

# Synthesis and Characterization of New Amphoteric Graft Copolymer of Sodium Carboxymethyl Cellulose with Acrylamide and Dimethylaminoethyl Methylacrylate

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Received 15 April 1997; accepted 18 October 1997

**ABSTRACT:** The graft copolymerization of sodium carboxymethylcellulose (NaCMC) with acrylamide (AM) and dimethylaminoethyl methylacrylate (DMAEMA) was conducted in an aqueous solution using ammonium persulfate (APS) and *N,N,N',N'*-tetramethylethylene diamine (TMEDA) as the initiator. The effects of various factors on grafting, such as temperature, pH, initiator concentration, and concentrations of AM, DMAEMA, and NaCMC were studied. The composition and thermal stability of the graft copolymers were characterized by infrared, elemental, and thermogravimetric analysis, and degradation activation energy and kinetic order were calculated. The relationship between its reduced viscosity and pH in aqueous NaCl was also investigated. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 879–885, 1998

**Key words:** cellulose; graft copolymer; amphoteric

## INTRODUCTION

The graft copolymerization of cellulose and its derivatives with hydrophilic monomers has received considerable attention during the past decades as a convenient way of introducing ionizable or other polar groups into the cellulose backbone. These graft copolymers are widely applied in many industries, such as in papermaking, textiles, petroleum, washing, and environment protection. However, the cellulose graft copolymers containing cationic and anionic groups have been scarcely studied.<sup>1–4</sup> Recently, a novel graft copolymer of sodium carboxymethyl cellulose with acrylamide and dimethylammonioethyl methylacrylate (CGAD) has been prepared in our laboratory, and we found that it could be applied in drilling mud and had the properties of filtrate loss controllability and inhibit clay swelling. This article was to provide the synthesis, characterization, and thermal stability of CGAD, and the further study will focus on its application.

## EXPERIMENTAL

### Materials

Sodium carboxymethylcellulose (NaCMC, commercial grade) was purified by washing with 80% alcohol, with a degree of substitution (D.S.) of 0.738, determined by conductometric titration<sup>5</sup> and an average molecular weight ( $M$ ) of  $1.2 \times 10^5$  determined by reduced viscosity.<sup>6</sup> Ammonium persulfate (APS; analytical grade) was purified by recrystallization from water, and dimethylaminoethyl methylacrylate (DMAEMA; commercial grade) was purified by distillation under reduced pressure. Acrylamide (AM; chemical grade) and *N,N,N',N'*-tetramethyl ethylene diamine (TMEDA; biochemical grade) were used without further purification.

### Graft Copolymerization

A definite amount of NaCMC was dissolved with stirring and warming in distilled water, and inert gas ( $N_2$ ) was bubbled through. After 30 min, initi-

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ators of APS solution and TMEDA solution were added to the reaction system. After 10 min, AM and DMAEMA (being neutralized with 6M HCl) were added. Graft copolymerization was conducted at 35°C for 6 h. The resulting product was precipitated by pouring the reaction mixture solution into ethanol, filtered and washed with ethanol for several times, then dried under reduced pressure to constant weight. The graft copolymerization product was extracted with acetone-distilled water mixture 3 times to remove the homopolymers to obtain the pure graft copolymer. The grafting parameters were calculated in the following manner.

$$\% \text{ graft yield: } (G\%) = (W_2 - W_0) \times 100/W_0$$

% graft efficiency:

$$(E\%) = (W_2 - W_0) \times 100/(W_1 - W_0)$$

% monomer graft conversion:

$$(C\%) = (W_2 - W_0) \times 100/W_3$$

where  $W_0$ ,  $W_1$ ,  $W_2$ , and  $W_3$  denote the weight of NaCMC, weight of graft copolymerization product, weight of graft copolymer, and weight of total monomers, respectively.

### Characterization

1. The infrared (IR) spectra of the graft copolymers were recorded with a NICOLET FT-20SX spectrophotometer KBr disk.
2. The composition analysis of the graft copolymer was determined by IR and elemental analysis.
3. The intrinsic viscosities of the graft copoly-

mers in NaCl solution of different concentrations were determined at 30°C by an Ubbelohde viscometer.

4. The thermal stability of the graft copolymer was determined by thermogravimetric analysis (TGA).

## RESULTS AND DISCUSSION

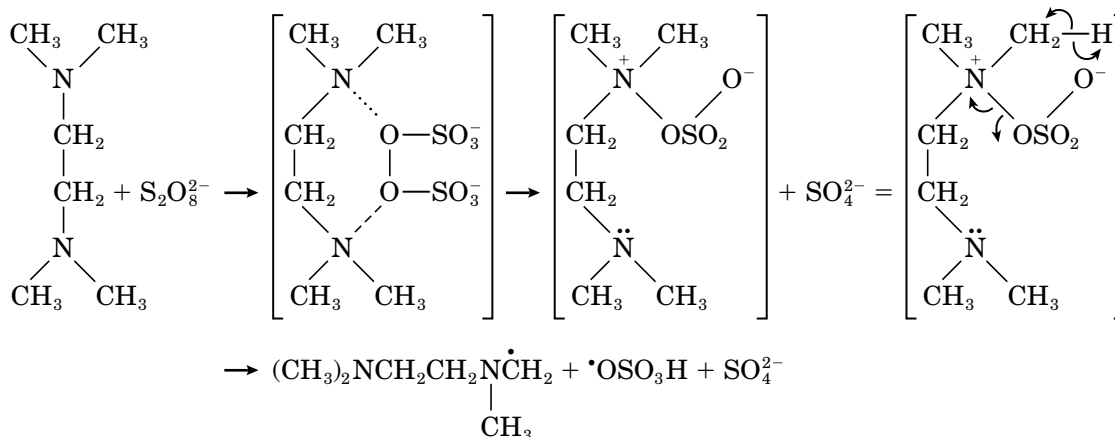
### Effect of Reaction Conditions on Grafting

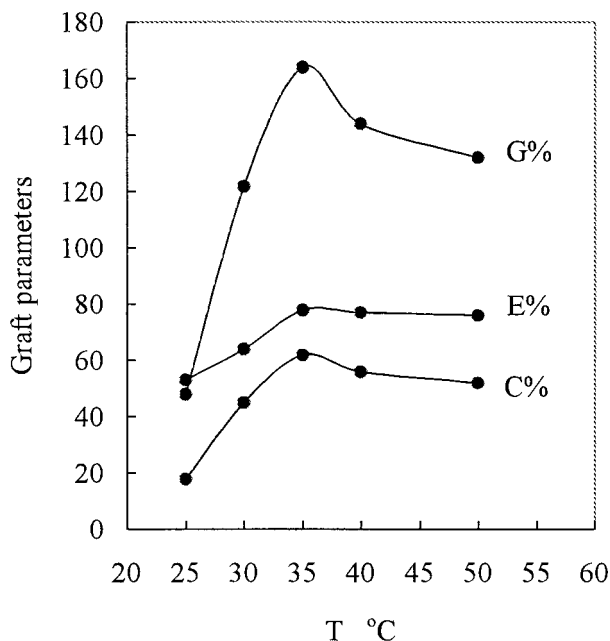
#### Reaction Temperature

Figure 1 presents the relationship between the reaction temperature and the grafting. At the temperature range of 35–45°C, maximum graft yield ( $G\%$ ), graft efficiency ( $E\%$ ), and monomer graft conversion ( $C\%$ ) were achievable. Both lower and higher temperatures than 35–45°C were unfavorable. At lower temperatures, the decomposing rate of the initiators was lower; and, at higher temperatures, the termination rate of polymerization was higher, both resulting in a decrease of the initiation efficiency or in a decrease of the values of  $W_1$  and  $W_2$ . As  $E\%$  depended on  $W_1$  (as a denominator) and  $W_2$  (as a numerator),  $E\%$  varied with temperature, less distinct than  $G\%$  and  $C\%$ , as shown in Figure 1.

#### Concentration of APS and TMEDA

Figures 2 and 3 show effects of APS and TMEDA concentrations on grafting. It is interesting to find that  $G\%$  and  $C\%$  attain maxima at the same concentration, that is,  $[APS] = 4.4 \times 10^{-3}M$  and  $[TMEDA] = 4.5 \times 10^{-3}M$ . This might be because APS and TMEDA could better form 1 : 1 complex of charge transfer and then produce easier more free radicals, leading to high efficiency of initiation, as illustrated in the following manner.<sup>7</sup>





**Figure 1** The effect of temperature on grafting. Conditions are as follows: [CMC] = 2g/dL; [AM] = 0.5M; [DMAEMA] = 0.1M; [APS] =  $4.4 \times 10^{-3}$ M; [TMEDA] =  $4.5 \times 10^{-3}$ M; pH 6; 6 h.

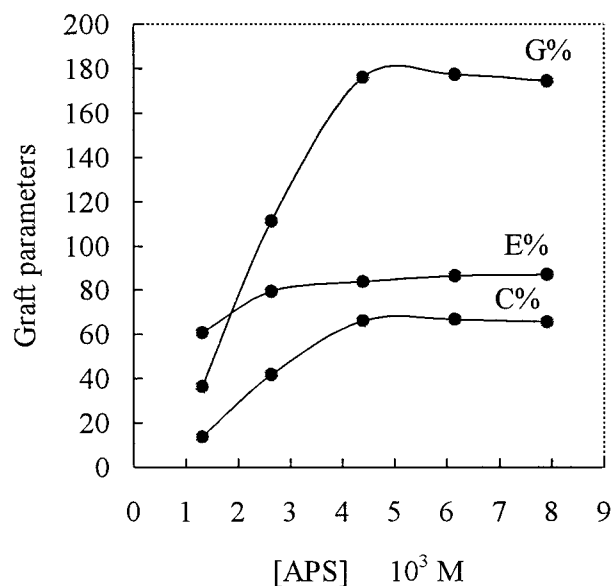
The variation of  $E\%$  was much milder due to its dependence on  $W_1$  and  $W_2$ , as mentioned above.

### pH

Figure 4 shows the influence of pH. At the range of pH 6–7, graft yield, graft efficiency, and monomer graft conversion attained maxima. This might be because, at lower pH, TMEDA was changed into a salt state and couldn't form a complex of charge transfer with APS, while at a higher pH, the initiator decomposed fast to result in an increase of the termination rate.

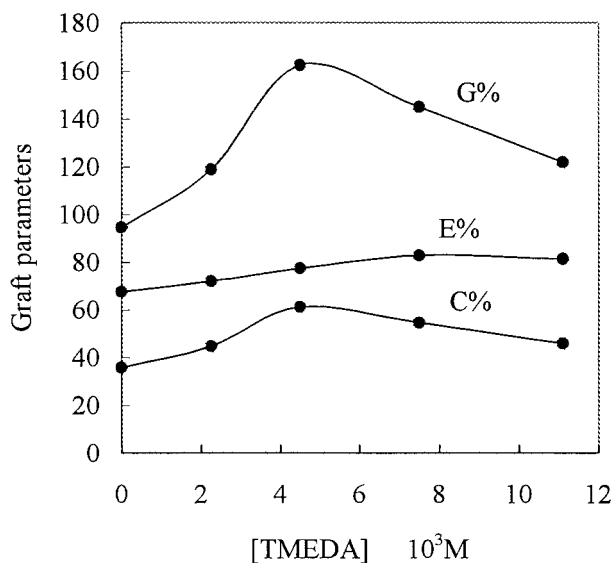
### Concentrations of NaCMC, AM, and DMAEMA in Feed

Table I illustrates the effect of concentration of NaCMC, AM, and DMAEMA on grafting. With an increase in the monomer AM or DMAEMA concentrations,  $C\%$  and  $G\%$  increased, indicating that more monomers were favorable for graft copolymerization. But, on the other hand, more polymerization product of the monomers (including homopolymers and copolymers) would form at high concentrations of AM and DMAEMA, so that  $E\%$  increased much slower and even appeared somewhat fluctuate. With an increasing NaCMC concentration,  $C\%$  and  $E\%$  increased, while  $G\%$  obviously dropped down. This showed that al-

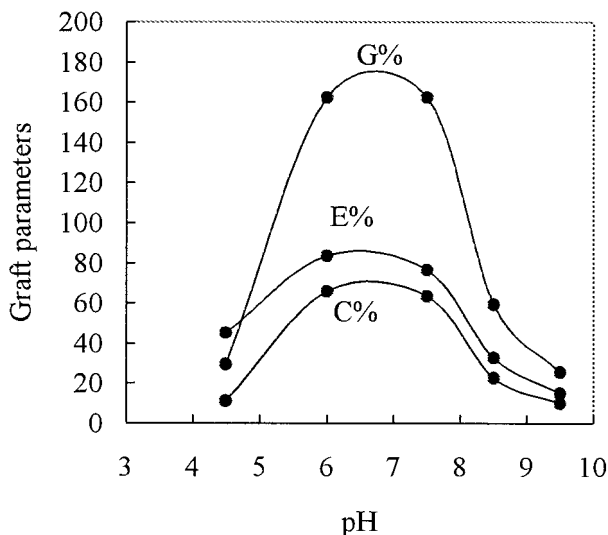


**Figure 2** The effect of [APS] on grafting. Conditions are as follows: [CMC] = 2g/dL; [AM] = 0.5M; [DMAEMA] = 0.1M; [TMEDA] =  $4.5 \times 10^{-3}$ M; pH 6; 35°C; 6 h.

though more NaCMC provided more chance for grafting, the utilization ratio of NaCMC (or graft yield) became smaller, as not enough AM as DMAEMA reacted with NaCMC. Therefore, it is important to control the concentrations of NaCMC, AM, and DMAEMA to get the best graft polymerization. According to the results listed in Table I,



**Figure 3** The effect of [TMEDA] on grafting. Conditions are as follows: [CMC] = 2g/dL; [AM] = 0.5M; [DMAEMA] = 0.1M; [APS] =  $4.4 \times 10^{-3}$ M; pH 6; 35°C; 6 h.



**Figure 4** The effect of pH on grafting. Conditions are as follows: [CMC] = 2g/dL; [AM] = 0.5M; [DMAEMA] = 0.1M; [APS] =  $4.4 \times 10^{-3}$ M; [TMEDA] =  $4.5 \times 10^{-3}$ M; pH 6; 35°C; 6 h.

the conditions for sample No. 6 may be the best one for the synthesis of the new amphoteric graft copolymer of NaCMC-AM-DMAEMA.

#### Proof of Grafting

The IR spectrum of the graft copolymer showed not only the characteristic absorption bands of NaCMC but also the characteristic bands of  $-\text{CONH}_2$  ( $1650 \text{ cm}^{-1}$ ) and  $-\text{NH}^+$  ( $2740 \text{ cm}^{-1}$ ), indicating that the graft copolymer contained the chain structure of AM and DMAEMA.

#### Composition Analysis of the Graft Copolymers

The composition of the graft copolymers was determined by IR and elemental analysis, as follows.

According to Beer's law and the results of elemental analysis, eqs. (1), (2), and (3) can be established.

$$A_{1650} = k_1 b C_{\text{AM}} = k_1 b W_{\text{AM}} / M_{\text{AM}} \quad (1)$$

$$A_{2740} = k_2 b C_{\text{DM}} = k_2 b W_{\text{DM}} / M_{\text{DM}} \quad (2)$$

$$W_{\text{AM}} / M_{\text{AM}} + W_{\text{DM}} / M_{\text{DM}} = N\% / 14 \quad (3)$$

where  $A_{1650}$  is the absorbance of characteristic band of  $-\text{CONH}_2$  in AM,  $A_{2740}$  is the absorbance of characteristic band of  $\text{N}^+\text{H}$  in DMAEMA,  $W_{\text{AM}}$  and  $W_{\text{DM}}$  are the percents of AM and DMAEMA in the graft copolymer, respectively, and  $M_{\text{AM}}$  and  $M_{\text{DM}}$  are the molecular weights of AM and DMAEMA.  $k_1$ ,  $k_2$ , and  $b$  are constants.

Then,  $W_{\text{AM}}$  and  $W_{\text{DM}}$  can be calculated by eqs. (4) and (5), as follows:

$$W_{\text{AM}} = M_{\text{AM}} B N\% / 14(B + 1) \quad (4)$$

$$W_{\text{DM}} = M_{\text{DM}} N\% / 14(B + 1) \quad (5)$$

where  $B = k_2 A_{1650} / k_1 A_{2740}$ ,  $k_2 / k_1$  can be obtained from the copolymer of AM with DMAEMA by IR and elemental analysis. The results were listed in Table II.

#### Dependence of Viscosity of the Graft Copolymer on pH in NaCl Solution

The reduced viscosity of graft copolymers, which were dissolved in 0.6M NaCl at different pH, is shown in Figure 5. All curves show minima indicating that all samples have the isoelectric points. At the isoelectric point, the positive charge ascribable to DMAEMA and negative charge ascribable

**Table I** Effects of Concentrations of NaCMC, AM, and DMAEMA on Grafting

No.	NaCMC (g/dL)	AM (M)	DMAEMA (M)	C%	G%	E%
1	1	0.5	0.1	33.6	179	61.7
2	2	0.5	0.1	61.2	162	77.3
3	3	0.5	0.1	78.2	137	85.4
4	4	0.5	0.1	73.6	86	87.2
5	2	0.3	0.1	18.0	37.0	61.7
6	2	0.6	0.1	85.1	256	89.8
7	2	0.7	0.1	87.6	321	83.4
8	2	0.6	0.025	59.1	135	69.6
9	2	0.6	0.05	68.3	174	78.2
10	2	0.6	0.2	88.3	313	79.2

Reaction conditions: [APS] =  $4.4 \times 10^{-3}$ M; [TMEDA] =  $4.5 \times 10^{-3}$ M; pH = 6; 6 h, 35°C.

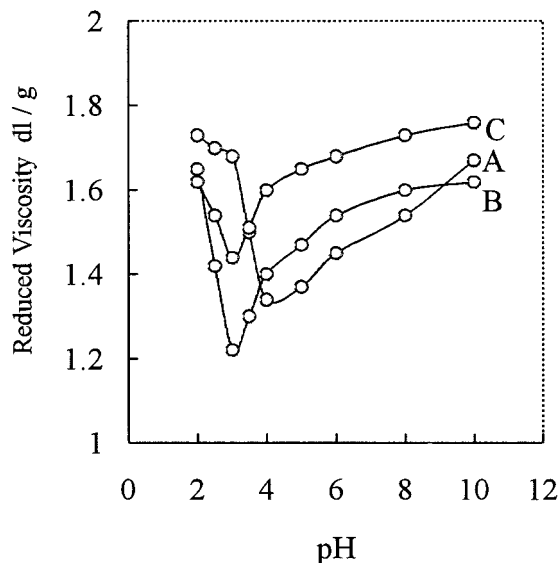
**Table II** The Compositions of the Graft Copolymers Obtained by IR and Elemental Analysis

No.	C	H	N	$A_{1650}/A_{2740}$	$B$	$W_{AM}\%$	$W_{DM}\%$	$W_{CMC}\%$
PAD	47.55	7.65	14.90	5.88		68.4	31.6	0
6	46.53	7.19	12.27	8.90	5.33	53.6	22.15	24.25
8	44.67	6.69	13.48	31.0	18.26	58.77	8.84	32.46
9	45.57	6.87	11.97	18.0	10.78	55.7	17.54	26.76
10	47.11	7.67	9.91	5.10	3.05	37.89	33.83	28.28

PAD is the copolymer of AM with DMAEMA; Nos. 6, 8, 9, and 10 were the samples listed in Table I.

to CMC become almost equal along a polymer chain leading to the coiling structure of the polymer chain, thus resulting in the minimum viscosity of the polymer solution. At a pH lower or higher than the isoelectric point, the viscosity of the solution becomes larger due to the presence of net charge (or the electrostatic repulsion) in the polymer chain, making the chain adopt an extended structure.

The plots of reduced viscosity versus pH for the graft copolymer (Table I, No. 6) dissolved in different concentrations of NaCl solution are shown in Figure 6. The addition of NaCl doesn't change the isoelectric point, but the reduced viscosity of the polymer solution increases with increasing NaCl concentration. This is because the intramolecular ionic attraction in the polymer chain can be suppressed at higher ionic strength.



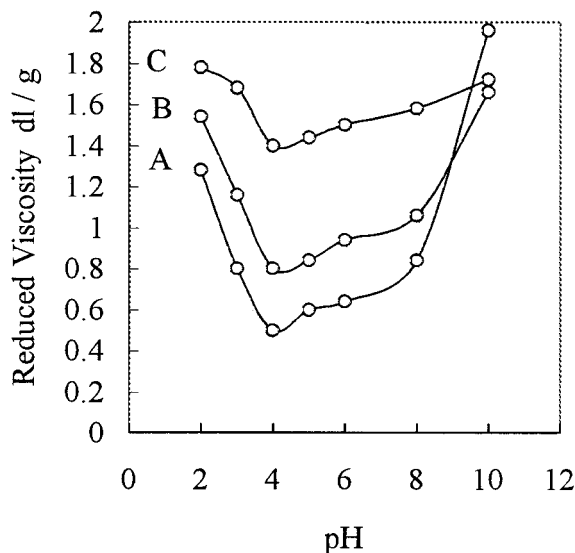
**Figure 5** Reduced viscosities of 0.1 g/dL of the graft copolymers in 0.6M NaCl solution in different pH conditions: (A) Table I, No. 6; (B) Table I, No. 9; (C) Table I, No. 8.

### Thermal Stability of Graft Copolymer

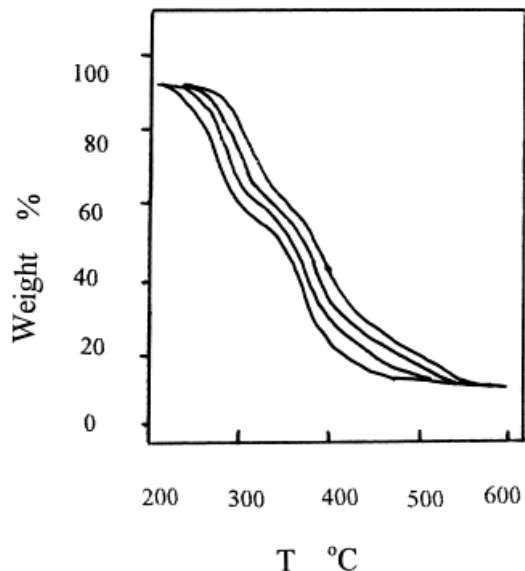
The TGA curves for the thermal degradation of a 5-mg graft copolymer (Table I, No. 6) are shown in Figure 7 at various heating rates in nitrogen atmosphere. The thermal degradation occurs in two stages. The first stage refers to degradation of the NaCMC main chain<sup>8</sup> and the ester of DMAEMA chain, and the second stage to the further degradation of the graft chain. It can be seen that the temperatures of the start of intense degradation ( $T_{start}$ ), the maximum peak at the first stage ( $T_{m1}$ ) and at the second stage ( $T_{m2}$ ), and 50% weight loss ( $T_{50\%}$ ) increase with an increase in the heating rate (see Table III).

The activation energy for a given weight fraction ( $W\%$ ) and the kinetic order of the degradation can be determined by the following equations by Ozawa's method<sup>9</sup>:

$$\text{Log } B + 0.457E/RT = K \quad (6)$$



**Figure 6** Reduced viscosities of 0.1 g/dL of the graft copolymer solution in different pH conditions: (A) 0.1M NaCl; (B) 0.3M NaCl; (C) 0.6M NaCl.



**Figure 7** The TGA curves of CGAD at various heating rates. TGA from left to right: 5, 10, 20, and 40°C/min.

$$\text{Log} |(1 - C)^{1-n} - 1| = \text{Log } B \quad (n \neq 1) \quad (7)$$

$$\text{Log} |\text{Ln}(1 - C)| = \text{Log } B \quad (n = 1) \quad (8)$$

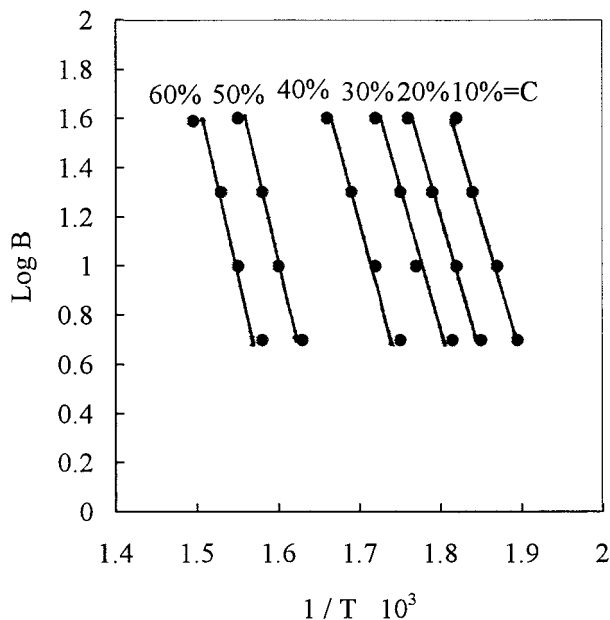
$$C = 1 - W/W_0 \quad (9)$$

where  $B$  is the heating rate,  $T$  is the temperature,  $K$  is a constant,  $E$  is the activation energy,  $R$  is the ideal gas constant,  $n$  is the reaction order, and  $W_0$  and  $W$  represent the initial weight and weight at any time. From the data of Figure 7, it is easy to obtain the heating rate  $B$  at any temperature  $T$ . Then, according to eq. (6), the activation energy of degradation can be found by plotting  $\text{Log } B$  against  $1/T$ , as shown in Figure 8. From Figure 8, the activation energies have been determined; that is,  $E_1 = 99.7 \text{ kJ/mol}$  (the first stage) and  $E_2 = 124.7 \text{ kJ/mol}$  (the second stage).

The logarithm of  $\text{Ln}(1 - C)$  plotted against the logarithm of heating rate ( $B$ ) in a nitrogen atmosphere is shown in Figure 9. The good linear

**Table III Heat Stability of the Graft Copolymer at Various Heating Rates in Nitrogen**

Heating Rate (°C/min)	$T_{\text{start}}$ (°C)	$T_{m1}$ (°C)	$T_{m2}$ (°C)	$T_{50\%}$ (°C)
5	246	282	362	374
10	262	289	365	378
20	267	296	393	385
40	269	309	415	393

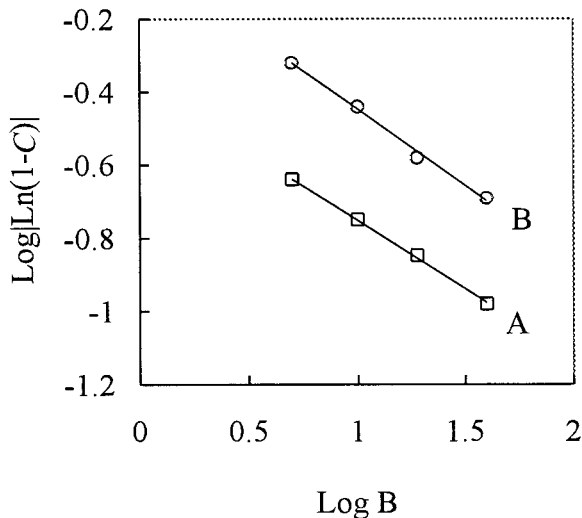


**Figure 8** The plots of logarithms of heating rate  $B$  versus  $1/T$  in nitrogen atmosphere.

relationship obtained means that the kinetic order is 1 for the thermal degradation of CGAD.

### CONCLUSIONS

The graft copolymer of sodium carboxymethylcellulose with AM and DMAEMA was synthesised by using APS-TMEDA as the initiator and was ascertained by IR. The effects of various factors



**Figure 9** The relationship between  $\text{Log} |\text{Ln}(1 - C)|$  and  $\text{Log } B$  obtained by Ozawa's method for  $n = 1$  in a nitrogen atmosphere: (A) 270°C; (B) 290°C.

on the graft copolymerization were studied in detail. Its composition was calculated by IR and elemental analysis.

The reduced viscosity of the graft copolymer in aqueous NaCl attains its minimum at the isoelectric point, and the minimum value of the reduced viscosity is increased by the addition of NaCl because the intramolecular ionic attraction of graft copolymer chain is suppressed at a high ionic strength.

Thermal degradation of the graft copolymer shows that the degradation has 2 stages, and their activation energies have been found, as follows:  $E_1 = 99.7$  kJ/mol and  $E_2 = 124.7$  kJ/mol. The kinetic order of degradation is 1.

This work was supported by Laboratory of Cellulose and Lignocellulosis Chemistry, Academia Sinica, and by Guang dong Provincial Natural Science Foundation.

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