

Polymerization and Thermal Behaviors of Poly[dimethyl(acrylamidopropyl)ammonium propane sulfonate] poly (DMAAPS)

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SYNOPSIS

The conversion in the free radical polymerization of zwitterionic sulfobetaine monomer [dimethyl(acrylamidopropyl)ammonium propanesulfonate](DMAAPS) was investigated under various conditions, such as, monomer concentration, reaction time and temperature, and various salts. The high conversion of DMAAPS monomer could be achieved under lower temperature. The conversion of DMAAPS is enhanced in the presence of various salts in aqueous solution, but is not very significant because the reactivity of DMAAPS is very rapid even at lower temperature and lower concentration of the monomer. The thermal behavior of poly(DMAAPS) was also studied under nitrogen and air atmosphere at various heating rates. The kinetic parameters such as activation energy, preexponential factor, and reaction order were determined by Ozawa's method. Thermal degradation of such a polymer occurs in two and three stages in nitrogen and air atmospheres, respectively. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Sulfobetaine monomers derived from dimethyl-aminoalkyl acrylates and/or dimethylaminoalkyl acrylamides are extensively used in industries concerned with textiles, dispersion agents, anti-static agents, surfactants, protective colloids, and coatings.¹⁻⁷ The aqueous solution properties of poly(betaines), such as carboxybetaine and sulfobetaine, have been extensively investigated.⁸⁻²⁵ Recently, the synthesis and aqueous solution properties of poly[dimethyl(acrylamidopropyl)ammonium propane sulfonate], poly(DMAAPS), were studied in previous reports.^{26,27} Such sulfobetaines and the corresponding cationic monomers were synthesized and clearly identified the ¹H-NMR signals of the aliphatics group near the lines due to the quaternary ammonium group of sulfobetaine monomers with the assistance of the respective cationic

monomers. Recently, we also reported that the minimum salt concentration and intrinsic viscosity of poly(DMAAPS) were related to the type and concentration of the salt used.²⁷

The kinetic features of the radical polymerization for zwitterionic monomers of the betaine type were rarely studied.^{11,12,20,28} For example, Topchiev et al.¹¹ measured individual rate constants dilatometrically in the polymerization of carboxybetaine in the absence and presence of sodium chloride in aqueous solution. Liaw²⁸ investigated the absolute rate constants in the free radical polymerization of sulfobetaine monomers [3-dimethyl(methacryloyloxyethyl)ammonium propane sulfonate (DMAPS) and 3-dimethyl(acryloyloxyethyl)ammonium propane sulfonate (DAAPS) in formamide and dioxane co-solvents.

The thermal degradation of the poly(DMAPS) had been reported in previous papers,^{29,30} although no previous attempts appear to have been made to study these sulfobetaines. The results of kinetic parameters of the degradation of poly(DMAAPS) and the effect of various conditions, such as the type and concentration of salt, reaction temperature, and re-

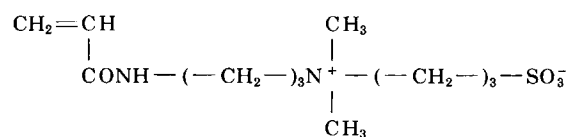
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action time on the polymeric conversion, are described in this article.

EXPERIMENTAL

Monomer Preparation

The monomer *N,N'*-dimethyl(acrylamidopropyl)-ammonium propane sulfonate (DMAAPS) was prepared as described previously.²⁶ The monomer was characterized by elemental analysis techniques and NMR as described above. It is found to be quite hygroscopic (mp 105°C).²⁶ The structure is given below:



Polymerization of DMAAPS

Into a 25 mL polymerization tube 10 mL (predetermined concentration) of DMAAPS monomer aqueous solution was introduced in the absence and/or presence of salt, and 1 wt % of 4,4'-azobis-4-cyanovaleric acid (ACVA) based on monomer weight. The contents of the tube were then purged with nitrogen and sealed. The tube was then placed in a

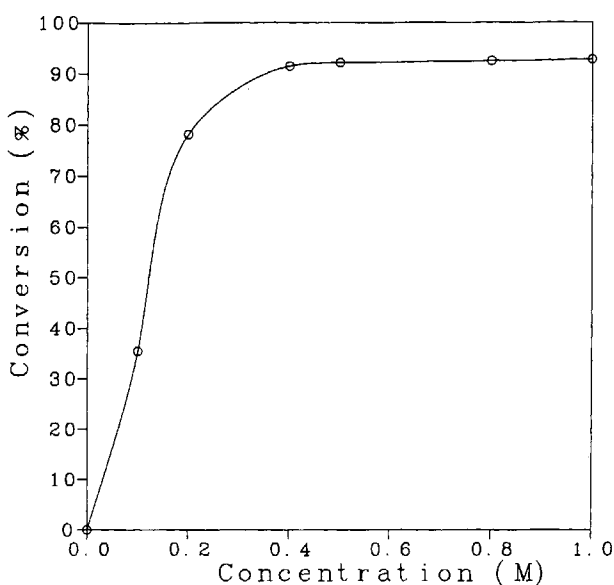


Figure 1 Conversion of polymerization as a function of DMAAPS at 80°C for 3.5 h.

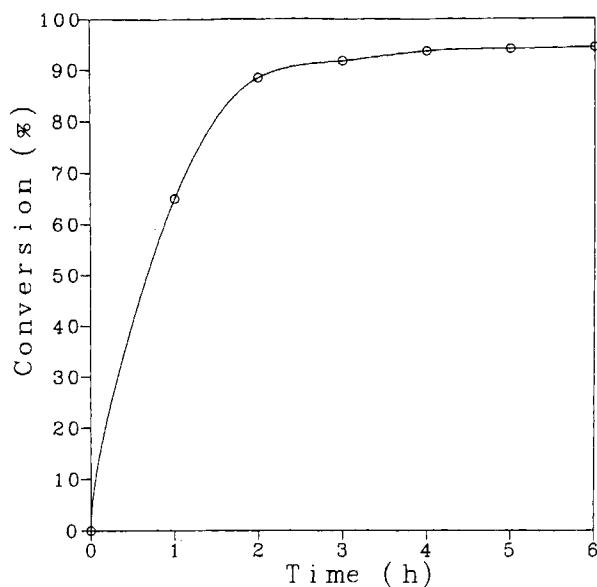


Figure 2 Conversion of polymerization of DMAAPS as a function of reaction time. [DMAAPS] = 0.5M, reaction temperature = 80°C.

thermostated bath at the predetermined temperature for a desired time. The polymer product was precipitated with acetone, washed with water to remove the unchanged monomer, and dried for about 24 h at 100°C, and then weighed.

Thermal Analysis

Thermal analysis was measured using Rikaku Thermoflex TG8110. The heating rate was at 5, 10, 15, and 20°C/min in nitrogen and air atmospheres. The flow rate was 50 mL/min and the sample weighing 12 mg was used.

RESULTS AND DISCUSSION

It is well known that poly(sulfobetaine)s or poly(carboxybetaine)s do not dissolve in water, but dissolve in aqueous salt solution. Their minimum salt concentrations are decreased with increasing ion radius of salt ions and their intrinsic viscosities are increased with increasing ion radius of salt ions when dissolved in salt solution. These occurrences are attributed to the site binding ability of the salt ions.^{20,25} The rate of polymerization for poly(betaine)s could be enhanced in the presence of salt because the salt would reduce the electrostatic repulsive force in betaines.^{11,12,25,28} Investigation of the polymerization conversion of DMAAPS in various conditions in-

Table I Effect of Reaction Temperature on Conversion of DMAAPS Polymerization^a

Temperature (°C)	Conversion (%)
45	78.4
50	81.0
60	83.6
80	85.1

^a [DMAAPS] = 0.25M, reaction time = 2 h.

involved monomer concentration, reaction time, reaction temperature, and various salts.

Effect of DMAAPS Concentration

The polymerization conversion of DMAAPS monomer in pure water at 80°C for 3.5 h shown in Figure 1 is increased with increasing concentration. The conversion is lower at lower monomer concentration, i.e., 0.1M, because the molecular weight of the polymer seems to be lower and the polymer cannot be precipitated in methanol. However, 90% conversion is attained when the monomer concentration increased slowly over 0.4M.

Effect of Reaction Time

The conversion shown in Figure 2 is increased with increasing reaction time for 0.5M DMAAPS concentration at 80°C. The result showed that the conversion reached over 60% for 1 h reaction time, and the conversion then increased slowly to 94.3% as polymerization proceeded from 2 to 6 h. From this result, it is known that the reactivity of DMAAPS is extremely rapid at this condition. Hence, the effect on the conversion of DMAAPS at lower concentration and lower temperature needs to be understood. The conversion shown in Table I has reached 78.4% for 0.25M monomer concentration at lower temperature (45°C) for the 2 h reaction time. It clearly demonstrates that the reactivity of DMAAPS is very rapid even at the lower temperature of 45°C.

Effect of Various Salts on the Conversion

It was found that the conversion of DMAAPS in salt solution was enhanced in our earlier study.³¹ Topchiev et al.¹² and Liaw et al.²⁸ also reported that the rates of polymerization for carboxybetaine, DMAPS, and DAAPS were increased in the presence of salt, respectively. The conversion shown in Table II is increased in the order no salt < Cl⁻ < Br⁻ < I⁻ for

Table II Effect of Various Salts on the Conversion of DMAAPS Polymerization^a

Salt	Concentration (M)	Conversion (%)
None	—	90.6
KCl	0.125	93.0
KBr	0.125	93.1
KI	0.125	93.4
LiCl	0.125	91.7
NaCl	0.125	92.6
KCl	0.125	93.0

^a [DMAAPS] = 0.315M, reaction time = 3.5 h, reaction temperature = 80°C.

KCl, KBr, and KI, respectively, for DMAAPS monomer solutions containing salt with a common cation (K⁺) but different anions. For chloride salt, the data also indicate an increase in the conversion of polymerization in the order no salt < Li⁺ < Na⁺ < K⁺ for LiCl, NaCl, and KCl, respectively. From the above result it can be seen that salt enhances the DMAAPS conversion. This phenomenon is consistent with sulfobetaine, such as DMAPS, but the salt effect is not significant here because the reactivity of DMAAPS is more rapid than that of DMAPS. Table III shows the effect of various concentrations of sodium chloride solution on the conversion of DMAAPS at 0.315M for 3 h. The result shown in Table III indicates an increase of conversion with increase of NaCl concentration. This occurrence reveals that the conversion can be enhanced through addition of salt because the electrostatic repulsive force of betaines can be neutralized in aqueous salt solution.^{11,20,25,27}

TG Curve Characteristic of Poly(DMAAPS)

The poly(DMAAPS) was quite hygroscopic at ambient temperature, so the thermogravimetric anal-

Table III Effect of Various NaCl Concentrations on the Conversion of DMAAPS Polymerization

NaCl Concentration (M)	Conversion (%)
0	90.57
0.125	92.57
0.625	92.86
1.250	94.15
2.500	95.00

^a [DMAAPS] = 0.315M, reaction time = 3.5 h, reaction temperature = 80°C.

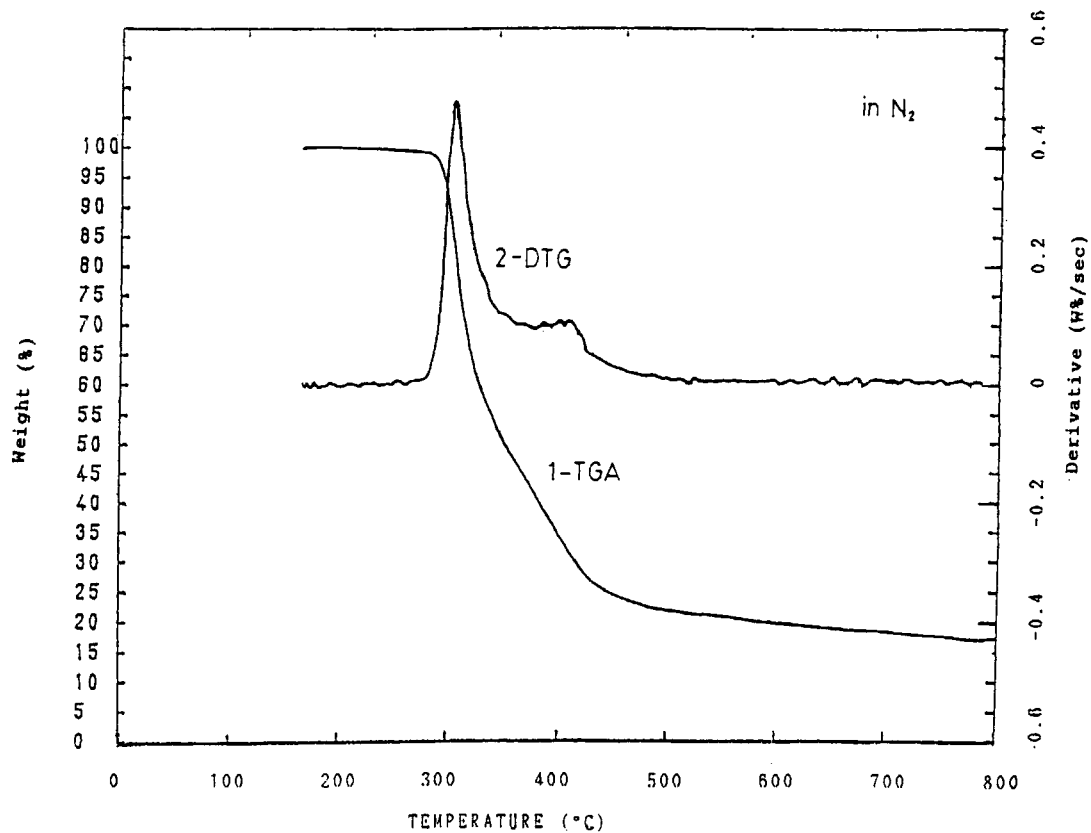


Figure 3 The curves of 1-TGA and 2-DTG obtained during the nitrogen atmosphere degradation of poly(DMAAPS).

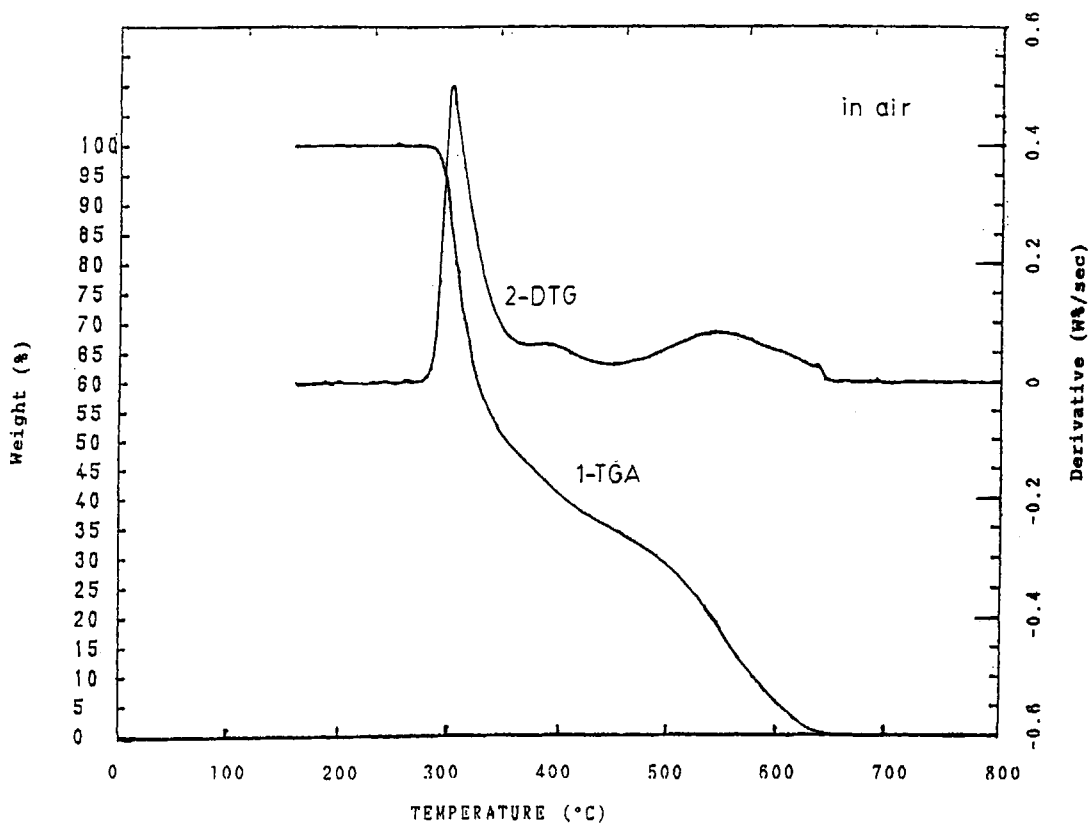


Figure 4 The curves of 1-TGA and 2-DTG obtained during the air atmosphere degradation of poly(DMAAPS).

Table IV Weight Loss of Poly(DMAAPS) in Nitrogen^a

Heating Rate (°C/min)	First Stage		Second Stage	
	Temperature (°C)	Weight Loss (%)	Temperature (°C)	Weight Loss (%)
5	272.3–294.5	39.2	294.5–396.9	34.2
10	282.1–309.1	41.8	309.1–420.0	33.4
15	288.5–311.4	42.1	311.4–443.4	33.6
20	293.9–324.8	42.3	324.8–444.7	34.4

^a Start temperature, 120°C; end temperature, 800°C.

ysis measured after the moisture was removed at 120°C for 5 min. The TG curve for the thermal degradation of a 12 mg poly(DMAAPS) sample is shown in Figures 3 and 4 with a heating rate of 20°C/min in nitrogen and air atmospheres, respectively. From Figures 3 and 4, it can be seen that thermal degradation of such a polymer occurs in two and three stages under nitrogen and air atmospheres, respectively. These degradation phenomena are similar to that observed for the poly(DMAPS) in our previous study.^{29,30}

The TG curve for poly(DMAAPS) in nitrogen atmosphere has two stages. In the first stage, weight loss starts at 294.0°C and continues to 324.8°C with 42.3% weight loss. The second stage (34.4%) is completed by 444.7°C. The weight percentage remaining at 800°C is 16.9%. However, the TG curve for poly(DMAAPS) in air atmosphere has three distinct stages; weight loss starts at 292.2°C and continues to 334.4°C with 47.8% weight. The second stage (22.8%) is completed by 497.7°C. The third stage (29.4%) is completed by 623.6°C, and no ash is left.

Tables IV and V show the percentage weight loss of poly(DMAAPS) in nitrogen and air atmosphere

and the corresponding temperature at the heating rate of 5, 10, 15, and 20°C/min, respectively.

Determination of Kinetic Parameters for the Thermal Degradation of Poly(DMAAPS)

The results of the thermogravimetry at various heating rates in nitrogen and air atmosphere are plotted against the absolute temperature in Figures 5 and 6, respectively.

The apparent activation energy was determined by Ozawa's³² method for a given value of weight fraction (wt %). According to it, the weight decreases to a given fraction at temperature T_1 for the heating rate of β_1 , at T_2 for β_2 , and so on. The following equation could be derived:

$$-\log \beta_1 - \frac{E_1}{2.303RT_1} = -\log \beta_2 - \frac{E_2}{2.303RT_2} \quad (1)$$

where E is the activation energy and R is the ideal gas constant. From Figures 5 and 6, the logarithms

Table V Weight Loss of Poly(DMAAPS) in Air^a

Heating Rate (°C/min)	First Stage		Second Stage		Third Stage	
	Temperature (°C)	Weight Loss (%)	Temperature (°C)	Weight Loss (%)	Temperature (°C)	Weight Loss (%)
5	272.3–300.5	43.0	294.5–396.9	25.8	472.0–550.0	31.2
10	280.0–318.1	44.6	309.1–420.0	24.0	490.9–570.0	31.4
15	287.6–324.1	47.5	311.4–443.4	22.0	494.0–620.0	30.5
20	292.2–334.4	47.8	324.8–444.7	22.0	502.0–623.6	29.4

^a Start temperature, 120°C; end temperature, 800°C.

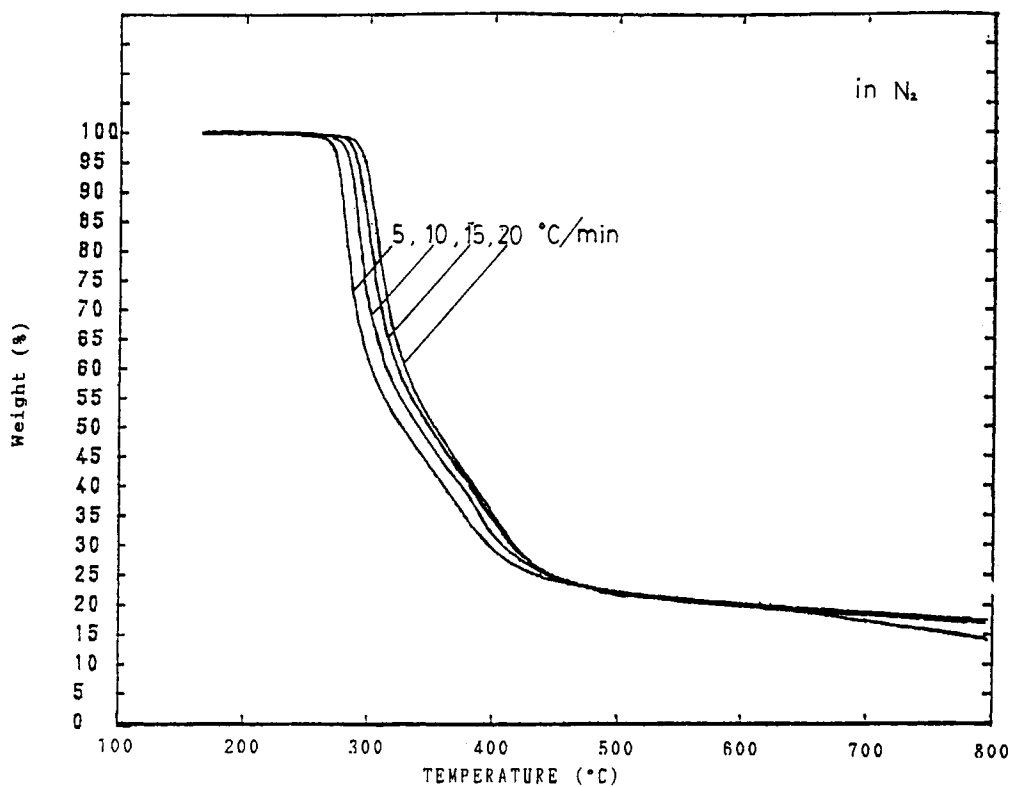


Figure 5 TG curves of poly(DMAAPS) at various heating rates in nitrogen atmosphere.

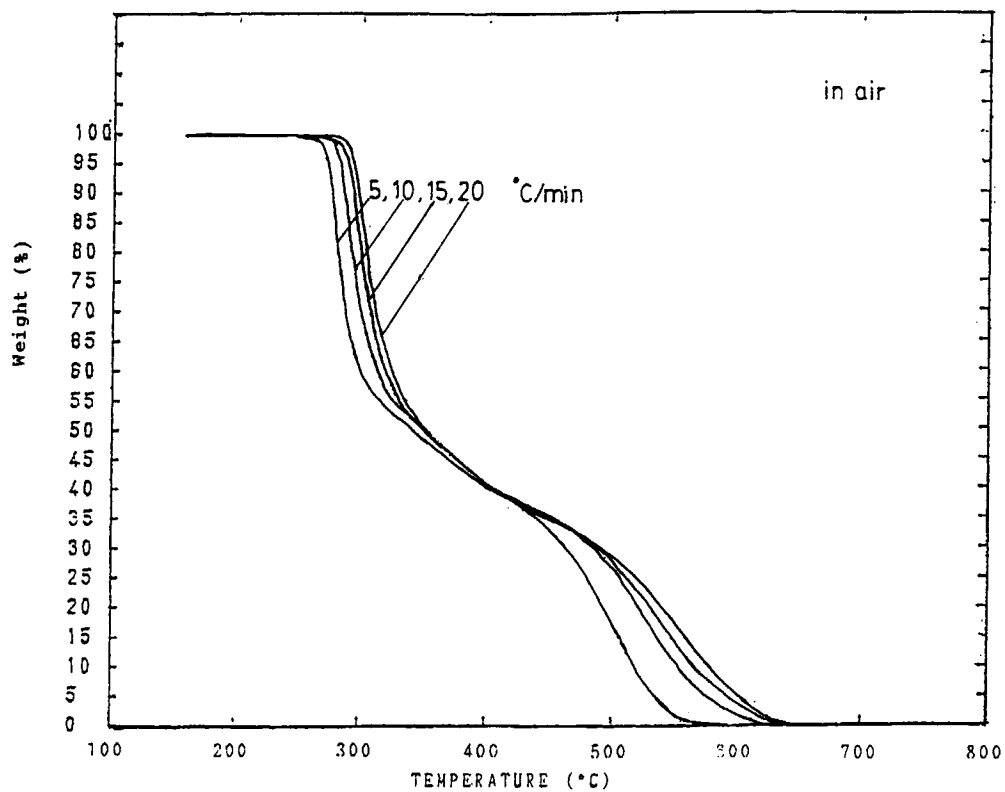


Figure 6 TG curves of poly(DMAAPS) at various heating rates in air atmosphere.

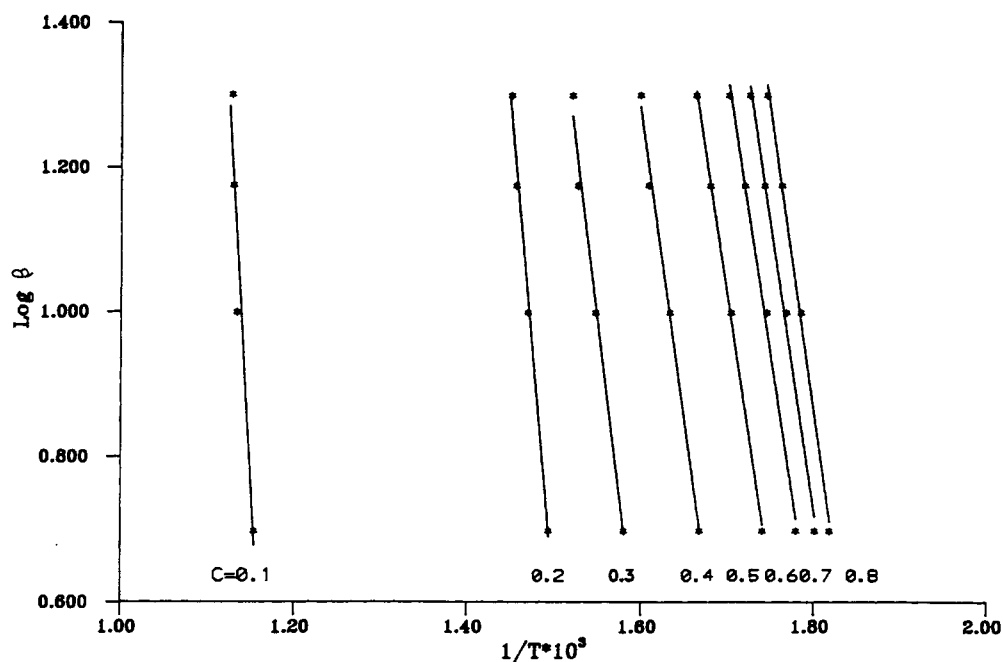


Figure 7 The plots of logarithms of heating rate and the reciprocal absolute temperature for indicated conversion of the degradation of poly(DMAAPS) in nitrogen atmosphere.

of the heating rates could be plotted against the reciprocal absolute temperature until the weight of the sample decreases to a given fraction. The results are shown in Figures 7 and 8. Straight lines are drawn using the linear regression method. From

these lines the activation energies and the pre-exponential factors are determined as listed in Table VI in nitrogen and air.

The kinetic order of the reaction could be derived by using Eq. (1)

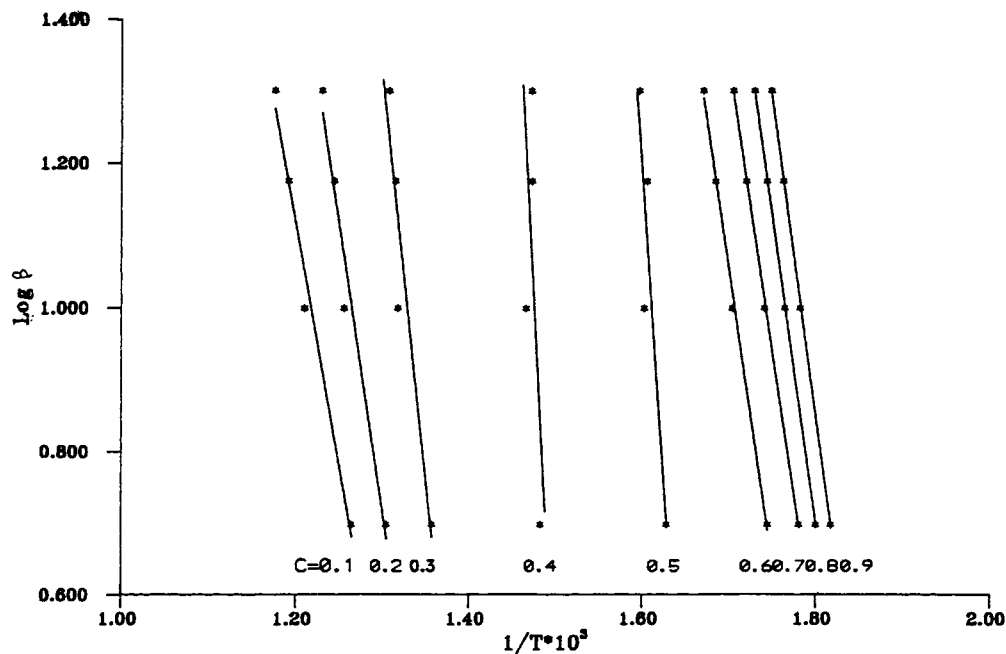


Figure 8 The plots of logarithms of heating rate and the reciprocal absolute temperature for indicated conversion of the degradation of poly(DMAAPS) in air atmosphere.

Table VI Activation Energies and Preexponential Factor of Degradation of Poly(DMAAPS) in Nitrogen and Air Atmosphere

Condition	First Stage		Second Stage		Third Stage	
	ΔE (kJ/mol)	$\log A^a$	ΔE (kJ/mol)	$\log A^a$	ΔE (kJ/mol)	$\log A^a$
In N ₂	150.1	12.2	200.5	14.2	—	—
In air	159.0	16.0	350.7	29.3	154.6	12.5

^a A is calculated by the Ozawa's method. The dimension of A is min^{-1} .

$$\log |\ln(1 - C)| = \log(AE/\beta R) - 2.35 - \frac{E}{2.303RT} \quad \text{for } n = 1 \quad (2)$$

where A is the preexponential factor, β is the heating rate, R is the ideal gas constant, and E is the activation energy.

The conversion (C) is defined by $C = 1 - (W/W_0)$, where W_0 and W represent the initial weight and weight at any time, respectively, and n is the reaction order. The logarithm of $|\ln(1 - C)|$ can be plotted vs the logarithm of heating rate (β) and is shown in Figures 9 and 10. Good linear relationship was obtained at constant temperature of 340°C, and 294.2; 530, 330, and 300°C for nitrogen and air atmospheres, respectively. These results indicate that the apparent kinetic order is unity under a nitrogen and air atmosphere, respectively.

CONCLUSIONS

The conversion of an aqueous solution of zwitterionic monomer DMAAPS increases as salt is added to it. When the radius of salt ion is large, the conversion of polymerization increased. This is because the electrostatic repulsive force of betaines can be neutralized in aqueous salt solution. The reactivity of DMAAPS is very rapid even at lower temperature and lower concentration of monomer. The thermal behavior of poly(DMAAPS) exhibited two and three stages of degradation under nitrogen and air atmosphere, respectively. These degradation phenomena are also similar to poly(DMAPS). The kinetic parameters of thermal degradation such as activation energies, preexponential factor, and reaction order were also determined.

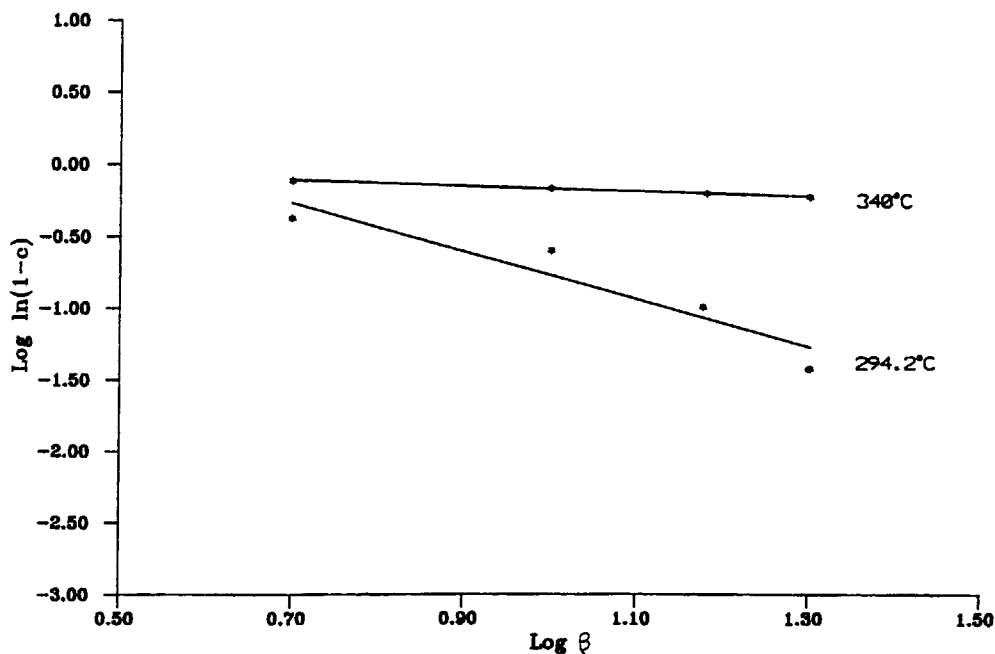


Figure 9 Relationship obtained by Ozawa's method for $n = 1$ in nitrogen atmosphere.

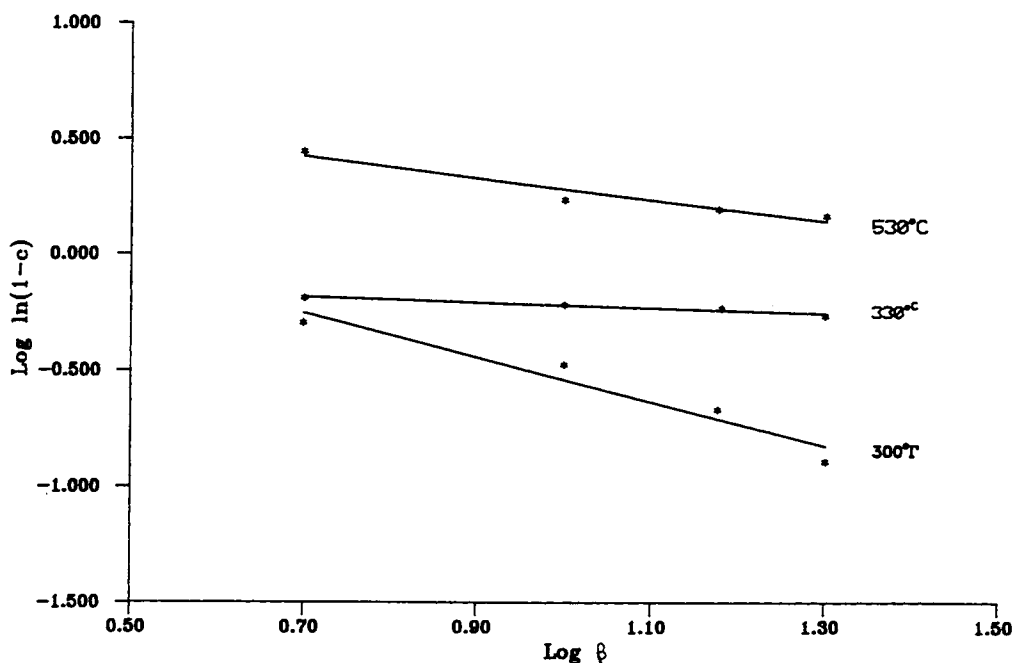


Figure 10 Relationship obtained by Ozawa's method for $n = 1$ in air atmosphere.

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