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SYNTHESIS AND CHARACTERIZATION OF POLY(DIALYLDIMETHYLAMMONIUM CHLORIDE-*g*-ACRYLAMIDE)

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ABSTRACT

Graft copolymers of poly(diallyldimethylammonium chloride), (poly-DADMAC), with acrylamide were synthesized using a ceric salt/nitric acid initiation system. The effects of concentration of initiator, monomer, and substrates were studied. Copolymers were characterized by viscometry and size-exclusion chromatography. The highest molecular weight (\bar{M}_w) of graft copolymer obtained was 1.70×10^6 . The compositions of copolymers are dependent upon the ratios of the concentration of monomer to the concentration of substrate. The highest content of DADMAC monomer unit in the copolymer was 33 wt%.

INTRODUCTION

As early as 1949, it was observed that radical cyclopolymerization of diallyldimethylammonium bromide resulted in water-soluble cationic polyelectrolytes [1]. This first cyclopolymer, in its chloride form (poly-DADMAC), has been used in many applications, such as papermaking, water treatment, and electrographic paper reproduction processes [2]. With a view to modifying properties of the polymer, random copolymerizations of DADMAC with vinyl monomers, especially acrylamide (AM), have been investigated [3].

In this work we attempted to synthesize a new type of copolymer from DADMAC and AM. For this purpose the copolymerization of DADMAC with acrylic acid at $\text{pH } 7.0 \pm 0.5$ in aqueous solution was first carried out. Then the products were treated with 3-chloro-1,2-propanediol to give prepolymers having $-\text{CH}_2-\text{CH}-\text{CH}_2$ groups, which can serve as grafting sites in



the presence of ceric ion. In this paper the effects of varying the concentrations of ceric ion, monomer, nitric acid, and substrate (prepolymer) on the extent of grafting and intrinsic viscosity of the graft copolymer will be discussed.

EXPERIMENTAL

Materials

AM, a commercially available reagent, was recrystallized from acetone, DADMAC, obtained from the Allied Company as a 60% aqueous solution of DADMAC, was used without further purification. Acrylic acid (AA) (Eastman Kodak Co.) was distilled before use. Ceric ammonium nitrate (G. F. Smith Co.) was used without purification.

Synthesis of Poly-DADMAC-*co*-2,3-Dihydroxypropyl Acrylate

DADMAC-*co*-AA copolymers were synthesized under the reaction conditions shown in Table 1. Into a 100-mL flask the desired quantities of AA and DADMAC were added. The pH of this solution was adjusted to 7.0 ± 0.5 with 0.5 *N* aqueous NaOH, and the solution was diluted to 50 mL with deionized water. V-50 (azobis(2-amidinopropane) dihydrochloride) was used as the initiator. The solution was then bubbled with nitrogen at room temperature for 30 min. Then the flask was kept in an oil bath maintained at 50°C for a specified time. The product was isolated by precipitating into a large amount of acetone.

The esterification of poly-DADMAC-*co*-AA was carried out at pH 9 and 115°C by refluxing with an excess of 3-chloro-1,2-propanediol [4] for 4 h. The molar ratio of the diol to AA was 3:1. After the reaction the neutralized solution was dialyzed against deionized water to remove all ions and small molecules using a membrane with a molecular weight cut-off of 2000.

TABLE 1. Synthesis of Prepolymers^a

Prepolymer	Polymerization conditions					Yield, %	[η], dL/g
	DADMAC/AA, mole ratio	V-50, mol/L	Temperature, °C	Time, h			
PP-1-1	10:1	0.01	50	20.7	99.3	2.70	
PP-2-1	20:1	0.01	50	9	99	2.68	
PP-2-2	20:1	0.01	50	17	99	2.60	
PP-3-1	40:1	0.01	50	24	95.3	2.75	
PP-4-1	71:1	0.01	50	24	99	2.40	

^aFor the conditions of esterification, see Experimental part.

Graft Copolymerization

The copolymerization was carried out according to Pledger et al. [5]. After a specified reaction time (24 h), the resulting copolymer was precipitated by adding the dilute reaction mixture dropwise to a large amount of acetone. The copolymer was then washed several times with small amounts of acetone and vacuum dried to constant weight at 40°C. Polymer yield, W , was calculated based on the following equation:

$$W = \frac{(\text{g of polymer recovered}) \times 100}{\text{g of prepolymer added} + \text{g of AM added}}$$

The copolymer sample for ^{13}C -NMR identification and elemental analysis was purified by repeatedly dissolving it in deionized water and reprecipitating it into acetone three times.

Intrinsic Viscosity

The viscosities of solutions of copolymers in 0.2 M aqueous Na_2SO_4 were measured with an Ubbelohde viscometer at $30 \pm 0.2^\circ\text{C}$. The intrinsic viscosity, $[\eta]$, was obtained by extrapolation of both reduced viscosities, η_{sp}/c , and inherent viscosities, $\ln \eta_r/c$, to infinite dilution.

Molecular Weights of Copolymers

Molecular weights of copolymers were obtained with the use of Waters Associates, Model 590, gel-permeation chromatograph equipped with a 757 UV detector, calibrated with polyacrylamide standards. The following conditions were used. Columns: glycerated controlled-pore glass beads, 3017 and 1273 Å; mobile phase, 0.2 M sodium sulfate; flow rate, 6 mL/min. The following equation was used to calculate the molecular weight:

$$\bar{M}_w = (6.9215 \times 10^6) - (1.0008 \times 10^5 V_R)$$

where V_R = retention volume in milliliters.

Elemental Analysis

Elemental analyses were conducted by Atlantic Microlab, Inc.

¹³C-NMR Spectra

The ¹³C-NMR spectra of D₂O solutions were recorded with a Varian XL-200 spectrometer system operating at 50.30 MHz.

RESULTS AND DISCUSSION

Radical copolymerizations of DADMAC with AA were carried out in order to introduce the grafting site onto the poly-DADMAC backbone. The resulting products were then subjected to esterification at pH 9 in the presence of 3-chloro-1,2-propanediol. The poly-DADMAC-*co*-2,3-dihydroxypropyl acrylates (prepolymers), synthetic conditions, and viscosity data are listed in Table 1.

Grafting studies of such prepolymers were carried out in the presence of Ce(NH₄)₂(NO₃)₆/HNO₃ and AM. We will discuss the influences of some reaction variables on graft copolymerization of the prepolymer with AM and the results of characterization of graft copolymers.

Effects of Reaction Parameters on Conversion and Intrinsic Viscosity of Copolymer

Effects of HNO₃ Concentration

The graft polymerization initiated by the Ce⁴⁺/HNO₃ initiation system is quite dependent on HNO₃ concentration [6] (see Fig. 1). The highest conversion occurred at [HNO₃] 4.5 mmol/L. At higher HNO₃ concentration ([HNO₃] above 6 mmol/L), both yield and [η] of the copolymer decreased rapidly with increasing HNO₃ concentration. This result might be due to a decrease of the initiation rate and/or an overabundance of protons, which may act as free radical terminators [7].

Effects of Monomer Concentration

The effects of the concentration of AM on the graft copolymerization are shown in Fig. 2. Both the extent of grafting and the [η] of the copolymer increased, as expected, with increasing concentration of AM. The reactivity of prepolymer PP-1-1 is higher than that of prepolymer PP-2-1. There was a tendency to form crosslinked products insoluble in water at higher AM concentrations. In the case of PP-2-1, the highest AM concentration to give good

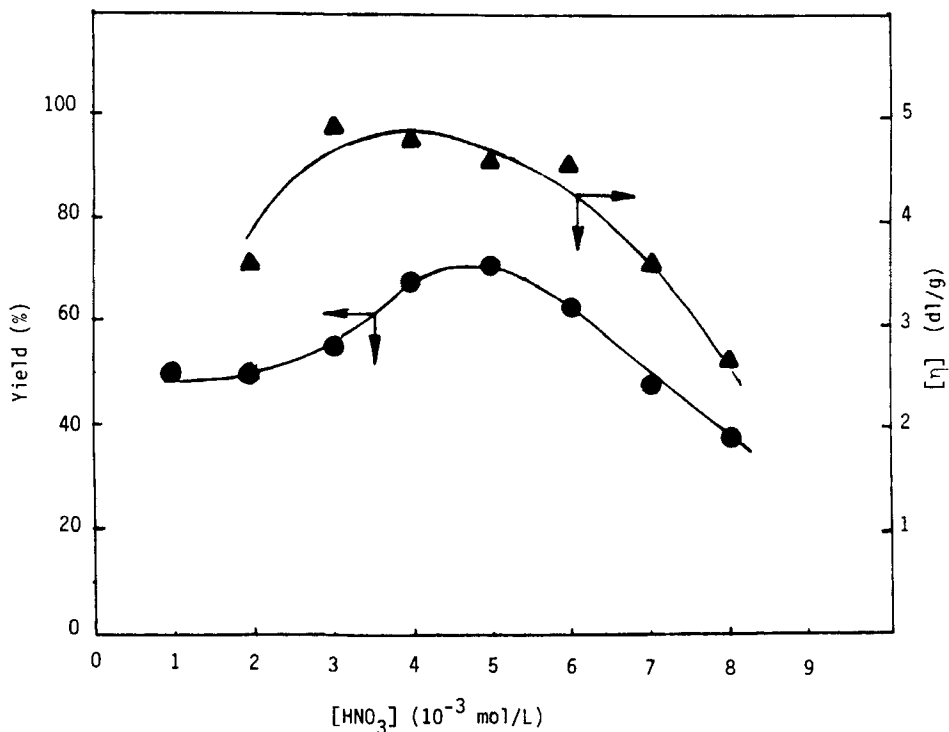


FIG. 1. Variation of yield and intrinsic viscosity with acid concentration. Prepolymer PP-2-1 = 0.25 g; reaction solution volume = 25 mL; $[\text{AM}] = 0.4 \text{ mol/L}$; $[\text{Ce}^{4+}] = 0.5 \text{ mmol/L}$; temperature = 30°C ; time = 24 h.

water-soluble products was about 1.2 mol/L; but for PP-1-1, the concentration was only about 0.25 mol/L.

Effects of Ceric Ion Concentration

It is evident from Table 2 that the extent of grafting and $[\eta]$ of the copolymer almost change synchronously with increasing Ce^{4+} level. Maximum conversion for this series was at 0.2 mmol/L $[\text{Ce}^{4+}]$. Increasing $[\text{Ce}^{4+}]$ from 0.2 to 1.5 mmol/L decreased yield and $[\eta]$, presumably as a result of faster radical termination due to reaction with Ce^{4+} .

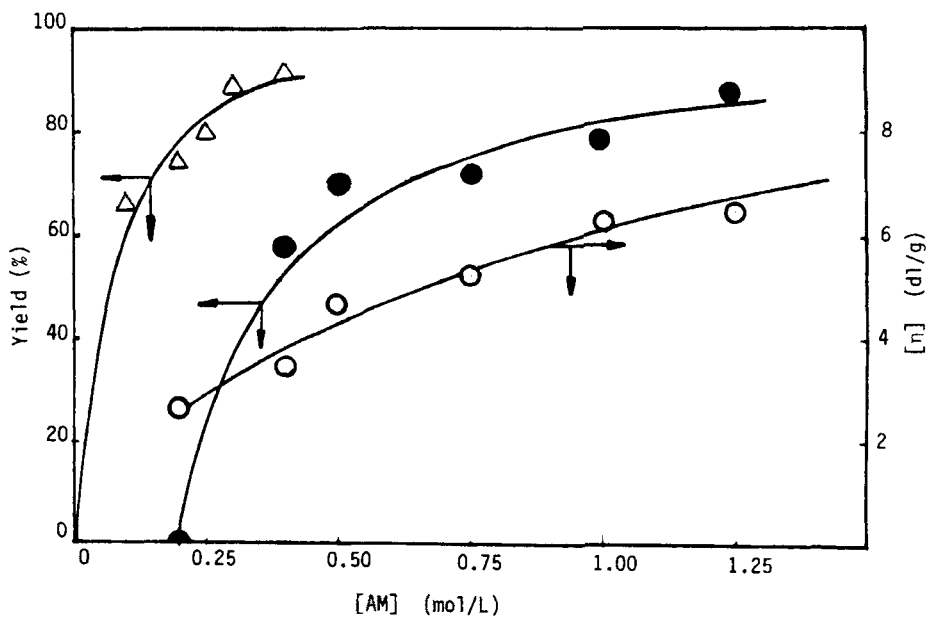


FIG. 2. Variation of yield and intrinsic viscosity with monomer concentration. Prepolymer = 0.15 g; reaction solution volume = 25 mL; $[Ce^{4+}] = 0.5$ mmol/L; $[HNO_3] = 5$ mmol/L; temperature = $30^\circ C$; time = 24 h. (Δ) PP-1-1, (\bullet) PP-2-1.

TABLE 2. Effects of Ce^{4+} Salt Concentration on Yield and Intrinsic Viscosity^a

Run no.	Ce^{4+} , mmol/L	Yield		$[\eta]$, dL/g	$\bar{M}_w \times 10^{-4}$
		g	%		
DA-C-1	0.08	0.420	43.6	5.53	146
DA-C-2	0.10	0.662	68.8	7.35	152
DA-C-3	0.20	0.694	72.1	6.20	—
DA-C-4	0.30	0.661	68.7	5.92	148
DA-C-5	0.50	0.602	62.5	4.83	134
DA-C-6	0.75	0.565	58.7	4.20	128
DA-C-7	1.00	0.514	53.4	4.20	124
DA-C-8	1.50	0.423	43.9	3.25	97

^aPolymerization conditions: solution volume = 25 mL, PP-2-2 = 0.252 g, AM = 0.71 g, $[HNO_3] = 4.5$ mmol/L, temperature = $30^\circ C$, polymerization time = 24 h.

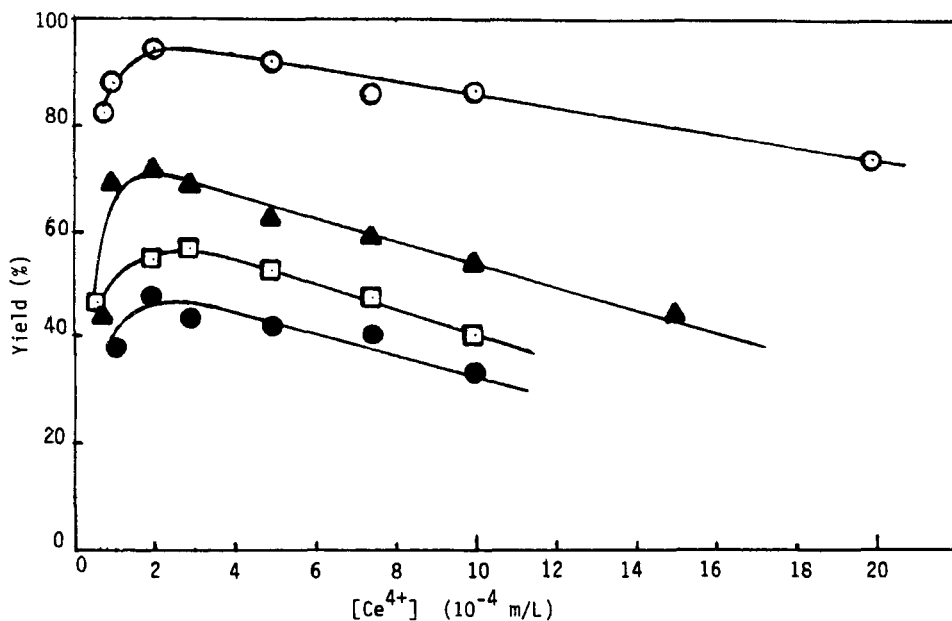


FIG. 3. Copolymerizability of various prepolymers as a function of ceric salt level. [Prepolymer] = 0.25 g/25 mL; [AM] = 0.4 mol/L; [HNO₃] = 4.5 mmol/L; temperature = 30°C; time = 24 h. (○) PP-1-1, (▲) PP-2-2, (□) PP-3-1, (●) PP-4-1.

Effects of Prepolymers

Four samples of prepolymer, PP-1-1, PP-2-2, PP-3-1, and PP-4-1, were synthesized (Table 1). The graft copolymerizability of four samples was tested under the same polymerization conditions (Fig. 3). The order of reactivity was PP-1-1 > PP-2-2 > PP-3-1 > PP-4-1. Figure 4 shows a plot of the highest yield in Fig. 3 vs the monomer feed used for preparing the prepolymer; a nearly straight line was obtained, showing that the larger the number of sites available for grafting, the greater is the grafting.

The effects of concentration of prepolymer on graft polymerization are summarized in Table 3. It appears that there is an optimal ratio of [prepolymer]/[Ce⁴⁺] for the high-yield formation of graft copolymer of high intrinsic viscosity.

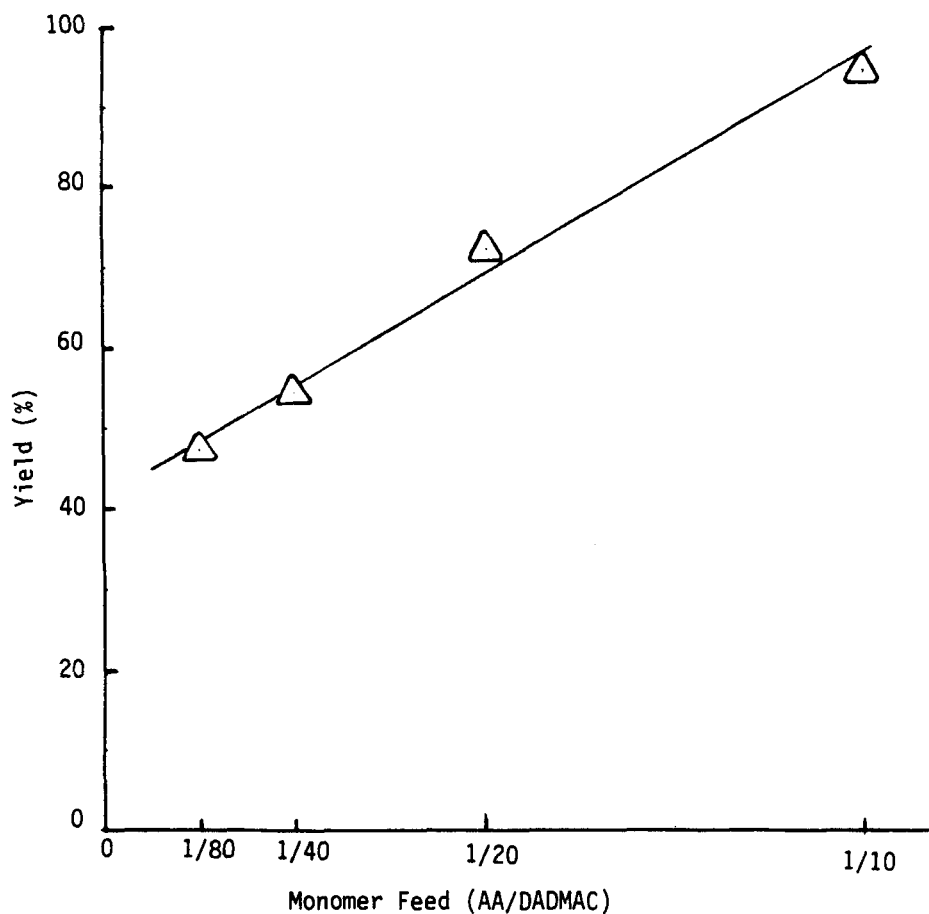


FIG. 4. Dependence of maximum yield on prepolymer composition. Abscissa: Monomer feed for preparation of prepolymer (Table 1).

Characterization

Molecular Weight of Copolymers

The results of size-exclusion chromatography (SEC) are shown in Tables 2-5. The trends of molecular weight with increasing $[\text{HNO}_3]$, $[\text{AM}]$, $[\text{Ce}^{4+}]$, and $[\text{prepolymer}]$ are similar to those of $[\eta]$, as expected.

TABLE 3. Effects of Concentration of Prepolymer on Yield and Intrinsic Viscosity^a

Run no.	Prepolymer, ^b g	Yield		$[\eta]$, dL/g	$\bar{M}_w \times 10^{-4}$
		g	%		
DA-P-1	0.10	0.297	36.7	3.34	121
DA-P-2	0.15	0.509	59.2	4.25	132
DA-P-3	0.20	0.601	66.0	5.20	141
DA-P-4	0.25	0.629	65.5	4.20	130
DA-P-5	0.30	0.650	64.5	4.17	130
DA-P-6	0.35	0.667	62.9	4.00	128

^aPolymerization conditions: solution volume = 25 mL, AM = 0.71 g, $[\text{Ce}^{4+}] = 0.5 \text{ mmol/L}$, $[\text{HNO}_3] = 5 \text{ mmol/L}$, temperature = 30°C, polymerization time = 24 h.

^bPrepolymer = PP-2-1.

TABLE 4. Effect of Acrylamide Concentration on Molecular Weight of Copolymer^a

Run no.	[AM], mol/L	$[\eta]$, dL/g	$\bar{M}_w \times 10^{-4}$
DA-A-1	1.25	6.5	160
DA-A-2	1.00	6.3	155
DA-A-3	0.75	5.3	153
DA-A-4	0.50	4.6	138
DA-A-5	0.40	3.4	130
DA-A-6	0.20	—	71

^aPolymerization conditions: solution volume = 25 mL, PP-2-1 = 0.15 g, $[\text{Ce}^{4+}] = 0.5 \text{ mmol/L}$, $[\text{HNO}_3] = 5 \text{ mmol/L}$, temperature = 30°C, polymerization time = 24 h.

TABLE 5. Effect of Nitric Acid Concentration on Molecular Weight of Copolymer^a

Run no.	[HNO ₃], mmol/L	[η], dL/g	$\bar{M}_w \times 10^{-4}$
DA-N-1	1	—	130
DA-N-2	2	3.55	126
DA-N-3	3	4.60	133
DA-N-4	4	4.80	137
DA-N-5	5	4.57	135
DA-N-6	6	4.56	132
DA-N-7	7	3.58	104
DA-N-8	8	2.65	67

^aPolymerization conditions: solution volume = 25 mL, PP-2-2 = 0.25 g, AM = 0.71 g, [Ce⁴⁺] = 0.5 mmol/L, temperature = 30°C, polymerization time = 24 h.

Composition of Copolymers

For use as cationic flocculants, charge density in the polymer is very important because it is closely related to properties of the polymer [3]. The content of cationic monomer units in the copolymer governs the charge density of the macromolecular chain, and it can be determined by elemental analysis. The elemental analyses data for two series of samples are listed in Table 6. Prepolymers PP-1-1 and PP-2-2 are well-defined in structure and may be written as follows:

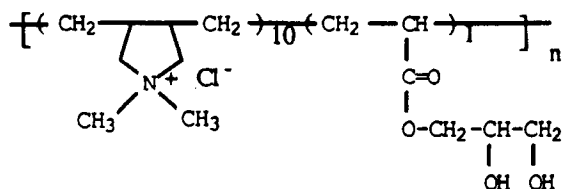
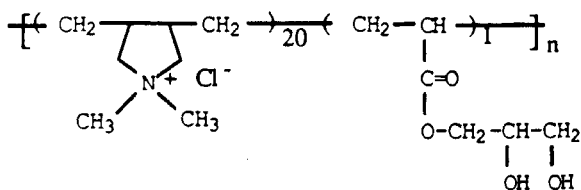


TABLE 6. Composition of Copolymer by Elemental Analysis

Sample	AM in feed, wt%	Cl, wt%	N, wt%	AM in copolymer, wt%
DA-P-1	87.6	2.50	16.82	87.2
DA-P-2	82.6	3.54	16.47	82.1
DA-P-3	78.0	3.62	16.86	82.0
DA-P-4	73.9	4.24	16.09	78.5
DA-P-5	70.3	5.26	15.49	73.3
DA-P-6	67.0	6.18	14.90	68.4
DA-63	58.6	5.09	14.37	71.8
DA-64	58.6	5.01	14.61	72.1
DA-65	58.6	4.97	14.34	72.1

and



(see Table 1). The moles of AM per repeat unit can be estimated on the basis of these structures. It can be seen from Table 6 that the content of AM monomer units in the polymer increased with increasing AM concentration in the feed. Moreover, the composition of the copolymer remained constant at constant feed composition although the other polymerization conditions were changed. Furthermore, in the case of PP-2-2, the composition of copolymers was very close to that of the feed. The reliability of the data was also checked by GPC (Table 7).

Proof of Grafting

The presence of a poly-DADMAC-*g*-AM copolymer in these reactions is evident because there is a substantial difference in solubility between the poly-

TABLE 7. Composition of Copolymer

Sample	AM ^a in sample, wt%	DADMAC ^b in sample, wt%	Composition of copolymer, ^c AM, wt%
DA-P-1	68.9	11.4	85.8
DA-P-2	69.3	16.1	81.1
DA-P-3	78.0	16.5	82.5
DA-P-4	70.0	19.3	78.3
DA-64	63.1	22.8	73.4

^aGPC method. Column: glycerated CPG, 74 Å; mobile phase, 0.2 M Na₂SO₄; flow rate, 3 mL/min.

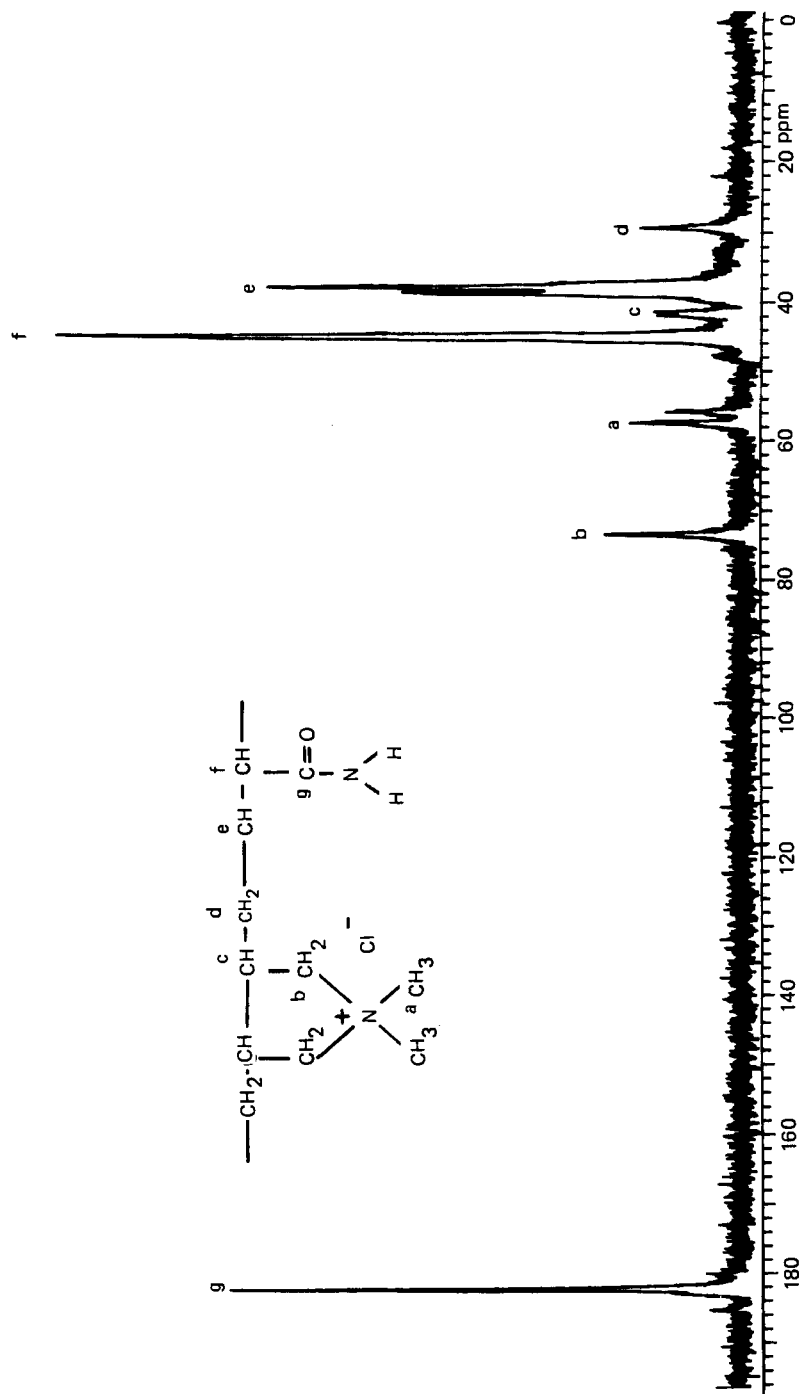
^bElemental analysis.

^cCalculated based on AM and DADMAC monomer units.

mer and the copolymer. The prepolymers are water soluble and soluble in some polar organic solvents, such as acetone, alcohols, etc. The copolymers are also water soluble, but they do not dissolve in acetone and isopropanol. Other evidence of grafting can also be provided by the ¹³C-NMR spectra of samples of the purified copolymers. A typical NMR spectrum is shown in Fig. 5. The peaks a, b, c, and d, which were identified with those [8] of poly-DADMAC, clearly indicate the presence of DADMAC monomer units in the matrix of PAM. However, the free prepolymer does not appear in the carefully purified copolymers.

CONCLUSIONS

Graft copolymerizations of the prepolymer with AM have been studied by means of viscometry, SEC, NMR, and elemental analysis. It may be concluded that the reactivity of prepolymers is closely related to the number of sites available for grafting on the molecular backbone. The effect of Ce⁴⁺ concentration on conversion, $[\eta]$, and molecular weight is significant with the other conditions kept constant. The highest molecular weight obtained was 1.70×10^6 , as measured by SEC. Elemental analyses indicated that the composition of the copolymers is dependent on the ratio of concentration of monomer to concentration of prepolymer, and that the high-

FIG. 5. A typical ^{13}C -NMR spectrum of the graft copolymer.

est amount of DADMAC monomer units incorporated into copolymer was 33 wt%.

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