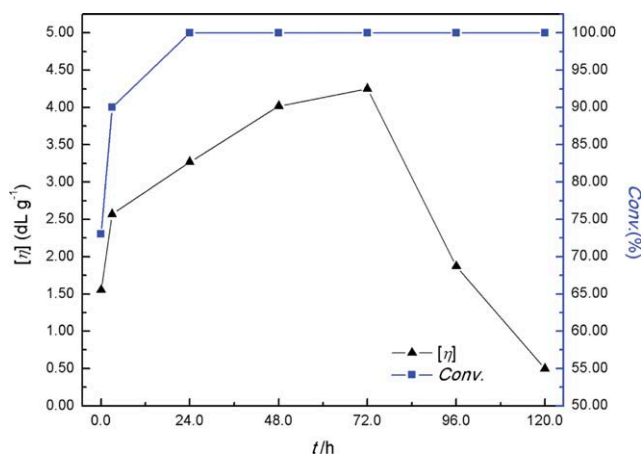

Figure 4 The effects of t on the products' $[\eta]$ and Conv. when $T_3 = 60°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

many) using tetramethylsilane as an internal standard. The semisolid state ^1H NMR spectra were recorded in C_3D_6O on an Avance 400 (SB) (Bruker, Germany).

The weight-average molar mass (M_w) of polymers were determined with a DAWN HELEOS GPC-MALLS system (Wyatt, USA) by using 0.50 mol/L NaCl solution as mobile phase. The polymer sample solution was filtered through a 0.45-μm membrane (Glass Microfiber filter, Whatman, Clifton, NJ). A value of $dn/dc = 0.170$ was used.[23]

The thermal degradation was recorded on DTG-60 (Shimadzu, Japan) by using a 0.8000 mg linear and crosslinked PDMDAAC sample in an aluminum pan. The scan was performed from 30 to 600°C at a heating rate of 10°C/min under a nitrogen atmosphere.

Solubility test

Flakes of the product gel (1.5 cm × 0.2 cm × 0.2 cm, length × width × height) with each kind of structures were put into a culture dish contained with 10-mL deionized water. They were kept to reach their
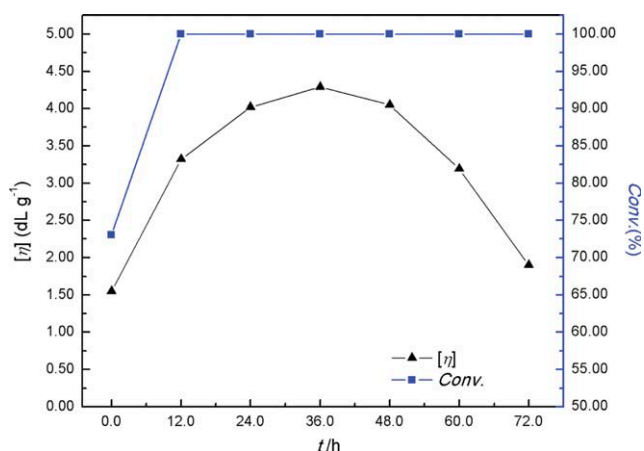

Figure 5 The effects of t on the products' $[\eta]$ and Conv. when $T_3 = 65°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
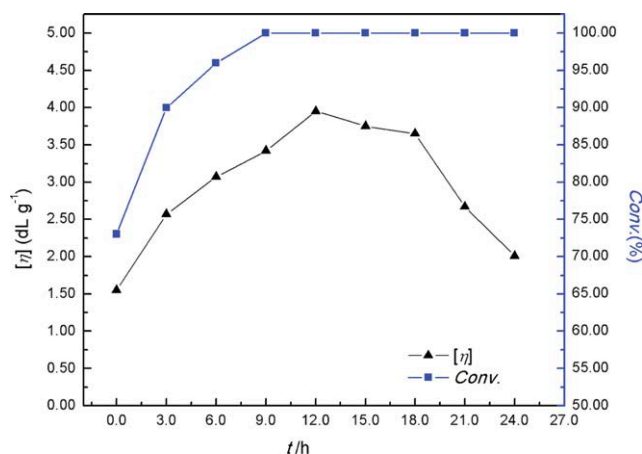
Figure 6 The effects of t on the products' $[\eta]$ and Conv. when $T_3 = 70°$C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

highest solubility under a weak stirring. After this, the product solution was dyed by adding 1 mL bromocresol green [m(bromocresol green):m(ethanol) = 1%] and took photographs using Sony T10 camera.

RESULTS AND DISCUSSION

The effects of maintaining time t on the products' $[\eta]$ and Conv., when T_3 was selected

Figures 2 to 6 show the effects of t on the products' $[\eta]$ and Conv., when T_3 was 50, 55, 60, 65, and 70°C, respectively. Their corresponding reaction conditions are shown in Table II.

It is easy to find out that all the curves have the similar changing regulation to each other despite their different values. We will take Figure 3 as an example to describe.

Figure 3 shows the effect of t on the products' $[\eta]$, i.e., molecular weight and Conv., when $T_3 = 55°$C. It is evident that $[\eta]$ increased rapidly from 1.55 to 4.69 dL g^{-1} when maintaining time t increased from 0 to 96 h. The Conv. increased from 73.03 to 100.00% when t increased from 0 to 48 h, and then maintained constantly during rest of the process. However, $[\eta]$ decreased quickly when the t increased further than 96 h, and finally $[\eta]$ was only 0.47 dL g^{-1} when t was 216 h as crosslinking occurred in the product. In fact, the molecular weight of the crosslink products is extremely increased, but the measurement of $[\eta]$ was carried out by testing the elute time of the sample solution filtered; therefore, $[\eta]$ was decreased as the crosslinking products were filtered out.

DISCUSSION

The effect of T_3 and t on polymer products' properties

t_1 means a time range that the PDMDAAC products' $[\eta]$ values were equal to or higher than 4.00 dL g^{-1}.

TABLE II
Summary of Reaction Conditions with Different T_3

No.	T_3 (°C)	Total reaction time (h)	Intervening time (h)
1	50.0	240	24
2	55.0	216	24
3	60.0	120	24
4	65.0	72	12
5	70.0	24	3

All the reactions were held in $T_1 = 46°$C and $T_2 = 50°$C and maintained for 3 h, respectively,[18] and then increased to the maintaining temperature T_3 for different time.

t_2 means a time point when the products' Conv. value reached 100.00%. $[\eta]_{max}$ means PDMDAAC products' highest $[\eta]$ value at each T_3. The t_1, t_2, and $[\eta]_{max}$ were summarized from Figures 2 to 6, respectively, and shown in Table III.

It is not so difficult to find out from Table I that when T_3 increased from 50 to 70°C, the starting point of t_1 decreased from 96 to 12 h gradually; meanwhile, the range of each t_1 was sharply decreased from 32 h (96–128 h) to shorter than 1 h (12–12 h) and the time t_2 decreased from 48 to 9 h gradually. Whereas the change of the $[\eta]_{max}$ values obtained at each T_3 did not obey the similar regulation of t_1 or t_2. It did obey a parabola type-liked regulation. And only a PDMDAAC product with a highest $[\eta]$ value of 4.69 dL g^{-1} in this research can be obtained when polymerization carried out at T_3 = 55°C for 96 h.

The reasonable explanation might be that the gradual increase of $[\eta]$ of PDMDAAC product in the preliminary period (before t_2) of T_3 term dominantly benefits from the increase of the monomer conversion, i.e., the polymerization of the residual monomer. Then, the significant increase of $[\eta]$ in the later period (after t_2) benefits mainly from the polymerization of the small amount of hanging double bonds and terminal double bounds. However, the latter has its limitation because of the crosslinking side reaction. In fact, the relationship of T_3 and its corresponding t for the PDMDAAC's $[\eta]$ to achieve the highest value obeys the rule of Arrhenius equation. That is to say, when the maintaining

TABLE III
Summary of t_1, t_2, and $[\eta]_{max}$ at Different T_3

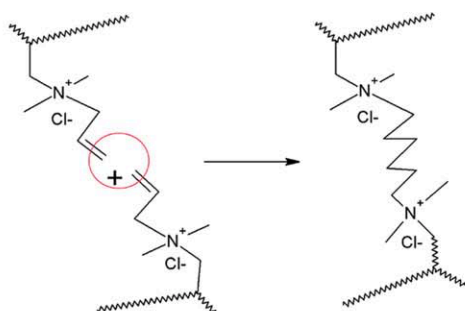| No.	T_3 (°C)	t_1 ($[\eta] \geq$ 4.0 dL g^{-1}) (h)	t_2 (Conv. $\geq$ 100.00%) (h)	$[\eta]_{max}$ (dL g^{-1})
1	50.0	96.0–128.0	48.0	4.31
2	55.0	72.0–144.0	48.0	4.69
3	60.0	48.0–72.0	24.0	4.25
4	65.0	24.0–28.0	12.0	4.29
5	70.0	12.0–12.0	9.0	3.95

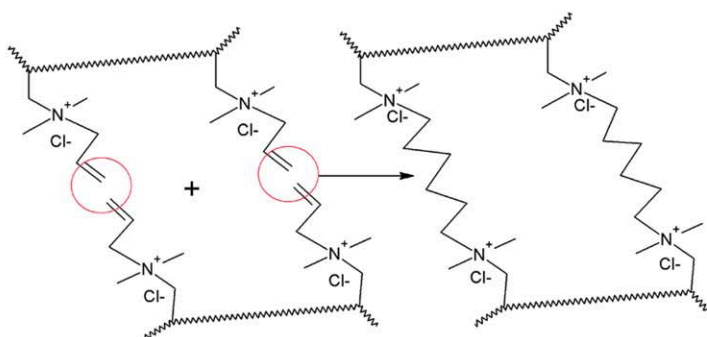Fig.7-1 the branch reaction process of PDMDAAC

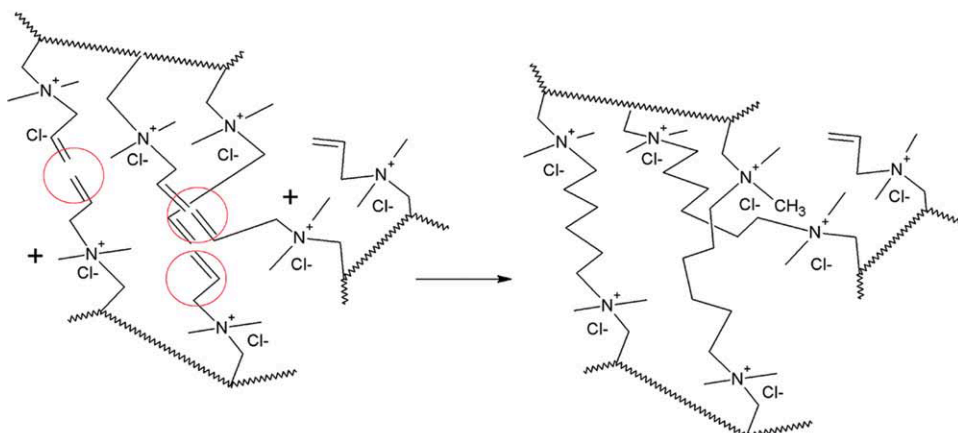Fig.7-2 the plane crosslink reaction process of PDMDAAC

Fig.7-3 the stereo crosslink reaction process of PDMDAAC

Figure 7 The possible structures of branched and crosslinked PDMDAAC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature T_3 is low, the corresponding polymerization velocity is not so fast, thereby, the time needed to achieve the same reaction proceeding (monomer conversion) is long. While T_3 is high, it contrarily becomes the dominance in the reaction proceeding before the crosslink reaction.

The effects of T_3 and t on products' structure

The possible reason for the occurring of the crosslink reaction

Based on the results mentioned above, the solubility of PDMDAAC product became worse when

TABLE IV
Phenomena of Typical PDMDAACs' Dissolution when T_3 = 55°C with Different t

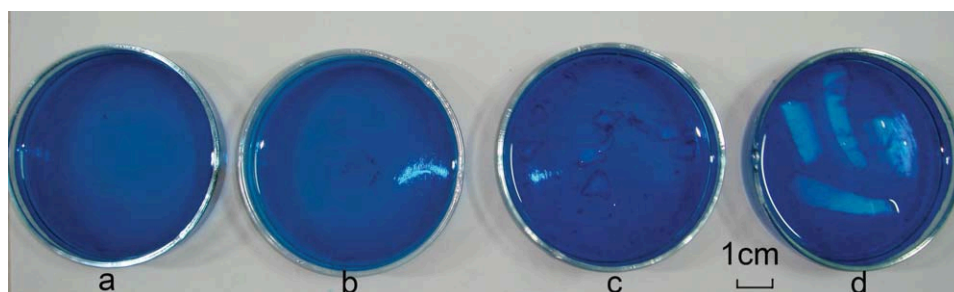| No.	Structure	Molecular weight	$[\eta]$ (dL g^{-1})	t_s (d)	Dissolution phenomena
1	Linear	Low	1.55	0.1	Swelling, then dissolved to homogeneous solution quickly[a]
2	Linear	High	4.69	1.0	Swelling, then dissolved to homogeneous solution slowly[b]
3	Branched	High	4.25	3.0	Swelling, then dissolved slowly with some insoluble flake[c]
4	Crosslinked	High	0.47	–	Swelling[d]

Figure 8 The phenomena of each typical structure of PDMDAAC products' dissolution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

maintaining time is longer than t_2, i.e., the dissolving time of product became longer, and the insoluble gel fragments appeared and became more, neither in deionized water nor in salt solution.

It is mainly because of the increased amount of hanging double bonds' bonding, which results not only in the propagation of the linear molecular chain but also in the branched and crosslinked chain in the product. They manifested the low solubility of the product and the sharp decrease of [η] value.

The macrostructures of branched and crosslinked PDMDAAC might be as described in Figure 7.

The solubility of crosslink product

It is obvious from Figure 7 that there are many differences between the linear and the branched or crosslinked molecular structures in PDMDAAC. This may be the main reason for the difference in dissolving time in room temperature (defined as t_s) and dissolution phenomena of these products.

For further understanding, the products obtained at $T_3 = 55°C$ with the reaction time t of 0, 96, 120,

and 216 h represents the linear product PDMDAAC with low- and high-molecular weight, the branched and crosslinked products, respectively. Table IV shows the dissolution phenomena and Figure 8 shows their corresponding photographs. (a–d) indicated in Table IV are the description to Figure 8.

It was significant from Table IV and Figure 8 that the solubility of the PDMDAAC products became worse gradually or even insoluble completely after dissolving for more than 3 days, with the increased degree of branch or crosslink in product molecules.

The dissolution process of PDMDAAC might be, first, a swollen gel produced by solvent water molecules gradually diffusing into the PDMDAAC structure. Second, this gel gradually disintegrates as more solvent enters into the gel, and as molecules of solvated polymer gradually leaves the gel and are carried into the solution. A homogenous polymer solution could be formed finally in this situation for the linear molecular product even though the swelling and dissolution process might take a longer time, particularly for the product with high-molecular weight.[24] However, dissolution time might be much longer or even the swelling gel cannot be dissolved due to the product with the branch or network structures. In this situation, dissolution phenomena
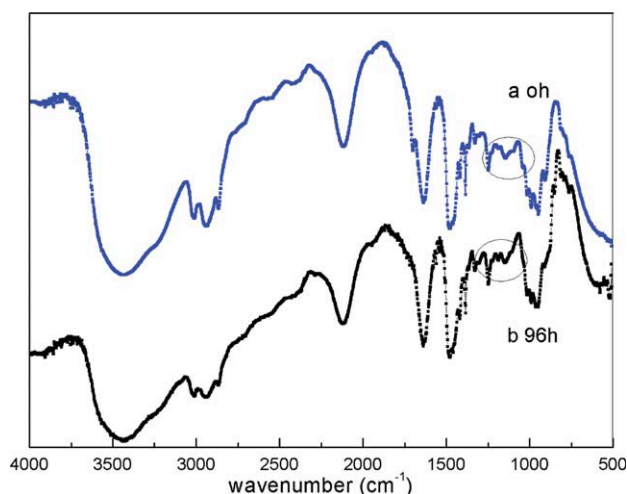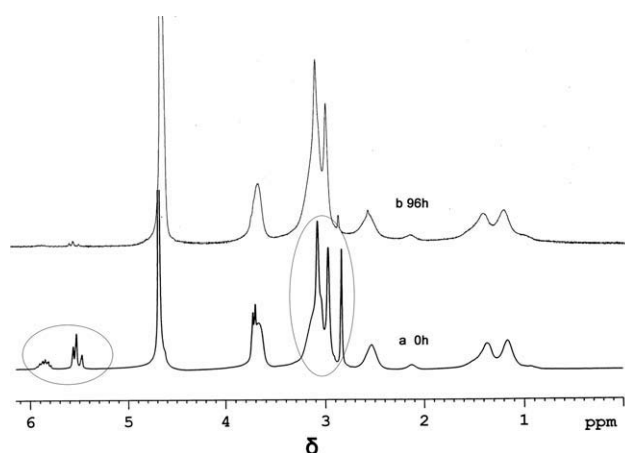

Figure 9 The FTIR spectra of PDMDAAC with different maintaining time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 10 The ^{1}H NMR spectra of PDMDAAC of different maintaining time.
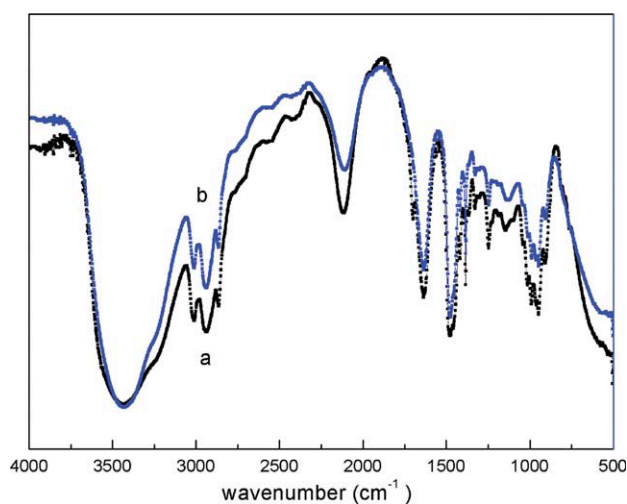
Figure 11 The FTIR spectra of crosslink (a) and linear (b) PDMDAAC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 12 The semisolid state ^{1}H NMR spectra of crosslink (a) and linear (b) PDMDAAC.

appeared as the insoluble fragments or even as the swelling flakes, which would directly influence the value of the products' intrinsic viscosity. Because the value was calculated by the eluting time of the polymer sample solution in Ubbelohde viscometer, this time would be sharp decrease after filtering off the branched and crosslinked molecules in the solution.

The difference of the product structures at T_3 for different reaction time

Based on Figure 3, the products with the reaction time t of 0 or 96 h at $T_3 = 55°C$ were selected to represent the linear PDMDAAC with low- or high-molecular weight. Figures 9 and 10 show the FTIR and ^{1}H NMR spectra of them, respectively.

The spectra of FTIR, Figure 9(a), exhibited that the characteristic absorption peaks of residual monomer in PDMDAAC ν_{C-H} 3025, 3080, 1929, 1424 cm^{-1} and δ_{C-H} 849–880 cm^{-1} were all weakened in Figure 9(b), and the spectra of ^{1}H NMR, Figure 10(a), exhibited the peaks $\delta = 5.5$ and 5.9 disappeared in Figure 9(b), which predicted that the residual monomers
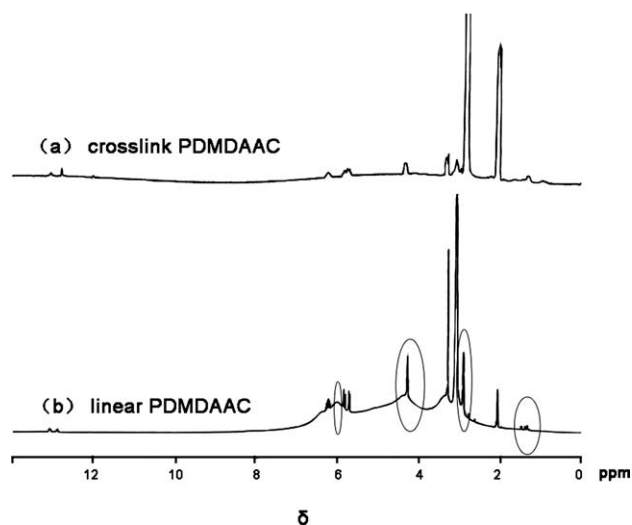
were polymerized completely, with the change of corresponding Conv. from 73.03 to 100.00%.

The product with the reaction time t of 216 h at $T_3 = 55°C$ was selected to represent the crosslinked product and characterized by the FTIR and semisolid state of ^{1}H NMR. The spectra of the crosslinked product were contrasted with that of the linear product with the reaction time t of 96 h at $T_3 = 55°C$. Figures 11 and 12 show the FTIR and semisolid state of ^{1}H NMR spectra, respectively.

No significant difference could be observed from the FTIR spectra (i.e., Fig. 11) of the linear and crosslinked PDMDAAC product, which means that the percent of crosslinking product is so low and cannot be detected by FTIR. However, the semisolid NMR spectra exhibited that the peak $\delta = 5.99$ which belonged to the hanging double bond in the spectrum of linear PDMDAAC, i.e., Figure 12(b) disappeared in the crosslinked PDMDAAC's spectrum, i.e., Figure 12(a). Selecting the peak $\delta = 5.99$ that belonged to the —CH$_3$ as the reference peak, the peaks of $\delta = 1.33$, 4.26, and 2.84 increased clearly in the spectrum of crosslinked PDMDAAC, i.e., Figure
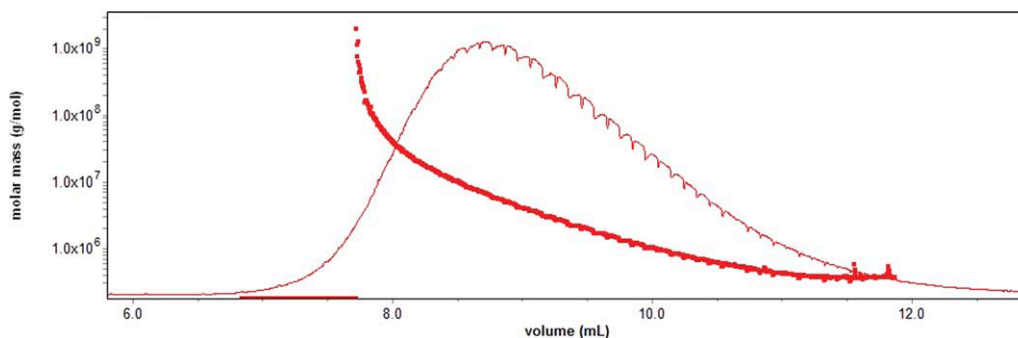

Figure 13 The chromatogram curve of PDMDAAC molecular weight versus elution volume (GPC-MALLS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
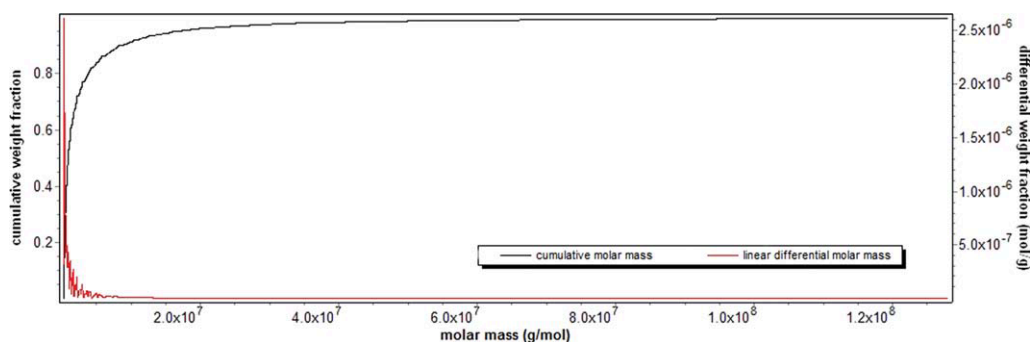
Figure 14 The molecular weight distribution of PDMDAAC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

12(a) when it was compared with the spectrum of linear product, i.e., Figure 12(b). Those peaks belonged to the —CH_2— of the main chain and branched chain, —CH— of the crosslink molecular, respectively. All of these indicated that the branched or crosslinked PDMDAAC was produced significantly by the reaction of the residual hanging or terminal double bond, when the reaction time was prolonged to 216 h.

GPS-Malls

Figures 13 and 14 show the calibration curve of molecular weight (the corresponding RI and one of the MALLS signals at 90°) and the molecular weight distribution of the linear product PDMDAAC with [η] 4.69 dL g^{-1}, respectively. The result from GPS-MALLS measurement demonstrated that, the M_w of PDMDAAC was 4.169 × 10^6, dispersion degree M_w/M_n was 5.109 and the R_g was127.7 nm.

DTA-TG

Figure 15 shows the thermal stability of linear and crosslinked PDMDAAC, and each characteristic datum was summarized in Table V. The PDMDAAC lost its weight in three stages. It should be noticed that the first stage is mainly loss contained water which reported by the literature,[15] and the other two stages loss weight are because of decomposition.

The comparison result can easily show that the characteristic datum is similar between linear and crosslinked PDMDAAC, however, the ΔH, T_s, and ΔT of linear product (3.28 kJ g^{-1}, 389.04°C, and 28.88°C, respectively) are much lower than crosslinked product (5.19 kJ g^{-1}, 395.60°C, and 35.86°C, respectively) in decomposition Stage I. It was mainly because that the crosslinking bond gave the product much more thermal stability.

CONCLUSIONS

The effects of maintaining reaction temperature T_3 and its corresponding reaction time t on the

PDMDAAC products' [η] and Conv. had been investigated. The soluble product with [η] 4.69 dL g^{-1} and Conv. 100.00% and partly soluble crosslinked product with "[η]" 0.47 dL g^{-1} and Conv. 100.00% were obtained, respectively. The [η] 4.69 dL g^{-1} of PDMDAAC was higher than the highest intrinsic viscosity value, i.e., molecular weight value reported in literatures until now, when a chemical initiation method was used. It was obviously known from the FTIR and NMR spectra of representative samples that the components and structures in the
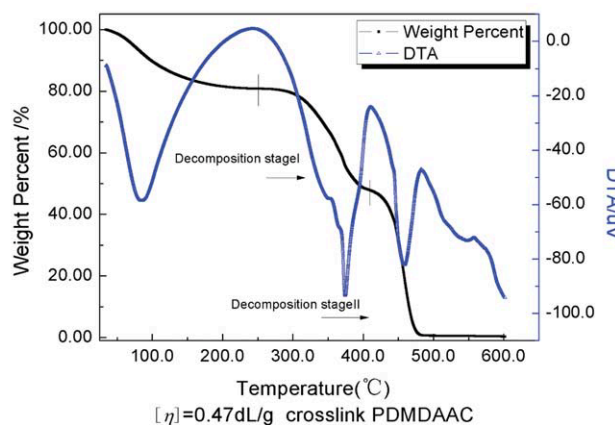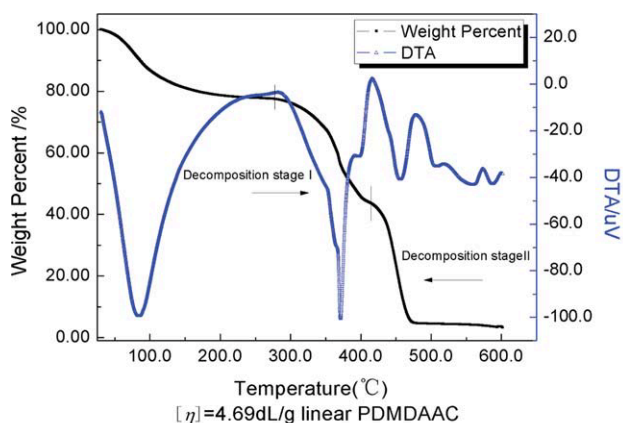

Figure 15 The TG-DTA thermography of linear and crosslink PDMDAAC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE V
Thermal Characteristic Datum of Linear and Crosslinking PDMDAAC

PDMDAAC	$[\eta]$ (dL g^{-1})	Decomposition stage I					Decomposition stage II				
		α (%)	ΔH (kJ g^{-1})	T_d (°C)	T_s (°C)	ΔT (°C)	α (%)	ΔH (kJ g^{-1})	T_d (°C)	T_s (°C)	ΔT (°C)
Linear	4.69	41.16	3.28	360.16	389.04	28.88	58.84	0.78	437.48	477.39	39.91
Crosslink	0.47	41.29	5.19	359.74	395.60	35.86	58.71	0.83	440.53	476.63	36.10

α was the lost weight percent, T_d was the onset degradation temperature, T_s was the softening temperature, and ΔT was the value that T_s misused T_d.

products PDMDAAC has significantly changed with the increase of reaction time in T_3 term. The DTA-TG thermography illustrated that PDMDAAC lost its weight in three stages and crosslinked product presented more thermal stability than linear product. These works performed above would supply a basement for researches on the forming mechanism, properties, and application of PDMDAAC with linear and crosslinked structures.

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