Water-Soluble Copolymers. III. Two-Step Terpolymerization of Acrylamide, Acrylic Acid, and Acryloyloxyethyl Trimethylammonium Chloride

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ABSTRACT: Terpolymerization of acrylamide (AM), acrylic acid (AA), and acryloyloxyethyl trimethylammonium chloride (DAC) was studied in aqueous solution by a two-step polymerization method, consisting of adiabatic polymerization until reaching a maximum temperature and following retaining temperature for maturation. A redox agent:promotor triad-initiating system was employed as an initiator. The effects of various parameters on terpolymerization were investigated. The optimum values were obtained at the DAC:AA molar feed ratio and the total monomer concentration, at the oxidant:reductant ratio and total redox agent concentration, and at the promotor concentration and redox agent:promoter ratio. The structure of the terpolymer was identified by Fourier transform infrared (FTIR) and ^{13}C NMR spectroscopy. And the terpolymer composition was agreed favorably with feed ratio. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3278–3284, 2007

Key words: acrylamide; acrylic acid; acryloyloxyethyl trimethylammonium chloride; terpolymerization

INTRODUCTION

Adiabatic calorimetric method is an important research approach of polymerization kinetics. Polyamide was first used to study on polymerization kinetics at 1965.[1] This method is of increasing interest for a wide variety of polymer production processes.[2–11] Kurenkov et al.[12] reported the adiabatic polymerization of acrylamide in concentrated aqueous solution in the presence of hydrolyzing agent. Kinetic orders with respect to the components of the reaction system were found. Pross et al.[13] measured inverse emulsion polymerization kinetic data of acrylamide by adiabatic as well as by isothermal calorimetry. Experimented results show a positive influence of the emulsifier concentration on the reaction rate and indicate the dominance of a bimolecular termination reaction with respect to the polymer radicals above a certain initiator concentration. Du et al.[14] reported the room temperature-initiated, self-heating copolymerization of acrylonitrile with vinyl acetate. Optimum values for the parameters were identified for both bulk and concentrated emulsion polymerization. However, the low heat of the reaction of vinyl acetate limits its amount in the system; the self-heating polymerization of room temperature initiation is suitable only when the acrylonitrile-to-vinyl acetate weight ratio is $\geq 7 : 3$. Du and coworkers[15] also studied high-rate polymerization of both acrylonitrile and butyl acrylate based on a concentrated emulsion. The initial polymerization was carried out adiabatically with self-heating until a temperature of about 70°C, and then followed by additional heating in a water bath at a higher temperature, up to a total polymerization time of 30 min. The conversion thus achieved was higher than that obtained via the adiabatic process alone.

Although extensive research has been conducted on ordinary polymer, very few studied have keen conducted on ampholytic polymers,[16–19] particularly about adiabatic copolymerization of amphoteric polyacrylamide. In the literature, the terpolymerizaton of acrylamide, acrylic acid, and acryloyloxyethyl trimethylammonium chloride was studied in aqueous solution by a two-step polymerization method, consisting of adiabatic polymerization until reaching a maximum temperature and following retaining temperature for maturation.

EXPERIMENTAL

Materials

Acrylamide (AM), obtained from SNF Flocculant (Taixing, China) was recrystallization from acetone. Technical-grade acryloyloxyethyl trimethylammonium chloride (DAC) monomer from Elf Atochem SA (Cedex, France) was used without further purification.

Acrylic acid (AA) monomer, obtained from Tianjin Chemical Reagent Co. (Tianjin, China) was used as supplied. 2,2'-azobis(2-amidinopropen)-dihydrochloride (AIBA) from Shanghai Hengyi Chemical Co. (Shanghai, China) was used as received without further purification. Potassium persulfate ($K_2S_2O_8$) and sodium bisulfite ($NaHSO_3$) from Guangzhou Chemical Manufacturer (Guangzhou, China) were used without further purification. The water was deionized water. Other reagents were GR grade and were used as received.

Adiabatic terpolymerization and retaining temperature for maturation

Three kinds of monomer solutions containing different concentrations of AM, AA, and DAC were first placed in a 500-mL flask provided with a magnetic stirrer. An aqueous solution of AIBA was then added. The system was purged with nitrogen for 15 min. The flask was sealed with a rubber septum and insulated, at room temperature. Subsequently, aqueous solutions of $K_2S_2O_8$ and $NaHSO_3$ were introduced with stirring, using syringes, respectively. A thermometer that penetrated the rubber septum to the center of the concentrated solution was employed to measure the temperature. As soon as the adiabatic terpolymerization system became a viscous solution, the stirring could no longer be continued. Whenever the system attained a maximum temperature, external heating in a water bath was provided for maturation of keeping temperature. The polymerization was conducted for 4 h; the gelatinous product was taken out from the flask, cut up, and dried. The weight ratio of the product to the total monomers before polymerization was taken as the monomer conversion.

Viscosity measurements

The intrinsic viscosity [η] of the polymer was used as a measure of the molecular weight. Polymer stock solution were made by dissolving amounts of polymer in $1.0M$ $NaNO_3$ solution. The solution were then diluted to 0.02 wt % by $1.0M$ $NaNO_3$ solution. Intrinsic viscosities of polymers were determined in a $1.0M$ $NaNO_3$ solution using an Ubbelodhe viscometer at 30°C. The intrinsic viscosities were evaluated using the combined method of the Huggins and Kramer equations (1) and (2), respectively:

$$\eta_{red} = [\eta] + k_1[\eta]^2 c \qquad (1)$$

$$\ln(\eta_{rel})/c = [\eta] + k_2[\eta]^2 c, \qquad (2)$$

where c is the mass concentration of the polymer, η_{red} is the reduced viscosity, η_{rel} is the relative viscosity, k_1 is the Huggins coefficient, and k_2 is the Kramer coefficient.

Characterization of terpolymer structure

The polymers were redissolved into deionized water and were further purified by precipitation in acetone, followed by vacuum drying for 2 days at room temperature. The Fourier transform infrared (FTIR) spectrum of the terpolymer sample was recorded on a Nicolet MAGNA-IR 760 FTIR spectrometer. The sample film was prepared using a KBr disc. The ^{13}C NMR spectrum of the terpolymer sample was obtained on a Bruker DRX-400 NMR spectrometer using 10–15 wt % aqueous (D_2O) polymer solution with DSS as a reference.

RESULTS AND DISCUSSION

The terpolymerization curves include two steps or three stages. In the adiabatic step, the temperature of the system increases first moderately, subsequently increases sharply for $\sim 40°C$, and then passes through a maximum. Finally, in the maturation step, the systemic temperature was kept via the addition heating from a water bath thermostat which compensated some heat losses. As the reaction was exothermic and the reactor (flask) was insulated, the temperature was retained until high conversion of the last reaction stage, so the temperature–time curve is actually a description of the polymerization kinetics.[20]

Effect of DAC:AA molar feed ratio

Table I shows that the incorporation of the comonomer DAC hindered the terpolymerization, reducing the 4-h conversions. The polymers produced at AA feed composition > 30 mol % were water-insoluble, which could be due to the imidization.[12] Figure 1 shows that the maximum temperature decreased with increasing DAC feed content. This occurred because the polymerization of both AA and AM was much more exothermic than that of DAC. Table I also shows that the polymeric intrinsic viscosity reached a maximum value at DAC feed composition = 30–50 mol %. When the DAC:AA molar feed ratio was lower than 4 : 1, the temperature of the system increased more fast (Fig. 1), which was due to the increased concentration of AM of the high reaction heat monomer in total monomer concentration, so the polymeric intrinsic viscosity decreased accordingly. However, at a higher DAC:AA molar feed ratio, the room initiated terpolymerization could hardly be employed, resulting in decreasing the polymeric intrinsic viscosity.
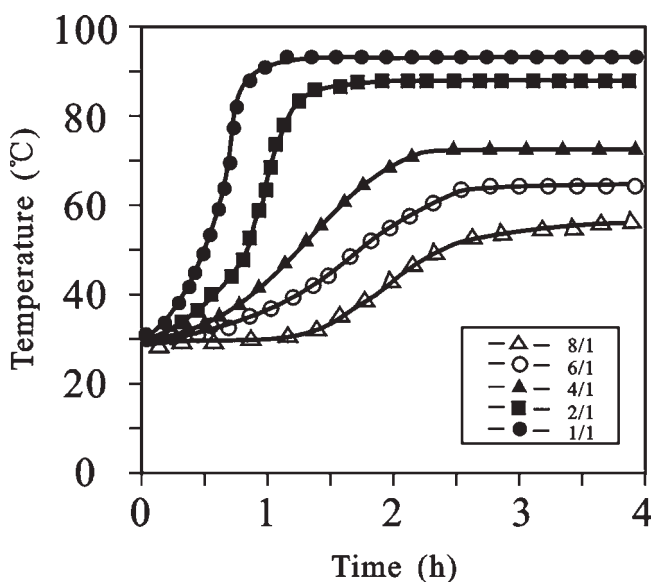
Effect of the monomer concentration

The effects of the monomer concentration are studied in Table II and Figure 2. Table II indicates that the 4-h conversion increased with increasing monomer con-

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TABLE I
Effect of AA Feed Composition and DAC:AA Molar Feed Ratio on Terpolymerization*

AA feed composition (mol %)	Molar feed ratio DAC:AA	4-h conversion (wt %)	Intrinsic viscosity (dL/g)
10	1 : 1	96	15.6
	2 : 1	93	17.9
	4 : 1	92	21.5
	6 : 1	87	19.7
	8 : 1	71	10.4
20	1 : 2	94	9.9
	2 : 2	91	16.4
	3 : 2	92	19.5
	5 : 2	77	20.7
	7 : 2	70	13.8
30	1 : 3	92	15.7
	2 : 3	93	17.6
	3 : 3	89	19.6
	4 : 3	76	14.2
	6 : 3	65	10.3

* Polymerization conditions: total monomer concentration = 2.5M; total redox initiator concentration = 4.5 $\times$ 10^{-4}M; AIBA = 2.7 $\times$ 10^{-3}M; K$_2$S$_2$O$_8$:NaHSO$_3$ molar ratio = 2 : 1.

centration. This was in line with the basic law for solution polymerization. Table II also shows that the intrinsic viscosity of the terpolymer increased, while the monomer concentration increased. However, the increase in the monomer concentration caused the temperature of the system to increase sharply until the maximum temperature was attained(Fig. 2); the higher the monomer concentration, the more conspic-

TABLE II
Effect of the Monomer Concentration on Terpolymerization*

Monomer conc (M)	4-h conversion (wt %)	Intrinsic viscosity (dL/g)
1.5	80	13.9
2.0	87	17.3
2.5	92	21.5
3.0	95	21.8
3.5	97	18.3

* Polymerization conditions: AA feed composition = 10 mol %; DAC:AA molar feed ratio = 4 : 1; AIBA = 2.7 $\times$ 10^{-3}M; total redox initiator concentration = 4.5 $\times$ 10^{-4}M; K$_2$S$_2$O$_8$:NaHSO$_3$ molar ratio = 2 : 1.

uous the effect, so the temperature dependence of the termination and chain transfer reactions was larger than that of the propagation reaction, which decreased the intrinsic viscosity of the terpolymer.

Effect of oxidant:reductant molar ratio

The effect of the oxidant (K$_2$S$_2$O$_8$):reductant (NaHSO$_3$) molar ratio is investigated in Table III and Figure 3. Table III indicates that there was an optimum oxidant: reductant molar ratio between 1 : 1–2 : 1. The 4-h conversion and the polymeric intrinsic viscosity decreased when the oxidant:reductant molar ratios were higher or lower than that. A probable interpretation was that when the proportion of reductant was low, not enough free radical could be produced to initiate the polymerization reaction, but if the amount of reductant was too

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Figure 1 Temperature–time plots for two-step heating systems of various DAC:AA molar feed ratio. Composition: AA, 10 mol %; DAC:AA (mol/mol): (1) 1 : 1, (2) 2 : 1, (3) 4 : 1, (4) 6 : 1, (5) 8 : 1. The other polymerization condition were as for Table I.
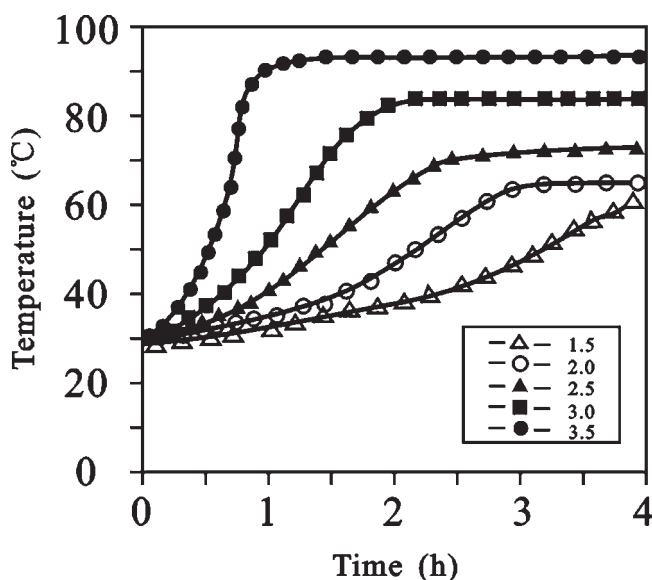
Figure 2 Temperature–time plots for two-step heating systems of various monomer concentration. The polymerization conditions were as for Table II.

TABLE III
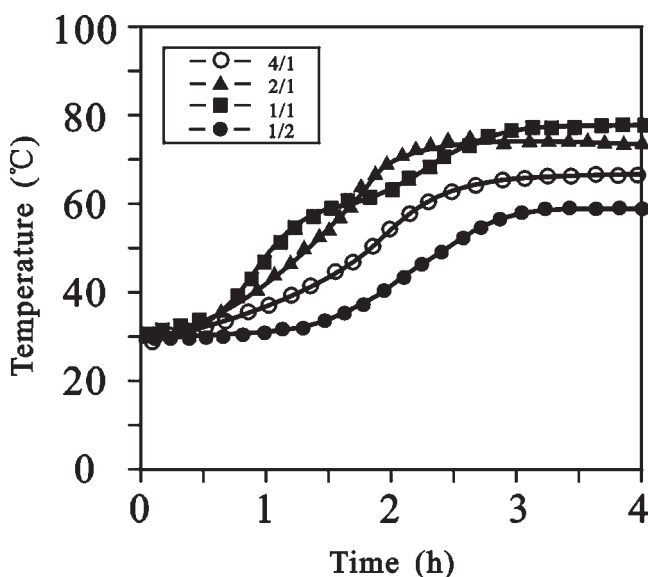#### Effect of Oxidant:Reductant Molar Ratio on Terpolymerization*

Oxidant:reductant molar ratio	4-h conversion (wt %)	Intrinsic viscosity (dL/g)
1 : 2	80	14.1
1 : 1	91	18.7
2 : 1	92	21.5
4 : 1	85	16.9

* Polymerization conditions: total monomer concentration = 2.5M; AA feed composition = 10 mol %; DAC:AA molar feed ratio = 4 : 1; AIBA = 2.7 × 10^{-3}M; total redox initiator concentration = 4.5 × 10^{-4}M.

large, the excess reductant would cause radical deactivation, decreasing the polymerization rate.

Effect of the redox initiator concentration

The effect of the redox initiator concentration on the 4-h conversion and the polymeric intrinsic viscosity is presented in Table IV and Figure 4. Table IV shows that the 4-h conversion increased with increasing the redox initiator concentration when the DAC:AA molar feed ratio was fixed. However, when the amount became greater than 4.5 × 10^{-4}M, the increase of the 4-h conversion became moderately. Additional information could be obtained by the temperature–time curves of Figure 4. Figure 4 indicates the increase in the maximum temperature with increasing redox concentration. Nevertheless, after the redox initiator concentration of ≥ 4.5 × 10^{-4}M, the maximum temperatures were almost the same, but the times at which they were reached were 1.0 h

TABLE IV
Effect of the Redox Initiator Concentration on Terpolymerization*

Total redox initiator conc (×10^{-4}M)	Molar feed ratio DAC:AA	4-h conversion (wt %)	Intrinsic viscosity (dL/g)
1.0	4 : 1	74	12.1
	6 : 1	71	11.9
2.0	1 : 1	89	—
	2 : 1	84	—
	4 : 1	81	15.5
	6 : 1	78	14.8
	8 : 1	59	—
4.5	1 : 1	96	—
	2 : 1	93	—
	4 : 1	92	21.5
	6 : 1	84	19.7
	8 : 1	71	—
7.0	1 : 1	97	—
	2 : 1	94	—
	4 : 1	93	17.2
	6 : 1	86	16.5
	8 : 1	73	—
10.0	4 : 1	94	15.3
	6 : 1	88	11.4

* Polymerization conditions: total monomer concentration = 2.5M; AA feed composition = 10 mol %; AIBA = 2.7 × 10^{-3}M; K$_2$S$_2$O$_8$:NaHSO$_3$ molar ratio = 2 : 1.

(curve -●-), 1.5 h (curve -■-), and 2.5 h (curve -▲-), respectively. This shows that a value near 4.5 × 10^{-4}M made up the optimum concentration. These experiments found that when an excess of redox initiator concentration was present, the reductant would react with and deactivate the radical.
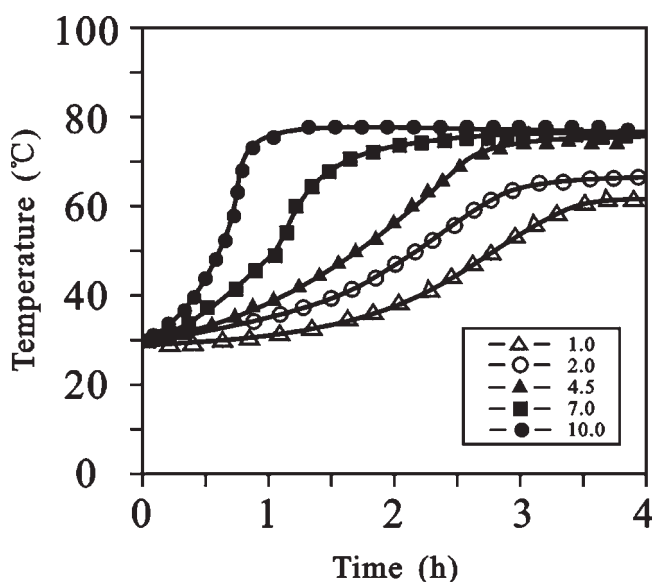

Figure 3 Temperature–time plots for two-step heating systems of various oxidant:reductant molar ratio (mol/mol). The polymerization conditions were as for Table III.

Figure 4 Temperature–time plots for two-step heating systems of various total redox initiator concentration. DAC:AA molar feed ratio = 4 : 1. The other polymerization conditions were as for Table IV.

TABLE V
Effect of Promotor Concentration on Terpolymerization*

Promotor conc ($\times 10^{-3}M$)	Redox agent: promotor molar ratio	DAC:AA molar feed ratio	4-h conversion (wt %)	Intrinsic viscosity (dL/g)
0.68	1 : 1.5	4 : 1	75	12.9
		6 : 1	61	9.8
1.35	1 : 3	1 : 1	91	12.4
		2 : 1	89	14.3
		4 : 1	87	16.7
		6 : 1	79	15.3
		8 : 1	63	9.1
2.70	1 : 6	1 : 1	95	15.6
		2 : 1	93	17.9
		4 : 1	92	21.5
		6 : 1	87	19.7
		8 : 1	71	10.4
4.05	1 : 9	1 : 1	97	13.9
		2 : 1	94	14.3
		4 : 1	93	18.6
		6 : 1	92	20.6
		8 : 1	86	14.5
6.80	1 : 15	4 : 1	95	16.2
		6 : 1	94	18.9
		8 : 1	89	14.1

* Polymerization conditions: total monomer concentration = $2.5M$; AA feed composition = 10 mol %; total redox initiator concentration = $4.5 \times 10^{-4}M$; $K_2S_2O_8$:NaHSO$_3$ molar ratio = 2 : 1.

Effect of the promotor concentration

The effect of the promotor (AIBA) concentration was investigated for the fixed redox initiator concentration = $4.5 \times 10^{-4}M$ and $K_2S_2O_8$:NaHSO$_3$ molar ratio = 2 : 1. The results were presented in Table V and Figure 5. Table V shows that the 4-h conversion increased with both the decrease of DAC:AA molar feed ratio and the increase of promotor concentration. Nevertheless, the effect of the promotor concentration on the polymeric intrinsic viscosity depended on the DAC:AA molar feed ratio:

1. *DAC:AA < 6 : 1.* Table V shows that the polymeric intrinsic viscosity reached a maximum value from 1.35 to $4.05 \times 10^{-3}M$. Figure 5 provides information on the terpolymerization kinetics, while the DAC:AA molar feed ratio was fixed at 4 : 1. As was generally observed, the larger the promotor concentration, the earlier the temperature maximum and the larger the temperature maximum value. However, when the promotor concentration became too high (e.g., $6.80 \times 10^{-3}M$) the polymeric intrinsic viscosity decreased rapidly. One could conclude that the promotor concentration of $2.70 \times 10^{-3}M$ constituted an optimum, which was equal to the redox agent:promotor molar ratio = 1 : 6, so the molecular weight of the product could be controlled by simply adjusting the promotor concentration.

2. *DAC:AA ≥ 6 : 1.* In this case, the optimum promotor concentration of the polymeric intrinsic viscosity was $4.05 \times 10^{-3}M$, i.e., redox agent:promotor molar ratio = 1 : 9. This was because the low heat of the reaction of DAC required a large pro-
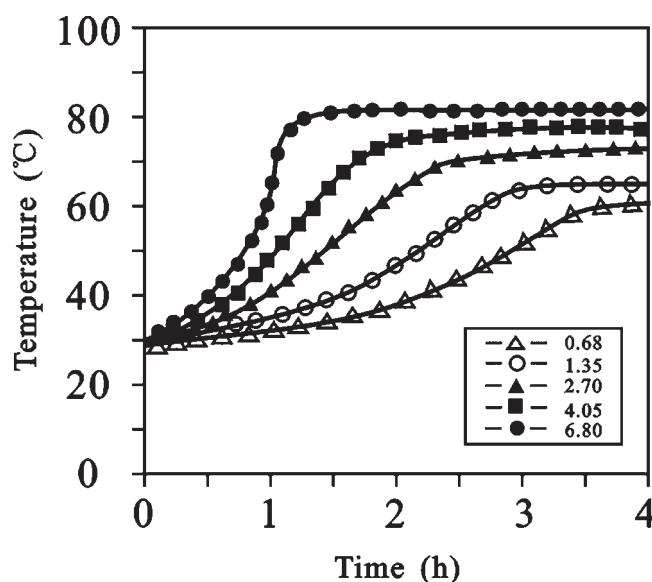

Figure 5 Temperature–time plots for two-step heating systems of various promotor concentration. DAC:AA molar feed ratio = 4 : 1. The other polymerization conditions were as for Table V.

motor concentration to maintain a high polymerization rate.

FTIR and ^{13}C NMR spectrum
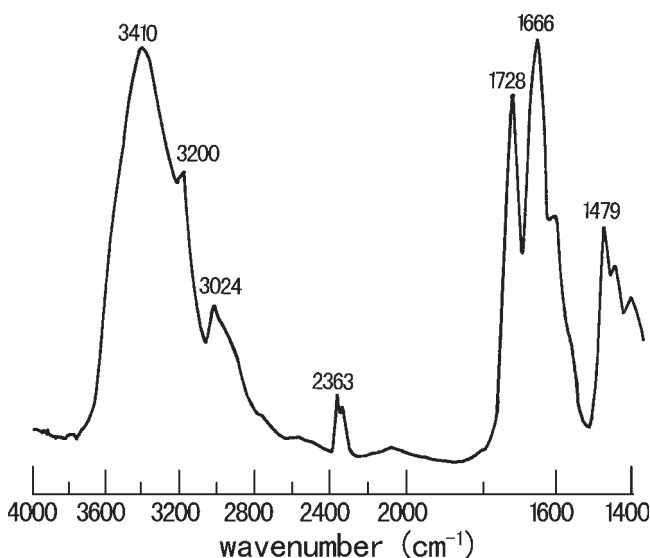
A typical FTIR spectrum of terpolymer sample (feed ratio of DAC:AA:AM (mol %), 40 : 15 : 45) is shown in Figure 6. A broad absorbance at 3410 cm^{-1} and an end sharp absorbance at 3200 cm^{-1} are characteristic peaks of —COOH group, represented —AA— unit. Similarly, the sharp absorbance at 1666 (—CONH$_2$) and at 1479 [—N$\oplus$(CH$_3$)$_3$] cm^{-1} are characteristic peaks of the —AM— and —DAC— units, respectively. Figure 7 shows the typical ^{13}C NMR spectrum of terpolymer sample (feed ratio of DAC:AA:AM (mol %), 40 : 15 : 45). The polymer composition was determined by integration of the carbonyl resonances and agreed favorably with feed ratio; i.e., the composition of the DAC:AA:AM terpolymer sample was 40 : 16 : 44 (mol %).

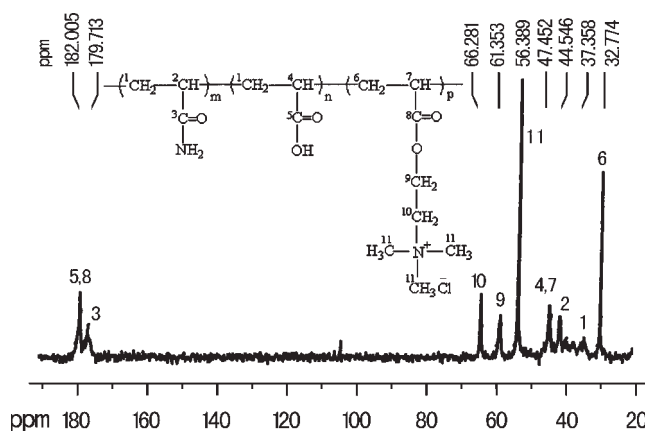## Consideration of the initiating mechanism of terpolymerization

Based on these experimental observations, we considered that the redox agent:promotor triad-initiating system initiated the terpolymerization by a two-step method. At room temperature, the following redox reaction between K$_2$S$_2$O$_8$ and NaHSO$_3$,

$$S_2O_8^{2-} + SO_3^{2-} \rightarrow SO_4^{2-} + SO_4^{\bullet-} + SO_3^{\bullet-},$$

led to two radical, thus initiating terpolymerization of AM, AA, and DAC. During the adiabatic polymeriza-

Figure 7 ^{13}C NMR spectrum of the terpolymer sample. Feed ratio of DAC:AA:AM: 40 : 15 : 45 (mol %).

tion, the temperature inside the flask increased first gradually, reached ca 40°C, after which the decomposition reaction of AIBA occurred as follows:
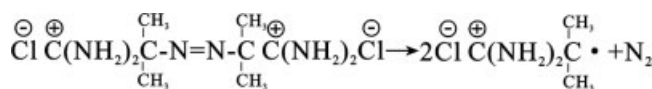
The radical concentration produced by the azo-initiator was multiple of that of redox initiator, it enhanced polymerization rate, and then the system temperature increased sharply. Since the azo-initiator could not produce side reaction, thus the polymerization conversion and the polymeric molecular weight could reach a very high level.

CONCLUSIONS

A two-step heating polymerization with a triad-initiating system was successfully applied to terpolymerization of AM, AA, and DAC. During the adiabatic step, the terpolymerization was initiated by K$_2$S$_2$O$_8$/NaHSO$_3$ redox system at room temperature, and then was promoted by AIBA at $\sim$ 40°C. After a maximum temperature, the retaining temperature was carried out for maturature. Under optimum conditions, the polymerization conversions were higher than 90 wt % within 4 h, and the polymeric intrinsic viscosity reached 21.5 dL/g.

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Figure 6 FTIR spectrum of the terpolymer sample. Feed ratio of DAC:AA:AM: 40 : 15 : 45 (mol %).

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