

Amine-Derivatized Poly(diallyldimethylammonium chloride) from *N*-Vinylformamide Copolymerization

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ABSTRACT: The reactivity ratios for the aqueous free-radical copolymerization of diallyldimethylammonium chloride and *N*-vinylformamide were found to be 0.13 and 1.92, respectively, from a Fineman–Ross analysis of a series of batch polymerizations. Because batch polymerization could not give a uniform product in a high yield with two monomers of such different reactivities, a semibatch procedure was developed in which the more reactive *N*-vinylformamide was added in 10 steps over the course of the copolymerization. The poly(diallyldimethylammonium chloride-*co*-*N*-vinylformamide) copolymers were hydrolyzed to give poly(diallyldimethylammonium chloride-*co*-vinylamine). The utility of the vinylamine/diallyldimethylam-

monium chloride copolymers was demonstrated by the preparation and characterization of three derivatives: (1) a copolymer with coupled dansyl groups for fluorescence detection; (2) a copolymer with coupled dansyl groups for ultraviolet–visible detection; and (3) an ultra-high-molecular-weight (1.6×10^6 Da) poly(diallyldimethylammonium chloride) by chain extension (coupling) with glycerol diglycidyl ether. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1068–1075, 2007

Key words: branched; cationic polymer; chromophoric polymer; fluorescent polymer; kinetics (polym.); polyamines; polyelectrolytes; synthesis; water-soluble polymers

INTRODUCTION

Poly(diallyldimethylammonium chloride) (PDADMAC) is a water-soluble cationic polymer first prepared in the 1950s and widely used in a number of applications. Wandrey et al.¹ recently published an excellent review of PDADMAC preparation, characterization, and applications. The popularity of PDADMAC reflects its great chemical and temperature stability, its low cost, and its efficacy in applications requiring water-soluble cationic polymers. However, the chemical stability of the pyrrolidinium and quaternary ammonium groups in PDADMAC is also a limitation: the homopolymer is virtually impossible to derivatize once it is formed. A further limitation of PDADMAC is that with conventional free-radical polymerization it is difficult to prepare the high-molecular-weight polymers desirable for flocculation and rheology-control applications. The highest PDADMAC molecular weight that we have found reported for an unfractionated polymer is 781,000 Da (mass average from static light scattering).² Fractionation gives values as high as 1,200,000 Da [undisclosed average measured by size exclusion chromatography (SEC)]³ and 920,000 Da (mass average from SEC).⁴

Copolymerization is the obvious route to extending the utility of PDADMAC. Wandrey et al.'s review¹ summarizes 220 articles covering all aspects of diallyldimethylammonium chloride (DADMAC) polymerization. Although a wide variety of comonomers have been reported, acrylamide seems to have received the most attention. The major difficulty with the DADMAC/acrylamide system is that acrylamide polymerizes much more quickly than DADMAC, requiring a semibatch polymerization strategy.

In this article, we describe the preparation of poly(diallyldimethylammonium chloride-*co*-*N*-vinylformamide) [poly(DADMAC-*co*-NVF)] copolymers that were hydrolyzed into the corresponding vinylamine copolymers. *N*-Vinylformamide (NVF),⁵ an isomer of acrylamide, is a water-soluble monomer, only recently commercially available, that is used for the preparation of polyvinylamine-based polymers and copolymers. We have found no reports of DADMAC copolymerization with NVF.

In addition to defining the prerequisites for obtaining a uniform copolymer, we illustrate the utility of amine-derivatized PDADMAC with examples of fluorescent labeling, chromophoric labeling, and molecular weight extension with a crosslinking agent.

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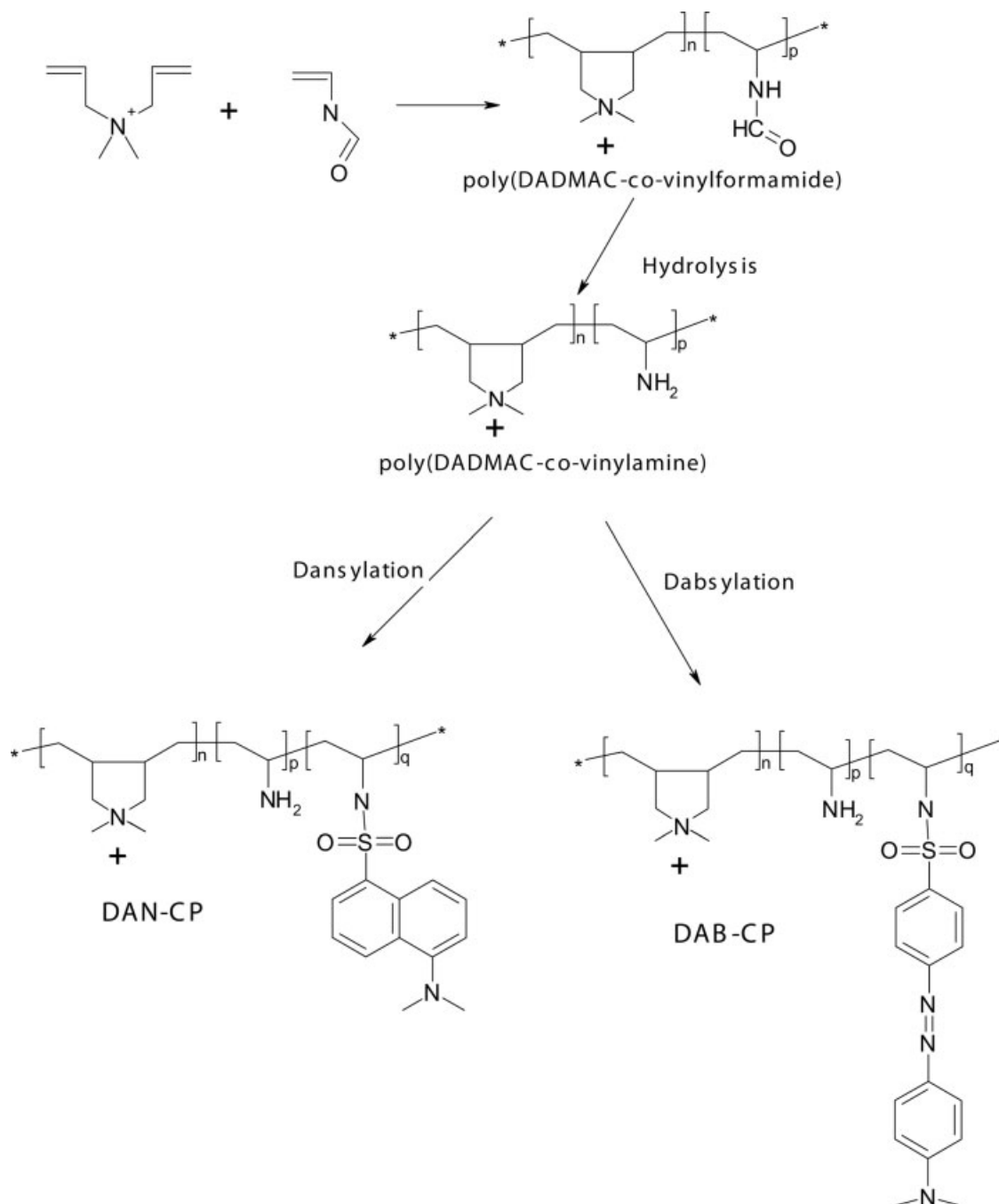
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EXPERIMENTAL

Chemicals

DADMAC (60 wt % aqueous solution; Aldrich, Oakville, Canada), 2,2'-azobisisobutyramidine dihydro-

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Scheme 1 Preparation and derivatization of the copolymers.

chloride (Wako, Osaka, Japan), and ethylenediaminetetraacetic acid dihydrochloride (EDTA; Wako) were used without further purification. NVF (Aldrich) was distilled under reduced pressure.

5-(Dimethylamino)naphthalene-1-sulfonyl chloride (dansyl chloride; Acros Pittsburg, PA), 4-(dimethylamino) azobenzene-4'-sulfonyl chloride (dabsyl chloride; Tokyo Kasei, Tokyo, Japan), 5-(dimethylamino)naphthalene-1-sulfonyl amide (dansyl amide; Tokyo Kasei), methyl orange, glycerol diglycidyl ether (Aldrich), and polyvinylsulfate potassium salt (PVSK; Wako) were

purchased and used without further purification. The other chemicals were reagent-grade. MilliQ water, (Millipore Ltd., Mississauga, ON, Canada), which was previously degassed by boiling, was used for the polymerizations.

Copolymer preparation

To determine the reactivity ratios, a series of batch polymerizations were conducted in which the total concentration of DADMAC and NVF was kept constant at 1.3 mol/L with the initial DADMAC concentration

TABLE I
Compositions of Poly(DADMAC-*co*-NVF) Polymers Isolated from Low-Conversion Batch Copolymerizations

f_1	n_1/n_2^a	Conversion (%)	F_1	M_1/M_2^b	$\frac{M_1/M_2}{n_1/n_2} \left(\frac{n_1}{n_2} - 1 \right)$	$\frac{(M_1/M_2)^2}{n_1/n_2}$
0.100	0.111	5.4	0.052	0.055	-1.913	0.225
0.201	0.252	6.3	0.110	0.124	-1.784	0.512
0.428	0.748	9.1	0.235	0.307	-1.688	1.823
0.599	1.494	9.5	0.335	0.504	-1.471	4.429
0.777	3.484	5.4	0.481	0.927	-0.275	13.1
0.896	8.615	9.8	0.630	1.703	3.56	43.6

^a Monomer ratio.

^b Molar ratio of DADMAC moieties to vinylformamide moieties in the copolymers.

varying between 0.13 and 1.17 mol/L. The aqueous monomer solutions were introduced into a 100-mL, three-necked glass flask, which was heated up to 45°C under bubbling nitrogen, and polymerization was initiated by the addition of an initiator (0.8×10^{-3} mol/L 2,2'-azobisisobutyramidine dichloride with 0.05% EDTA). The copolymerization was terminated at a conversion below 10% by the addition of hydroquinone.

The copolymers were precipitated in isopropyl alcohol and purified by repeated precipitations from water into isopropyl alcohol. The purified copolymers were dried to a constant weight in a vacuum desiccator under P_2O_5 . The contents of the cationic group (DADMAC) were determined by a colloid titration method⁶ with PVS_K as the titrant and 6-(*p*-toluidino)-2-naphthalenesulfonic acid potassium salt as the indicator. The colloid titration gave the equivalent weights (EWs) of the copolymers, from which the molar frac-

tion of DADMAC residues (F_1) was calculated with the following equation:

$$EW = \frac{162.1F_1 + 71.1(1 - F_1)}{F_1} \quad (1)$$

A semibatch copolymerization was used to prepare a uniform copolymer. To 500 mL of 15% aqueous DADMAC (0.46 mol) with an initiator (1.0×10^{-3} mol/L) at 50°C under stirring in a nitrogen atmosphere, 50 mL of 5.7% aqueous NVF (0.04 mol) was added in 10 equal shots over 10 h. Between each addition of NVF, a small amount of the reaction mixture was withdrawn and analyzed for the cationic content by colloid titration. The final product was precipitated in isopropyl alcohol and vacuum-dried.

Copolymer hydrolysis

Poly(DADMAC-*co*-NVF) was hydrolyzed to poly(diallyldimethylammonium chloride-*co*-vinylamine) [poly(DADMAC-*co*-vinylamine)]. According to the method of Gu et al.,⁷ 15 g of the copolymer was dissolved in 47 mL of water with stirring, and this was

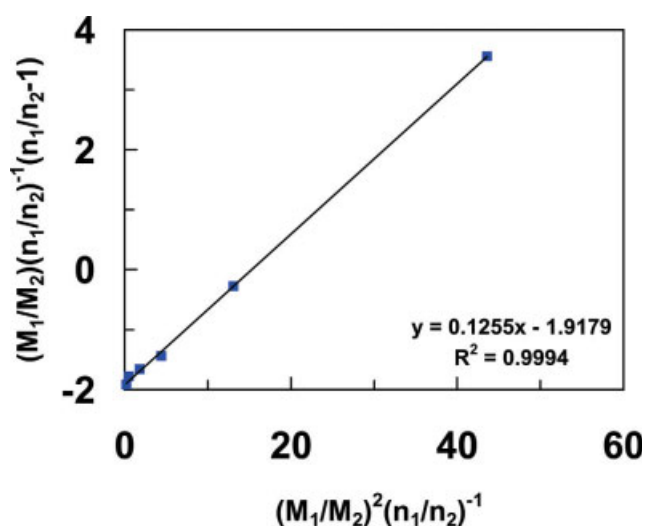


Figure 1 Fineman-Ross plot of the results listed in Table I. M_1/M_2 is the ratio of DADMAC and NVF moieties in the polymer, and n_1/n_2 is the corresponding ratio of the monomers. The slope is r_1 , and the intercept is $-r_2$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

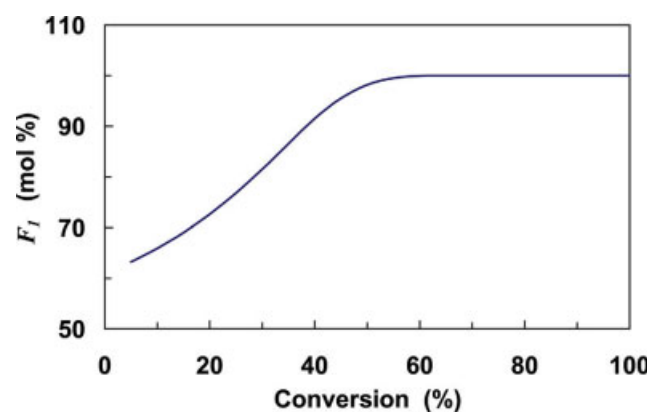


Figure 2 Calculated instantaneous molar fraction of the DADMAC moieties in the copolymer (F_1) as a function of the batch polymerization conversion. The initial DADMAC/NVF monomer ratio was 9 : 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
 M_w Values of Poly(diallyldimethylammonium chloride-co-vinylamine)s Extended with Glycerol Diglycidyl Ether

Sample	1	2	3	4	PDADMAC-L	PDADMAC-H
Reaction time (day)	0	2	3	4	—	—
M_w (kDa)	290	740	1100	1600	100 (100–200)	440 (400–500)

The values in parentheses are the values given by Aldrich for the commercial PDADMAC samples.

followed by the addition of 3 mL of 10N NaOH. The mixture was stirred for 10 h at 60°C under a nitrogen atmosphere. The product was neutralized with chilled HCl until the color of methyl orange changed from yellow to red, and then it was added to isopropyl alcohol to precipitate the product. The isolated copolymer was dissolved in water and precipitated from isopropyl alcohol two more times to purify the copolymer. The degree of hydrolysis was determined from the difference in the colloid titration values under acidic (ca. 3) and alkaline (ca. 12) conditions, and the results were confirmed by $^1\text{H-NMR}$ of poly(diallyldimethylammonium chloride-co-vinylamine) measured in D_2O .

Labeling of the copolymer

To 3 g of poly(DADMAC-co-vinylamine) dissolved in 12 mL of a sodium carbonate/sodium bicarbonate buffer (11 mL of 0.2M NaHCO_3 plus 1 mL of 0.05M Na_2CO_3 , pH 8.5) was added 6 mL of dimethylformamide (DMF). A freshly prepared dansyl chloride solution (0.45 g in 4.5 mL of DMF) was added slowly and was allowed to react at room temperature for 1 h. The product was neutralized with chilled 3M HCl and puri-

fied by three rounds of precipitation from water/acetone. The dansyl group content was calculated from the elemental sulfur content, which was determined at the Tokyo Institute of Technology Center of Analysis. The dansyl chloride functionalized copolymer was prepared in the same way.

Copolymer crosslinking with glycerol diglycidyl ether

Glycerol diglycidyl ether (2 g) was added to 80 g of a 10% aqueous hydrolyzed copolymer solution at room temperature under stirring. A part of the mixture was removed every day, diluted with water, dialyzed, and freeze-dried.

The molecular weights were measured by static light scattering with a Brookhaven BI-ISTW (New York, NY), which was equipped with a 5-mW Ne-He laser. The aqueous copolymer solutions were 1 : 1 diluted with a 1.0M NaCl solution, purified by filtration through 5- μm -pore-size membrane filters, which removed dust particles, and diluted with 0.5M NaCl.⁸ The scattering data analysis was performed with Brookhaven's Zimm plot analysis software^{9,10} with 0.176 mL/g for the refractive index increment dn/dc .²

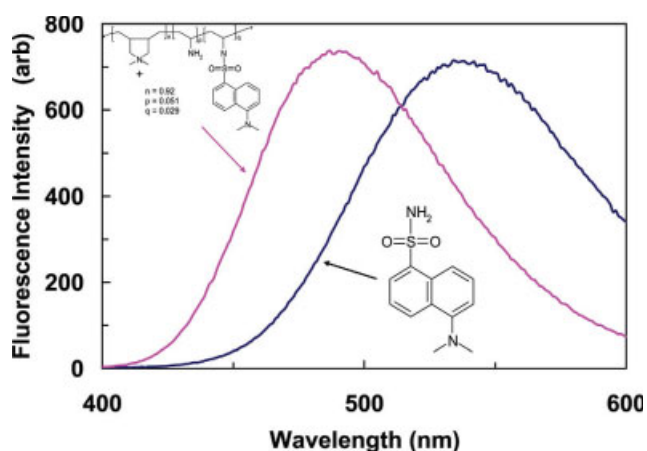


Figure 3 Comparison of the fluorescence emission intensity of the 25 ppm dansyl-labeled poly(diallyldimethylammonium chloride-co-vinylamine) copolymer with 15 ppm dansylamide. The excitation wavelengths corresponded to the maximum absorption: 328 nm for dansylamide and 319 nm for the copolymer. The pH was 6.3. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

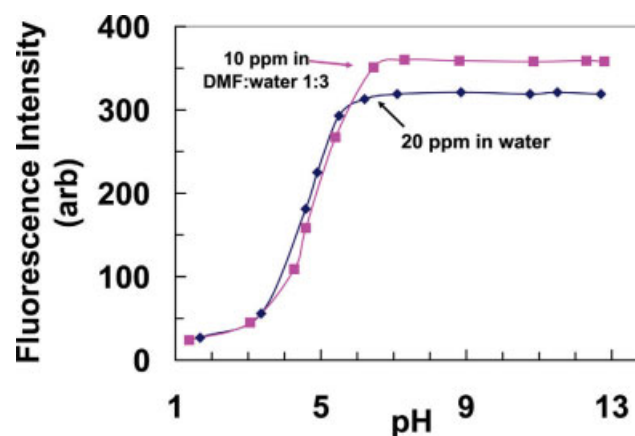


Figure 4 Influence of the pH on the fluorescence of the dansyl-labeled poly(diallyldimethylammonium chloride-co-vinylamine) copolymer. For the measurements in DMF and water (1:3 v/v), the excitation wavelength was 328 nm, and the intensity was measured at 490 nm. For the measurements in water, the excitation wavelength was 319 ppm, and the emission was measured at 500 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

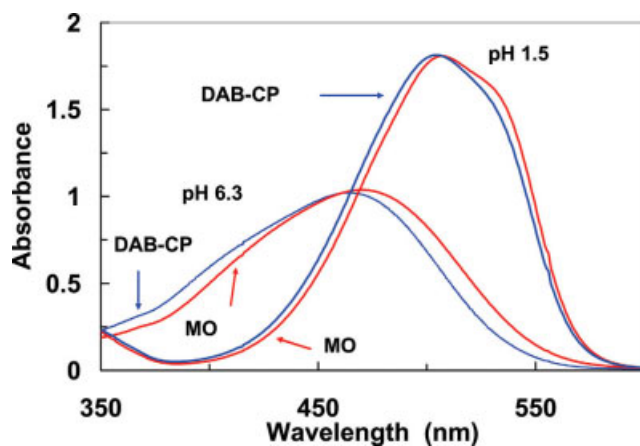


Figure 5 Adsorption spectra of DAB-CP (400 ppm) and methyl orange (MO; 9.3 ppm) at pHs 1.5 and 6.3. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Copolymer preparation

A series of batch copolymerizations employing various ratios of DADMAC (monomer 1) to NVF (monomer 2) were terminated at low conversions, and the product was purified. The structures of the monomers and polymers are shown in Scheme 1. The copolymer composition was determined by colloid titration,⁶ and the results are summarized in Table I. The Fineman–Ross plot^{10,11} of the copolymer composition data is shown in Figure 1, and the corresponding reactivity ratios are $r_1 = 0.13$ and $r_2 = 1.92$. The DADMAC/NVF reactivity ratios are consistent with the reactivity ratios for DADMAC (0.02–0.04) and acrylamide (4.6–6.7) reported by Brand et al.¹² because for both systems $r_1 < 1$ and $r_2 > 1$. These results indicate that NVF polymerizes much more quickly than DADMAC. To illustrate difficulties with batch polymerization, the instantaneous polymer composition was calculated as a function of the conversion with eq. (2), the Mayo–Lewis equation,¹⁰ together with eq. (3), the Meyer–Lowry equation,¹³ where F_1 is the instantaneous molar fraction of DADMAC moieties in the copolymer, x is the conversion, and f_1 and f_2 are the molar fractions of the DADMAC and NVF monomers:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (2)$$

$$x = 1 - \left(\frac{f_1}{f_{1,0}} \right)^\alpha \left(\frac{1-f_1}{1-f_{1,0}} \right)^\beta \left(\frac{f_{1,0} - \delta}{f_1 - \delta} \right)^\gamma \quad (3)$$

where

$$\alpha = \frac{r_2}{1 - r_2}$$

$$\beta = \frac{r_1}{1 - r_1}$$

$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)}$$

and

$$\delta = \frac{1 - r_2}{2 - r_1 - r_2}$$

The calculations in Figure 2 show that in a batch copolymerization, the first polymer formed will be rich in NVF, whereas all the NVF monomer will be consumed when the overall conversion is only 50%. Therefore, semibatch polymerizations are required for uniform products.

In a semibatch polymerization, in which NVF was added in 10 equal increments over 10 h, the copolymer composition was measured between each NVF addition. The DADMAC content in the copolymer ranged from 91 to 93% over the course of the polymerization.

Hydrolysis

NVF residues in the semibatch copolymer were converted to primary amines by alkaline hydrolysis.^{7,14} The structures before and after hydrolysis are shown in Scheme 1. Despite the severe hydrolysis conditions (i.e., 10 h in 0.6M NaOH at 60°C), a colorless product was obtained, reflecting the stability of the pyrrolidinium ring formed by DADMAC cyclization. The degree of hydrolysis, determined by colloid titration, was 95%, which corresponded to an amine content of 8 mol % in the copolymer. ¹H-NMR confirmed that most of the amide protons (7.5–8.2 ppm) were removed in the hydrolysis procedure. The molecular weight determined by static light scattering was 2.90×10^5 (see Table II).

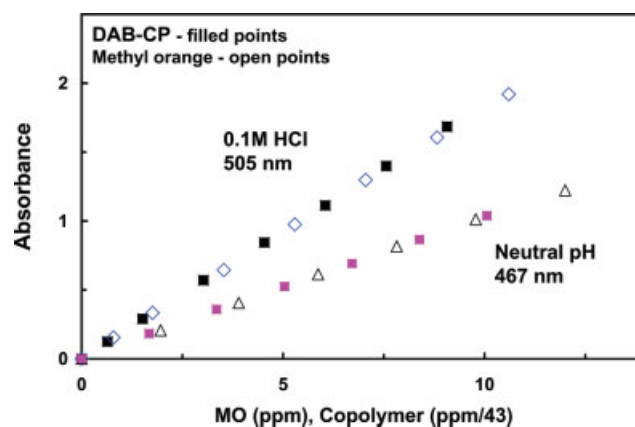
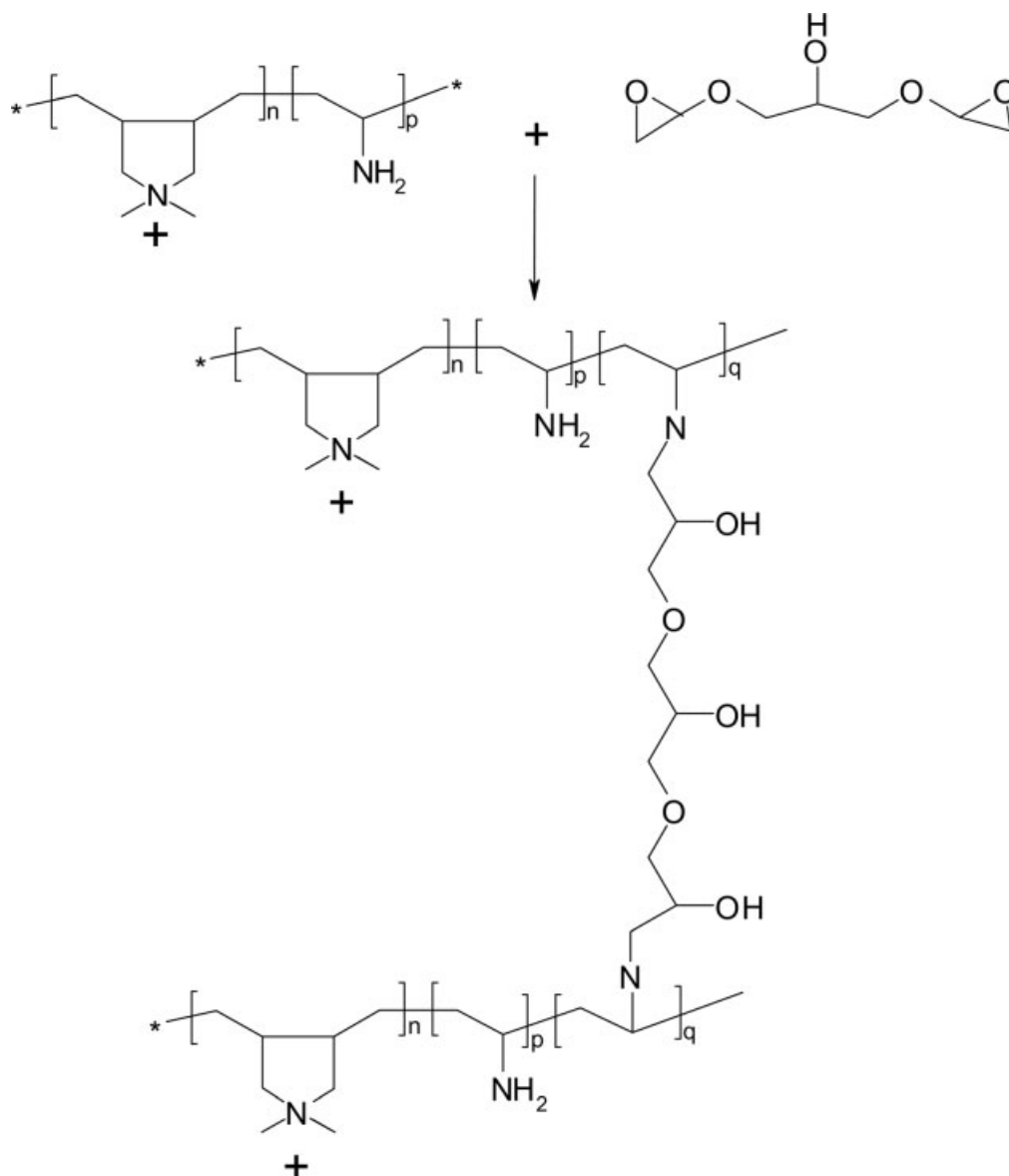


Figure 6 Fitting of the absorbance of DAB-CP to that of methyl orange (MO) under acidic and neutral conditions. Dividing the copolymer concentration by 43 gave the best fit for both data sets, which corresponded to a dabsyl content of 1.1 mol % in the copolymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 2 Crosslinking of poly(diallyldimethylammonium chloride-*co*-vinylamine).

Fluorescent labeling

The poly(DADMAC-*co*-vinylamine) copolymer was fluorescently labeled by dansyl chloride coupling to the amine groups (see Scheme 1).¹⁵ Dansylation of amine is usually performed by the addition of an acetone solution of dansyl chloride to a slightly alkaline aqueous-to-dilute solution of the compound to be labeled. Initial coupling attempts involving dansyl chloride solutions in acetone were unsuccessful. This may reflect the low solubility of both the polymer and dansyl chloride in the water and acetone mixture. The replacement of acetone with DMF gave good results (see the Experimental section for details). The degree of dansylation was estimated from the sulfur content (0.53%) of the labeled copolymer: 36% of the amine groups were substituted, and this corresponds to an

approximately 30% yield based on the quantity of added dansyl chloride.

The dansyl-labeled poly(diallyldimethylammonium chloride-*co*-vinylamine) (DAN-CP) showed interesting fluorescent properties. In a previous work, Tanaka and Ödberg¹⁶ showed that dansylated polyacrylamide with 10 mol % quaternary cationic groups had the same maximum wavelength for the fluorescent emission as dansylamide, a small-molecule analogue. Figure 3 compares the emission spectra of a dansyl-labeled poly(diallyldimethylammonium chloride-*co*-vinylamine) copolymer and dansylamide. The wavelength of the maximum emission was 48 nm less than that of dansylamide, suggesting some interactions with adjacent amino and quaternary ammonium groups in our copolymer.

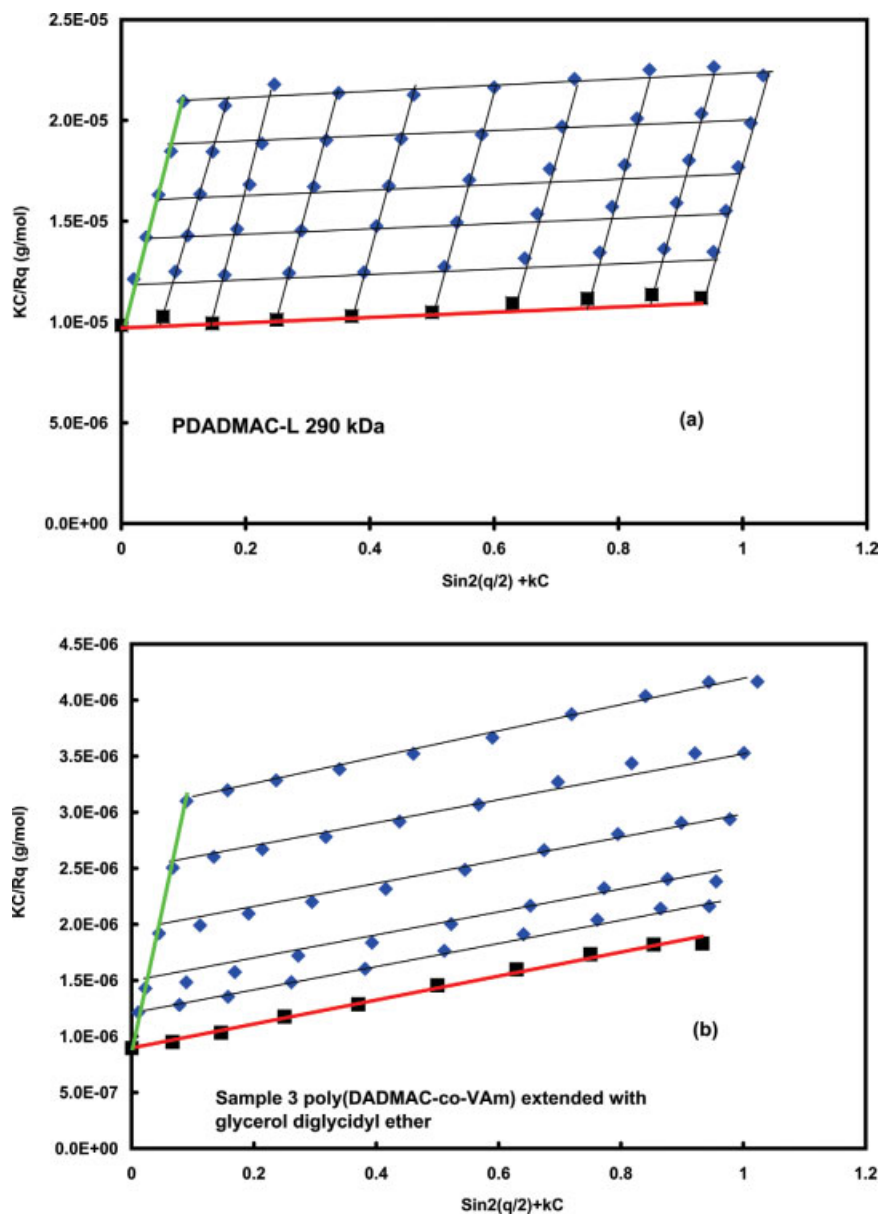


Figure 7 Zimm plots for (a) PDADMAC-L (Aldrich; see Table II) and (b) poly(diallyldimethylammonium chloride-*co*-vinylamine) [poly(DADMAC-*co*-VAm)] extended with glycerol diglycidyl ether (sample 3, Table II). The polymer concentrations were (a) 1, 2, 3, 4, and 5 mg/mL and (b) 0.25, 0.5, 1, 1.5 and 2 mg/mL. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The effects of the pH on the fluorescence intensities of the dansyl-labeled copolymer in DMF/water (1 : 3 v/v) and in water are shown in Figure 4. Above pH 6, the fluorescence intensity is constant, but it decreases quickly with pH decreasing below 5.5 to reach roughly zero at pH 2. The pH sensitivity of the dansyl fluorescence is well known and has been explained by quenching caused by energy transfer from excited protonated dansyl groups to unprotonated dansyl groups.¹⁷

Although fluorescent labeling is widely used in biomedical, biological, and fundamental studies, it is not always suitable for some process chemistry research.

For example, pH swings and the variable presence of metal ions limit the utility of fluorescent polymers in papermaking technology research. Thus, we also developed approaches for the dye labeling of DADMAC copolymers.

Chromophore labeling

Poly(DADMAC-*co*-vinylamine) was conjugated with the dansyl group {4-[4-(dimethylamino)phenylazo]-benzene}, which is a derivative of methyl orange (see Scheme 1). In Figure 5, the absorption spectra of dansyl-labeled poly(DADMAC-*co*-vinylamine) (DAB-CP)

are compared with those of methyl orange at pHs 1.5 and 6.3. Above pH 5, the solutions were yellowish-brown, whereas under acidic conditions the color intensity increased by about 1.8, and the color was deep red. Because the absorption spectra of methyl orange and the copolymer were similar, the absorption from methyl orange stock solutions was used to estimate the chromophore content of the copolymer. This approach is illustrated in Figure 6, which compares the absorbance–concentration curves for methyl orange and the copolymer under acidic and neutral conditions. Dividing the copolymer mass concentration by 43 gave very good agreement between the methyl orange and the labeled copolymer under both pH conditions. The conversion factor of 43 corresponds to a dabsyl content of 1.1 mol % in the copolymer, which, in turn, corresponds to about 15% conversion of the primary amine groups. The only assumption in this analysis is that the molar absorption of methyl orange equals that of copolymerized dabsyl moieties.

High-molecular-weight PDADMAC by crosslinking

PDADMAC can be readily synthesized by radical polymerization in an aqueous solution, which gives an effective and inexpensive product for many applications.¹ The structures are shown in Scheme 2. However, some applications, such as flocculation, require very high molecular weight, water-soluble cationic polymers. Such polymers have not been prepared with DADMAC.

Amine-containing PDADMAC copolymers offer the opportunity to increase the molecular weight by the coupling of two or more chains. The challenge is to limit the coupling reaction to prevent crosslinked gel formation. An experiment was conducted with glycerol diglycidyl ether as the coupling agent. The samples were isolated and characterized as a function of the reaction time. The weight-average molecular weight (M_w) was measured by light scattering, and the results are summarized in Table II, together with the results for two commercial PDADMACs. Examples of Zimm plots are shown in Figure 7. Our measurements for the commercial samples were within the range given by the supplier. The molecular weight of the reacted copolymer increased from 290 to 1600 kDa over 4 days

of reaction. Longer reaction times gave gels. These results suggest there is potential to extend the molecular weight of amine-derivatized PDADMAC.

CONCLUSIONS

Copolymers of DADMAC and vinylamine were prepared for the first time by the alkaline hydrolysis of copolymers of DADMAC and NVF. Because the reactivity ratio of NVF (1.92) was much higher than that of DADMAC (0.13), semibatch polymerization was required for a uniform product. The utility of amine-derivatized PDADMAC was illustrated by three reactions: (1) the coupling of dansyl chloride to give a fluorescently labeled polymer, (2) the coupling of the dabsyl group to give a chromophorically labeled polymer, and (3) the chain extension with glycerol diglycidyl ether to give very high molecular weight PDADMAC.

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