

Latexes of Starch-Based Graft Polymers Containing Polymerized Acrylonitrile

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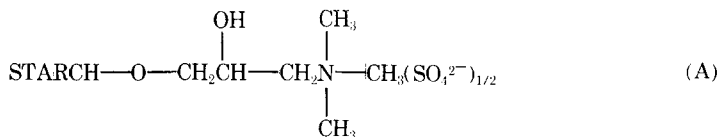
Synopsis

The scope of graft reactions to produce starch-based latexes was extended by graft polymerization of acrylonitrile (AN) onto gelatinized cationic starch possessing quaternary amine functionality and by graft terpolymerization of AN and *t*-butylaminoethyl methacrylate (TBAEM) onto gelatinized starch by cerium(IV) initiation at 25°C. Grafting onto starches containing highly basic quaternary amines gave polyacrylonitrile [poly(AN)] grafts having about one fourth the number-average molecular weight (\bar{M}_n) (178,000–232,000) of those produced by grafting AN onto starches containing the less basic tertiary amine groups. Sonification at 20 KHz of graft polymerization reaction mixtures having up to 8% solids reduced viscosities from 400–3000 cP to 10–40 cP. Diameters of dried particles measured about 300–1500 Å. Shaker-type agitation during grafting onto starch having quaternary amine groups produced poly(AN) chains with lower \bar{M}_n values than those produced during blade stirrer-type agitation. \bar{M}_n values of grafted poly(AN) decreased with increasing reaction time, degree of substitution of amine in the starch, gelation time of cationic starch at 95°C, and cerium(IV) concentration. AN was copolymerized with TBAEM at molar ratios of 14–85:1 in grafting onto gelatinized starch to yield copolymer side-chain grafts analyzing 8–52:1 of polymerized AN to TBAEM moieties.

INTRODUCTION

Previous work¹ described the preparation of starch graft copolymer latexes by a two-step reaction process. The steps involved preparation of N,N-diethylaminoethyl (TA) ether derivatives of starch (S) followed by graft polymerization of acrylonitrile (AN) onto gelatinized TAS by cerium(IV) initiation. Reaction mixtures (pH 5.5) sonified at 20 kHz air dried at room temperature and also at 70°C to hard transparent films. Scanning electron microscope (SEM) examinations showed the latexes to be composed of particles which, when coated with 200 Å of a gold–palladium alloy, had diameters of about 0.05–0.15 μ . Uncoated particles in the lower range are believed to be about the size of individual grafted copolymer molecules.

We extended latex preparation from grafting onto cationic starch having tertiary amine¹ functionality to grafting onto cationic starch having the more basic quaternary amine (QA) functionality. AN was graft polymerized onto gelatinized starch having QA functionality shown in formula (A) to produce QAS products with up to 50% grafted poly(AN) moiety:



Convenience that could be achieved in a one-step latex preparation process by possible graft copolymerization of AN and a vinylamine possessing cationic character onto a noncationic starch prompted us to investigate graft copolymerization reaction of AN and *t*-butylaminoethyl methacrylate (TBAEM) onto gelatinized starch.

Previously, we designated cationic starch PAN graft polymer in which the cationic starch had tertiary amine groups as CS-PAN; we will now use the notation TAS-*g*-poly(AN) in which *g* denotes graft. Where side chain grafts are copolymers, *co* will be inserted between the two monomer designations.

In preliminary evaluations, starch graft latexes functioned as useful materials in rubber and paper. Presumably, the small size of the latex particle and the high glass transition temperature of PAN made QAS(0.22% N)-*g*-poly(AN) (1:1) an excellent reinforcer in AN-butadiene copolymer (HYCAR, 1092-30) rubber. Also, the cationic character of the latex particles causes them to adsorb onto cellulose fibers in papermaking to improve dry strength of the paper.

We wish to report conditions for preparing QAS-*g*-poly(AN) and S-*g*-poly(AN-*co*-TBAEM) of varying polyvinyl side-chain content and of varying number-average molecular weight (\bar{M}_n) of poly(AN) as determined by gel permeation chromatography (GPC).

EXPERIMENTAL

Materials

Unmodified Hercules Starbake wheat starch (12.5% moisture) was used without further refinement.

Eastman's practical-grade AN was flash distilled under reduced pressure at 40°C, and the distillate was then stored in the dark at 3 to 4°C.

Ceric ammonium nitrate was Fisher Certified ACS grade. Solutions were prepared in 1N HNO₃ and then aged 24 hr at room temperature in a darkened hood before use.

Dimethylformamide (DMF) for the GPC study was refined by pumping it at a pressure of 2 psi up a stainless steel tower (2.4 in. × 4 ft) packed with Linde molecular sieve No. 4A and then down through a Selas microporus 015 porcelain filter. Lithium bromide was dissolved in DMF at a concentration of 200 ppm for the GPC instrument.

TBAEM reagent was purchased from Rohm and Haas, and 3-chloro-2-hydroxypropyltrimethylammonium chloride from Story Chemical Corp. as a 52% solution containing a maximum of 100 ppm 1,3-dichloropropanol and 5 ppm epichlorohydrin. Both reagents were stored in the dark at 3 to 4°C and used without further refinement.

Preparation of QAS

The procedure for making TA ether derivatives of starch described previously^{1,2} was also used to make QAS. Starch (220 g) was added to 500 ml water containing sodium sulfate, sodium hydroxide, and the QA, 3-chloro-2-hydrox-

TABLE I
Preparation of Quaternary Amine Starches (QAS)^a

NaOH, g	Amine, ^b g	QAS N, %
5	7.28	0.22 ^c
6	14.04	0.39
7	16.00	0.42
11	26.0	0.69

^a Each preparation was made at 55°C by reaction with 220 g Hercules Starbake wheat starch (12.5% moisture; 0.02% N) in 500 ml water containing 83.5 g sodium sulfate for 6 hr.

^b 3-Chloro-2-hydroxypropyltrimethylammonium chloride.

^c The amine degree of substitution in QAS having 0.22% N is 0.026.

propyltrimethylammonium chloride. The reaction mixture was stirred at 55°C for 6 hr, after which time it was cooled to room temperature and the pH adjusted to 5.5 with 1*N* sulfuric acid. The insoluble product was separated from the liquid by centrifugation. Residual salts in the product were removed by first slurring with distilled water, then centrifuging, and finally decanting the supernatant liquid. QAS was washed with absolute ethyl alcohol to remove water after which the product was filtered and air dried in a force-draft hood. Amounts of reagents used in the reactions and the nitrogen contents of the products are listed in Table I.

Preparation of QAS-*g*-Poly(AN)

QAS (24 g) was gelatinized by heating under nitrogen in 600 ml distilled water at 95°C with stirring. The solution was cooled to 25°C, at which temperature monomer and cerium(IV) additions were made. Some preparations were made in round-bottomed flasks in which reaction mixtures were stirred at about 240 rpm with rotating glass blades. Other preparations were made in glass-stoppered Erlenmeyer flasks in which reaction mixtures were shaken on a Burrell wrist-action shaker at the highest setting. In some experiments, monomer was added to gelatinized QAS and shaken or stirred 20 min before addition of cerium(IV) reagent, whereas in others the sequence of monomer to cerium(IV) addition was reversed. After a 3-hr reaction, graft dispersions (pH 1.8–2) were blended at a high rate of shear for 3 min in a Waring Blender. The latex formed was then blended at a low rate of shear while acidity was adjusted to pH 5.5 with 1*N* NaOH.

Solid QAS-*g*-poly(AN) products were isolated from latex preparations by precipitation with 3–4 volumes of ethyl alcohol. After analysis, 2 g graft copolymer was hydrolyzed in 200 ml 1*N* HCl at 95 to 100°C for 2 hr. The resulting acid-insoluble poly(AN) was dissolved in DMF–LiBr solvent, and \bar{M}_n was characterized by GPC. Extractions of only 7–10% solids from QAS-*g*-poly(AN) products by boiling in water for 2 hr and extraction of only 3–5% homopolymer poly(AN) by DMF at 25°C over a three-day period were regarded as evidence of AN grafting³ onto QAS.

Preparation of S-*g*-Poly(AN-*co*-TBAEM)

Starch (24 g) was heated in 600 ml water under nitrogen at 95 to 100°C with stirring for 1 hr and then cooled to 25°C. AN and about 20 ml of an aqueous

TABLE II
Graft Terpolymerization of Acrylonitrile (AN) and *t*-Butylaminoethyl Methacrylate (TBAEM) onto Gelatinized Starch by Cerium(IV) Initiation at 25°C^a

Prepa- ration no.	AN/ TBAEM, mole/ mole	Starch graft product N, %	Isolated side-chain graft				
			N, %	Cl, %	Pol. AN/pol. TBAEM, mole/mole	\bar{A}_n , ^b A	D_c ^c
1	85.63	13.74	25.16	0.56	112.7 ^d (52.6) ^e	15,800	3.00
2	28.55	12.34	22.87	2.13	26.2 (16.5)	17,000	2.85
3	14.26	10.22	20.46	3.90	12.1 (8.28)	19,900	2.80

^a Starch (24 g) was gelatinized at 95°C under nitrogen for 60 min. The AN:anhydroglucose unit (AGU) and AGU:cerium(IV) mole ratios were 3 and 50, respectively. Graft reactions were conducted in round-bottomed flasks for 3 hr with stirring.

^b Number-average molecular size determined by gel permeation chromatography (GPC).

^c Molecular dispersity.

^d Ratios were based on polymerized AN values derived from the equation (% N/14) - (% Cl/35.5) = moles of polymerized AN, and polymerized TBAEM values based on % Cl/35.5.

^e Ratios were based on values derived from the equation % N = % polymerized AN (0.264) + (100 - % Cl - % polymerized AN)(0.0749).

solution containing TBAEM adjusted to pH 4 were added to the starch solution under nitrogen and stirred for 20 min. Graft polymerization was initiated by addition of 0.2M cerium(IV) in 1N HNO₃, and the reaction was continued for 3 hr when it was blended 3 min at a high rate of shear before adjusting to pH 5.5 while blending at a low rate of shear.

A portion of the latex preparation was precipitated with 3-4 volumes of ethyl alcohol, and solids were recovered by filtration. The product was dried at 25°C in a force-draft hood. The starch moiety of the graft was removed by hydrolysis in 1N HCl at 95° to 100°C for 2 hr. The copolymer side chain was dissolved in DMF-LiBr solvent and characterized by GPC. Amounts of reagents used to make S-*g*-poly(AN-*co*-TBAEM) latexes, as well as the composition of the copolymer side chains, are listed in Table II.

Compositions of isolated copolymer side chains with respect to polymerized AN and TBAEM moieties were calculated from both the chloride and nitrogen analyses. Calculations stressing chloride analyses were based on the premise that only polymerized TBAEM moiety contains chloride and that wt-% relationships followed the equation

$$\frac{\%N}{14} - \frac{\%Cl}{35.5} = \text{moles of polymerized AN} \quad (1)$$

Other calculations were also made on the basis that both moieties in the copolymer side chain contain nitrogen and that wt-% relationships follow the equation

$$\%N = \% \text{ polymerized AN}(0.264) + (100 - \%Cl - \% \text{ polymerized AN})(0.0749). \quad (2)$$

Sonification

Reaction dispersions blended 3 min were poured into 2-oz bottles which were then cooled in ice water. The probe tip of a Heat Systems ultrasonic probe,

which measured 1 cm^2 , was immersed to the depth of 1 cm below the surface of the dispersion which was then sonified 3 min at 20 kHz. The probe was powered by a Branson supply unit.

GPC Analyses

Solutions of isolated side-chain grafts were made in DMF containing 200 ppm LiBr according to a procedure described previously.⁴ DMF-LiBr solutions containing 0.06% polymer side-chain grafts were filtered sequentially through fine, very fine, and ultrafine sintered glass filters with the aid of vacuum to ensure removal of microgel that could plug GPC columns. Molecular size distribution profiles of polymer samples were determined on the analytical mode of a Waters Associates Ana-Prep GPC. Samples (2 ml) were injected into the instrument, operated at 70°C and a pumping rate of 1.0 ml/min, with DMF-LiBr as the eluting solvent. Effluent from the sample bank, which was made up of two columns ($122 \text{ cm} \times 0.7 \text{ cm o.d.}$) packed with Styragel having exclusion limits of 10^7 and $1.5 \times 10^4 \text{ \AA}$, was analyzed at a sensitivity of $8\times$. The sample bank was calibrated with narrow range-dispersity polystyrene standards supplied by Waters Associates.

The log of the molecular size A for polystyrene standards dissolved in DMF-LiBr solvent is a linear function of count number C and has the following relationship:

$$\log A = 10.558 - 0.45840C$$

Molecular sizes of poly(AN) and poly(AN-*co*-TBAEM) molecules, including those eluted between the interstitial volume of the system and the elution volume of the largest standard, were determined from this equation. Molecular weights were calculated according to a computer program described previously.⁵

Scanning Electron Microscopy

Sample preparation of latexes for examining and subsequent photographing in a Cambridge Stereoscan Mark IIA SEM is the same as described previously.¹ Single droplets of 0.06% concentration of latexes were permitted to dry at 25°C on a microscope cover glass, which was then cemented to an aluminum specimen stud and coated (200 Å) with a gold-palladium (60-40) alloy at 4×10^{-5} torr.

RESULTS AND DISCUSSION

Grafting AN onto gelatinized starch³ or TAS¹ in a round-bottomed flask under stirring produced poly(AN) side chains with \bar{M}_n values of about 1 million. Surprisingly, grafting AN onto gelatinized cationic starches containing QA instead of tertiary amines produced poly(AN) grafts having \bar{M}_n values of about one quarter million. Since similar amounts of reagents were used and since similar yields of grafting were obtained in all preparations (Table III), how the cationic charge on the starch backbone influences structure of grafted side chains deserves more study. Elucidation of the effects of cationic charge might permit tailoring of graft polymer structure to meet certain enduse specifications.

Type of agitation used in grafting reactions influences \bar{M}_n values of grafted poly(AN). \bar{M}_n values of poly(AN) from grafting AN onto gelatinized QAS in

TABLE III
Influence of Cationic Functionality (CF) of Starch on Number-Average Molecular Weight (\bar{M}_n) of Grafted Polyacrylonitrile [Poly(AN)]^a

CF	N, %	Agitator	AGU/Ce(IV)	Starch graft product N, %	Poly(AN) \bar{M}_n
TAB ^b	0.42	ST ^c	40	12.25	1,094,000
TA	0.42	SH ^d	40	13.50	506,000
QA	0.39	ST	45	13.07	232,000
QA	0.39	SH	45	12.81	178,000

^a Cationic starch (24 g), gelatinized in 600 ml water by heating under nitrogen for 30 min, was cooled to 25°C and reacted with AN and cerium(IV) reagent. The AN:AGU molar ratio was 3.1 and the reaction time, 3 hr.

^b Tertiary amine.

^c Reaction was conducted in a round-bottomed flask using a rotating blade stirrer at 240 rpm.

^d Reaction was conducted in a stoppered Erlenmeyer flask clamped to a Burrell wrist-action shaker.

Erlenmeyer flasks when shaker action was used were lower than values of poly(AN) from grafting reactions in round-bottomed flasks when stirring action was used. This effect parallels previous results reported for grafting AN onto gelatinized TAS.

Viscosity differences were also noted in QAS-*g*-poly(AN) and TAS-*g*-poly(AN) reaction mixture dispersions that had been blended 3 min. In general, 7% to 8% TAS-*g*-poly(AN) dispersions that were not sonified had Brookfield viscosities (30 rpm) on the order of 1500–3000 cP, whereas dispersions of QAS-*g*-poly(AN) of similar poly(AN) contents and solid concentrations had viscosities on the order of 500 cP. Perhaps viscosity is related, in part, to the intensity of the charge on the polymer particle as well as to the \bar{M}_n of the grafted side chains. Sonification of 50-ml volumes at 20 kHz for 1 to 3 min at 5 to 10°C reduced viscosities of QAS-*g*-poly(AN) dispersions to about 10 cP and TAS-*g*-poly(AN) dispersions to 15–40 cP.

Reaction mixture dispersions of QAS-*g*-poly(AN) adjusted to pH 5.5 and blended 3 min dried on glass at 25° and 75°C to form hard, somewhat hazy, films. However, sonification of TAS-*g*-poly(AN) latexes gave dispersions that dried on glass at 25° and 75°C to hard, transparent films that were adhesive.

Although detailed studies relating to decreases in viscosities of QAS(0.22% N)-*g*-poly(AN) reaction mixtures through sonification have not been made, it is suspected that viscosity may be related, at least in part, to regions of association between QAS-*g*-poly(AN) particles, probably through the starch moiety, that are readily disassociated through cavitation. However, sonic radiation did not have adverse effects on \bar{M}_n values of grafted poly(AN); in fact, in all dispersions [TAS-*g*-poly(AN) and QAS-*g*-poly(AN)] somewhat higher \bar{M}_n values of poly(AN) resulted from sonified dispersions. Poly(AN) isolated from a nonsonified QAS(0.22% N)-*g*-poly(AN) dispersion (made by shaking agitation) had an \bar{M}_n of 147,000, whereas poly(AN) isolated from the corresponding sonified dispersion had an \bar{M}_n of 184,000.

SEM examination of both sonified and nonsonified QAS-*g*-poly(AN) dispersions at 0.06% concentration showed both contained particles that dried to balls having diameters of 300–1500 Å. The smaller sizes are believed to be within

TABLE IV
Influence of Gelatinization Time on Grafting AN onto QAS(0.22% N) at 25°C^a

Gelation time, hr	QAS- <i>g</i> -poly(AN) N, %	Poly(AN) \bar{M}_n	<i>D</i>
0.08	13.51	372,000	3.59
0.50	13.07	232,000	2.79
1.0	12.66	220,000	2.71

^a Reactions were conducted in round-bottomed flasks using stirrer agitation. The AN:AGU and AGU:Ce(IV) mole ratios were 3.69 and 45, respectively.

TABLE V
Influence of QA in Starch on Grafting AN^a

QAS N, %	QAS- <i>g</i> -poly(AN) N, %	Poly(AN) \bar{M}_n	<i>D</i>
0.22	13.21	712,000	2.43
0.39	9.02	300,000	3.78
0.42	9.00	230,000	3.90
0.69	8.96	131,000	4.10

^a QAS was gelatinized at 95°C for 30 min. A blade stirrer was used, and the reaction time was 3 hr at 25°C. The AN:AGU and AGU:Ce(IV) mole ratios were 3.69 and 90, respectively.

the range calculated for individual QAS-*g*-poly(AN) molecules. Larger particles may be aggregates of the smaller ones.

Dependence of the amount of AN grafted onto QAS(0.22% N) at 25°C over a 3-hr period on gelatinization time at 95°C is similar to the dependence reported for grafting onto TAS(0.42% N) (Table IV). Increasing gelatinization time from 0.08 to 1 hr resulted in QAS-*g*-poly(AN) products of lower nitrogen values. \bar{M}_n values of isolated poly(AN) products, as well as their molecular dispersities (*D*), decrease with increased gelatinization time.

The amount of amine derivatization of starch not only significantly influences the amount of AN grafted onto gelatinized QAS, but also significantly influences the \bar{M}_n value of grafted poly(AN) (Table V). As nitrogen content of QAS increased from 0.22 to 0.69, add-on decreased by 32% and \bar{M}_n of poly(AN) decreased more than fivefold. Lower degrees of polymerization and lower poly(AN) \bar{M}_n values [at AGU:Ce(IV) of 90] may suggest possible reaction of amine or reducing groups (formed under alkaline conditions during starch derivatization) with cerium(IV) or with polymer radicals. Loss of cerium(IV) before it initiates graft reaction would lower yields. Increases in polymer radical terminations would decrease \bar{M}_n values of isolated poly(AN). Perhaps amines also influence polymer radical termination.

Grafting AN onto gelatinized QAS (0.22% N) at 25°C at an AGU to cerium(IV) molar ratio of 45 was rapid; more than 50% AN was polymerized in 30 min (Table VI). Decreases in \bar{M}_n of poly(AN) samples isolated from graft mixtures after 0.5 to 3 hr reaction times were noted along with decreases in *D*. Increasing variations of \bar{M}_n and *D* values indicate polymerization systems of increasing heterogeneity.

Cerium(IV) concentration in the grafting reaction is also a factor influencing

TABLE VI
Variables Affecting \bar{M}_n of Poly(AN) Grafted to QAS(0.22% N) Gelatinized at 95° C for 30 Min

Variables	QAS- <i>g</i> -poly(AN) N, %	Poly(AN) \bar{M}_n	<i>D</i>
Reaction time, ^a hr			
0.5	8.5	231,000	2.96
1.0	10.66	215,000	3.37
3.0	12.81	178,000	4.17
AGU:Ce(IV), ^b mole:mole			
45	13.07	232,000	2.79
90	13.00	712,000	2.43
180	11.14	781,000	1.87

^a Grafting conducted at 25° C at AN:AGU and AGU:Ce(IV) mole ratios of 3.69 and 45, respectively.

^b Stirrer agitation was used and the AN:AGU mole ratio was 3.69. Reaction time was 3 hr.

\bar{M}_n and *D* of poly(AN) grafted onto QAS(0.22% N) (Table VI). In going from 180 AGU per cerium(IV) to 90 AGU per cerium(IV), differences in \bar{M}_n values of poly(AN) isolated from grafting reactions were only on the order of 10%. However, doubling the cerium(IV) concentration from 90 AGU per cerium(IV) to 45 significantly decreased \bar{M}_n from 712,000 to 232,000. Although one might expect lower \bar{M}_n values with increasing initiator concentration, the sudden decrease in \bar{M}_n may suggest increasing importance of initiator in poly(AN) radical termination at high cerium(IV) concentrations.

Increasing the AN concentration in graft reactions permits preparation of products of higher poly(AN) contents. A QAS(0.22% N)-*g*-poly(AN) containing 13% N was made from gelatinized QAS(0.22% N) by grafting at an AGU to cerium(IV) ratio of 90° at 25° C and by using a blade stirrer. The product consisted of 1 part starch and 0.97 part poly(AN) by weight. Doubling the cerium(IV) concentration in the grafting reaction permitted formation of a product having

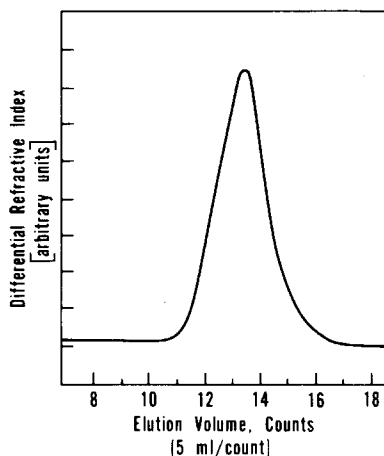


Fig. 1. Gel permeation chromatography elution curve of poly(acrylonitrile-*co*-*t*-butylaminoethyl methacrylate hydrochloride) (Table II, preparation 3) in dimethylformamide-lithium bromide (200 ppm) at 0.06% concentration.

17% N, which value indicates the graft to consist of 1 part starch and 1.8 parts poly(AN).

TBAEM, an amine methacrylate, was successfully copolymerized with AN onto gelatinized starch by cerium(IV) initiator to yield starch graft latexes with cationic charges on the side chains in a one-step process (Table II). The respective solid contents of preparations 1, 2, and 3 (Table II) were 7.8%, 7.2%, and 8.2%. Viscosities of reaction mixture dispersions were reduced from 440–1200 cP to 10–25 cP by sonification for 3 min. Positive charges on these, as well as other latex particles (300–1500 Å in the dried state), were demonstrated by means of a streaming-current detector. Films cast and dried on glass at 25° or 70°C were clear and adhesive.

Proof of grafting was demonstrated by hot-water and DMF extractions. Solids isolated from the nonsonified reaction mixture of S-*g*-poly(AN-*co*-TBAEM) latex preparation (Table II, preparation 2) were extracted first with water at 95°C for 2 hr and then with DMF at 25°C for three days. The water-soluble residue amounted to 9.5% and the DMF-soluble residue, to 3% of the initial solids. Solids isolated from the sonified reaction mixture (Table II, preparation 2) and extracted with water and DMF under the conditions described above gave 12% water solubles and 6% DMF solubles.

Compositions of isolated graft side chains were calculated from their nitrogen and chloride contents. Greater percentages of polymerized TBAEM in the poly(AN-*co*-TBAEM) side chains were calculated from eq. (2) which emphasizes a nitrogen balance than were calculated from eq. (1) which emphasizes chloride analysis. These results suggest that not all amino groups have bonded chloride. Interestingly, based on nitrogen values, graft side chains contain greater percentages of polymerized TBAEM moiety with respect to AN than were added as monomers to the reaction mixtures.

The GPC profile of isolated poly(AN-*co*-TBAEM) (preparation 3, Table II, Fig. 1), which is typical of other copolymer profiles, had a *D* of 2.8 and no evidence of bimodal character. Certainly, no distinct indication of a complicated polymer mixture is evident. Since the *Q* factor⁶ for the copolymer is not known, the copolymers were characterized by GPC as to number-average molecular sizes (\bar{A}_n), which may be regarded as a relative measure of \bar{M}_n values. As the mole fraction of TBAEM moiety in the reaction mixture increases, \bar{A}_n of the copolymer side chains increases.

The mention of firm names or trade products does not constitute an endorsement by the U.S. Department of Agriculture over other products or firms not mentioned.

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