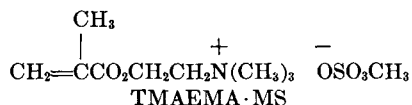


**Graft Copolymers by Simultaneous  $^{60}\text{Co}$ -Irradiation  
of Starch, Acrylamide, and *N,N,N*-Trimethylaminoethyl  
Methacrylate Methyl Sulfate**

**Introduction**

Previously, we have studied the graft polymerization of mixtures of acrylamide and *N,N,N*-trimethylaminoethyl methacrylate methyl sulfate (TMAEMA·MS)



onto starch that had been preirradiated with cobalt 60.<sup>1</sup> Since starch-graft copolymers of this type function as flocculants<sup>2</sup> and also as retention aids in papermaking,<sup>3</sup> we are currently seeking to optimize methods for their synthesis. We now report the simultaneous irradiation of starch and mixtures of the two monomers, a method which, for these graft copolymers, offers definite advantages over initiation by preirradiated starch. Although the simultaneous  $^{60}\text{Co}$ -irradiation of polysaccharide-monomer mixtures is a well-known procedure for graft polymerization, a study of our particular monomer system has not been previously reported.

**Experimental**

**Materials.** Unmodified wheat starch was Huron Starbake from Hercules, Inc., and contained 14% water. Acrylamide was Eastman reagent grade, and TMAEMA·MS was supplied as a 40% solution in water (Sipomer Q-5) by Alcolac Chemical Corp. Both monomers were used as received.

**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 1.16–1.14 Mrad/hr, as calculated from the initial dosimetry provided by the manufacturer and the decay rate of cobalt 60. Polymerizations were conducted with starch in both the swollen and unswollen states.

Reactions with swollen starch initiated by simultaneous irradiation were carried out in 2-oz screwcap glass bottles. Starch (16.2 g, dry basis, 0.1 unit mole) was added to a solution of 2.83 g (0.01 mole) TMAEMA·MS and 13.5 g (0.19 mole) acrylamide in 20 ml of either water or water-ethylene glycol. The amount of water included what was in the TMAEMA·MS solution but did not include the equilibrium moisture present in the starch. After the slurry was stirred gently and heated on a steam bath to give a thick paste which would not settle on standing, the bottle was tightly capped. The mixture was allowed to stand at room temperature for 30 min and was then irradiated with cobalt 60 (5.2 min for 0.1 Mrad). The irradiated mixture was kept 2 hr at room temperature, and the tough rubbery solid was cut into small pieces that were soaked overnight in about 1-liter water which contained 0.5 g hydroquinone. The mixture was centrifuged and the swollen solid was extracted three times with cold water and once with 95% ethanol. The solid was finally washed onto a filter with acetone and vacuum dried at 60°C. The combined water extract was dialyzed and freeze dried. For calculation of percentage conversion, all the synthetic polymer in this fraction was considered to be homopolymer, although infrared analysis showed roughly 15–20% (by weight) carbohydrate.

In the reaction with unswollen starch initiated by simultaneous irradiation, 40.6 g (dry basis, 0.25 unit mole) starch was blended with a solution of 1.42 g (0.005 mole) TMAEMA·MS and 6.75 g (0.095 mole) acrylamide in 10 ml water. The mixture was first evacuated to 50 mm and repressured with nitrogen (this procedure was repeated

four times). The mixture was then irradiated with cobalt 60 to a total dose of 0.1 Mrad. Products were isolated as described previously. The water-soluble fraction contained about 15% carbohydrate.

For comparison, a reaction initiated by preirradiated starch was carried out in which 32.4 g (dry basis, 0.2 unit mole) starch was irradiated in a 2-oz screwcap bottle under air to a dose of 0.1 Mrad. The irradiation was performed in an ice-filled Dewar flask, and the temperature of the starch sample during irradiation was about 5°C, as determined in a separate experiment. To facilitate addition of dry solids, the polymerization was run in a polyethylene-covered beaker equipped with a thermometer, a nitrogen inlet, and a spatula to permit stirring of the viscous reaction mass. A solution of 5.7 g (0.02 mole) TMAEMA·MS in 40 ml water was placed in the beaker and purged with a slow stream of nitrogen for 1 hr. Solid acrylamide (27.0 g, 0.38 mole) was added and the mixture stirred for 1 min to attain complete solution. The irradiated starch was then added (4 min after removal from the cobalt 60 source) and the mixture stirred thoroughly. The reaction mass was allowed to stand for 2 hr, during which time the temperature rose from 17° to 41°C (in the first 13 min) and then slowly dropped. Products were isolated as described previously. The water-soluble fraction contained about 15% carbohydrate.

**TMAEMA·MS in Polymeric Products.** Mole percentages of TMAEMA·MS in grafted and ungrafted synthetic polymers were calculated from 100 MHz NMR spectra, as determined in 5% D<sub>2</sub>O solutions which contained 9% sodium chloride to reduce viscosity. Spectra were run on a Varian HA-100 spectrometer, and signals at  $\delta$  3.21 (N-methyl groups of TMAEMA·MS, 9 protons) and  $\delta$  1.66 ( $-\text{CH}_2-$  of polyacrylamide, 2 protons) were integrated. The accuracy of the method has been verified with known polymer mixtures.<sup>1</sup>

**Hydrolysis of the Starch Moiety of Graft Copolymers and Molecular Weight of Grafted Polymer.** The weight per cent grafted synthetic polymer in starch-graft copolymers (per cent add-on) was calculated by two methods: gain in weight of starch after graft polymerization and weight loss of the graft copolymer after removal of the starch moiety by depolymerization with enzyme. The enzymatic hydrolysis procedure with Diazyme L30 (Miles Laboratories, Inc.) was similar to one we reported earlier,<sup>4</sup> except that no inorganic salts were added to exchange the anionic counterions of the quaternary ammonium salts before isolation of the polymer.

The number-average molecular weight of the grafted branch fraction was determined in 0.15N sodium chloride solution on a Melabs Model CSM-2 membrane osmometer equipped with a B-19 membrane (Schleicher and Schuell Co.).

Intrinsic viscosities of grafted branches in dl/g at 30°C were determined with Cannon-Fenske viscometers in 1N sodium nitrate.

## Results and Discussion

Simultaneous irradiations were performed with starch in the form of either unswollen granules or granules that had been swollen by heating in an aqueous solution of monomer. Polyacrylamide, poly(TMAEMA·MS), and copolymers of the two are water soluble; however, graft copolymers prepared from unmodified starch remain largely insoluble in cold water owing to their intact granule structure. Graft copolymers can therefore be freed of ungrafted synthetic polymer and unreacted monomer by extraction with cold water, and the ungrafted polymer isolated by dialysis and freeze drying of the water extract. We have characterized water-washed graft copolymers by determining the per cent add-on (see experimental part), the intrinsic viscosity of grafted polymer, and the TMAEMA·MS content of grafts, which for all polymers was lower than that in the initial monomer mixture.

Results of graft polymerizations of a mixture of 5 mole-% TMAEMA·MS and 95 mole-% acrylamide onto unmodified wheat starch are collected in Table I. In the first four reactions, a slurry of starch in the monomer solution was heated in a screwcap bottle to the indicated temperature; the bottle was capped, left to stand for 30 min, and

TABLE I  
Starch-Graft Copolymers Prepared by Simultaneous Irradiation

Starch, mole <sup>a</sup>	Water, ml	EG <sup>b</sup> , ml	Pretreatment	Monomers, <sup>c</sup> mole	Irradiation dose, Mrad	% Add-on <sup>d</sup>		Grafted branches TMAEMA·MS, mole-%	Conversion of monomers, %		Solubility of graft copolymer, <sup>g</sup> %
						By weight gain	By weight loss		To graft	To homopolymer <sup>f</sup>	
0.1	20	0	64°C, no N <sub>2</sub>	0.2	0.25	43	43	3.7	1.5	74	14 (3.4)
0.1	20	0	64°C, no N <sub>2</sub>	0.2	0.1	43	40	4.3	1.6	75	15 (3.6)
0.1	19	1	66°C, no N <sub>2</sub>	0.2	0.1	39	39	3.5	1.3	64	20 (2.6)
0.1	15	5	73°C, no N <sub>2</sub>	0.2	0.1	30	32	2.6	1.6	42	38 (3.0)
0.25	10	0	25°C, N <sub>2</sub>	0.1	0.1	16	15	1.4 <sup>h</sup>	1.8	93	7 (4.2)
0.2	40	0	preirradiation	0.4	0.1	31	26	3.9	2.0	44	7 (9.3)

<sup>a</sup> Mole anhydroglucose unit (MW = 162).

<sup>b</sup> EG = ethylene glycol.

<sup>c</sup> Monomer mixture composed of 5 mole-% TMAEMA·MS and 95 mole-% acrylamide. TMAEMA·MS = N,N,N-trimethylaminoethyl methacrylate methyl sulfate.

<sup>d</sup> Weight gain: % add-on determined by gain in weight of starch after graft polymerization. Weight loss: % add-on determined by loss in weight of graft copolymer after depolymerization of the starch moiety with enzyme.

<sup>e</sup> dl/g at 30°C in 1N sodium nitrate.

<sup>f</sup> Number in parentheses is the mole-% TMAEMA·MS in this fraction, based on 100% synthetic polymer.

<sup>g</sup> Graft copolymer (0.5 g) in 37.5 ml water was heated for 30 min at 100°C. Cooled mixture was centrifuged for 20 min at 5000 × g and the solubility calculated from the weight of solid in an aliquot of supernatant.

<sup>h</sup>  $\bar{M}_n = 157,000$ . Calculated grafting frequency, using % add-on by weight gain: 5100 anhydroglucose units per grafted branch.

then irradiated. Temperatures given in Table I are those at which starch first formed a paste that was thick enough to preclude its settling during reaction. This temperature was 64°C with water as the reaction medium; however, higher temperatures were needed with water-ethylene glycol. High monomer conversions were achieved without a nitrogen purge of the monomer solution, since dissolved oxygen is apparently removed sufficiently by heating. The reaction mass after irradiation was tough and rubbery but swelled in water at room temperature when cut into small pieces.

The first two reactions of Table I show the low irradiation doses which will give a high conversion of monomers to polymer. Irradiation doses of 0.25 Mrad and 0.1 Mrad gave similar results, except the intrinsic viscosity of the grafted polymer was somewhat higher at the lower dose. Consequently, all other reaction mixtures were irradiated to 0.1 Mrad. Doses lower than 0.1 Mrad were not examined but could probably be used.

The third and fourth reactions of Table I show the effect of added ethylene glycol on graft polymerization. Conversions of monomers to homopolymer were higher, and the intrinsic viscosities of grafted branches were lower with increasing amounts of ethylene glycol in the reaction mixture.

In the fifth reaction (Table I), simultaneous irradiation was performed with starch in granular form; however, amounts of starch, water, and the two monomers were adjusted so that the final mixture was still a free-flowing solid after blending at room temperature. Since no heat was applied to the reaction mixture, atmospheric oxygen was displaced with nitrogen before irradiation. The conversion of monomers to polymer was quantitative, although the larger starch:monomer ratio required for an outwardly dry reaction of this type gave a graft copolymer with a lower per cent add-on. Also, the molecular weight of grafted polymer was significantly lower than for the other simultaneous irradiations.

The last reaction in Table I was made with preirradiated starch so that results might be compared with a simultaneous irradiation reaction run under similar conditions (the second reaction). Conversion of monomers to polymer and the per cent add-on of the graft copolymer were both higher for the simultaneous irradiation procedure; however, there were no large differences in the intrinsic viscosity and TMAEMA-MS content of grafted branches.

There are several advantages of simultaneous irradiation over preirradiation for this system of monomers. In addition to high conversions of monomer to polymer at low irradiation doses and elimination of the nitrogen purge when reaction mixtures are heated before irradiation, simultaneous irradiation reactions are easier to run. Also, there is no time interval between irradiation and addition of irradiated starch to monomer; hence, radical decay is minimized and there is maximum utilization of available radicals. The simultaneous irradiation of outwardly dry blends of granular starch, monomer, and water is probably the simplest method for the preparation of these graft copolymers. The quantitative conversion of monomers to polymer and the high conversion to grafted polymer would eliminate the need for an isolation step in any practical process, and, at most, only a drying step would be required.

Our results are novel in that little or no crosslinking of synthetic polymer takes place. Also, the conversion of monomers to grafted polymer, rather than homopolymer, is greater than one might expect from a simultaneous irradiation reaction.<sup>5</sup> One explanation for the apparent absence of irradiation-induced crosslinking<sup>6</sup> is the low irradiation doses used in our reactions, and thus the relatively short irradiation times needed with our high-intensity cobalt 60 source (5.2 min for 0.1 Mrad). Although some conversion of monomers to polymer takes place during the irradiation period, a considerably longer period of time is required to attain high conversions, due to the high viscosity of the reaction mass. Much of the synthetic polymer formed in the reaction has therefore not been subjected to gamma irradiation. Furthermore, at the high starch concentrations used in our reactions, crosslinking in both the presence and absence of irradiation would be inhibited through the action of starch as a chain transfer agent during the polymeri-

zation. Chain transfer to starch would also be one factor contributing to the high conversions to grafted polymer as compared with homopolymer.

The lower intrinsic viscosity for grafted polymer at 0.25 Mrad as compared with 0.1 Mrad also deserves comment. Since the time during which starch free radicals are generated (irradiation time) is relatively short while the time needed to attain high monomer conversions is relatively long, the formation of lower molecular weight grafts at higher irradiation doses is not surprising. If a large number of grafts are initiated in the presence of a given amount of monomer and the conversion to polymer is constant, these grafts will necessarily be of lower molecular weight than those formed from a lesser number of initiating sites.

Although the graft copolymers from unmodified wheat starch shown in Table I are only partially soluble in water at 100°C, water solubility is improved if starches are reduced in molecular weight (e.g., acid-modified or hypochlorite-oxidized starches). With the proper selection of modified starch, we have produced graft copolymers that approach complete solubility in water close to room temperature. These soluble graft copolymers are not described in detail at this time because fractional precipitation would be necessary to separate homopolymer, and such a fractionation scheme has not yet been developed.

We are indebted to Dr. D. Weisleder for NMR spectra.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

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Received August 13, 1973  
Revised January 21, 1974