Preparation of Soapless Latexes by Sonification of Starch-Based Poly(isoprene–*co*–acrylonitrile) Graft Reaction Mixtures

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Synopsis

Graft copolymerization of isoprene (IP) and acrylonitrile (AN) onto gelatinized starch (S) and cationic starch having quaternary amine functionality through cerium(IV) initiation gave grafted side chains of poly(IP–*co*–AN). Grafts of various compositions are obtained by controlling the amounts and ratios of monomers added to starch. IP alone does not homograft onto gelatinized starch at 25° or 50°C by cerium(IV) initiation and requires the presence of an "initiator–monomer" such as AN to obtain copolymer side chains. Although cografting of IP and AN onto starch depends on AN to initiate radical chains, the ratio employed of the two monomers is critical for graft polymerization to occur. For example, at a molar ratio of IP to AN of 1 or greater, little polymer was produced; at molar ratios in the range of 0.4 to 0.67, considerable amounts of polymer were produced; and at a molar ratio of 0.13 or less, polymerization of AN was greatly retarded. Concentration of HNO_3 in the cerium(IV) reagent and reaction temperature also influence the grafting reaction. Lower HNO_3 concentrations favor grafting at 50°C, while higher acid concentrations favor grafting at 25°C. Starch graft reaction mixtures were sonified at 20 kHz to form latexes that air dry to clear pliable films. Poly(IP–*co*–AN) obtained by acid hydrolysis of the starch portion of the grafts failed to dissolve in either dimethylformamide or benzene, thus indicating presence of crosslinks. S–*g*–poly(IP–*co*–AN), having about one third starch and grafted side chains averaging about 2 parts polymerized IP per part of polymerized AN, was masticated on steel rolls at 100°C to a tough pliable film which was subsequently vulcanized to a rubber.

INTRODUCTION

We reported earlier[1] that reaction mixtures of graft copolymers made by grafting acrylonitrile (AN) onto gelatinized cationic starch possessing tertiary amine functionality (TAS) by cerium(IV) initiation at 25°C sonify at 20 kHz to latexes. These consisted of positively charged particles which contained the charge in the starch moiety and which in the dry state measured about 300–1500 Å in diameter. The latexes air dried on glass at 25 or 70°C to clear hard films which crazed on aging. Graft reactions in which shaker-type agitation was used produced poly(AN) side chains whose number-average molecular weights ($\overline{M}_n$) were about one half the values of those obtained from reactions in which stirrer-type agitation was used.

Later we reported[2] that reaction mixtures of starch grafts made by cerium(IV) initiation at 25°C by grafting AN onto gelatinized cationic starch possessing quaternary amine functionality (QAS) also sonify to yield latexes consisting of positive-charged particles which, in the dry state, measured about 300–1500 Å in diameter. The type of cationic starch used influenced graft structure.

Grafting onto gelatinized QAS permitted formation of poly(AN) side chains with $\overline{M}_n$ values only about one fourth those obtained from grafting onto gelatinized TAS. Differences found in $\overline{M}_n$ values of poly(AN) isolated from TAS grafts that were due to the type of agitation used in the graft reaction were also found in poly(AN) isolated from QAS grafts. Further, it was shown that stable graft latexes could also be made in which the cationic charges were in the side chains. Latexes made by sonification of reaction mixtures of starch grafts consisting of gelatinized starch and copolymer side chains of polymerized AN and t-butyl-aminoethyl methacrylate (TBAEM) air dried at 25°C to clear, hard films.

More recently[3] we extended both starch graft polymer reactions and starch graft latex preparations to include a diene monomer. Chloroprene (CP) graft polymerized as readily as AN onto gelatinized starch and QAS through cerium(IV) initiation at 25°C. Reaction mixtures sonified at 20 kHz to stable latexes that air dried to clear films. These films, however, unlike those made from latexes of TAS–g–poly(AN), remained soft and pliable on aging.

Starch–polychloroprene [S–poly(CP)] latexes are of interest, since unsaturation permits curing and thus could increase the potential application of starch grafts. The possibility of making starch grafts from dienes other than CP prompted us to investigate possible graft polymerization of IP and graft copolymerization of IP and AN onto gelatinized starch and QAS by cerium(IV) initiation.

We wish to report conditions for preparing starch grafts and QAS grafts containing polymerized IP and AN as well as conversion of the reaction mixtures to latexes.

EXPERIMENTAL

Unmodified General Mills Aytex-P wheat starch (12% moisture) was used without further refinement.
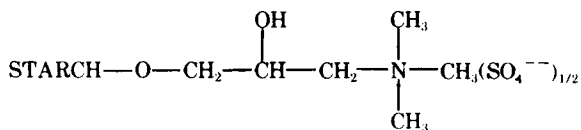
Eastman's practical-grade AN was flash distilled under reduced pressure at 40°C, and the distillate was then stored in the dark at 3–4°C.

Eastman's practical-grade IP was distilled at atmospheric pressure in a flash evaporator, and the distillate was then stored in the dark at 3–4°C.

Ceric ammonium nitrate was Fisher Certified ACS grade. Solutions were made in $1N$ and $0.1N$ HNO_3 as well as in distilled water. Solutions were used within 10 min after their preparation.

Preparation of QAS

The procedure for making granular QAS with 0.24% N by reaction of granular wheat starch and 3-chloro-2-hydroxypropyltrimethylammonium chloride in the presence of sodium sulfate under basic conditions to yield granular starch with quaternary amine functinality shown below was described previously:[2]

$$STARCH-O-CH_2-\underset{\underset{}{\overset{\overset{OH}{|}}{}}{CH}}-CH_2-\underset{\underset{\overset{|}{CH_3}}{\overset{\overset{CH_3}{|}}{}}}{N}-CH_3(SO_4^{--})_{1/2}$$

Preparation of QAS–*g*–Poly(IP–*co*–AN)

Gelatinization of QAS (0.24% N; 8% moisture) was achieved by heating 30.3 g in 700 ml distilled water, under nitrogen, with stirring for 30 min. Three hundred grams of dispersion, cooled to 25°C, was poured under nitrogen into a 500-ml screw-cap glass bottle that had been wrapped with surgical adhesive tape. A solution consisting of a mixture of monomers was added to the bottle which was then capped and shaken. The screw cap was made of thermoset plastic and fitted with a Teflon gasket 0.5 mm thick. Ceric ammonium nitrate was dissolved in either distilled water or nitric acid (0.1*N* or 1.0*N*) to make a 0.2*M* solution which was then added to the dispersion. Finally, the mixture was tumbled (45 tumbles per min) up to 16 hr at 50°C in an Aminco (American Instruments Company) constant-temperature polymerization bath. Reaction mixtures (pH 2–2.5) cooled to 25°C and then blended 3 min in a Waring Blender were adjusted to pH 5.5 with 1*N* NaOH.

Solid starch-graft products were isolated from blended dispersions by precipitation with several volumes of ethyl alcohol. Carbon, hydrogen, and nitrogen analyses of graft products made by the same procedures were found to agree within a ±3% range. Samples (2 g) of starch grafts were hydrolyzed in 200 ml 1*N* HCl at 95–100°C for 2 hr to yield poly(IP–*co*–AN).

Extraction of only about 5–10% water solubles from isolated starch grafts with boiling water and no extraction of homopolymer from the same solids with benzene or dimethylformamide (DMF) at 25°C over a three-day period was regarded as evidence of grafting.

Reaction mixtures that had been blended were poured into 2-oz bottles, cooled in ice water, and then sonified for 1–3 min at 20 kHz by the method described previously.[3]

Calculations

Compositions of QAS–*g*–(IP–*co*–AN) products were calculated from their carbon, hydrogen, and nitrogen analyses, as well as from their percentages of oxygen that were estimated by differences. Calculations were made on a 100-g sample basis so that percent element values were regarded as gram amounts present in the sample. As a first approximation in calculating the approximate amount of starch moiety present in the 100-g sample, it was assumed that the contribution of nitrogen in QAS to the analytical percent nitrogen in comparison to the contribution in the polymerized AN moiety was not significant. The amount of polymerized AN in the 100-g sample was calculated from eq. (1). Gram amounts of carbon and hydrogen present in the polymerized AN moiety were calculated from eqs. (2) and (3):

$$\%N \times \frac{53}{14} = \% \text{ polymerized AN moiety} \tag{1}$$

$$\%N \times \frac{36}{14} = \% \text{ carbon} \tag{2}$$

$$\%N \times \frac{3}{14} = \% \text{ hydrogen} \tag{3}$$

These values, substracted from the analytical values, give the weights of carbon,

hydrogen, and oxygen remaining in the starch and polymerized IP moiety (starch–IP). From these weights, a new percentage carbon value was calculated which corresponds to carbon in starch–IP. Insertion of this value in eq. (4),

$$88.2 - (\% \text{ carbon}) = 0.438 \times (\% \text{ starch}) \tag{4}$$

and solution of this equation gives percent starch in starch–IP. Equation (4) was derived from a carbon balance based on total carbon in starch–IP. From the percent starch value, the grams of starch in the original 100-g sample was calculated.

From a knowledge of both the percent nitrogen in QAS and the approximate percent starch in the starch graft copolymer, it was possible to adjust the original analytical analyses to exclude carbon, hydrogen, nitrogen, oxygen, and sulfur due to QA functionality in starch. The percent nitrogen in the adjusted analysis relates only to the amount of polymerized AN moiety.

Calculations described above dealing with the original analytical analyses were repeated with the adjusted analyses to give percentages of starch, polymerized AN, and IP moieties in starch graft copolymers.

RESULTS AND DISCUSSION

To establish conditions for making copolymers of starch that contain unsaturation, gelatinized starch was reacted with mixtures of IP and AN (0.666 molar ratio) at 25 and 50°C with 0.2M cerium(IV) reagents made up in 1N and 0.1N HNO_3 (Table I). Low yields of polymer were obtained when graft reactions were conducted with stirring for 4 hr at 25°C; however, at this temperature, higher yields were obtained by use of cerium(IV) dissolved in 1N HNO_3 than in 0.1N HNO_3. Greater reaction was achieved at 50°C in capped glass bottles in which tumbling action was used. Under these conditions, use of cerium(IV) dissolved in 0.1N HNO_3 produced much more polymer than use of cerium(IV) dissolved in 1N HNO_3. Perhaps greater acidity at 50°C hydrolyzed some starch to produce reducing endgroups (carbonyls) that are capable of consuming starch–cerium(IV) complexes,[4] or perhaps these endgroups react with polymer chain radicals thereby terminating polymerization reaction. Although the initial molar ratio of IP to AN was 0.666 in each case, more polymerized IP than AN moieties were found in the products.

TABLE I

Effect of Temperature and Acid Concentration in Cerium(IV) Reagent on Graft Polymerization of 10.22 g Isoprene (IP) and 12 g Acrylonitrile (AN) in Gleatinized Starch[a]

Temp.,[b] °C	HNO_3, N	Polymer produced, g	Polymerized AN moiety, g (% conv.)	Polymerized IP moiety, g (% conv.)	(IP)/(AN)[c]
50	1.0	4.15	1.64 (13.7)	2.59 (25.4)	1.23
25	1.0	0.96	0.43 (3.6)	0.53 (5.2)	0.96
50	0.1	6.97	2.15 (17.3)	4.82 (47.2)	1.73
25	0.1	0.59	0.17 (1.4)	0.34 (3.3)	1.60

[a] Starch (11.4 g) was contained in 300 g dispersion. Polymerization time 4 hr, at an anhydroglucose unit (AGU) to cerium (IV) ratio of 50.3.

[b] Reactions at 50°C were conducted with tumbling-type agitation (45 tumbles per min) in closed glass bottles while reactions at 25°C were conducted with stirrer-type agitation in round-bottomed flasks.

[c] Mole ratio of monomers polymerized.

A study was made of the rate at which IP and AN polymerized in gelatinized starch at 50°C when cerium(IV) dissolved in 0.1N HNO₃ was used as a graft reaction initiator and tumbling action was used to agitate the mixture. Conversion–time plots (Fig. 1) of IP and AN polymerization show evidence of heterogenous polymerization during the first 3 hr of reaction. Similar plots obtained for graft polymerization of AN onto gelatinized starch[5] were explained on the basis of buried polymer radicals. Since IP is insoluble in water, and since resulting starch grafts become increasingly more insoluble with reaction time, it would not be surprising if buried polymer radicals were also involved in grafting IP and AN onto starch.

Even though the initial molar ratio of IP to AN in cograft reactions was 0.666, more polymerized IP than AN moieties were found in all products analyzed above 1 hr of reaction time.

The rate at which IP and AN cograft onto gelatinized starch is many times less than the rate at which AN alone grafts onto starch. Acrylonitrile graft polymerizes onto gelatinized starch at 25°C [4.33 AN/anhydroglucose unit (AGU); 182 AGU/cerium(IV)] over a 30-min period[5] to give a product analyzing 50% poly(AN), while IP and AN (2.1 IP and 3.21 AN/AGU) required more time, 16 hr, a higher temperature, 50°C, and more cerium(IV), 50.3 AGU/cerium(IV), to produce a product analyzing about 50% poly(IP–co–AN).

Since IP alone neither homopolymerizes nor adds to graft sites in gelatinized starch treated with cerium(IV) (Table II), it is reasonable to conclude that in cografting AN and IP, it is AN monomer that first adds to form starch–AN radicals which then react to form copolymer side chains.

Initial molar ratios of monomers in the reaction mixtures are critical in making products of various compositions. Graft reactions were conducted in which the weights of IP and starch were kept constant and the weight of AN varied (Table II). Although AN is necessary for grafting, the presence of amounts corresponding to an IP-to-AN molar ratio of 1 failed to produce much polymer; significant amounts of polymer were produced when the initial ratio was 0.66, and the presence of greater amounts of AN to a ratio of 0.40 produced even more
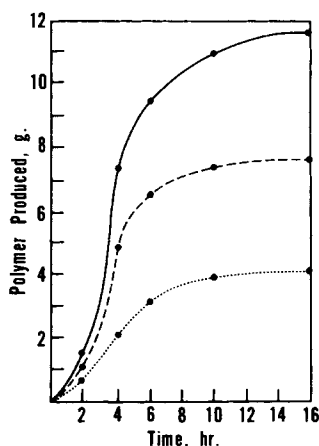

Fig. 1. Variation of polymer produced with respect to time by graft copolymerization of 11.4 g gelatinized starch with 10.2 g isoprene (IP) and 12 g acrylonitrile (AN) at 50°C for 4 hr; 50.3 anhydroglucose units (AGU)/Ce(IV): (—) total polymer produced; (- - -) polymerized IP moiety; (·····) polymerized AN moiety.

TABLE II

Influence of Increasing AN in a Constant Weight of IP on Composition of Polymer Produced by Graft Polymerization Onto Gelatinized Starch by Cerium(IV) Initiation[a]

AN, g	Polymer produced, g	Polymerized AN moiety, g (% conv.)	Polymerized IP moiety,	IP/AN,[b] M/M	(IP)/(AN),[c]
0	0	—			
4	0.444	0.121 (3.04)	0.323 (3.16)	1.97	2.71
8	1.34	0.65 (8.13)	0.69 (6.73)	1.0	0.87
12	6.97	2.15 (17.30)	4.82 (47.19)	0.67	1.73
16	8.16	2.96 (18.54)	5.21 (51.00)	0.50	1.37
20	11.17	4.81 (24.14)	6.36 (62.24)	0.40	1.03

[a] Weight of IP was 10.22 g, weight of gelatinized starch in 300 g of its dispersion was 11.4 g, and ratio of AGU per cerium(IV) (0.1N HNO$_3$) was 50.3. The polymerization temperature was 50°C and reaction time, 4 hr.

[b] Initial molar ratios.

[c] Mole ratio of monomers polymerized.

polymer. In all experiments increasing the amount of AN increased the percent conversions of both AN and IP to polymer. Also, all products contained more IP than AN polymerized moieties.

Plots of total weights of polymer produced and weights of polymerized IP and AN moieties against weights of AN in the initial reaction mixtures produced curves (Fig. 2) that exhibited breaks typical of equivalence relationships. The breaks are followed by slight plateaus and then by rises in the curves.

Although AN grafts readily onto gelatinized starch, addition of only minor amounts of IP and AN (0.133 molar ratio) retards polymerization of AN at 50°C (Table III), even though high conversions of IP to the polymerized moiety occur. A plot of data showed that minimum polymerization of AN occurs at a molar ratio of IP to AN of 0.065. Since AN radicals are about 50 times more reactive to IP than to AN itself and react with IP to form the more stable (less reactive) IP radical,[6] the slow rates of graft polymerization and low degrees of conversion of monomers to polymer undoubtedly involve the stability of the IP radical relative to the AN radical, as well as possible termination mechanisms favoring IP radical
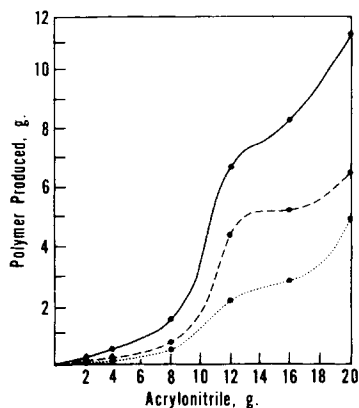

Fig. 2. Amounts of polymer produced with AN after 4-hr graft copolymerization reaction at 50°C. Amounts of gelatinized starch and IP were 11.4 g and 10.2 g, respectively; 50.3 AGU/Ce(IV): (—) total polymer produced; (- - -) polymerized IP moiety; (·····) polymerized AN moiety.

TABLE III

Influence of Increasing IP in a Constant Weight of AN on Composition of Polymer Produced by Graft Polymerization Onto Gelatinized Starch by Cerium(IV) Initiation[a]

IP, g	Polymer produced, g	Polymerized AN moiety, g (% conv.)	Polymerized IP moiety, g (% conv.)	IP/AN,[b] M/M	(IP)/(AN)[c]
0	8.35	8.35 (68.75)	0		
2.04	3.36	1.77 (14.76)	1.86 (91.04)	0.133	0.819
3.40	5.07	2.09 (17.40)	2.98 (87.44)	0.221	1.12
6.81	6.31	2.27 (18.90)	4.04 (59.32)	0.440	1.40
10.22	6.97	2.15 (17.30)	4.82 (47.10)	0.666	1.73
20.43	3.47	1.15 (9.57)	2.32 (11.40)	1.333	1.57

[a] Weight of AN was 12 g, weight of gelatinized starch in 300 g of its dispersion was 11.4 g, and ratio of AGU per cerium(IV) ($0.1N$ HNO$_3$) was 50.3. Polymerization temperature was 50°C and the reaction time, 4 hr.

[b] Initial molar ratios.

[c] Mole ratio of monomers polymerized.

interactions. Inhibiting effects of minor amounts of certain monomers on the polymerization of other monomers due to very large differencces in their relative reactivities are well known.[7]

Maximum weight yields were obtained over a 4-hr reaction period by use of an initial molar ratio of IP to AN of 0.666. Use of greater molar ratios resulted in lesser yields of polymer.

Just as the ratio of monomers in the initial reaction mixture is a factor that influences the composition and the amount of polymer produced, so also is the ratio of starch to monomers a factor that influences the yields and composition of polymer produced (Fig. 3). Products are produced having about twice as much polymerized IP moiety as AN from reaction mixtures having a monomer-to-starch weight ratio of 2 (IP-to-AN molar ratio of 0.666), while higher yields of products having about as much polymerized IP as AN are produced when the monomer-to-starch weight ratio is 3.

Ungrafted polymer, which is normally removed from solids of starch graft reaction mixtures by extraction with appropriate solvents, was not obtained by extraction of S–g–poly(IP–co–AN) reaction mixtures with benzene or DMF. Further, acid hydrolysis of 2-g samples in 100 ml $1N$ HCl for 2 hr at 100°C,
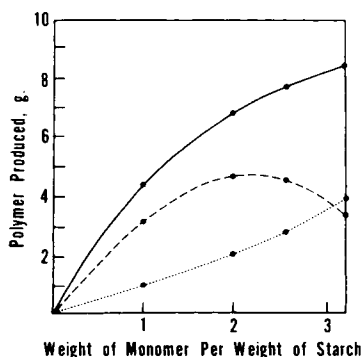

Fig. 3. Variation of polymer produced with respect to total amount of IP and AN (molar ratio 0.666) used in graft copolymerization onto 11.4 g gelatinized starch for 4 hr at 50°C; 50.3 AGU/Ce(IV): (—) total polymer produced; (- - -) polymerized IP moiety; (·····) polymerized AN moiety.

conditions sufficient to hydrolyze the starch portions, gave rubbery residues that swelled but failed to dissolve in either benzene or DMF. Insolubility of the residues suggests that crosslinking of side chains and any homopolymer that might have formed had occurred. Interestingly, we reported similar insolubilities for S–poly(CP) reaction mixtures as well as insolubility of isolated poly(CP) side chain grafts in benzene and concluded that crosslinking of chains had occurred.

Previously, we reported that sonification of gelatinized cationic starch–g–poly(AN), –(TBEAM–co–AN), –(methyl acrylate), and –(CP) reaction mixtures at 20 kHz for 1–3 min produce low-viscosity latexes. The sonification technique for making latexes from starch grafts was extended to S–g–poly(IP–co–AN). Reaction mixtures (8–10% solids), adjusted to pH 5.5 and blended 3 min, were sonified in 50-ml aliquots for 1–3 min to low-viscosity dispersions.

Although starch was gelatinized at 100°C in order to disrupt the granule and disperse the amylose and amylopectin, we suspect that these macromolecules exist, under our conditions of grafting, as large hydrated aggregates. Monomers undoubtedly graft to form aggregate particles and sonification merely disrupts these, probably through the starch moieties,[1] into smaller individual starch graft latex particles.

Even though grafted side chains of S–g–poly(IP–co–AN) may be crosslinked, latex dispersions evaporate at 25° or 75°C to form clear films that are soft and do not craze on aging. Undoubtedly, the polymerized IP moiety improved the flow properties of the graft polymer.

Although the sequence of cerium(IV) to monomer addition is not an important variable in grafting onto gelatinized starch, it is important in both grafting AN and cografting IP and AN onto gelatinized cationic starch.[1] Also, the acidity of the cerium(IV) reagent influences the degree of grafting at 50°C. Greater grafting occurs when the cerium(IV) is dissolved in distilled water than when it is dissolved in $0.1N$ HNO_3. In subsequent grafting studies, therefore, we added monomer to gelatinized QAS (0.24% N) first and then cerium(IV) reagent which was made up in distilled water.

The rate of cografting IP and AN onto gelatinized QAS (0.24% N) at 50°C when cerium(IV) initiator was dissolved in distilled water (Table IV) was more rapid in the initial stages of reaction than the rate of grafting onto gelatinized starch when cerium(IV) was dissolved in $0.1N$ HNO_3 (Fig. 1). Again, higher acidity

TABLE IV
Rate of Polymerization of IP and AN in Gelatinized Quaternary Amine Cationic Starch (QAS) at 50°C[a]

Time, hr	Polymer produced, g	Polymerized AN moiety, g (% conv.)	Polymerized IP moiety, g (% conv.)	(IP)/(AN),[b]
1	1.29	0.504 (4.20)	0.79 (7.73)	1.22
2	2.70	1.19 (9.92)	1.51 (14.76)	0.99
4	6.05	2.21 (18.41)	3.84 (37.63)	1.35
6	8.25	2.99 (24.89)	5.26 (51.52)	1.37
16	13.77	4.94 (41.15)	8.33 (81.54)	1.31

[a] Gelatinized QAS (0.24% N) (11.5 g) in 300 g dispersion was treated with cerium(IV) reagent made up in distilled water [50 AGU/cerium(IV)] and then allowed to react with IP (10.22 g) and AN (12 g).

[b] Refers to mole ratio of monomers polymerized; initial mole ratio of IP to AN was 0.666.

at 50°C may produce more reducing endgroups that could have adverse effects on graft reactions.

Inhibiting effects due to minor amounts of IP on the graft polymerization of AN in gelatinized starch systems (Table III) were also observed in grafting AN in gelatinized QAS (0.24% N) (Table V). Maximum amounts of polymer having a maximum percentage of polymerized IP are produced in graft reactions in which the initial IP-to-AN molar ratio is 0.666. Also, rates of conversion of IP to polymer are high when IP concentrations are small.

Isoprene failed to homograft onto gelatinized QAS (0.24% N) (Table VI). However, cografting of IP and AN does occur in the presence of increasing amounts of AN. Decreasing the initial ratio of IP to AN in the reaction mixture increases the amount of copolymer produced and decreases the ratio of polymerized IP to AN moiety in the copolymer.

Insolubility of the isolated copolymer side chains in either DMF or benzene prevented characterization with respect to molecular size and dispersity. Even copolymers formed at low conversions failed to dissolve in DMF or benzene.

TABLE V

Effect of Increasing IP in a Constant Weight of AN on Composition of Polymer Produced by Graft Polymerization Onto Gelatinized QAS (0.24% N) by Cerium(IV) Initiation[a]

IP, g	Polymer produced, g	Polymerized AN moiety, g (% conv.)	Polymerized IP moiety, g (% conv.)	IP/AN,[b] M/M	(IP)/(AN)[c]
0	10.38	10.38 (86.51)			
2.04	3.30	1.46 (12.17)	1.84 (90.20)	0.133	0.98
3.4	4.80	1.89 (15.75)	2.91 (85.60)	0.221	1.20
6.81	5.55	2.07 (17.25)	3.48 (51.10)	0.440	1.31
10.22	6.07	2.15 (17.93)	3.92 (38.36)	0.666	1.42
20.43	4.98	1.74 (14.50)	3.24 (15.86)	1.330	1.45

[a] Gelatinized QAS (0.24% N) (11.5 g) in 300 g dispersion was treated with cerium(IV) reagent made up in distilled water [50 AGU/cerium(IV)] and then allowed to react with AN (12 g) and IP for 4 hr at 50°C.
[b] Initial molar ratios.
[c] Refers to mole ratio of monomers polymerized.

TABLE VI

Influence of Increasing AN in a Constant Weight of IP on Composition of Polymer Produced by Graft Polymerization onto Gelatinized QAS (0.24% N) by Cerium(IV) Initiation[a]

AN, g	Polymer produced, g	Polymerized AN moiety, g (% conv.)	Polymerized IP moiety, g (% conv.)	IP[b]/AN M/M	(IP)[c]/(AN)
0	0				
4	1.90	0.46 (11.41)	1.44 (14.13)	1.97	2.44
8	3.52	1.13 (14.16)	2.39 (23.39)	1.00	1.65
12	6.07	2.15 (17.93)	3.92 (38.35)	0.66	1.42
16	6.45	2.49 (15.57)	3.96 (38.74)	0.50	1.24
20	8.31	3.38 (16.89)	4.93 (48.19)	0.40	1.14

[a] Gelatinized QAS (0.24% N) (11.5 g) in 300 g dispersion was treated with cerium(IV) reagent made up in distilled water [50 AGU/cerium(IV)] and then allowed to react with IP (10.22 g) and AN at 50°C for 4 hr.
[b] Initial molar ratios.
[c] Refers to mole ratio of monomers polymerized.

A S–g–poly(IP–co–AN) (1.5:2:1) was made by reaction of 19 g AN of 17 g IP with 11.4 g cerium(IV)-treated starch [50.3 AGU/cerium(IV)] at 50°C for 16 hr. Interestingly, the side chain had the same composition as a nitrile rubber, and on a particle basis we suspect that the elastomeric moiety encapsulates the starch. The dry solid product was found to masticate on rubber-mill rolls at 100°C to a tough pliable film. Further, vulcanization of the film produced a rubber having strength properties at least comparable to or better than a commercial carbon black-reinforced nitrile rubber we tested. This is highly suggestive that starch in starch-graft nitrile rubber functions as a reinforcer.

Undoubtedly, other monomers that normally do not homograft onto starch by cerium(IV) initiation can be incorporated in starch in graft form by cografting with monomers that normally homograft and that have suitable copolymer reactivities.

References

1. L. A. Gugliemelli, C. L. Swanson, F. L. Baker, W. M. Doane, and C. R. Russell, *J. Polym. Sci.*, 12, 2683 (1974).

2. L. A. Gugliemelli, C. L. Swanson, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, 20, 3175 (1975).

3. L. A. Gugliemelli, C. L. Swanson, W. M. Doane, and C. R. Russell, *J. Polym. Sci. B*, 14, 215 (1976).

4. L. A. Gugliemeli, W. M. Doane, C. R. Russell, and C. L. Swanson, *J. Polym. Sci. B*, 10, 415 (1972).

5. L. A. Gugliemelli, C. L. Swanson, and W. M. Doane, *J. Polym. Sci.*, 11, 2451 (1973).

6. G. Odian, *Principles of Polymerization*, McGraw-Hill, New York, 1970.

7. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.