

Polysaccharide-g-Polystyrene Copolymers by Persulfate Initiation: Preparation and Properties

INTRODUCTION

The preparation of biodegradable plastics and the use of plant-derived natural polymers as extenders and replacements for petrochemical-based polymers are both active fields for research. Our research in these areas has centered on the synthesis and structure-property relationships of polysaccharide graft copolymers. Several years ago, we reported the synthesis of starch-*g*-polystyrene by the simultaneous cobalt-60 irradiation of starch-styrene mixtures¹ and the subsequent extrusion processing of these graft copolymers into strong, continuous plastics that exhibited little or no die swell.² A recent report by Henderson and Rudin³ also describes the extrusion of starch-*g*-polystyrene. The literature also contains a number of references to cellulose-*g*-polystyrene.⁴

Since cobalt-60 is not yet commonly employed as a free radical initiator in the large-scale production of polymers, we sought a chemical initiation method that might be used as an alternative to high-energy irradiation. Ceric ion, although routinely used with a number of monomer systems to prepare polysaccharide graft copolymers,⁵ failed to initiate polymerization in our experiments with starch and styrene. In this report, we will describe the preparation of starch-*g*-polystyrene and cellulose-*g*-polystyrene by a simple method that involves heating semisolid mixtures composed of the polysaccharide, styrene, and an aqueous solution of potassium persulfate. The reproducibility of these polymerizations and the extrusion processing of starch-*g*-polystyrene (after removal of a portion of the starch by hydrolysis) will also be described.

EXPERIMENTAL

Materials

Globe Pearl Corn Starch was from CPC International and contained 10% moisture. Cellulose was bleached softwood pulp (Alberta Hi-Brite) from St. Regis Paper Co., and analyses showed 0.06% lignin and 85.8% α -cellulose, the remainder being pentosans. Cellulose was stirred with water, filtered, and allowed to air dry to a moisture content of 6.3%; it was then broken up before reaction by stirring in a Waring Blender. Styrene (Eastman) was extracted with 5% sodium hydroxide and then with water immediately before reaction.

Graft Polymerizations

Starch. To a paste prepared from 333 g (300 g, dry basis) of starch and 150 g of styrene was added a solution of 3.0 g of potassium persulfate in 75 mL of water, and the resulting mixture was thoroughly blended. Air was displaced by four evacuations (to 50 mm) followed by repressuring (to atmospheric pressure) with nitrogen, and the mixture was heated in an 80°C oven for 3 h. A temperature of 100°C was reached during polymerization. The reaction mass was ground in a blender with ethanol to reduce particle size, and the polymer was washed with ethanol and dried.

A 10.0-g portion of each polymer was wet with 4 mL of water⁶ and was then exhaustively extracted with benzene to remove homopolymer. Grafted polystyrene was separated from starch by treating 6.00 g of benzene-insoluble graft copolymer with periodic acid followed by sodium methoxide in methanol, according to the method of Gugliemelli et al.⁷ This method was tested on a known sample of polystyrene and was shown to be nondegrading. Weight percent polystyrene in graft copolymers (% add-on) was calculated from weight loss after the periodate-base starch degradation.

Molecular weights of grafted polystyrene and polystyrene homopolymer for the nine repeat reactions were determined by GPC in tetrahydrofuran solution on a Waters Model ALC/GPC 244 Liquid Chromatograph (Table I). Four Waters μ -Styragel columns were used (10^5 , 10^4 , 10^3 , and 500 Å) with an injection volume of 200 μ L and a flow rate of 1 mL/min. Polystyrene standards were used. Standard deviation (σ) on \bar{M}_w and \bar{M}_n measurement was 11,400 and 19,300, respectively. The higher value of σ for \bar{M}_n is due to the sensitivity of \bar{M}_n to small fluctuations in the baseline and

TABLE I
Starch-*g*-Polystyrene Preparations: Polystyrene Molecular Weights

Prep. no.	Polystyrene grafts			Homopolymer (benzene extractable)		
	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
1	423,000	201,000	2.10	387,000	150,000	2.58
2	513,000	155,000	3.31	339,000	142,000	2.39
3	519,000	184,000	2.82	425,000	222,000	1.91
4	629,000	271,000	2.32	421,000	150,000	2.81
5	533,000	191,000	2.79	370,000	132,000	2.80
6	468,000	121,000	3.87	378,000	136,000	2.78
7	524,000	182,000	2.88	322,000	135,000	2.39
8	503,000	181,000	2.78	376,000	145,000	2.59
9	521,000	227,000	2.30	353,000	136,000	2.60
Mean	515,000	190,000	2.80	375,000	150,000	2.54

is about 15% of the \bar{M}_n value in the worst cases. Use of four replicate molecular weight determinations reduced the standard deviation to less than 10% of reported \bar{M}_n for the averages reported in this work.

Cellulose. Except for the amounts of starting materials used, reactions with cellulose and extractions of crude polymers with benzene were carried out as described for starch. To remove cellulose from graft copolymers to give grafted polystyrene for GPC analysis, cellulose-*g*-polystyrene was treated first with sodium periodate solution and then with sodium methoxide in methanol, as described earlier.⁸ Solubility of the grafted polystyrene in benzene was determined by overnight stirring of 0.2 g of polymer in 100 g of benzene. The gel fraction was separated by centrifugation (30 min at 30,000 $\times g$), and a weighed portion of the supernatant was freeze dried to determine the dry weight of soluble polymer. Molecular weights were determined on the soluble fractions.

Microscopy

Samples were examined and photographed at 1,000 \times in a Hitachi ISI scanning electron microscope. Specimens were spread with a spatula onto aluminum stubs, where they adhered without the use of silver paint or adhesive. When fractured granules were desired, the specimen was masticated with a spatula on the surface of the stub. Specimens were then coated with a 200-Å layer of gold-palladium (60-40) alloy.

Partial Hydrolysis of Starch-*g*-Polystyrene

Hydrochloric Acid. 300 g of starch-*g*-polystyrene (not extracted with benzene) was blended with excess 0.01*N* hydrochloric acid and separated by filtration. The acid-washed polymer was then heated under reflux for 30 min with 3 L of 0.01*N* hydrochloric acid. The insoluble polymer was separated by filtration, washed with water (pH adjusted to 7 for the final wash), and dried under vacuum at 60°C. The hydrolysis was repeated on four other batches and products were combined. The combined product contained 58% polystyrene (by weight) as determined by weight loss after removal of the starch component.

Enzyme. Three hundred grams of starch-*g*-polystyrene (not extracted with benzene) was suspended in 3 L of water containing 0.132 g of $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$, and the pH was adjusted to 7.0 with sodium hydroxide solution. 30 g of Takatherm enzyme solution (Miles Laboratories, Inc.) was added, and the mixture was stirred at 85-90°C for about 20 h. The insoluble polymer was separated by filtration, washed with water, and dried under vacuum at 60°C. The hydrolysis was repeated four times, and the combined product was given a second enzyme hydrolysis using the same procedure. The final product contained 40% polystyrene (by weight) as determined by weight loss after removal of the starch component.

Extrusion and Testing of Starch-*g*-Polystyrene

Partially hydrolyzed starch-*g*-polystyrene with 58% add-on (100 g) was weighed into a Waring Blender, and 15 g of either dibutyl phthalate or glycerol was washed in with 35 mL of ethanol.

Mixtures were thoroughly blended, and the solids were then spread onto open trays to allow the ethanol to evaporate.

Plasticized and unplasticized starch-*g*-polystyrene samples were extruded through a 3/4-in. C. W. Brabender extruder with *L/D* ratio of 20:1. The screw had a 2:1 compression ratio and was driven by a variable speed Brabender Plasti-Corder. Temperature of the barrel and slit die ($1 \times 1/16$ in.) was 175°C. Plastic specimens used for testing were given two passes through the extruder. Dumbbell-shaped tensile specimens were machined on a Tensil Kut specimen cutter (Sieburg Industries, Inc.). Specimens were tempered for 4 days at 22.2°C and 50% relative humidity before testing on an Instron testing machine at a 5 cm/min crosshead speed.

RESULTS AND DISCUSSION

When a semi-solid mixture of starch, styrene, water, and potassium persulfate in a weight ratio of 100:50:25:1 is heated, an exothermic polymerization takes place to give a reaction product containing 26–28% polystyrene (by weight), the major portion of which is apparently grafted to starch. Nine identical polymerizations were run to examine the reproducibility of this reaction and also to obtain sufficient polymer for extrusion processing. Conversion of styrene to polymer ranged from 68% to 79%. Polystyrene not extractable with benzene was assumed to be grafted, and this fraction amounted to 82–88% of the total polystyrene formed, the remaining 12–18% being benzene-extractable homopolymer. Benzene-extracted polymers contained 24–26% polystyrene, by weight.

Molecular weights and molecular weight distributions for both homopolymers and grafts (after removal of starch) were determined by GPC analysis for the nine repeat experiments (Table I). Polystyrene grafts had mean \bar{M}_w and \bar{M}_n values of 515,000 and 190,000, respectively, whereas mean values of \bar{M}_w and \bar{M}_n for the homopolymers were 375,000 and 150,000. One-way analysis of variance was applied to estimate the variations in \bar{M}_w and \bar{M}_n that one might expect between replicate ex-

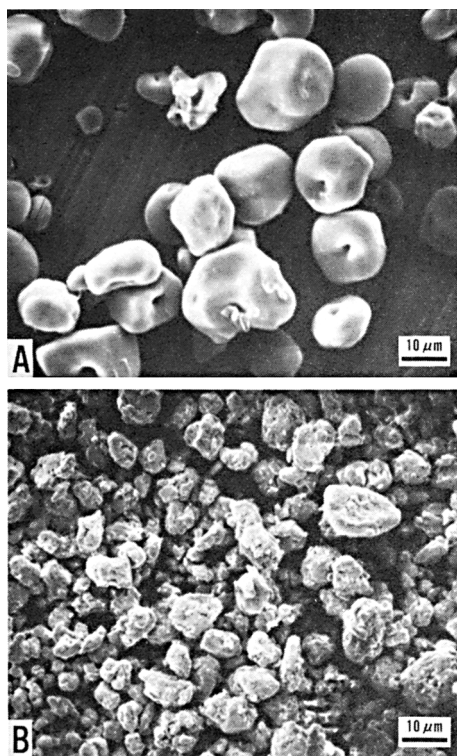


Fig. 1. (A) Starch-*g*-polystyrene; not extracted with benzene; 26–28% add-on. (B) Polystyrene remaining after removal of starch from the polymer shown in (A). Polystyrene granules fractured by mastication.

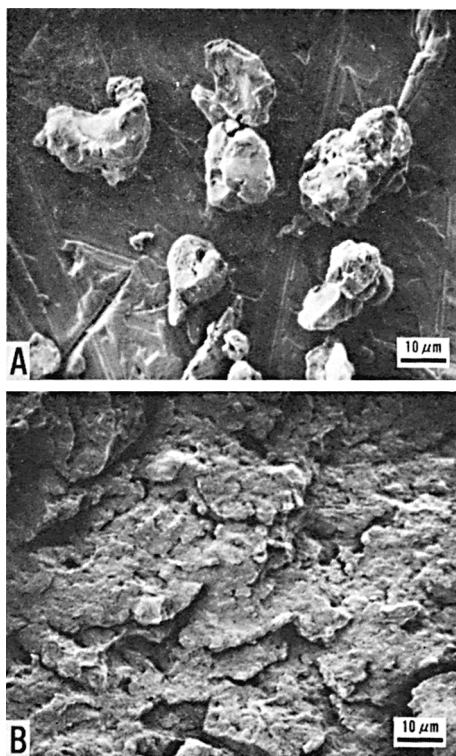


Fig. 2. (A) Starch-*g*-polystyrene; partially hydrolyzed with 0.01*N* HCl; 58% add-on. (B) Fracture surface of tensile test specimen prepared by extrusion of the polymer shown in (A).

periments, independent of the lack of reproducibility inherent in our GPC procedure (see Experimental). Standard deviations (8 degrees of freedom) for \bar{M}_w and \bar{M}_n were 54,800 and 40,700, respectively, for polystyrene grafts and were 33,900 and 26,300, respectively, for polystyrene homopolymers.

Like the cobalt-60 initiated graft copolymer,⁹ persulfate-initiated starch-*g*-polystyrene retains a similarity in appearance to corn starch granules [Fig. 1(A)], even though reaction temperatures greatly exceed the gelatinization temperature of starch. Moreover, when viewed through a polarizing microscope, nearly all starch-*g*-polystyrene granules still show birefringent patterns typical of unmodified starch.¹⁰ Apparently, there is insufficient water in our system to permit starch gelatinization. Although evidence suggested surface grafting in cobalt-60 initiated graft polymerizations,⁹ scanning electron microscopy provided no such evidence for our persulfate-initiated products. Fracturing some of the eroded-appearing polystyrene granules that remained after removal of the starch component gave only small fragments [Fig. 1(B)] and did not reveal the hollow centers that

TABLE II
Effects of Plasticizers on Tensile Properties of Starch-*g*-Polystyrene^a

Plasticizers	UTS ^b	Elongation at break (%)
None	2.8	2.1
Dibutyl phthalate	1.5	1.8
Glycerol	0.34	3.1

^a Polystyrene content: 58%, by weight.

^b Ultimate tensile strength (kg/mm²).

TABLE III
Preparation of Cellulose-g-Polystyrene: Comparison of Cellulose with Starch as Substrate for Grafting

Polysaccharide (g)	Reactants ^a		Styrene conversion (%)	Graft copolymer, benzene-insol.		Polystyrene grafts		Homopolymer, benzene-sol.					
	Styrene (g)	Water (mL)		% total add-on	Insol. gel (%)	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	% of total	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	
Cellulose (30)	150	50	58	38	33	0	438,000	118,000	3.71	62	269,000	70,000	3.84
Cellulose (30)	100	100	80	36	30	20	612,000	167,000	3.66	64	433,000	99,000	4.37
Cellulose (30)	50	150	80	61	22	25	616,000	114,000	5.40	39	490,000	119,000	4.12
Cellulose (30)	15	185	62	84	8	—	—	—	—	16	272,000	54,000	5.04
Starch (300)	150	75	68-79	95-97	24-26	0	515,000 ^b	190,000 ^b	2.80 ^b	3-5	375,000 ^b	150,000 ^b	2.54 ^b

^a Reactions with cellulose used 1.0 g of $K_2S_2O_8$. Reaction with starch used 3.0 g of $K_2S_2O_8$.

^b Mean values from nine repeat experiments.

one might expect if polystyrene were located primarily near the granule surface and if the granule centers were thus composed largely of ungrafted starch. We must, therefore, conclude that polymerization takes place not only on the surface but throughout the starch granule matrix as well. Also, the maintenance of birefringence after graft polymerization suggests that grafting takes place in amorphous regions of the granule.

Although we have reported the extrusion of starch-*g*-polystyrene copolymers with 40% and 48% add-on,² the polystyrene content of our present products is too low to permit such processing. A logical solution to this problem is hydrolytic removal of a portion of the starch to yield a graft copolymer with a higher styrene:starch ratio. Although enzymatic hydrolysis afforded a product that contained 40% polystyrene and that showed no birefringence, this particular product also resisted our attempt at extrusion. Refluxing 0.01*N* hydrochloric acid increased the polystyrene content to 58%; and at this level of addition, the polymer could be easily extruded to a plastic with an ultimate tensile strength of 2.8 kg/mm.² Despite the granulelike appearance of this partially hydrolyzed starch-*g*-polystyrene [Fig. 2(A)], a fracture surface of the extruded plastic [Fig. 2(B)] shows little or no granule structure remaining. This is in contrast to fracture surfaces of starch-*g*-poly(methyl acrylate),¹¹ where the remains of grafted starch granules were still visible. Partial hydrolysis of starch apparently makes starch-*g*-polystyrene granules more susceptible to breakdown under the conditions of extrusion.

Since starch-*g*-polystyrene plastics are brittle, the effects of plasticizers at a level of 15 parts per 100 parts polymer were briefly examined (Table II). Both dibutyl phthalate (a plasticizer for the styrene portion¹²) and glycerol (a plasticizer for the starch portion¹³) reduced the ultimate tensile strengths of extruded polymers without having a significant effect on brittleness, as approximated by the % elongation at break. Glycerol produced the most drastic reduction in tensile strength, lowering this value by almost a factor of 10. Other techniques, such as the cograftering of rubbery polymers, should therefore be investigated to reduce brittleness in these polymers.

A series of potassium persulfate-initiated reactions was next run with cellulose as the substrate for graft polymerization (Table III). It was not possible to use the same solid:liquid ratios with cellulose that we used for starch because of the higher fluid uptake shown by cellulose; much of this fluid no doubt was trapped between fibers rather than absorbed. Whereas 300 g of starch required about 225 g of liquid (styrene plus water) to thoroughly wet the polysaccharide and to produce a semisolid paste, cellulose required roughly a tenfold increase in the amount of liquid used. For the reactions in Table III, the weights of cellulose, potassium persulfate, and total liquid were held constant, whereas the ratio of styrene to water was varied. Even at a 5:1 weight ratio of styrene:cellulose, the resulting cellulose-*g*-polystyrene contained only 33% (by weight) polystyrene, most of the polymer formed being benzene-soluble homopolymer (probably formed between the fibers). Lower values for % add-on were obtained at lower styrene:cellulose ratios, and a cellulose:styrene ratio comparable to that used for the starch reactions produced a graft copolymer with only 8% add-on. Conversions of styrene to homopolymer in all reactions were higher than for the reactions with starch. Another difference between starch and cellulose reactions was the presence of a significant gel fraction in the polystyrene grafts isolated after removal of the cellulose components of the graft copolymers. Also, molecular weight distributions of grafts and homopolymers were broader for the cellulose-derived polymers.

We are indebted to Dr. W. F. Kwolek for assistance with the statistical analyses, to F. L. Baker for the scanning electron micrographs, to R. G. Fecht for the determination of tensile properties, and to Dr. U. Khoo for birefringence determination by polarizing microscopy.

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Received February 1, 1983

Accepted March 3, 1983

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