Cationic Starch-Polyacrylonitrile Graft Copolymer Latexes*

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Synopsis

Acrylonitrile (AN) was graft-polymerized onto gelatinized cationic starch (CS) possessing diethylaminoethyl ether groups by cerium(IV) initiation to give stable latex-like copolymer dispersions. Dispersions of the latex copolymers, having up to 50% grafted polyacrylonitrile (PAN), air- and heat-dry on glass to clear, adhesive films. Sonification of up to 8% dispersions at 20 KHz reduced their viscosities from 1500-3000 cP to 15-40 cP. Scanning electron microscopy revealed that both nonsonified and sonified dispersions consist of ball-like particles measuring about 0.05-0.15 μm in diameter when dry. The films are formed by coalescence of these particles. The degree to which AN grafts onto CS at ambient temperature is related to the nitrogen content of CS, gelatinization time of CS at 95°C, sequence of AN and cerium(IV) addition, concentration of cerium(IV), concentration of AN, and severity of reaction agitation. Number-average molecular weight values of PAN were about 10⁶ when grafting was conducted under stirring and about 5 x 10⁵ when conducted under shaking action.

INTRODUCTION

We observed that reaction mixtures obtained by grafting acrylonitrile (AN) onto gelatinized starch in an aqueous medium could be centrifuged to produce highly turbid supernatants. These turbid dispersions contained several per cent solids and dried at room temperature to highly translucent films. Nitrogen content of the solids indicated the presence of 20-30% polyacrylonitrile (PAN). The colloidal nature of the dispersions suggested to us the possibility of making starch graft copolymer latexes. Extension of the studies to cationic starch (CS) demonstrated that grafting AN or methyl acrylate (MA) onto gelatinized CS possessing diethylaminoethyl ether groups produced turbid dispersions containing about 30% grafted PAN or poly(methyl acrylate) (PMA) in the dispersed phase. These dispersions dried on glass at room temperature or at 70°C to produce hard, clear, transparent films. Reported here are: (1) reaction conditions for preparing cationic starch–polyacrylonitrile (CS–PAN) graft copolymers of varying PAN contents, (2) number-average molecular weights (Mn) by

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gel-permeation chromatography (GPC) and molecular dispersities of the PAN moiety, and (3) dispersion stability of sonified CS–PAN. Also reported is the examination of the particulate structure of CS–PAN by scanning electron microscopy (SEM).

**EXPERIMENTAL**

**Materials**

Unmodified Hercules Starbake wheat starch containing 13.5% moisture was used without further refinement.

The AN was freed from inhibitor by flash distillation under reduced pressure at 40°C, and the distillate was then stored in the dark at 3–4°C.

Ceric ammonium nitrate was Fischer 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) employed in GPC determination of $M_n$ of PAN samples was dried 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 microporous 015 porcelain filter.

**Preparation of CS**

Diethylaminoethyl ether derivatives of starch were prepared according to the methods of Caldwell.² Starch (220 g) was slurried in a solution containing 500 ml of water and the appropriate amounts of sodium sulfate, sodium hydroxide, and 2-chlorodiethylaminoethyl hydrochloride. The slurry was heated with stirring at 55°C for 6 hr, after which time it was cooled to 25°C and then adjusted to pH 5.5. After the solids were separated by centrifugation, the supernatant was discarded. Residual salts in the product were removed by sequentially slurrying with distilled water, centrifuging and then discarding supernatants three times. Wet CS was slurried in absolute ethyl alcohol, filtered, and finally air-dried in a force

<table>
<thead>
<tr>
<th>Preparation</th>
<th>Sodium hydroxide, g</th>
<th>Amine, g</th>
<th>N in CS, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.82</td>
<td>3.5</td>
<td>0.13</td>
</tr>
<tr>
<td>2</td>
<td>4.07</td>
<td>6.75</td>
<td>0.26</td>
</tr>
<tr>
<td>3</td>
<td>4.82</td>
<td>13.50</td>
<td>0.42</td>
</tr>
<tr>
<td>4</td>
<td>5.50</td>
<td>15.50</td>
<td>0.51</td>
</tr>
<tr>
<td>5</td>
<td>11.00</td>
<td>27.00</td>
<td>0.90</td>
</tr>
</tbody>
</table>

² Each preparation was made at 55°C by reaction for 6 hr with 220 g of Hercules Starbake wheat starch (13.5% moisture; 0.02% N) in 500 ml of water containing 83.5 g of sodium sulfate.

² 2-Chlorodiethylaminoethyl hydrochloride.

² The degree of amine substitution in a CS having 0.26% N is 0.029.
draft hood. Conditions to make products of varying nitrogen values are tabulated in Table I.

**Preparation of CS–PAN**

CS (22 g) was gelatinized in 500 ml of distilled water under nitrogen at 95°C for 5–60 min. The solution was then cooled to 25°C at which temperature initiation and graft reactions were conducted. In one series of preparations, graft reactions were made with 250 g of CS dispersion in stoppered, 500-ml Erlenmeyer flasks shaken on a Burrell wrist-action shaker. In a second series, reactions were conducted under rotating blade stirrer action in round-bottomed flasks. In some experiments ceric ammonium nitrate in nitric acid solution (aged 24 hr) was added to gelatinized CS, and the mixture was either shaken or stirred 20 min before addition of freshly distilled AN. In others, AN was added to gelatinized CS, and the mixture was either shaken or stirred 20 min before addition of the cerium (IV) reagent. After 3 hr, mixtures (pH 1.8–2) were transferred to blender jars and blended about 3 min at high speeds to smooth creams. Blending was continued for 1 min at low speeds, while acidities were adjusted to the desired pH with 1N NaOH.

In each preparation, a portion of the reaction mixture was added to four volumes of ethyl alcohol to precipitate solids for analysis and polymer characterization. Proof of AN grafting onto gelatinized CS (0.42% N) was demonstrated by methods described previously. Samples (6 g each) of solid CS–PAN products analyzing approximately 2:1, 1:1, and 1:2 CS to PA by weight were extracted with 300 ml of DMF at room temperature for 3 days. The isolated DMF-soluble homopolymer PAN was 0.2–0.3 g in each product and had $M_n$ values of 150,000 to 200,000 by GPC.

**Sonification**

For 3 min, 50 ml of CS–PAN reaction mixtures contained in 2-oz. bottles immersed in ice water was sonified at 20 kHz with a Heat Systems ultrasonic probe equipped with a Branson power supplier. The probe tip measured about 1 cm.

**GPC Analyses**

Solutions of PAN were prepared according to a procedure described previously. DMF solutions containing 0.06% PAN were filtered through ultrafine sintered glass filters with vacuum applied. Molecular sizes of polymer were determined from chromatograms prepared on the analytical mode of a Waters Associates Ana-Prep GPC. The sample bank consisted of two columns (4 ft × 3.8 in., o.d.) packed with Styragel having exclusion limits of 10^6 and 1.5 × 10^4 Å. The instrument was operated at 70°C and at a pumping rate of 1.0 ml/min with DMF as the eluting solvent. Narrow-range dispersity polystyrene standards, supplied by Waters Associates, were dissolved in DMF at 0.06% concentrations and used to calibrate the
sample column bank. After 2 ml of filtered PAN solution was injected on
the column bank, the effluent was analyzed at a sensitivity of 8X.

The log of the molecular size \( A \) for polystyrene standards is a linear func­
tion of count number \( C \) and has the following relationship (least-squares computation):

\[
\log A = 10.073 - 0.43101C
\]

Molecular sizes of all PAN 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 the computer program described previously.4

Scanos. Scanning Electron Microscopy

Specimens were prepared for viewing by first placing one droplet of
0.06% graft copolymer dispersion on a microscope cover glass and then
drying at 25°C. The cover glass was broken, and a section containing
deposited polymer particles was placed on an aluminum specimen stud.
Conductive silver paint was applied to the edge of the glass to cement it to
the stud. The specimen and stud surface were then coated with a thin
layer (200 Å) of gold–palladium (60–40) alloy at 4 × 10^{-5} torr in a Denton
vacuum evaporator equipped with a rotating-tilt stage which allows uni­
form coating of the sample. The coating permits a good electron path
from the sample to the stud and thus prevents charging of the specimen
surface which could deform the image. Finally, samples were examined and
photographed in a Cambridge Stereoscan Mark II A SEM.

RESULTS AND DISCUSSION

Grafting AN onto CS

Kinetic studies of grafting AN onto starch by cerium(IV),5 as well as
oxidative ashing studies,6 are consistent with schemes involving cerium(IV)
complexation with starch, followed by formation of radicals that initiate
polymerization. Cationic starch is similar to starch, in that CS also forms
complexes with cerium(IV).7 However, the degree of substitution (DS)
of amine in CS influences degree of grafting (Fig. 1, curve 1). Greater
amounts of cerium(IV) are needed to achieve similar degrees of grafting as
the DS with respect to amine in CS increases. Reduction in the amount of
grafting with increasing DS is suggestive that more cerium(IV) is being
reduced to cerium(III) without initiating polymerization of AN. Perhaps
cerium(IV) reacts with reducing groups whose formation and concentration
is related to conditions of CS preparation.

Addition of AN to the gelatinized CS before the cerium(IV) was added
gave a higher PAN add-on than the converse sequence of addition (Fig. 1,
curves 2 and 3). If, indeed, reducing groups are present in gelatinized CS,
then addition of cerium(IV) after AN could conceivably give greater add-on
of PAN. Cerium(IV) reacts several hundred times faster with carbonyl
Fig. 1. Influence of reaction conditions on relationship between per cent nitrogen in cationic starch (CS) and per cent nitrogen in CS-polyacrylonitrile (CS-PAN) products at 25°C. Cationic starch was gelatinized at 95°C for 1 hr: (1) Ce(IV) was added to gelatinized CS and stirred 20 min before addition of 20 ml of acrylonitrile (AN) [160 anhydroglucose units (AGU)/Ce(IV)]; (2) Ce(IV) was added to CS and stirred 20 min before addition of 20 ml of AN [80 AGU/Ce(IV)]; (3) 20 ml of AN was stirred in CS 20 min before addition of Ce(IV) [80 AGU/Ce(IV)].

Fig. 2. Influence of gelatinization time of CS (0.42% N) on AN polymerization at 25°C. Cerium(IV) was added to CS before AN, 80 AGU/Ce(IV).

than with diol groups to give free-radical intermediates that could be lost before they initiate grafting reaction with monomers. However if CS had been innudated with AN, then capture of free radicals by AN before they are lost is quite possible.

Gelatinization time of CS (0.42% N) influences the degree of PAN add-on (Fig. 2). Increasing the gelatinization time from 5 to 60 min at 95°C
Preparation of DS–Polyacrylonitrile (CS–PAN) at 25°C

<table>
<thead>
<tr>
<th>Preparation</th>
<th>H₂O, ml</th>
<th>AN, g</th>
<th>AN:CS, mole:mole</th>
<th>Ce(IV), Ce(IV), mole:mole</th>
<th>CS–PAN product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>24</td>
<td>1.22 (3.69)</td>
<td>7.1</td>
<td>10.7</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>28</td>
<td>1.42 (4.29)</td>
<td>7.1</td>
<td>5.1</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>48</td>
<td>2.44 (7.38)</td>
<td>7.1</td>
<td>7.1</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>24</td>
<td>1.22</td>
<td>7.1</td>
<td>9.35</td>
</tr>
<tr>
<td>5</td>
<td>1000</td>
<td>24</td>
<td>1.22</td>
<td>14.2</td>
<td>12.25</td>
</tr>
<tr>
<td>6</td>
<td>1000</td>
<td>48</td>
<td>2.44</td>
<td>14.2</td>
<td>13.42</td>
</tr>
</tbody>
</table>

a Acrylonitrile (AN) was added to 19.5 g of CS (0.42% N) that had been gelatinized at 95°C for 30 min and then cooled to 25°C. The mixture was stirred 20 min before addition of cerium(IV). Stirring was continued for 3 hr.
b AGU = anhydroglucose unit; corrected for weight of amine sulfate salt.
c Per cent nitrogen of total solids precipitated from the dispersion.

decreased nitrogen in the CS–PAN products from about 15% (56% PAN) to 9% (33% PAN).

Acrylonitrile:CS weight ratios greater than 1.22 at a cerium(IV) concentration of one cerium(IV) per 80 anhydroglucose units (AGU) had adverse effects on grafting AN onto CS (0.42% N) (Table II). Increasing the AN concentration by about 16% (preparations 1 and 2) decreased PAN add-on more than 50%. Even increasing the water content in the graft reaction (preparation 3) by 100% and the AN:CS ratio from 1.42 to 2.44 did not give so great a PAN add-on as when the AN:CS ratio was 1.22 (preparation 1). Increasing the water content of the reaction from 250 ml (preparation 1) to 500 ml (preparation 4) decreased the PAN add-on from 42 to 35%. Higher PAN add-on was achieved by increasing the weight of cerium(IV) from 1.4 × 10⁻³ mole (preparations 3 and 4) to 2.8 × 10⁻³ mole (preparation 5).

The type of agitation during grafting influences the GPC $M_n$ of PAN isolated from the reaction mixture by acid hydrolysis (Table III). Graft copolymerization of AN with both CS (0.42% N) and CS (0.51% N) produced PAN of $M_n$ about 10⁶ when reaction was conducted in a round-bottomed flask at 25°C under mild stirring with a rotating blade at 180 rpm and $M_n$ about 5 × 10⁶ when reaction was conducted in a stoppered Erlenmeyer flask under more vigorous wrist-shaking agitation of the Burrell shaker at its highest setting. Since amounts of AN grafted are similar under both conditions, as evidenced by nitrogen values of CS–PAN products, about twice the number of apparent chains are produced when agitation is more vigorous.

The sequence of AN and cerium(IV) addition at the 40 AGU to cerium(IV) ratio (Table IV) appears to influence the PAN add-on more when graft copolymerization is conducted with stirring action in a round-bot-
TABLE III
Influence of Stirring and Shaking Action During Preparation of CS-PA on the Molecular Weight of Isolated PA

<table>
<thead>
<tr>
<th>Preparation</th>
<th>N in CS, %</th>
<th>Agitator</th>
<th>N in CS-PA, %</th>
<th>$M_n$ of PAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.42</td>
<td>STb</td>
<td>12.25</td>
<td>1,094,000</td>
</tr>
<tr>
<td>2</td>
<td>0.42</td>
<td>SHc</td>
<td>13.50</td>
<td>506,000</td>
</tr>
<tr>
<td>3</td>
<td>0.51</td>
<td>ST</td>
<td>12.32</td>
<td>1,017,000</td>
</tr>
<tr>
<td>4</td>
<td>0.51</td>
<td>SH</td>
<td>12.83</td>
<td>455,000</td>
</tr>
</tbody>
</table>

*a Reactions were conducted at respective AN:AGU and AGU:Ce(IV) mole ratios of 3.69 and 40 at 25°C for 3 hr.

*b Reaction was conducted in a round-bottomed flask using a rotating blade stirrer at 180 rpm.

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

TABLE IV
Influence of AN to Ce (IV) Addition Sequence on Grafting AN to Gelatinized CS (0.51% N) at AN:AGU and AGU:Ce (IV) Resp. Mole Ratios of 3.69 and 40 at 25°C for 3 Hr

<table>
<thead>
<tr>
<th>Preparation</th>
<th>Addition sequence</th>
<th>Agitation</th>
<th>N in CS-PA, %</th>
<th>$M_n$ of PAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AN before Ce(IV)</td>
<td>ST</td>
<td>12.31</td>
<td>1,017,000</td>
</tr>
<tr>
<td>2</td>
<td>Ce(IV) before AN</td>
<td>ST</td>
<td>9.96</td>
<td>1,069,000</td>
</tr>
<tr>
<td>3</td>
<td>AN before Ce(IV)</td>
<td>SH</td>
<td>12.83</td>
<td>455,000</td>
</tr>
<tr>
<td>4</td>
<td>Ce(IV) before AN</td>
<td>SH</td>
<td>13.72</td>
<td>505,000</td>
</tr>
</tbody>
</table>

tomed flask at 25°C for 3 hr than with wrist-shaking action in a stoppered Erlenmeyer flask. Sequence of AN to cerium(IV) addition does not appear to affect $M_n$ of isolated PAN under these conditions.

CS-PA Dispensers

Opaque, aqueous reaction mixtures of CS-PA (containing up to 8% solids composed of up to 50% grafted PAN) which had been blended for 3 min (see Experimental) and whose acidities after adjustment ranged from pH 1.8 to 7 formed supported films at 25°C and 75°C that were hard and adhesive but slightly hazy in appearance. These dispersions had Brookfield viscosities of 1500–3000 cP at 30 rpm and 25°C. However, reaction mixtures subjected to ultrasonic treatment at 20 kHz for 1–3 min at 5–10°C formed more fluid, latexlike dispersions having Brookfield viscosities of 15–40 cP at 30 rpm and 25°C. These dispersions gave films that were hard, adhesive and remarkably glasslike in appearance. The low viscosity of sonified CS–PAN (1:1) reaction mixtures, their stability, and the transparency of cast films, suggest their utility as latexes.

Attempts to redisperse solid CS-PA (1:1) obtained by alcohol precipitation of dispersions were not successful. Further, attempts to pre-
pare CS–PAN (1:1) latexes by grafting onto granular cationic starch were also not successful.

SEM showed that both nonsonified and sonified dispersions dried at 0.06% concentrations to ball-like particles measuring about 0.05–0.15 μ in diameter (Fig. 3). These dimensions are in the range of known latexes. The hundredfold decreases in viscosity of CS–PAN dispersions following sonification may be explained by possible regions of association between particles at high concentrations that are subsequently destroyed or disrupted by ultrasonic energy. Also, it is possible sonification causes some degradation of starch chains.

Sonification, which has a marked influence on the viscosity of CS–PAN (1:1) dispersions, has little effect on the $M_n$ of PAN isolated from dispersions by acid hydrolysis. PAN isolated from CS (0.51% N)–PAN (1:1) dispersions made by stirring action and then sonified for 12 min at 20 kHz had an $M_n$ value of 1,290,000, whereas PAN isolated from the nonsonified dispersion had an $M_n$ value of 1,070,000. Similarly, PAN isolated from CS (0.51% N)–PAN (1:1) made by shaker action and then sonified had an $M_n$ of 450,000, whereas PAN isolated from the nonsonified dispersion had an $M_n$ of 418,000.

Preparation of SEM specimens by nebulizing 0.06% CS (0.51% N)–PAN (1:1) dispersions with a stream of nitrogen onto cover glasses produced ball particles 3–5 μ in diameter which are believed to be artifacts. SEM examination at 50,000× revealed the particles have a granular texture which suggests the small balls (0.05–0.15 μ) in the droplet had coalesced on drying to make a single large particle.

CS–PAN reaction mixtures, sonified after aging for at least 1 week after their preparation, contained some anomalous ball particles measuring about 1–3 μ in diameter. SEM examination of droplets from sonified dispersions
showed that some large ball-like particles were scattered about a field of smaller particles, and sometimes large cubic and hexagonal crystals were observed. Crystals or large anomalous particles did not appear in reaction mixtures that were sonified within 24 hr after being prepared.

Formation of latexes by classical emulsion polymerization is attributed to polymerization of vinyl monomers within soap or detergent micelles to form polymer particles that are stabilized by subsequent protective colloid action of adsorbed surfactants. Formation of starch graft latexes did not involve soap or detergent, but perhaps there are analogies to emulsion polymerization. Much of gelatinized CS exists in the form of highly hydrated amyllopectin macromolecules (or microgel) possessing cationic charges. AN, upon stirring, probably permeates the intermolecular structure of CS. Graft copolymerization initiated within the amyllopectin molecule by cerium(IV) forms a particle consisting of PAN in highly hydrated starch possessing cationic charges. Perhaps the charges contribute to the stability of the particle dispersion.

In explaining kinetics of grafting AN onto gelatinized starch during the early stages of reaction, it was assumed that highly solvated soluble starch molecules hinder intra- and interpolymer association of grafted PAN—an effect which, in turn, limits coalescence of polymer particles. With superimposing of the charge effect of cationic groups, seemingly intra- and inter-PAN association to give coalescence of polymer particles would be even more restricted and would explain the latexlike properties of CS–PAN reaction mixtures.

Transparency of CS–PAN latex films seems to be related to the charge on the starch. Reaction mixtures of S–PAN (1:1), made from gelatinized starch according to methods described previously, at pH 5.5 and about 8% solids sonified at 20 kHz for 3 min to form milky dispersions having viscosities of 25–40 cP. These dispersions dried on glass at 25°C to form films that were hard and adhesive but hazy in appearance.

Sonified CS–PAN (1:1) dispersion stored at room temperature for 6 months did not form sediments but sometimes increased in viscosity to about 100–200 cP. Aged dispersions, however, became fluid on shaking or sonifying.

CS (0.51% N)–PAN (1:1.6) reaction mixtures also sonified to fluid dispersions. Films made from these dispersions were highly translucent but not so clear as those made from CS (0.51% N)–PAN (1:1).

Since the preparation of CS–PAN products and the properties of their dispersions have raised several questions, we feel there is need for continued investigation both with AN and other vinyl monomers. Future work will evaluate the scope of our preparative method in making a series of starch graft copolymer latexes with a broad range of properties.

We thank Mmes. C. E. McGrew and B. R. Heaton for performing the Kjeldahl analyses.

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


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