

Graft Polymerization of Styrene onto Starch by Simultaneous Cobalt-60 Irradiation

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Synopsis

Starch-*g*-polystyrene copolymers have been prepared by the simultaneous ^{60}Co -irradiation of starch-styrene mixtures, and copolymers have been characterized with respect to weight per cent polystyrene (% add-on) and also the molecular weight and molecular weight distribution of polystyrene grafts. In a typical polymerization, 4 g each of starch and styrene were blended with 1 ml water and 1.5 ml of an organic solvent; the resulting semisolid paste was irradiated to a total dose of 1 Mrad. With ethylene glycol, acetonitrile, ethanol, methanol, acetone, and dimethylformamide as the organic solvent, values for % add-on ranged from 24% to 29%. The highest % add-on (43%) and the highest conversion of styrene to grafted polymer (76%) were obtained when the organic solvent was omitted, and water alone was used. When water was also omitted, polymerization of styrene was negligible; however, graft copolymer was formed in the absence of water when either ethylene glycol or ethanol was added. Attempts were unsuccessful to achieve a % add-on greater than 43% by doubling the amount of styrene in the polymerization recipe. Mixtures of equal weights of starch and styrene are relatively nonviscous, but these mixtures thicken when either water or ethylene glycol is blended in. Reasons for this thickening action and the possible influence of thickening on the graft polymerization reaction were explored.

INTRODUCTION

Use of renewable, agriculturally derived products, such as polysaccharides, as extenders and replacements for synthetic, petroleum-based polymers is currently an active area for research. Graft polymerization of synthetic polymers onto a polysaccharide backbone perhaps offers one of the best ways to utilize polysaccharides for this purpose. The Northern Laboratory has made an extensive investigation of graft polymerizations onto starch^{1,2} and, as one phase of this continuing program, has initiated a study of the grafting of thermoplastic polymers. As a first step in such research, we examined the cobalt 60-initiated polymerization of styrene onto unmodified corn starch.

The literature contains few reports of starch-styrene copolymerizations. To initiate graft polymerizations, Kargin and co-workers³ used ozone; Patel et al.,⁴⁻⁶ metal ion-peroxide systems; and Reyes et al.,⁷ electron beam irradiation. In our study, we examined the synthesis of starch-*g*-polystyrene by the simultaneous cobalt-60 irradiation of starch-styrene mixtures and characterized the resulting graft copolymers. In an unpublished contract report for the U.S. Department of Agriculture, Reyes⁸ showed that starch-*g*-polystyrene could be prepared by the simultaneous irradiation of starch and styrene in either methanol-water or

ethylene glycol-water; her observation served as a starting point for our latest work.

The formation and physical properties of plastics from starch-*g*-polystyrene copolymers will be reported separately.

EXPERIMENTAL

Materials

Granular globe pearl corn starch (CPC International; 13.9–15% water) was used in all experiments, except for two reactions with freeze-dried starch. To prepare the freeze-dried starch, a 5% suspension of Globe pearl corn starch in water was stirred at 95°C for 30 min, and the gelatinized starch dispersion was freeze dried. The dry starch was allowed to stand at 25°C and 100% relative humidity until a water content of 13.8% was reached.

Styrene, Eastman reagent grade, was distilled through a 22-in. Vigreux column before use (bp 54°C/30 mm). Organic solvents were reagent grade and were used as received. In a run made without added water, absolute ethanol was further dried by passing through a column of molecular sieve.

Graft Polymerizations

The cobalt 60 source was a Gammacell 200 unit from Atomic Energy of Canada, Ltd. The dose rate at the center of the chamber was 1.01–0.89 Mrad/hr, as calculated from the initial dosimetry data provided by the manufacturer and the decay rate of cobalt 60. The accuracy of these values was confirmed by Fricke dosimetry.⁹

Reactions were carried out in 2-oz screwcap glass bottles. A mixture of starch, styrene, and solvent was thoroughly blended with a spatula, and the resulting paste was evacuated to 50 mm and repressured with nitrogen. This evacuation and repressuring procedure was repeated four times. The mixture was then irradiated with cobalt 60 and allowed to stand at room temperature for 2 hr. Ungrafted polystyrene and unreacted monomer were removed from the reaction mass by four extractions with benzene. For reactions run without water, 1 ml water was added before benzene extraction.¹⁰ Infrared analysis of polystyrene isolated from the benzene extracts showed little or no carbohydrate. The graft copolymer after solvent extraction was washed onto a fritted glass funnel with ethanol and dried in a vacuum oven at 60°C. The weight per cent grafted polystyrene in the graft copolymer (% add-on) was calculated from the gain in weight of starch after graft polymerization.

Isolation of Grafted Polystyrene

A suspension of 4.00 g graft copolymer in 250 ml of 0.5*N* hydrochloric acid was heated under reflux for 2 hr. The solid was removed by filtration, washed with water and ethanol, and dried *in vacuo* at 60°C. To maximize surface area, and thus the penetration of acid into the hydrophobic polymer particles, the polymer was next dispersed in benzene and freeze dried. The freeze-dried solid was wet with 10 ml methanol, 250 ml of 0.5*N* hydrochloric acid was added, and the

methanol was stripped off under vacuum. This methanol pretreatment was necessary to achieve good wetting of the hydrophobic polymer with hydrochloric acid solution. The resulting suspension was heated under reflux for 2 hr, and the grafted polystyrene was isolated by filtration, washed, and dried. Carbohydrate content was about 5%, by infrared. The % add-on was calculated by loss in weight of the graft copolymer after removal of starch by acid depolymerization.

Molecular Weights and Grafting Frequencies

Molecular weights of polystyrene were calculated from intrinsic viscosities in benzene at 30°C according to the equation¹¹

$$[\eta] = 1.06 \times 10^{-4} \bar{M}_n^{0.735}$$

Grafting frequencies, as expressed by the average number of anhydroglucose units (AGU) per grafted polystyrene branch, were calculated from the molecular weight of grafted polystyrene and the average between the % add-on values obtained from weight gain and from weight loss.

Selected samples were also dissolved in dimethylformamide solution (containing 200 ppm lithium bromide) and analyzed by gel permeation chromatography on a Waters Anaprep unit. Two 4 ft \times $\frac{3}{8}$ in. columns were packed with Styragel (10^7 and 10^4 Å) and were calibrated against characterized polystyrene standards provided by Waters Associates. The pumping rate was 1 ml/min, and the column temperature was 75°C.

RESULTS AND DISCUSSION

Graft Polymerization and Polymer Characterization

In all reactions, ungrafted polystyrene was removed from the graft copolymer by extraction of the reaction mass with benzene at room temperature. Although the graft copolymer was highly swollen in benzene, infrared spectra showed little or no carbohydrate carried over into the benzene extract. Exhaustive extraction (room temperature) of one graft copolymer with 90:10 (vol) dimethyl sulfoxide:water, which is a good solvent for corn starch, dissolved less than 5% of the polymer. To isolate grafted branches for molecular weight determination, starch was removed from the graft copolymer by hydrolysis with 0.5*N* hydrochloric acid. The molecular weights of both grafted polystyrene and ungrafted homopolymer were determined from intrinsic viscosity measurements in benzene, and selected samples were also analyzed by gel permeation chromatography. In all reactions, the molecular weight of grafted polystyrene was higher than that of homopolymer. Under our hydrolysis conditions, refluxing mineral acid did not change the intrinsic viscosity of a commercial polystyrene sample of molecular weight 200,000.

Our initial graft polymerizations were carried out by thoroughly blending mixtures of 4 g each of starch and styrene, 1 ml water, and 1.5 ml of a number of common organic solvents and then irradiating these mixtures to a total dose of 1 Mrad (Table I). Polymerizations run in the presence of ethylene glycol, acetonitrile, ethanol, methanol, acetone, or dimethylformamide gave similar values for % add-on (24–29% for all reactions), whereas molecular weights of

TABLE I
Graft Polymerizations in Aqueous-Organic Reaction Media^a

Organic solvent	% Add-on ^b		MW of graft ^c	Grafting frequency, AGU/graft ^d	% Conversion		MW of homopolymer ^e
	Wt. loss	Wt. gain			To graft	To homo-polymer	
Ethylene glycol	29	29	500,000	7,560	40	12	196,000
Acetonitrile	25	26	502,000	9,050	34	4	178,000
Ethanol	26	26	465,000	8,170	36	7	162,000
Methanol	29	29	570,000	8,610	42	10	209,000
Acetone	24	25	420,000	7,990	33	6	155,000
Dimethylformamide	27	28	650,000	10,600	40	13	282,000
None (water only)	43	43	785,000	6,420	76	15	365,000

^a Polymerization recipe: 4.0 g starch, 4.0 g styrene, 1.5 ml organic solvent, 1.0 ml water, irradiation dose of 1.0 Mrad.

^b Wt. gain: % add-on determined by gain in weight of starch after graft polymerization. Wt. loss: % add-on determined by loss in weight of graft copolymer after depolymerization and removal of the starch moiety with mineral acid.

^c Calculated from intrinsic viscosity in benzene at 30°C: $[\eta] = 1.06 \times 10^{-4} \bar{M}_n^{0.735}$.

^d AGU = Anhydroglucose unit.

grafted polystyrene varied from 420,000 to 650,000. Graft copolymers are infrequently grafted, as indicated by the large number of AGU per grafted polystyrene branch (7,560 to 10,600).

The highest % add-on (43%) and the largest number of grafted branches resulted when the organic solvent was omitted and water alone was used. The molecular weight of grafted polystyrene under these conditions was 785,000, and the grafting frequency was 6,420 AGU per graft. Total conversion of monomer to polymer was more than 90%, and a 76% conversion of monomer to grafted polystyrene was realized. Temperature of the reaction mass during one such polymerization, as measured by a thermistor probe, reached a maximum of 47°C after 35–40 min in the cobalt 60 source. A tenfold increase in the amounts of reactants produced a maximum temperature of 86°C, since heat from the exothermic polymerization was not so readily dissipated from the larger mass.

Since the highest conversion of monomer to grafted polymer was obtained in the absence of organic solvents, a series of reactions was run in the presence of water alone to determine the influence of reaction conditions on graft copolymer formation (Table II). Comparison of the first and second reactions of Table II showed that irradiation to a total dose of 0.5 Mrad rather than 1 Mrad reduces the % add-on, the number of grafted branches (larger AGU/graft), and the conversion to grafted polymer. Graft molecular weight remained virtually unchanged. A 2.5-fold increase in the amount of water blended with starch and styrene (third reaction) lowered graft molecular weight somewhat, but produced no gross changes in graft copolymer composition. Eliminating added water (fourth reaction) resulted in little or no polymerization. In the fifth reaction of Table II, even though the amount of styrene was doubled, % add-on did not increase. Twofold increases in both styrene and water (sixth reaction) and warming the reaction mass to 65°C before irradiation (last reaction) caused only minor changes in composition of the final polymer.

Since mineral acid reportedly increases radiation-induced graft polymerization of styrene onto cellulose,¹² the fifth reaction of Table II was repeated, except that 1M sulfuric acid was substituted for water. These conditions, however, gave no increase in % add-on.

TABLE II
Graft Polymerizations in Water. Influence of Reaction Conditions^a

Styrene, g	Water, ml	Dose, Mrad	% Add-on		MW of graft ^b	Grafting frequency, AGU/graft	% Conversion		MW of homo- polymer ^b
			Wt. loss	Wt. gain			To graft	To homo- polymer	
4.0	1.0	1.0	43	43	785,000	6,420	76	15	365,000
4.0	1.0	0.5	30	32	725,000	9,960	48	5	350,000
4.0	2.5	1.0	40	41	590,000	5,350	68	17	328,000
4.0	0	1.0	—	2(max)	—	—	—	—	—
8.0	1.0	1.0	40	41	636,000	5,770	35	7	267,000
8.0	2.0	1.0	40	40	795,000	7,361	34	5	224,000
8.0 ^c	2.0	1.0	43	44	636,000	5,100	40	5	274,000

^a All reactions used 4.0 g starch.

^b Calculated from intrinsic viscosity in benzene at 30°C.

^c Starch-styrene-water mixture heated to 65°C and cooled to room temperature before irradiation.

TABLE III
 Graft Polymerizations in Organic Solvents in the Absence of Water^a

Organic solvent	% Add-on		MW of graft ^b	Grafting frequency, AGU/graft	% Conversion		
	Wt. loss	Wt. gain			To graft	To homo-polymer	MW of homo-polymer ^b
Ethylene glycol	32	30	525,000	7,210	44	21	275,000
Ethanol	21	22	955,000	21,500	28	5	—
Acetonitrile	—	4(max)	—	—	—	—	—

^a Polymerization recipe: 4.0 g starch, 4.0 g styrene, 1.5 ml organic solvent, irradiation dose of 1.0 Mrad.

^b Calculated from intrinsic viscosity in benzene at 30°C.

Next, a series of three reactions was run in the presence of selected organic solvents, but in the absence of any added water to determine what effect these conditions might have on the composition of the reaction product (Table III). The highest % add-on was obtained in ethylene glycol, and the graft copolymer composition was remarkably similar to the reaction run in the presence of water (first reaction of Table I). A significant conversion to grafted polystyrene was also realized in ethanol, although the high molecular weight for grafted polystyrene was surprising. These two solvents contained only 0.10% and 0.14% water, respectively, as determined by Karl Fischer titration. In the presence of acetonitrile, there was little conversion of styrene to polymer.

The addition of monomer to preirradiated starch is a general method of preparing graft copolymers,¹³ and, with certain monomers, this technique is as commonly used as the simultaneous irradiation of starch-monomer mixtures we describe here. In order that the two irradiation techniques might be directly compared under our reaction conditions, 4 g starch was preirradiated to a total dose of 1 Mrad, and a heterogeneous mixture of 8 g styrene and 2 ml water was then blended in under an atmosphere of nitrogen. Although amounts of reactants, irradiation dose, and reaction time were the same as for the sixth reaction of Table II, the % add-on in the final product was only about 5%.

Selected samples of grafted polystyrene were analyzed by gel permeation chromatography as a check on the molecular weights calculated from intrinsic viscosities and also to estimate molecular weight distributions. Weight-average molecular weights for grafted polystyrene in the fourth reaction of Table I (methanol solvent) and the last reaction of the same table (water only) were 730,000 and 817,000, respectively. The corresponding number-average molecular weights were 202,000 and 257,000; however, these values are less reliable because of the difficulty in accurately measuring the low molecular weight ends of the distribution curves. Values of the \bar{M}_w/\bar{M}_n ratios, therefore, lie between 3 and 4 for these two samples. Although molecular weights calculated from intrinsic viscosities are considerably different from values for \bar{M}_n determined by gel permeation chromatography, intrinsic viscosities are still valuable to compare polystyrene samples rapidly within a given series.

Physical State of Starch-Styrene Mixtures

Suspensions of starch in styrene, at the concentrations used in our experiments, settled rapidly; and the viscosity of these suspensions resembled that of styrene itself. Adding a styrene-miscible organic solvent, followed by thorough mixing, changed the appearance of the mixture little. However, adding water in the presence or absence of organic solvents gave a mixture that thickened when it was triturated with a spatula; thorough mixing gave a semisolid mass that had a paste-like consistency and did not settle on standing. Outwardly, it seemed as if the addition of water caused the starch to absorb essentially all the liquid. A similar behavior was observed when ethylene glycol, which is also not miscible with styrene, was stirred into a starch-styrene mixture in the absence of water.

Since conversions of styrene to grafted polymer were highest in the presence of either water or ethylene glycol, we investigated more fully whether the thickening phenomenon of starch-styrene mixtures, when they were blended with water, might be directly related to grafting efficiency. Examining starch-water-styrene mixtures under a light microscope revealed immediately that thickening was not due to gross swelling of individual starch granules, although a change in granule appearance from opaque to translucent with opaque centers, when excess styrene was added, suggested that granules did absorb styrene. Starch granules that had been in contact with water-styrene were still strongly birefringent. Moreover, when a semisolid paste of starch-water-styrene, which contained little or no free liquid, was centrifuged for 20 min at about $200 \times g$, there was some separation of solid and liquid phases, and 16% of the originally added styrene could be poured off.

Since marked granule swelling and loss of birefringence were not observed, and since the styrene component of the semisolid mixture of starch-water-styrene could be partially separated by low-speed centrifugation, it seemed that the thickening action could be best ascribed to a clumping and sticking together of individual starch granules due to the highly hydrophilic surfaces formed by the absorption of added water. Because large and irregularly shaped clumps pack together less uniformly than individual granules, they would trap more liquid in the interstices. This same conclusion applies to mixtures of starch, styrene, and ethylene glycol; since ethylene glycol, like water, is hydrophilic and not miscible with styrene and would thus also be selectively absorbed by starch. In 1943, Kruyt and Van Selms^{14,15} observed a similar thickening phenomenon with mixtures of rice starch, carbon tetrachloride, paraffin oil, and water and proposed a similar explanation.

The next question was whether added water was a primary cause of the high conversions to grafted polystyrene or whether high conversions were instead due to the water-induced physical trapping of styrene in close proximity to each starch granule, i.e., the fact that starch-water-styrene mixtures will not separate on standing. Evidence that the physical state of starch-monomer mixtures is not of prime importance was obtained from graft polymerization onto a starch sample which had been isolated by freeze drying an aqueous dispersion of gelatinized starch. Because starch in this form has a high surface area, it absorbs styrene without separating into two phases; however, polymerization was still

negligible in the absence of added water. When water was added to the mixture of freeze-dried starch and styrene, a graft copolymer with 34% add-on was isolated.

The reaction run in ethanol in the absence of water (second reaction, Table III) provides additional evidence that the physical state of the reaction mass is not the primary factor in determining whether graft polymerization will or will not take place. In this reaction, no thickening of the starch-styrene-ethanol reaction mass occurred on mixing; however, a graft copolymer with more than 20% add-on was produced.

The high conversions to grafted polystyrene in the presence of added water is probably due to several factors, one of which is the radiolysis of water within the starch matrix.¹⁶ Radiolysis products of water (e.g., hydroxyl radical) can abstract hydrogen atoms from starch to generate free radicals on the starch backbone, which can subsequently react with styrene to initiate graft polymerization. A similar radiolysis of ethylene glycol and ethanol to yield free radical products may also be visualized;¹⁷ however, the concentration of ethanol within the starch granule should be significantly lower than that of water or ethylene glycol because of the miscibility of ethanol with styrene. This reduced concentration would account for the relatively low % add-on observed with ethanol.

Although styrene is commonly considered to be water insoluble, it is soluble to a small extent (0.032% at 25°C). Thus, another important reason why the addition of water and other hydroxylic solvents leads to graft polymerization is that these solvents diffuse readily throughout the starch matrix and therefore serve to establish contact between solvated styrene molecules and free-radical sites on the hydroxyl-containing starch backbone. Although there is no gross starch granule swelling in these hydroxylic solvents at room temperature, graft polymerization with granular starch may also be facilitated by a loosening and opening of the granule structure as the solvent penetrates the granules and hydrogen bonds with individual starch molecules. The ability of a particular solvent to promote graft polymerization is apparently not strictly a function of its water miscibility, since little polystyrene was produced in acetonitrile when water was absent.

Since the starch we used already contained about 14–15% water, one may ask why additional water must be added before graft polymerization will proceed. It is known that water at a concentration of about 14% is intimately associated with starch, as in a hydrate.¹⁸ Water in excess of this amount is absorbed by the starch granules, but is less tightly bound. The extent to which water molecules are strongly hydrogen bonded to the glucopyranose units of starch molecules may be the factor determining whether or not graft polymerization of styrene is initiated.

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