

Graft Copolymers from Thiolated Starch and Vinyl Monomers

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Synopsis

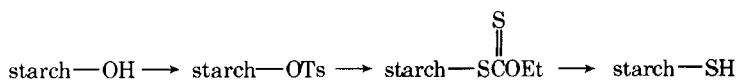
Thiol starches of degree of substitution (D.S.) 0.005-0.162 were prepared by displacing starch tosyloxy groups with xanthate and treating the resulting xanthate esters with either sodium hydroxide or sodium borohydride. Acrylonitrile, styrene, acrylamide, acrylic acid, and dimethylaminoethyl methacrylate were grafted onto the thiol starches with hydrogen peroxide as initiator. The peroxide caused both grafting of monomer and coupling of thiol groups to disulfide. Treating graft copolymers with sodium borohydride regenerated thiol groups from disulfide groups so that the grafting sequence could be repeated. By regenerating the thiol groups and repeating the grafting steps, high add-on and high-frequency starch graft copolymers were prepared. During four grafting sequences, acrylonitrile reacted with D.S. 0.162 thiol starch to give graft copolymers that contained increasing amounts of polyacrylonitrile (46.0-66.5%). Grafting frequency increased from 183 to 71 anhydroglucose units (AGU)/graft, while molecular weights of the grafted chains ranged between 20,000 and 25,200. The final product was hydrolyzed with potassium hydroxide solution to a copolymer, which absorbed up to 400 ml water per gram. Styrene was grafted onto thiol starch to give products containing 34.4-69.5% polystyrene with 986-3520 AGU/graft and having molecular weights of grafted chains between 276,000 and 364,000. Graft copolymers containing 48.9% polyacrylamide, 21.2% poly(acrylic acid), and 77.7% poly(2-methacryloyloxyethyltrimethylammonium acetate) were obtained under similar conditions.

INTRODUCTION

Starch graft copolymers having high add-on, high grafting frequencies [fewer than 100 anhydroglucose units (AGU)/graft], and short chains are often difficult to obtain by free-radical processes, and their properties have been little explored. Acrylonitrile (AN) has been reacted with starch by ceric ion¹ initiation to give products having 600-4000 AGU/graft and graft molecular weights of 75,000-800,000. When this monomer is grafted onto starch by the ferrous ion-hydrogen peroxide system,² higher grafting frequencies (300-1000) and lower molecular weights (4,000-90,000) of the grafts result.

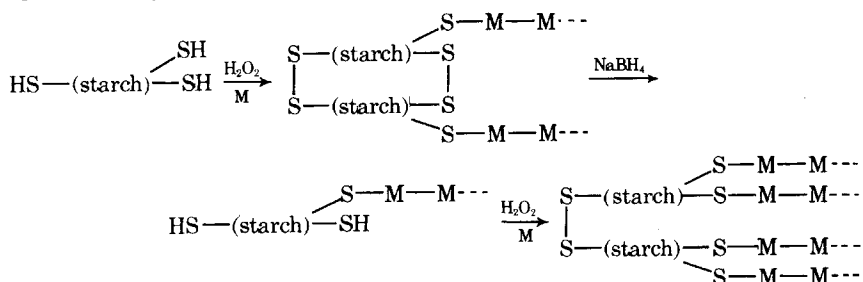
Grafting frequencies are notably increased when part of the redox system involved in free-radical grafting is incorporated in the polysaccharide backbone. Redox grafting involving cellulose xanthate and AN³ gives 80-100 AGU/graft and graft molecular weights of 13,000-15,000. This system has a disadvantage in that the grafts are attached to the polysaccharide in part through thioester linkages that are cleaved by hydrolysis.⁴ The preparation of hydrolyzed polysaccharide-polyacrylonitrile graft copolymers, for which there are many potential uses,⁵ requires alkali-stable grafting linkages.

We have introduced thiol groups into starch by the sequence⁶



(where OTs is tosyloxy) so that the grafts would become attached through stable thioether linkages and so that copolymers with frequently attached side chains could be prepared.

In addition to AN, the monomers styrene, acrylamide, acrylic acid, and dimethylaminoethyl methacrylate (DMAEMA) were also grafted onto thiol starches in the presence of hydrogen peroxide. The peroxide caused both grafting of monomer at the thiol site and coupling of the thiol groups to disulfide. Treating graft copolymers with sodium borohydride regenerated thiol groups so that the grafting sequence could be repeated. In this way, add-on and grafting frequency could be greatly increased over what is normal in a single grafting step. The process may be illustrated as follows:



where M = monomer. These monomers provide hydrophobic and hydrophilic graft copolymers containing neutral, anionic, and cationic functionalities. Dispersed graft copolymers were obtained by hydrolyzing the insoluble starch-polyacrylonitrile graft copolymers with potassium hydroxide solution.

EXPERIMENTAL

Ultraviolet (UV) and visible spectra were determined on a Beckman Model DB recording spectrophotometer. Infrared (IR) spectra were determined on potassium bromide discs with a Perkin-Elmer Model 137 spectrophotometer. Acrylonitrile and styrene (Eastman practical grades) were distilled before use. Acrylamide (Eastman, practical), acrylic acid (Eastman, inhibited), and DMAEMA (Rohm and Haas, inhibited) were used without further purification. Hydrogen peroxide (30%) was Baker reagent grade.

Tosyl starches and Starch Xanthate Esters (StSCSOEt)

To prepare tosyl starches, pearl corn starch (30.0 g) was suspended in 3:2 pyridine:water (300 ml) and heated to 85°C under constant stirring to gelatinize the starch. Water was then removed as an azeotrope (bp 93–94°C), and pyridine was added periodically to replace the volume distilled. When temperature reached 113–114°C, the distillation was discontinued and the resulting mass was cooled. Tosyl chloride (0.5–10.0 g) was added and the mixture stirred overnight at room temperature. The product was precipitated in 4:1 ethanol:water (1 liter). The solid was removed by filtration, washed with ethanol and hexane, and dried 1 hr at 100°C.

Tosyl starches (27–33 g) were dispersed in water (500 ml), and sodium ethylxanthate (30 g) was added. The reaction was kept 3–4 hr at 65°C or overnight at room temperature. Acetic acid was added periodically to maintain neutrality. After cooling, excess xanthate was destroyed with 1*N* hydrochloric acid (200 ml). The product was precipitated by the addition of 3 liters of ethanol, filtered, re-suspended in ethanol, filtered again, washed with hexane, and dried for 1 hr at 100°C.

Product samples (10–50 mg) were kept 5 min in 1*N* hydrochloric acid (10 ml) on a steam bath. Solutions were cooled and diluted to 100 ml. The UV absorption was measured at 282 nm and the xanthate ester degree of substitution (D.S.) derived as follows:

$$\text{moles of SCSOEt in sample: } \frac{A}{\epsilon l} \times \frac{1}{10}$$

where A is the absorption at 282 nm for the cell path length $l = 1$ cm and 1/10 liter volume; and ϵ is the average molar extinction coefficient (12,000) for the xanthate ester group.⁸

Approximate moles of AGU of starch taken is expressed as $w/162$, where w is the sample weight in grams and 162 is the equivalent weight of the AGU unit:

$$\text{D.S.}_{\text{SCSOEt}} = \frac{\text{moles of SCSOEt in sample}}{\text{moles of AGU units in sample}} = \frac{\frac{A}{\epsilon l} \times \frac{1}{10}}{\frac{w}{162}} = \frac{A \times 16.2}{12,000 \times w}$$

Thiol Starches

Starch xanthate esters (10 g) were dispersed in 0.1*N* sodium hydroxide (200 ml) at 75–80°C for 5 min under nitrogen. The mixture was agitated in a blender 10 min at 50°C and cooled. After neutralizing with 1*N* hydrochloric acid (20 ml), ethanol (1 liter) was added, and the product was removed by filtration, washed with ethanol, filtered, washed with hexane, filtered again, and vacuum dried 1 hr at 50°C.

Alternatively, the thiol starch was prepared directly by suspending tosyl starch (30.0 g) in water (500 ml) and treating with sodium ethylxanthate (30.0 g) for 4 hr on the steam bath. After cooling, 10*N* hydrochloric acid (25 ml) was added, and the products were filtered and washed thoroughly with water, ethanol, and hexane and then vacuum dried at 50°C.

Determination of Free and Total Thiol

For free thiol, samples (10–20 mg) were suspended in 1*N* hydrochloric acid (10 ml) and kept on the steam bath 5 min under nitrogen. After the suspension was cooled, water (80 ml) was added. Trisodium phosphate (3.0 g) and Ellman's reagent⁹ (1 ml) were added, and the solution was diluted to 100 ml. Optical density was determined at 420 nm, and thiol D.S., by the formula

$$\text{D.S.}_{\text{SH}} = \frac{A \times 16.2}{10,670 \times w}$$

where A is the optical density at 420 nm, w is the sample weight in grams, and 10,670 is the average extinction coefficient of several known thiols determined under similar experimental conditions.⁹

For total thiol, a method was used that was applicable to all samples containing disulfides and various sulfur-containing esters, which could be reduced to thiols. A sample (10–20 mg) was suspended in water (10 ml) which contained sodium borohydride (0.2 g). It was stirred 5 min on the steam bath under nitrogen, and 10*N* hydrochloric acid (1.5 ml) was added. After another 5 min, the mixture was cooled before being diluted with water (80 ml); thiol concentration was determined as described for free thiol.

Grafting and Recycling Reactions

For grafting, suspensions of thiol starch in water (1–5%) were warmed to 75°C as nitrogen was continuously bubbled through the reaction mixture. Sodium borohydride (0.1–2.0 g) was added to the suspension and allowed to react for 15 min. The reaction mixture was cooled to room temperature, and excess sodium borohydride was destroyed with 10*N* hydrochloric acid. After 15 min, the reaction mixture was buffered at pH 5 with a mixture of glacial acetic acid and 12.5*N* sodium hydroxide (3:2 v/v). Monomer (1–20 g) and hydrogen peroxide (30%, 0.04–1.00 ml) were added, and the total was stirred at room temperature 4 hr. Products were isolated by either filtration or centrifugation and then washed with water, ethanol, and hexane. Yields of products were determined after vacuum drying 1 hr at 100°C.

To recycle, the graft copolymers were resuspended in water and the grafting reaction was repeated. When acrylamide, acrylic acid, and DMAEMA were used, graft copolymers were obtained directly upon centrifugation since the homopolymers were water soluble. In graft copolymers derived from AN and styrene, products had to be extracted with suitable solvents to remove homopolymer.

Analyses of Graft Copolymers

Crude polyacrylonitrile (PAN) and polystyrene graft copolymers (1.0 g) were extracted 16 hr with *N,N*-dimethylformamide (DMF, 100 ml) for PAN graft copolymers or benzene (100 ml) for polystyrene graft copolymers to remove homopolymer. Insoluble material from centrifugation was resuspended in a similar volume of extractant and recentrifuged. The insoluble portion was washed with ethanol and dried. Homopolymer was determined from the weight of the residue after evaporation of the solvent. A portion (1.0 g) of the graft copolymers was kept on the steam bath 4 hr in 1*N* hydrochloric acid (100 ml) to hydrolyze the starch portion to glucose. The insoluble grafted side chains were isolated after washing with water, ethanol, and hexane; they were then vacuum dried 1 hr at 100°C and weighed. Grafting efficiencies were determined from the ratios of grafted side chain to total vinyl polymer (grafted portion plus homopolymer).

Polyacrylamide and poly(2-methacryloyloxyethyltrimethylammonium acetate) graft copolymers were suspended in water and centrifuged and resuspended several times in water to remove homopolymer, excess monomer, and salts. After the insoluble portion was washed with ethanol and vacuum dried, the per cent

graft was determined from the nitrogen content, assuming the grafted portion to contain polyacrylamide or poly(2-methacryloyloxyethyltrimethylammonium acetate) groups in the polymeric chain. Grafting was confirmed by appearance in the IR of either amide C=O at 6.0 μm or ester C=O at 5.8 μm .

Portions of poly(acrylic acid) (PAA) graft copolymers were washed thoroughly with 0.5*N* hydrochloric acid and water to convert all sodium carboxylate groups to carboxyl. Conversion was confirmed by appearance of C=O at 5.9 μm in the IR. After washing with alcohol and vacuum drying, samples (10–30 mg) were suspended in water (50 ml) and treated with standardized 0.02*N* sodium hydroxide (5 ml). After 2 hr, the excess base was titrated with standardized 0.02*N* hydrochloric acid to pH 8.5,¹⁰ and the percentage PAA in the graft copolymer was calculated.

Molecular Weights

Grafted side chains of polyacrylonitrile or polystyrene (0.2–0.3 g) were suspended in DMF or benzene (37 ml) and shaken overnight. Generally, less than 5% remained insoluble. After the solutions were centrifuged, filtered, and diluted to 50 ml, intrinsic viscosities were determined with No. 75 Cannon–Fenske viscometers. Molecular weights of PAN and polystyrene were obtained according to known formulae.^{3,11}

Hydrolysis of PAN Graft Copolymers

Thiol starch subjected to four grafting cycles with AN (1.0 g of polymer not extracted with DMF and containing 73% PAN) was suspended in 4% potassium hydroxide (40 ml) and kept 2 hr on the steam bath. The mixture was cooled and acidified with 10*N* hydrochloric acid (6 ml). The gummy suspension was centrifuged and the residue transformed into a powder upon trituration with acetone. Recovery was 0.97 g. IR showed no nitrile absorption, but exhibited carboxyl (5.9 μm) and amide (6.0 μm) absorptions in similar proportions. The product contained 5.9% nitrogen corresponding to 4.2 mmole amide per gram. Titration with 0.1*N* sodium hydroxide to neutrality gave 4.9 mmole carboxyl per gram. At neutrality, a clear gel formed, which retained about 200 ml water per gram. When pH of the gel was adjusted to 9 and the gel dried to a film, it could be rehydrated to hold about 400 ml water per gram.

RESULTS AND DISCUSSION

Tosyl starches of D.S. 0.010–0.288 were obtained by varying the amount of tosyl chloride in the reaction mixture. Treatment of the tosyl starches with sodium ethylxanthate under neutral or buffered conditions gave a partial displacement of tosyloxy groups.

D.S._{SCSOEt} values of 0.007–0.062 determined by the UV method represent conversions of 48–70% (Table I). When these esters were treated with sodium hydroxide solution, D.S._{SH} values of 0.005–0.045 were lower than expected. Apparently under alkaline conditions some liberated thiol groups react with undisplaced tosyl groups to form sulfide groups:

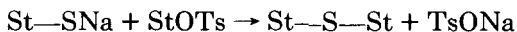


TABLE I
 Preparation of Thiol Starches

D.S.-OT _s ^a	D.S.-SCSOEt ^a	D.S.-SH ^a	Conversion of OTs to SCSOEt, %	Conversion of OTs to SH, %
0.010	0.007	0.005	70	50
0.056	0.027	0.025	48	45
0.129	0.062	0.045	48	35
0.200	—	0.123 ^b	—	61
0.288	—	0.130 ^b	—	45

^a D.S.-OT_s, D.S.-SCSOEt, and D.S.-SH are degrees of substitution of starch tosyl, xanthate ester, and thiol groups, respectively.

^b Treatment with NaBH₄ gave D.S.-SH of 0.157 and 0.162.

This kind of displacement reportedly occurs intramolecularly in the model compound 1,2-O-isopropylidene-3-deoxy-3-thio-6-O-tosyl- α -D-glucofuranose upon treatment with sodium hydroxide.¹² The tendency for thiol groups to displace residual tosyl groups was confirmed by IR spectra. A tosyl starch of D.S. 0.84 was treated with sodium ethylxanthate to give a product having similar proportions of xanthate ester (8.2 μ m) and tosyl (8.4, 8.5 μ m) groups. Saponification with sodium hydroxide or sodium borohydride gave a highly insoluble material, which contained negligible thiol by the Ellman reagent. IR showed loss of xanthate ester groups, as expected, but also a large decrease in tosyl groups. Since treating the original tosyl starch with alkali under similar conditions caused no loss of tosyl groups, the thiol groups generated probably displaced residual tosyl groups to give sulfide with loss of thiol.

When tosyl starches were treated with sodium ethylxanthate solution on the steam bath and the mixtures allowed to become alkaline, thiol starches were produced directly without isolation of the intermediate xanthate esters. In this way, overall conversions of tosyl to thiol were greater, as indicated in Table I, where D.S.-SH of 0.123 and 0.130 were obtained from D.S.-OT_s of 0.200 and 0.288. Treatment of these products with sodium borohydride slightly increased D.S.-SH to 0.157 and 0.162, probably due to decomposition and reduction of residual ester and disulfide groups.

The product of D.S.-SH 0.130 was used in grafting AN and styrene and that of D.S.-SH 0.123 in grafting acrylamide, acrylic acid, and DMAEMA. Repeated treatments of graft copolymers with monomer and hydrogen peroxide after regeneration of thiol groups significantly increase grafting and progressively decrease residual thiol available for the next cycle (Table II). Reactivities of monomers in these systems may be described both in terms of monomer interactions with —SH groups and of interactions of monomer units with one another. These reactivities result in add-on, expressed as increasing percentage of polymer in the graft copolymer. Add-on capability results from several factors of reactivity in these cycles and represents an index of practical significance wherein the overall performance of monomers may be compared. The weight increase with each cycle and ultimate add-on are greatest for DMAEMA and styrene, intermediate for acrylamide and AN, and least for acrylic acid. In several instances, as in the second cycle of grafting AN, polymer content increased little. The low add-on may have been caused by poisoning of the redox system due to insufficient

TABLE II
Influence of Repeated Cycles Upon Grafting of Various Monomers Onto Thiol Starch

Monomer	Cycle no.	Polymer in graft copolymer, %	Residual D.S. _{SH} ^a	Cumulative D.S. _{SH} consumed
Acrylonitrile ^b	0	—	0.16 ^c	—
	1	46.0	0.06	0.10
	2	61.4	0.04	0.12
	3	63.6	0.03	0.13
	4	66.5	0.02	0.14
Acrylonitrile ^d	0	—	0.16 ^c	—
	1	15.8	0.10	0.06
	2	38.4	0.08	0.08
	4	47.9	0.06	0.10
Styrene ^d	0	—	0.16 ^c	—
	2	34.4	0.06	0.10
	3	56.4	0.03	0.13
	4	69.5	0.02	0.14
Acrylamide ^d	0	—	0.16 ^c	—
	2	22.7	0.06	0.10
	3	37.6	0.04	0.12
	4	48.9	0.03	0.13
Acrylic acid ^d	0	—	0.16 ^c	—
	3	18.8	0.03	0.13
	4	21.2	0.03	0.13
Dimethylaminoethyl methacrylate ^d	0	—	0.16 ^c	—
	2	54.1	0.05	0.11
	3	77.7	0.03	0.13

^a D.S._{SH} of thiol in starch portion of copolymer after reduction with NaBH₄.

^b Grafting at 1% thiol starch.

^c D.S._{SH} of initial thiol starch upon NaBH₄ treatment.

^d Grafting at 5% thiol starch.

removal of by-products, such as hydrogen sulfide and carbon disulfide, normally flushed out with nitrogen after regenerating thiol groups. Usually, grafting ability was restored in subsequent cycles as by-products diminished.

Copolymers from reactions of thiol starches with AN or styrene were heated with 1*N* hydrochloric acid to hydrolyze the starch portions and leave grafted side chains. Intrinsic viscosities were obtained in suitable solvents; also, molecular weights and grafting frequencies were determined.

Grafting frequencies increase with both acrylonitrile and styrene as cycles are repeated (Table III). Molecular weights are in the same range for a given series and are much higher for polystyrene than polyacrylonitrile. In the acrylonitrile series, increasing thiol starch concentration from 1% to 5% and keeping reactant ratios the same reduced molecular weights of grafted side chains from about 20,000 to 10,000, but trends in grafting frequencies were similar. The second acrylonitrile series of Table III corresponds to the acrylonitrile series of Table II. Grafting efficiencies in terms of polymer found as grafts were 75–80% in both acrylonitrile series and 82–86% in the styrene series.

The approach to limiting values of grafting frequencies (for example, 71

TABLE III
Effect of Repeated Cycles Upon Grafting Frequencies and Average
Molecular Weights of Grafted Side Chains

Monomer	Cycle no.	AGU/grafted chain	Molecular weight	D.S. of graft ^a	Thiols used in grafting, ^b %
Acrylonitrile ^c	1	183	25,200	0.006	6.0
	2	83	21,400	0.012	10.0
	3	71	20,000	0.014	10.8
	4	71	22,900	0.014	10.0
Acrylonitrile ^d	1	256	7,760	0.004	6.7
	2	106	10,700	0.009	11.3
	4	76	11,200	0.013	13.0
Styrene ^d	2	3,520	298,000	0.0003	0.3
	3	1,320	276,000	0.0008	0.6
	4	986	364,000	0.0010	0.7

^a D.S. of graft = grafted chains/AGU.

^b Thiols used in grafting, % = (D.S. of graft/cumulative D.S._{SH} consumed) × 100 (see Table II for cumulative D.S._{SH} consumed).

^c 1% Thiol starch.

^d 5% Thiol starch.

AGU/grafted chain for polyacrylonitrile in Table III) may be due to an increasing difficulty for the monomer units to approach the regenerated grafting sites as the amount of grafting increases. Where starch thiol radicals initiate and terminate the same polymer chain, crosslinking would make it more difficult for the monomer to reach the active sites. The higher grafting frequencies in acrylonitrile copolymers over styrene copolymers (6.7% to 13% of total thiol used in grafting acrylonitrile vs. 0.3–0.7% for styrene, Table III) may be due to the greater polarity of acrylonitrile leading to easier penetration of monomer to the grafting sites.

The crude product from the final graft copolymerization with acrylonitrile (Table III, fourth cycle, first series) was hydrolyzed 2 hr on the steam bath in 4% potassium hydroxide. Acidification gave a product having no nitrile groups but amide and carboxyl groups in nearly equal proportions. The yield of saponified graft copolymer suggested that almost all grafting sites were alkali stable. When the product was adjusted to pH 9 and dried, a film formed that took up about 400 ml water per gram.

This process of regenerating remaining thiol groups and grafting opens possibilities for many new types of graft copolymers. For example, styrene and AN might be grafted either as mixtures or sequentially during regeneration cycles.

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