Synthesis of a New Cationic Acrylamide–Dicyanodiamide Macromer and Its Copolymerization with Acrylamide

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ABSTRACT: Acrylamide–dicyanodiamide macromer (M) is a new cationic condensation polymer of acrylamide (Am), dicyanodiamide (D), formaldehyde (F), and ammonium chloride (NH_4Cl) with C=C as one of the end groups. The process of condensation was monitored by high-pressure liquid chromatography, and C=C was identified by ^1H NMR. Investigation on the kinetics of reactions between Am and F as well as D and F supported the suggestion about the polycondensation mechanism. In the synthesis of M, feed composition remarkably affected its molecular weight ($\bar{M}_w$) and structure. The higher the ratio of Am/D, the lower $\bar{M}_w$, and a fraction of molecular chains contains more than one C=C; conversely, the lower the content of Am, the higher $\bar{M}_w$, and some molecular chains contain no C=C. M can polymerize with Am to produce graft copolymers, which has been confirmed by GPC. Two copolymers were obtained by adjusting the dosage of Am. The charge density, molecular weight, and molecular structure of the copolymers have been characterized, and their viscosity behavior in aqueous solutions has been studied.

Introduction

A considerable amount of research effort has been made in the area of the preparation of tailor-made comblike graft copolymer, because the diversity of the polymeric nature of the segments in graft copolymers can provide a wide range of properties depending on the amphiphilicity, surface activity, and compatibility of the segments. For this purpose, the macromer method may be one of the most promising approaches. Macromer represents a polymer containing a polymerizable group at one end of the chain so that it can polymerize with various comonomers forming graft copolymers of well-defined structure and composition to meet the requirement of specified molecular design.

The polycondensate of dicyanodiamide (D) and formaldehyde (F) is a cationic polyelectrolyte having wide-ranging uses[1,2] due to its high charge density, but, on the other hand, its low molecular weight limits its efficiency in practical applications. As the amide group can also react with F, we expect that it is possible to prepare a new cationic macromer by polycondensation of D, F, and acrylamide (Am) together, and then the macromer can possibly polymerize with vinyl monomer (e.g., Am) to produce a graft cationic polyelectrolyte of high molecular weight.

There are many methods for the synthesis of macromers, such as anionic polymerization,[3-6] cationic polymerization,[7,8] free-radical polymerization,[9,10] and polycondensation.[11] The active group C=C was introduced either by using functional initiators or by end-capping with a functional reagent, so that C=C could be definitely located at the end of the macromer chain. But for the D, F, and Am reaction system, the polycondensation process is comparatively complicated, since the three reactants can react with each other. The site of C=C is not clear, and the feed composition may influence considerably the structure and molecular weight of the products (including macromer and graft copolymers). In the present paper, the optimum conditions for the preparation of the macromer and its copolymer with Am have been explored, and their charge density, molecular weight, and the other molecular structural parameters have been determined. It was found that this new cationic macromer could be prepared easily, consisting of a C=C active group at the end of the macromer chain which could polymerize with Am (or other vinyl monomers), producing a graft copolymer whose molecular weight and charge density could be controlled on purpose.

Experimental Section

Materials. Acrylamide (Am; Shanghai Factory of Chemical Reagent) was recrystallized twice from a mixed solvent of benzene and methanol. Dicyanodiamide (D; Sanming Factory of Chemical Reagent) was recrystallized twice from ethanol. Reagent-grade formaldehyde (F; 37% formalin) and ammonium chloride (NH_4Cl; Beijing Factory of Chemical Reagent) were used without further purification. Reagent-grade ammonium persulfate and sodium sulfite (Guangzhou Factory of Chemical Reagent) were used as initiators. Reagent-grade acetone and 2-propanol (Guangzhou Factory of Chemical Reagent) were used as precipitants. Reagent-grade tetrahydrofuran (THF; Shanghai Factory of Chemical Reagent) and ammonium acetate (Guangzhou Factory of Chemical Reagent) were used in the measurement of GPC. Reagent-grade methanol and benzene (Beijing Factory of Chemical Reagent) were used in the purification of Am. Reagent-grade bromine, iodine, hydroxyamine hydrochloride, and sodium thiosulfate (Guangzhou Factory of Chemical Reagent) were used as titrants. Reagent-grade dimethyl sulfoxide (DMSO; Guangzhou Factory of Chemical Reagent) was used as solvent in the measurement of ^1H NMR. Reagent-grade sodium chloride (Taishan Factory of Chemical Reagent) was used in the determination of viscosities and molecular weights.

Macromer Preparation. A total of 0–0.05 mol of Am, 0.5 mol of D, 0.55 mol of NH_4Cl, and 90 mL of 37% formalin (1.1 mol) were mixed in 40 mL of deionized water, and the polycondensation was run at 80 °C for 2 h. Five macromers of various molecular weights were obtained by controlling the dosage of Am. The products were purified by precipitation in acetone and dried at 50 °C under vacuum.

Investigation on the Reaction Kinetics of Am–F and D–F Systems. Am and D were reacted separately with F at various temperatures. Their initial concentrations were $[Am]_0 = 0.33$ mol·L^{-1}, $[D]_0 = 0.33$ mol·L^{-1}, and $[F]_0 = 0.67$ mol·L^{-1}. Aliquots of the reaction mixtures were taken out at certain time intervals for analysis in the following respects: products identified by IR spectra, the content of C=C by the bromination method,

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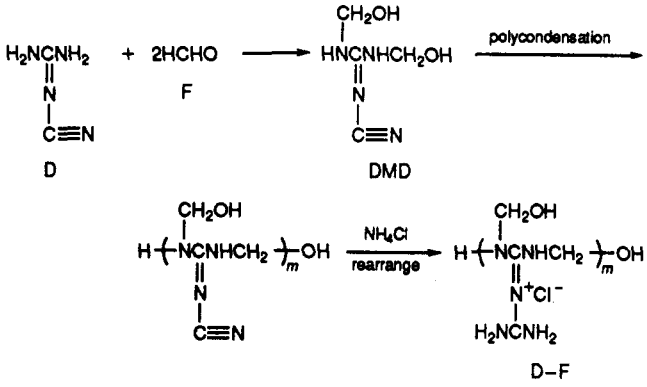
unreacted F by hydroxyamine hydrochloride, and the hydroxymethyl group by iodometric titration. The data of reaction kinetics for Am–F and D–F systems were then obtained from the above analytical results.

Graft Copolymer Preparation. A total of 0.15 g of ammonium persulfate, 0.1 g of sodium sulfite, 10 g of macromer, and 5–15 g of Am were mixed in 300 mL of deionized water and heated with stirring at 70 °C for 24 h under N_2. Two graft copolymers with different molecular weigths, P(M–Am)-I and P(M–Am)-II, were obtained by adjusting the dosage of Am. Copolymers were isolated by pouring the reaction solution into acetone, filtered, and dried at 50 °C under vacuum. The removal of PAm homopolymer which possibly formed during copolymerization was carried out as follows: The copolymer product was ground into a fine powder, extracted by refluxing with a large quantity of mixed solvent (2-propanol/deionized water = 1/1 (v/v)), and then filtered at 50 °C. The extraction was repeated with a fresh mixed solvent each time until no PAm homopolymer could be detected in the filtrate.

Measurements. High-pressure liquid chromatography (HPLC) was performed on an Altex Model 153 instrument equipped with a Waters Bondapak μ-C18 column (3.91 mm i.d. × 25 cm) under the following conditions: carrier solvent MeOH/H_2O = 50/50 (v/v), elution speed 0.5 mL/min, column temperature 30 °C, detector UV (254 nm). Gel permeation chromatography (GPC) was performed on a Waters GPC instrument equipped with a M-Bondagel E125 column, carrier solvent 0.25 mol/L CH_3COONH_4/THF = 75/25 (v/v), elution speed 0.5 mL/min, column temperature 60 °C, detector UV (254 nm). ^1H NMR spectra of reaction products in DMSO were obtained at 90 MHz on a JEOL FX-90Q instrument using tetramethylsilane (TMS) as an internal standard at 25 °C. The colloidal conductometric titration was carried out using a DDS-11A type conductometric titration apparatus. Molecular weight determination was made by a low-angle laser light scattering (LALLS) method using Chromatix KMX-6. The viscosity of the copolymer aqueous solutions was determined at 30 ± 0.05 °C using a Cannon–Ubbelohde dilution-type viscometer.

Results and Discussion

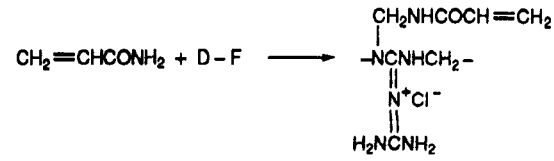
1. Synthesis of Macromer by the Polycondensation of Am, D, and F. According to Spiethoff,[12] the condensation process between D and F in the presence of NH_4Cl is



Since intermolecular reaction of the terminal active H–N< of one oligomer with the pendant $-CH_2OH$ groups of other oligomers is much more difficult than with the terminal $-CH_2OH$ due to steric effects, the possibility of a producing branch product is very small. In general, only linear condensation takes place.

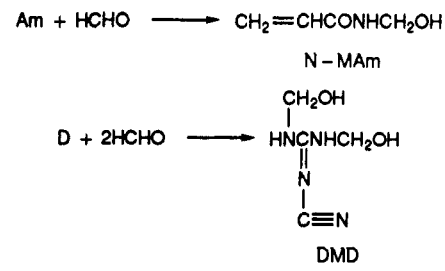
But in the synthesis of macromer, the case is much more complicated. As both Am and D can react easily with F, the polycondensation of Am, D, and F may be carried out in either mode shown as follows.

Mode A. Am participates in the reaction after D has condensed with F. The C=C in the above product is



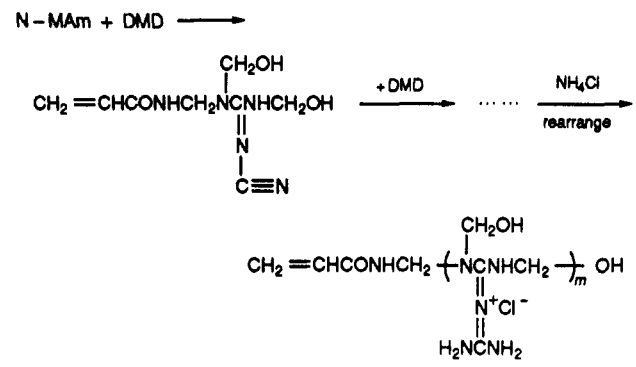
located in the side chain.

Mode B. Both Am and D react with F simultaneously.



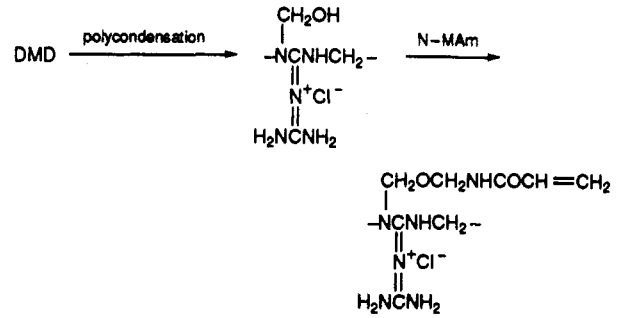
Then the following three reaction modes may possibly take place:

B(a). N-MAm immediately condenses with DMD to produce macromer.



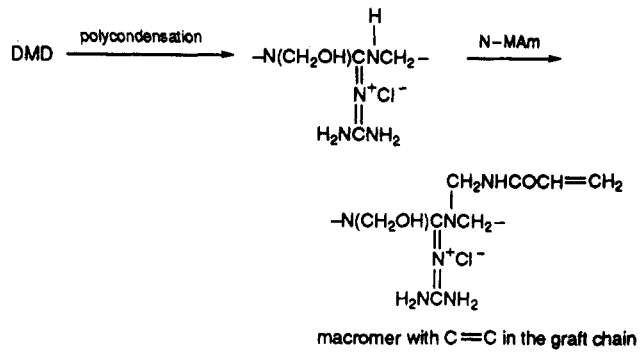
macromer with C=C at the end of the main chain

B(b). N-MAm reacts with the pendant –OH groups of oligomers formed by the polycondensation of DMD.



macromer with C=C in the graft chain

B(c). N-MAm reacts with the active H in the backbone of the DMD polycondensation oligomers. In both A and



macromer with C=C in the graft chain

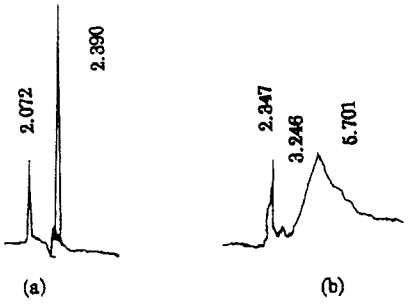


Figure 1. HPLC curves of the reaction system at different reaction times (Am/D = 1/10 (mol), carrier solvent MeOH/H_2O = 50/50 (v/v)): (a) 0 min; (b) 10 min.

B modes, when Am is fed in excess, Am (or N-MAm) will react further with either terminal -OH (or -H) or pendant -OH (or -H), so that there will be two or more C=C groups in the macromer molecule. Obviously, owing to the cross-linking formation, it is very unfavorable for the macromer to polymerize with vinyl monomer to produce a water-soluble copolymer. Therefore, the feed composition control plays an important role in the synthesis of the macromer.

The analysis mentioned above shows that the reactions between Am, D, and F are quite complicated. The site of C=C in the macromer is not clear, and the feed composition may influence considerably the structure and molecular weight of the macromer and its copolymers with vinyl comonomers. In order to examine the mode of polycondensation and the structure of the macromer, the following explorations have been done.

1.1. Study of the Mechanism of Polycondensation. The HPLC curves for the Am-D-F reaction system were taken at the beginning of mixing and 10 min after mixing. The results are shown in Figure 1. It has been found from our experiment that the elution times of pure Am and D in HPLC using the mixture of MeOH and H_2O (50/50 v/v) as carrier solvent are 2.077 and 2.359 min. Hence, in Figure 1a, peaks at 2.072 min (9.09% by weight) and 2.390 min (90.9% by weight) refer to the elution times of pure Am and D, respectively, since no reaction occurs at the beginning. After 10 min, the content of D lowers to 20.43% (2.35 min) and the Am peak has disappeared (Figure 1b); i.e., Am has been completely consumed within 10 min. In Figure 1b, the peaks at 2.721 min (3.0067% by weight), 3.246 min (3.843% by weight), 5.071 min (72.6110% by weight) are the elution times of other products with different structures and molecular weights. As these other products had nothing to do with our study, they were not further examined.

The above results indicate qualitatively that the reactivity of Am with F may be higher than that of D with F. In order to compare their reactivities quantitatively, the reaction kinetics of Am + F and D + F have been investigated as follows.

a. Am + F. Theoretically, the investigation should be made at the temperature (80 °C) at which the polycondensation Am + F + D was carried out, but the reaction of Am + F was too fast at 80 °C, unfavorable to get accurate kinetic data. Thus, the reaction was studied at 30–50 °C. The relationship between product concentration and reaction time is shown in Figure 2.

The reaction can be expressed as:

$$\underset{\text{Am}}{CH_2{=}CHCONH_2} + \underset{\text{F}}{HCHO} \underset{k_{A^-}}{\overset{k_A}{\rightleftarrows}} \underset{\text{N-MAm}}{CH_2{=}CHCONHCH_2OH}$$

The reverse reaction can be neglected due to the high

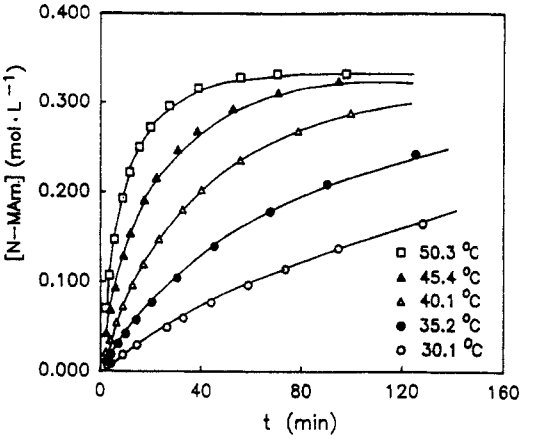


Figure 2. Relationship between the concentration of N-MAm and reaction time.

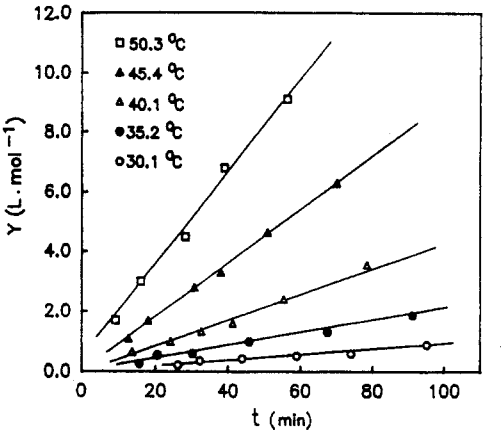


Figure 3. Relationship between Y and the reaction time for the Am + F reaction.

conversion of Am. If the reaction is assumed to be second-order, the rate of Am consumed is given by:

$$dx/dt = k_A([A]_0 - x_A)([F]_0 - x_A) \qquad (1)$$

where $[A]_0$ and $[F]_0$ denote initial concentrations of Am and F (mol/L), x_A is the concentration of N-MAm (mol/L), k_A is the rate constant of reaction (L/mol·min), and t is the reaction time.

Upon integration, a second-order rate expression is obtained:

$$Y = \frac{1}{[A]_0 - [F]_0} \ln \frac{[F]_0([A]_0 - x_A)}{[A]_0([F]_0 - x_A)} = k_A t \qquad (2)$$

The linear plots of the data are shown in Figure 3, which reveals that the assumption of a second-order reaction is correct. The slopes of straight lines are rate constants (k_A). The plot of ln k_A against the reciprocal of the reaction temperature T is shown in Figure 4, from which k_A at 80 °C is obtained by extrapolation, and equal to 7.35 L/mol·min.

b. D + F. Reaction products of D with F are closely related to temperatures. It was found[12] that mono- or bis-hydroxymethylated products were obtained at low temperature (<44 °C) and polycondensation occurred at higher temperature. It is very difficult to study reaction kinetics of D with F at 80 °C due to the complicated composition of the products. Thus, study was carried out at temperatures lower than 40 °C. The relationship of the concentration of the product with the reaction time is shown in Figure 5.

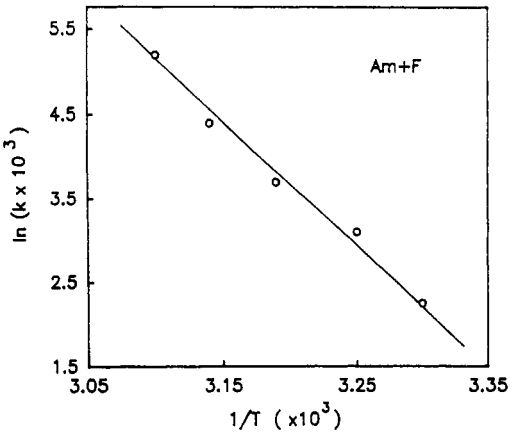


Figure 4. Relationship between ln k_A and $1/T$ for the Am + F reaction.

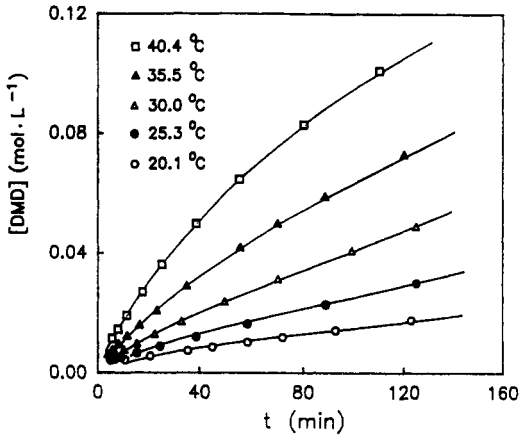
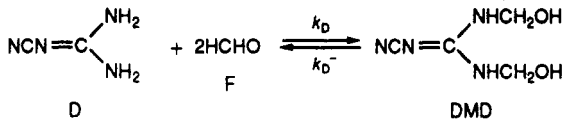


Figure 5. Relationship between the concentration of DMD and the reaction time.

The reaction between D and F can be expressed as:



If the reaction is assumed to be third-order and the reverse reaction can be neglected, then the reaction rate is expressed:

$$dx/dt = k_D([D]_0 - x_D)^2([F]_0 - 2x_D) \quad (3)$$

Upon integration, eq 3 can be transformed into eq 4 under the condition of $[F]_0 = 2[D]_0$.

$$Z = \frac{1}{4}\left[\frac{1}{([D]_0 - x_D)^2} - \frac{1}{[D]_0^2}\right] = k_D t \quad (4)$$

A linear relationship is observed between Z and t (Figure 6), indicating the correctness of the assumed third-order reaction. The k_D at 80 °C was obtained by extrapolation of the linear plot of ln k_D vs $1/T$ (Figure 7), and its value is 1.28 $L^2/mol^2 \cdot min$.

The above kinetic data on the Am + F and D + F reactions convince us of the high reactivity of Am (k_A is 5.76-fold of k_D), so polycondensation according to mode A was completely excluded. Then do the three ways in mode B occur at the same time? It has been reported[13] that only at high temperatures and under strong acidic conditions can the anhydro reaction between the hydroxymethyl groups take place. In addition, study confirmed[14] that the number of active hydrogen atoms (i.e., possessing reactivity) of a D molecule is three at most though there exist four hydrogen atoms per D molecule.

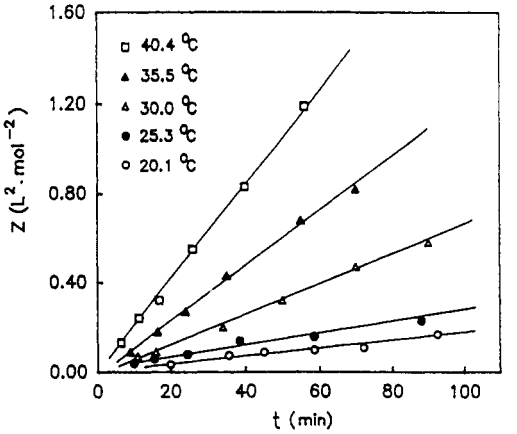


Figure 6. Relationship between Z and the reaction time for the D + F reaction.

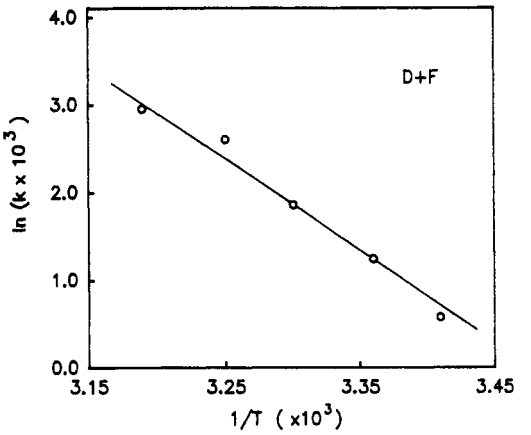


Figure 7. Relationship between ln k_D and $1/T$ for the D + F reaction.

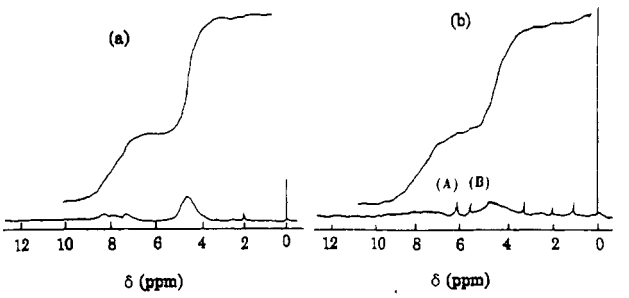
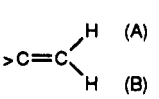


Figure 8. ^1H NMR spectra of the D–F condensation polymer (a) and macromer-IV (Am/D = 0.072 (mol)) (b) (solvent: DMSO).

Therefore, the hydrogen in backbones of D–F has no reactivity, which is the main reason that only linear polymer is obtained and no cross-linking occurs when D polycondenses with F.[15] According to the above analysis, the possibility of modes B(b) and B(c) is also excluded. Thus, the only conclusion is that the polycondensation follows mode B(a) and the C=C group locates at the end of the main chain.

1.2. Identification of C=C. The presence of C=C in the macromer has been identified further by comparison of the ^1H NMR spectrum of macromer (Figure 8b) with that of polycondensate D–F (Figure 8a) which does not consist of $C=CH_2$. It is very clear that there are dual peaks in Figure 8b, but no such peaks in Figure 8a. The assignments of the dual peaks are as follows:



$\delta_A = 6.1$ ppm, $\delta_B = 5.5$ ppm

1.3. Effect of the Dosage of Am on the Molecular Weight of Macromer. The molecular weight of the

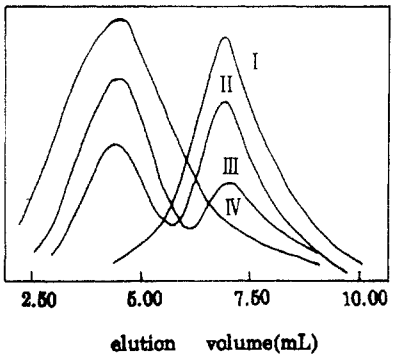


Figure 9. Gel permeation chromatography of the polymerization products of macromers with Am (reaction time: 24 h).

Table 1. Relationship between Am/D (mol) with $\bar{M}_w$ and τ of the Macromer

macromer	M-I	M-II	M-III	M-IV	M-V
Am/D	0	0.03	0.05	0.072	0.10
$\bar{M}_w \times 10^{-3}$	3.51	3.39	3.28	2.53	1.75
$A_2 \times 10^3$	-1.38	-1.61	-3.17	-4.26	-5.90
$\tau \times 10^3$ (C equiv/g)	5.54	5.49	5.41	5.35	5.28

macromers was determined by the LALLS method with 0.1 mol/L of an aqueous NaCl solution as solvent, and products were filtered and purified before determining their molecular weight. Good results were obtained, and the effect of feed composition on the molecular weight is shown in Table 1. Am is a monofunctional monomer, whereas D is a bifunctional one. Thus, it is inevitable that the dosage of Am considerably affects the molecular weight of the products if Am participates in polycondensation. It is very obvious that the higher the Am/D ratio (mol), the lower the $\bar{M}_w$ of the macromer. It implies further that the Am unit is attached to the end of the macromer chain. In the case where the content of Am is high enough, the Am unit would attach to both ends of the macromer chain.

1.4. Charge Density of the Macromer. Macromers were titrated conductometrically with an anionic polyelectrolyte, poly(vinyl sulfate potassium) (PVSK), and the obtained charge density τ (C equiv/g) is listed in Table 1. If each monomer unit of macromers contains a cationic group, then the calculated charge density should be 5.57×10^{-3} (C equiv/g), which is fairly identical with the experimental results, indicating that NH_4Cl has completely reacted. The gradual drop of τ from M-I to M-V attributes to the increase of the Am content.

2. Synthesis of the Graft Copolymer P(M-Am) by the Copolymerization of the Macromer with Am. The five macromers (see Table 1) were copolymerized with Am under the same conditions in aqueous solutions for 24 h. It was found that all the copolymer products were water-soluble except that of M-V, probably due to the cross-linking between the copolymer molecules resulting from the excessive content of Am in M-V (i.e., due to the existence of C=C at the two ends of M-V). The other four products, purified by precipitation and extraction, were detected by GPC analysis as shown in Figure 9. M-I is virtually a polycondensate of D and F containing no C=C, so it does not participate in copolymerization with Am. The single peak at 0.7 mL in curve I corresponds to the elution volume of D–F. In curve IV, the peak at 7.0 mL disappears, while another single peak appears at 4.3 mL. That means all of M-IV has been used up and only the copolymer Am-IV is eluted with a elution volume at 4.3 mL. In curves II and III, there exist dual peaks at 7.0 and 4.3 mL, indicating that a fraction of M-II (69.3%, by weight) and M-III (32.7%, by weight), which consists of neither Am structural units nor a C=C active group, does not participate in copolymerization. It can be concluded that the copolymerization ability of the macromer becomes stronger with enhancing the ratio of Am/D and the optimum Am/D is 0.072 in the present research.

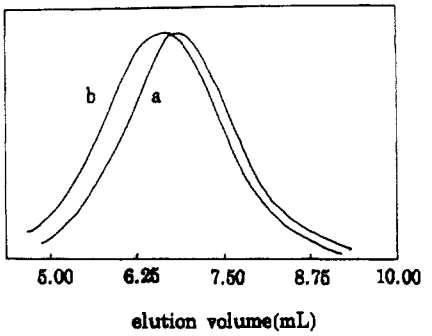


Figure 10. Gel permeation chromatography of macromer-IV (a) and its homopolymer (b) (reaction time: 24 h).

Table 2. Molecular Characteristic Parameters of Two Copolymers

P(M-Am)	$\tau \times 10^3$, C equiv/g	W_g	$\bar{M}_w \times 10^{-4}$
I	3.98	71.4	40.2
II	2.65	47.6	57.8

The GPC curve for the homopolymer of M-IV which was prepared under the same conditions of copolymerization mentioned above is shown in Figure 10b. It is practically identical with curve a for macromer-IV. It implies that the self-polymerization of M-IV during copolymerization is nearly impossible due to the steric effect.

3. Characterization of Copolymer P(M-Am). Two graft copolymers P(M-Am)-I and P(M-Am)-II with different charge densities and molecular weights have been prepared by polymerizing M-IV with different dosages of Am. The charge density τ (C equiv/g) of P(M-Am) was determined by conductometric titration, and the weight fraction (W_g) of the graft chain can be calculated by: $W_g = 179.5\ \tau$, where 179.5 is the molecular weight of the structural unit in the macromer. The molecular weight of the copolymers was determined by the LALLS method with 0.1 mol/L of NaCl as solvent. All these results are listed in Table 2.

A distinctive feature of graft copolymers obtained by using macromers is that the molecular weight of the macromer, $\bar{M}_g$, which forms a graft chain can be determined beforehand. Thus, as long as the overall molecular weight of the copolymer, $\bar{M}_o$, and the weight fraction of the graft chain, W_g, are known, other parameters of molecular structure can be calculated as follows.[16]

(a) Molecular weight of the backbone:

$$\bar{M}_b = \bar{M}_o(1 - W_g)$$

(b) Average number of the graft chain:

$$\bar{N}_g = \bar{M}_o(W_g/\bar{M}_g)$$

(c) Molecular weight of the segment between two adjacent graft points in the backbone:

$$\bar{M}_{gg} = \bar{M}_b/\bar{N}_g$$

Thus, the above structural parameters can be easily obtained with known data $\bar{M}_o$ ($\equiv\bar{M}_w$ in Table 2), $\bar{M}_g$ ($\equiv$molecular weight of macromer-IV in Table 1), and W_g (in Table 2). The results are listed in Table 3.

4. Viscosity of P(M-Am) in Aqueous Solutions. The plot of η_{sp}/C vs C for P(M-Am) in water shows the

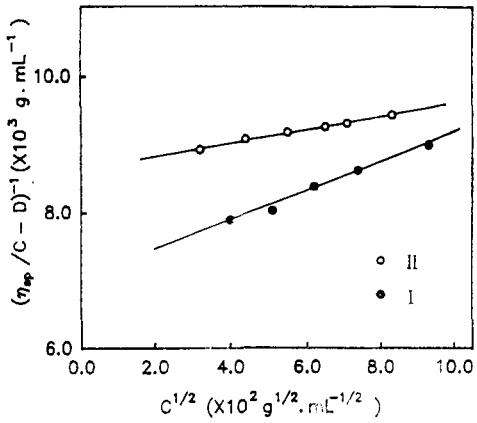


Figure 11. Relationship between $(\eta_{sp}/C-D)^{-1}$ and $C^{1/2}$ for P(M–Am) in H_2O.

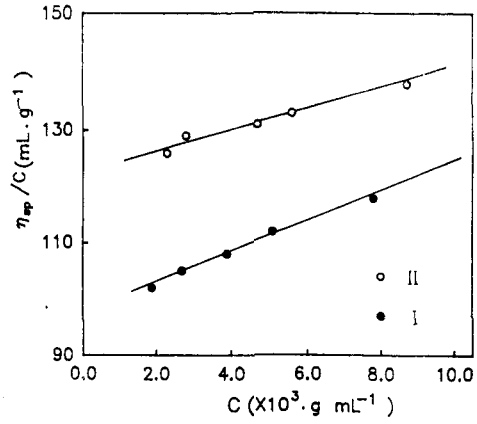


Figure 12. Relationship between η_{sp}/C and C for P(M–Am) in 0.1 mol/L of an aqueous NaCl solution.

Table 3. Structural Parameters and [η]'s for P(M–Am)

	structural param			[η]	
P(M–Am)	$\bar{M}_b \times 10^{-4}$	$\bar{N}_g$	$\bar{M}_{gg} \times 10^{-3}$	in H_2O	in NaCl soln
I	11.5	113	1.02	1.40×10^3	98.2
II	30.3	109	2.78	1.15×10^3	125

typical polyelectrolyte behavior. Then [η] in water can be obtained by a linear plot of $(\eta_{sp}/C-D)^{-1}$ vs $C^{1/2}$ (Figure 11) according to the Fuoss relation:[17]

$$\eta_{sp}/C = \frac{A}{1+BC^{1/2}} + D \qquad (5)$$

[η] in 0.1 mol/L of a NaCl solution is also easily found by a linear plot of η_{sp}/C vs C as shown in Figure 12. All [η]'s are listed in Table 3.

It is very interesting to find that [η], or the extent of coiling of P(M–Am), is closely related to the structural parameters. In water, $[\eta]_{II} < [\eta]_I$, although the molecular weight of P(M–Am)-II is higher than that of P(M–Am)-I and its backbone length ($\bar{M}_b$) is 2.63 times that of P(M–Am). This is obviously attributed to the stronger electrostatic repulsion between the cationic groups stemming from the smaller $\bar{M}_{gg}$ of P(M–Am)-I. But, once the polyelectrolyte effect has been suppressed in a NaCl solution, $\bar{M}_b$ plays an important role in governing the dimension of P(M–Am). The larger $\bar{M}_b$, the less extent it coils up, leading to $[\eta]_{II} \gg [\eta]_I$.

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