JOURNAL OF APPLIED POLYMER SCIENCE VOL. 21, 761–772 (1977)

Amylose Graft Polymers Made by ^{60}Co Gamma-Irradiation*

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Synopsis

Model products were needed to elucidate structure–property relationships in a starch graft polymer research program. Simultaneous irradiation of amylose and acrylamide in oxygen-free, dilute aqueous solutions gave graft polymers with maximum add-on of about 16%. The graft polymers were separated from homopolymer and subfractionated by incremental additions of nonsolvent (methyl or ethyl alcohol) to irradiated aqueous reaction media. The graft polymers were fairly homogeneous in graft content. Effects were determined of ratios of monomer to substrate, dose rate, and total dose on yield, graft content, intrinsic viscosity, and homopolymer characteristics. Under some conditions, crosslinks probably formed between graft side chains. Large differences in solution properties of a synthetic mixture of separately irradiated amylose and acrylamide and an irradiated solution of amylose and acrylamide indicated that grafting had occurred. Further evidence for true grafting was based on the action of a selective precipitant, *n*-butyl alcohol, on graft polymer solutions.

INTRODUCTION

Starch graft polymers prepared from starches containing both amylose and amylopectin are, consequently, mixtures of amylose and amylopectin graft polymers. Therefore, relationships of structural characteristics of starch graft polymers, such as graft content or graft molecular weight, to properties (e.g., flocculating ability) are not clear-cut. This work describes development of procedures for the preparation of graft polymers of amylose, the linear component of starch. In addition to serving as models for understanding the structure–property relationships in starch graft polymers, amylose graft polymers might themselves possess unique and valuable properties.

There are a limited number of preparations described in the literature covering amylose graft polymer preparation. They include ultraviolet irradiation of amylose film in the presence of acrylonitrile and a photosensitizer,[1] base-catalyzed addition of amylose to 1-acrylamido-1-deoxy-D-glucitol,[2] free-radical initiation using manganic sulfate and reaction with methyl methacrylate and methyl acrylate,[3] ceric ammonium nitrate initiation and reaction with acrylonitrile,[4] and iron(II) peroxide initiation and reaction with styrene.[5] The grafting procedures involving γ-radiation used simultaneous solution irradiations for styrene[6] and acrylamide[7] monomers. The dose rate in Mishina's study[7] was

* Presented at 167th American Chemical Society meeting, Los Angeles, California, March 31–April 5, 1974.

about 1/26th of that used here. A preirradiation method has also been reported for grafting acrylamide.[8]

In preliminary experiments, preirradiation of amylose was unsuccessful in grafting reactions with aqueous oxygen-free acrylamide solutions. Electron spin resonance analyses indicated that relative to granular starch, extremely poor yields of trapped radicals were obtained when amylose of 1% moisture content was irradiated under nitrogen at 0°C to an absorbed dose of 1 Mrad. Therefore, amylose graft polymers were prepared exclusively by simultaneous solution irradiations, with acrylamide serving as a representative water-soluble vinyl monomer. Amylose, fractionated from tapioca starch, was chosen as the substrate polymer because its high molecular weight minimized retrogradation problems.

RESULTS AND DISCUSSION

Irradiation Solvent

Polar solvents suitable for simultaneous irradiation of amylose and acrylamide are limited in number. In addition to solubility requirements of the reactants, solubility of the polymeric products affects propagation rates and the separating of graft polymer from homopolymer. Furthermore, alkaline solvents were precluded because irradiated amylose is alkali sensitive and because amide groups in polyacrylamide hydrolyze. Solvent radiolysis products also differ in their effects on either polymerization or degradation of polymers in the grafting reaction. Dimethyl sulfoxide (DMSO), water, and combinations of these solvents seemed most promising on the basis of known properties. A well-known solvent for starch and amylose,[9] 90% DMSO (90:10; DMSO:water, by volume), is also a solvent for acrylamide and polyacrylamide. Water generally meets the same solubility criteria as 90% DMSO, but its use is complicated somewhat by retrogradation of amylose.

The relative effects of DMSO–water and water solvents on radiation depolymerization of dissolved amylose and polyacrylamide and rate and extent of acrylamide polymerization are important to solvent selection. In a companion study,[10] G (amylose scission) values were determined for amylose, 1% solutions, irradiated in nitrogen saturated aqueous solvents of varying DMSO content. G values of 2.3 and 30 were associated with 99.8% DMSO and water, respectively. A value of 5, for 90% DMSO, can be obtained by interpolation of the data. Such a range in susceptibility to scission probably would be reduced by vinyl monomers in simultaneous irradiation reactions. Similarly, polyacrylamide that was irradiated to a total absorbed dose of 1 Mrad in 99.8% DMSO (2% solution) had an intrinsic viscosity decrease of only 4%. However, the extent of any crosslinking reactions in DMSO and their contribution to viscosity stability are unknown.

Acrylamide was irradiated (ambient temperature and air) in both 90% DMSO and water to various total absorbed doses to determine the solvent effects on polymerization (Fig. 1). Polymerization rate in 90% DMSO was slow compared to that in water. Results in 99.8% DMSO were similar to those in 90% DMSO, and the molecular weight of polyacrylamide formed by a total dose of 0.09 Mrad was estimated to be about 5600 from intrinsic viscosity–molecular weight rela-

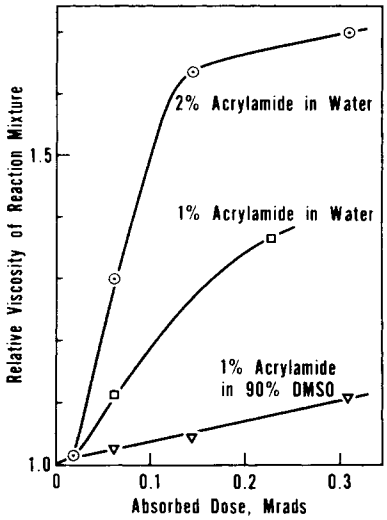

Fig. 1. Irradiation polymerization of acrylamide in water and 90% dimethyl sulfoxide (DMSO) at 23°C in air.

tionships.[11] Also, total conversion of monomer to polymer was very low compared to reaction in water. Saturation of aqueous 2% acrylamide solution with nitrogen did increase significantly the relative viscosity obtained with an absorbed dose of 0.06 Mrad,but did not affect the relative viscosity of a 1% solution of acrylamide irradiated in 90% DMSO.

Chemical reaction or molecular association of solvent radiation products and substrate occurred with both amylose and acrylamide irradiated in 99.8% DMSO. Thus, sulfur contents of 0.06% and 0.58% were observed in reaction products of amylose and acrylamide, respectively, when they were irradiated (ambient temperature and air) to an absorbed dose of 1 Mrad. The sulfur-containing amylose and polyacrylamide were recovered quantitatively from the reaction media by freeze drying following dialysis against distilled water to remove DMSO.

Water was used for all subsequent experiments because DMSO-based solvents proved unsuitable for simultaneous irradiations of amylose and acrylamide.

Polymerization of Acrylamide

Several experiments were performed to determine the relationship of total absorbed dose and dose rate to yields and intrinsic viscosity of polyacrylamide prepared from acrylamide irradiated in water (Fig. 2). Intrinsic viscosity reached a steady state that is the result of degradation, crosslinking, and forming of new polymer at total absorbed doses in the range of 0.1 to 0.3 Mrad.

The influence of acrylamide concentration, dose rate, and total absorbed dose on the relative molecular weight of polyacrylamide was also estimated (Fig. 3). These data show the amounts of methyl alcohol required to titrate irradiated solutions to an initial turbidity. Presumably, molecular weights were inversely related to the methyl alcohol concentration at which turbidity was first observed. However, note that such a relation might be affected somewhat by differences in molecular weight distribution. Also, differences in polymer concentration

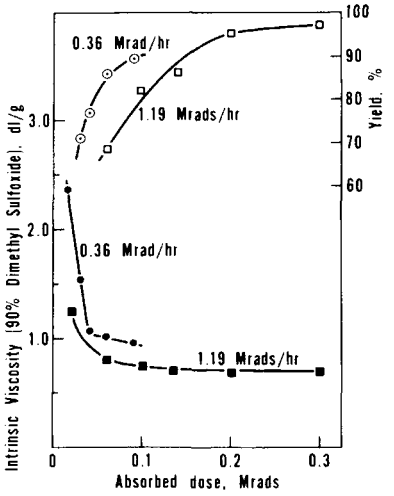

Fig. 2. Influence of dose rate and total absorbed dose on intrinsic viscosity and yield of polyacrylamide obtained by irradiation of 4% aqueous solution of acrylamide at 23°C in air.

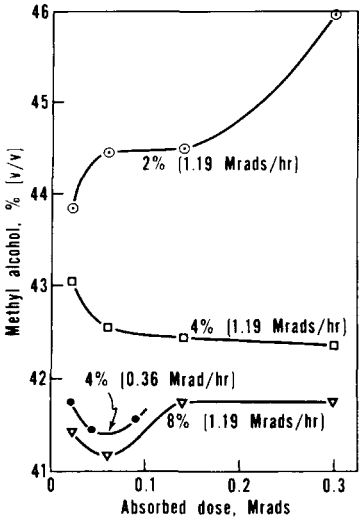

Fig. 3. Effects of irradiation conditions on apparent molecular weight of polyacrylamide as inferred from the methyl alcohol concentrations (v/v) at which initial turbidity occurs in 0.5% solutions at 23°C.

resulting from variation in the extents of conversion, particularly at low absorbed doses, may alter the nonsolvent concentration required for initial turbidity. The apparent molecular weight steady states observed in Figure 2 for the irradiated 4% solutions are confirmed here, and they are also evident at 8% concentration. A decrease in dose rate from 1.19 to 0.36 Mrad/hr at 4% acrylamide concentration gave the expected increase in molecular weight. In the 2% solution, the apparent decline in molecular weight obtained with absorbed doses above about 0.12 Mrad probably results from the domination of irradiation depolymerization over crosslinking because of the low concentration of polymer.

The net effect of concomitant crosslinking and depolymerizing during irradiation was determined for a 1% solution of polyacrylamide irradiated in the

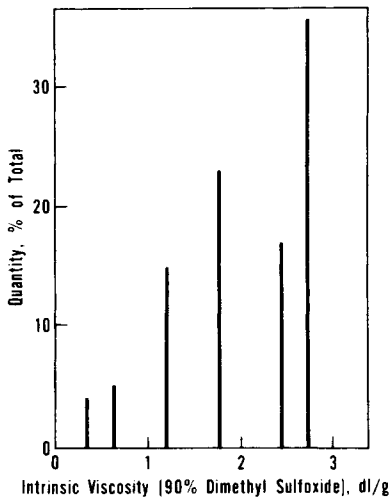

Fig. 4. Molecular size distribution of polyacrylamide prepared by irradiation at 23°C under nitrogen to 0.057 Mrad total absorbed dose at 8% concentration of acrylamide.

absence of monomer. The intrinsic viscosity (in 90% DMSO) declined from the original value of 1.02 to 0.95 dl/g with 0.06 Mrad total absorbed dose, and it was 1.24 dl/g at 0.12 Mrad. The solution formed a solid gel at 0.3 Mrad.

Polyacrylamide prepared by irradiation under nitrogen of an 8% solution to an absorbed dose of 0.057 Mrad was fractionated by incremental additions of nonsolvent (ethyl alcohol). Intrinsic viscosity distribution for the principal fractions (Fig. 4) is characterized by two peaks. Presumably, the peak observed at the higher intrinsic viscosity, which represents about 35% of the whole polymer, results from crosslinking reactions. Polyacrylamide derived from irradiation (0.057 Mrad) of a 4% acrylamide solution was analyzed by gel permeation chromatography (GPC) and found to have normal single-peak distribution.

Solubility of Amylose Graft Polymers

Amylose graft polymers were separated from solutions of simultaneously irradiated amylose and acrylamide by fractional precipitation. Methyl alcohol was the most effective nonsolvent of those tried owing to the wide spread of alcohol concentrations at which graft and homopolymer are initially precipitated (Table I). Amylose ($[\eta]_{90\%\ DMSO}$ = 1.92 dl/g) solutions under similar conditions developed an initial turbidity when the methyl alcohol concentration was 8.6%.

There was a possibility for coprecipitation of molecularly associated nongrafted amylose and polyacrylamide during nonsolvent additions. However, amylose was cleanly separated from a 2:1 synthetic mixture of amylose and polyacrylamide by methyl alcohol precipitation.

General Reaction Conditions

Reaction conditions for grafting by simultaneous irradiation were selected to minimize both crosslinking of grafted and nongrafted polyacrylamide and depolymerizing of amylose and to maximize monomer conversion. The selection

TABLE I
Solubility of Amylose Graft Polymer and Polyacrylamide at 27°C in Several Nonsolvent–Water Mixtures

Solvent	Nonsolvent concentration (v/v) in aqueous polymer solutions[a] at incipient precipitation, %	
	Amylose graft[b] polymer	Polyacrylamide[c]
Methanol	11.4	45.7
Ethanol	22.0	40.2
Acetone	17.4	34.7

[a] Nonsolvent was added slowly, while maintaining constant temperature, to 1% aqueous polymer solutions.

[b] Prepared by γ irradiation, 0.057 Mrad total absorbed dose under nitrogen, of an aqueous solution (2% amylose, 4% acrylamide).

[c] Prepared by γ irradiation, 0.057 Mrad total absorbed dose under nitrogen, of an aqueous 4% solution of acrylamide, $[\eta]_{90\%\ DMSO} = 1.25$ dl/g.

TABLE II
Amylose Graft Polymers Precipitated from Reaction Media[a] with Progressively Higher Nonsolvent Concentrations

Ethyl alcohol concentration, %	Graft polymer		
	Add-on, %	Yield (amylose basis), %	Intrinsic viscosity, dl/g
	2% Acrylamide		
18	4.3	59.9	2.22
20	4.3	58.9	2.26
22	5.2	70.3	1.76
25	7.5	87.2	1.92
	4% Acrylamide		
18	9.1	42.6	2.40
20	8.6	48.6	2.12
22	9.5	62.1	—
25	7.2	82.3	—

[a] Reaction media originally contained 2% amylose and either 2% or 4% acrylamide in water before irradiation to a total absorbed dose of 0.057 Mrad. Precipitations were performed at 25°C.

of 2% amylose as the upper concentration limit was guided by the desirability to maintain good fluidity of the reaction medium and to avoid "gel effects."[12]

Fractional precipitation of simultaneously irradiated amylose–acrylamide to recover uncontaminated graft polymer was approached initially by additions of nonsolvent over a range of concentrations to aliquots of the reaction medium (Table II). According to these data, the graft polymers are fairly homogeneous in graft content. Total conversion of monomer to graft and homopolymer was 49.6%, 60.6%, and 67.0% for 2%, 4%, and 8% acrylamide concentrations, respectively.

A simultaneously irradiated (0.057 Mrad and nitrogen saturated) reaction mixture of 2% amylose and 4% acrylamide was fractionated to determine relative solubilities of components and effectiveness of separations. The cumulative

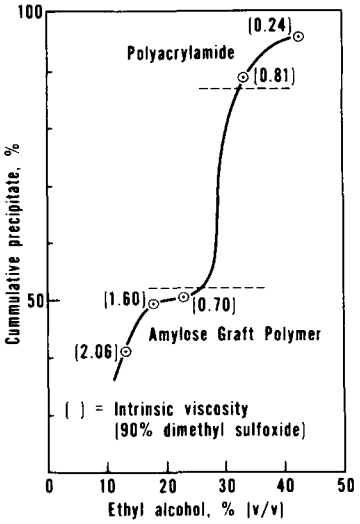

Fig. 5. Fractional precipitation at 15°C of a simultaneously irradiated (0.057 Mrad total absorbed dose, nitrogen saturated) solution of 2% amylose and 4% acrylamide. Intrinsic viscosities (90% DMSO) are given in parentheses.

precipitation curve (Fig. 5) indicates that the two polymer types were separated with ethyl alcohol. Precipitation begins at lower concentrations of ethyl alcohol than would be anticipated from data in Table I. This difference was because of the 15°C temperature, which greatly facilitated separation of the syrupy precipitates of graft polymers. In Figure 5, the intrinsic viscosities (90% DMSO) of the fractions are given in parentheses. The first, high molecular weight fraction with an intrinsic viscosity of 2.06 was 81% of the total weight of material precipitated in the 0–25% ethyl alcohol concentration range and had a 10.3% add-on.

The first fraction in Figure 5 was subfractionated by redissolving and reprecipitating twice, using progressively lower concentrations of methyl alcohol as the nonsolvent each time. The first and second precipitations were 58% and 26% by weight of the original amylose graft polymer, respectively. The polyacrylamide content and intrinsic viscosity of the whole fraction and of the reprecipitated graft polymers are compared in Table III. The data in Table III indicate that the original graft polymer is fairly homogeneous.

The molecular weight distribution of an isolated amylose graft polymer, pre-

TABLE III
Subfractionation of Amylose Graft Polymer[a] with Methyl Alcohol

Fraction	Per cent of original graft polymer, wt %	Add-on, %	Intrinsic viscosity, dl/g
Original	100	10.3	2.06
First reprecipitate	58	7.2	2.08
Second reprecipitate	26	7.1	1.93

[a] Amylose graft polymer is first fraction ($[\eta]_{90\%\ DMSO}$ = 2.06 dl/g) in Fig. 5.

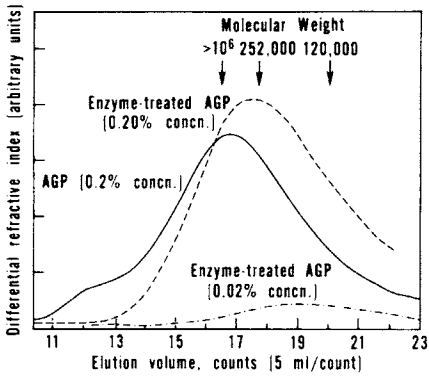

Fig. 6. Gel permeation chromatographic elution curves of amylose graft polymer (AGP) (10% add-on) before and after digestion with an amylolytic enzyme.

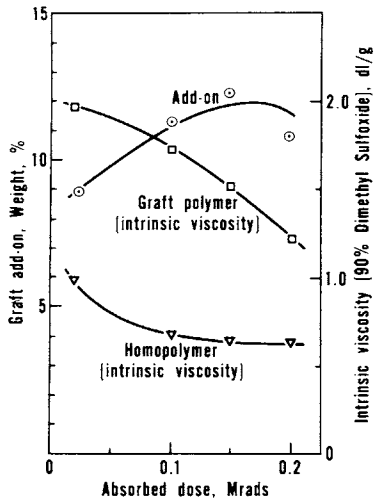

Fig. 7. Effects of total absorbed dose on characteristics of graft and homopolymer in simultaneous solution irradiation (50°C, nitrogen saturated) of 2% amylose and 4% acrylamide.

pared by conditions identical to those used in Figure 5, was examined by GPC. The distribution curve (Fig. 6) displayed a shoulder in the high molecular weight region that is too large to be attributed to amylopectin contamination. A solution of graft polymer was digested with amylolytic enzymes, dialyzed, and reapplied to the GPC column. Because the enzyme hydrolyzate, which contained a 6% carbohydrate residue, did not contain any high molecular weight polyacrylamide, presumably the shoulder may be graft polymer crosslinked through the side chains. The molecular weight scale shown in Figure 6 was determined by positions of peaks of fractionated polyacrylamide (polymerized by irradiation) of known number-average molecular weight (by osmometry). The molecular weight of the amylose before grafting was calculated from intrinsic viscosity to be 800,000 according to the Mark–Houwink equation of Banks and Greenwood.[13]

The effects of total absorbed dose in simultaneous irradiations of 2% amylose and 4% acrylamide solution (nitrogen saturated) on add-on and the intrinsic viscosity of both amylose graft polymer and homopolymer are given in Figure 7. The add-on increases to a maximum with increased dose, and its apparent decline thereafter must be attributed to graft polymer degradation and enhanced solubility of highly grafted fragments in the precipitating medium. The latter possibility is supported by results of qualitative tests with iodine in the alcoholic supernatants from which the graft polymers were precipitated that gave increasing color intensities for solutions associated with higher total absorbed doses. The intrinsic viscosity–absorbed dose relationship for homopolymer was almost identical to that in Figure 2.

The decline in intrinsic viscosity (90% DMSO) of amylose graft polymer with increasing absorbed dose cannot be attributed entirely to molecular weight decrease. For example, if it is assumed that the molecular weight of the graft polymers had reached a steady state, lower intrinsic viscosities could result from progressively higher graft content because DMSO is not as good a solvent for the grafted side chains as it is for amylose.

Evidence for Grafting

Two experiments were made that provided evidence for true grafting or the bonding of polyacrylamide to amylose. The first test was based on the stability of grafted amylose to retrogradation. Aqueous solutions of 2% amyle, 2% acrylamide, and of amylose and acrylamide both at 2% concentrations were irradiated under grafting conditions. A fourth solution was a 1:1 blend of half of each of the irradiated 2% amylose and 2% acrylamide solutions and will be referred to as the "synthetic mixture." Irradiated water was then added on a 1:1 basis to the remaining halves of the irradiated solutions of amylose and acrylamide and to the irradiated amylose–acrylamide solution so that all four solutions had equal concentrations of either amylose or acrylamide. After standing for 80 hr, the irradiated mixture was unchanged in appearance while massive precipitation occurred in both the amylose and the synthetic mixture. However, the possibility existed that amylose irradiated with the vinyl monomer had been protected from degradation and, therefore, would be less likely to retrograde. Solutions of nonirradiated amylose, with and without polyacrylamide, were prepared, and amylose retrogradation occurred within 80 hr for both.

Precipitation occurred sooner and to a greater extent in the synthetic mixture than in the irradiated amylose control. This difference is attributed to the action of polyacrylamide acting as a flocculant to accelerate precipitation of molecular associations of amylose in early stages of formation.

The second experiment to test true grafting was based on the selective separation of amylose from solution by complexing with *n*-butyl alcohol. It was expected that amylose graft polymers would form the complex as grafting frequency was low. When a solution of 2% amylose graft polymer, 10.3% add-on, was treated with *n*-butyl alcohol, a precipitate formed. This precipitate, representing 90% of the original graft polymer in the solution, contained 9.3% polyacrylamide. Graft polymer remaining in solution was apparently too highly substituted to form an insoluble complex. A parallel experiment with a solution of amylose and polyacrylamide, present in the same ratio as in the graft polymer,

gave a precipitate that contained only 1% polyacrylamide. Polyacrylamide alone was not precipitated by *n*-butyl alcohol. These results, in addition to providing evidence for true grafting, suggest that amylose grafts that do not have too high a grafting frequency can be separated from homopolymer by *n*-butyl alcohol.

Graft Polymer Properties

General conditions and procedures for preparation and isolation of amylose graft polymers derived from this work are given in the experimental section. These conditions were used to prepare a series of amylose graft polymers, five of which are described in Table IV. The graft polymers, which had been recovered as solids by freeze drying, dissolved easily in warm water with stirring. Retrogradation was not a problem except for those grafts having add-ons less than 5%.

The add-ons (Table IV) are directly related to the ratio of acrylamide to amylose. The intrinsic viscosity of the graft polymers is independent of the amount of grafted polymer side chains. However, the Brookfield viscosity of 2% solutions of the graft polymers at 25°C is directly related to add-on. Results, based on isolation of graft side chains after amylolytic enzyme digestion, indicate that grafting frequency generally was low, 12,000 to 24,000 anhydroglucose units/graft. The molecular weight of the isolated side chains varied directly from 125,000 to 430,000 with the ratio of acrylamide to amylose when other reaction conditions were the same. The side chain that was fractionated on the GPC column (Fig. 6) has a broad molecular weight distribution that is nearly identical with polyacrylamide homopolymer prepared by irradiation polymerization.

EXPERIMENTAL

Equipment

All irradiations were conducted in a Gammacell 200 (Atomic Energy of Canada Limited) with a ^{60}Co source having an activity of about 8000 curies. Dose rate was varied by lead attenuators from 0.36 to 1.14 Mrad/hr. Dosimetry data were provided by the manufacturer.

TABLE IV
Amylose Graft Polymers

Irradiation conditions			Viscosity		
Acrylamide/amylose, wt/wt	Dose rate, Mrad/hr	Total absorbed dose, Mrad	Intrinsic dl/g	Paste, cps[a]	Add-on, %
2	1.14	0.057	2.10	14.0	6.2
4	1.14	0.057	2.05	21.2	15.7
2	0.57	0.041	1.98	—	8.2
4	0.57	0.041	2.21	24.5	15.4
2	0.57	0.029	2.05	14.0	7.5

[a] Brookfield, 2% aqueous solution, 25°C.

Intrinsic viscosities were determined in 90:10 DMSO:water at 25°C ± 0.05°C in size 100 Cannon-Ubbelohde-type capillary viscometers.

Paste viscosities of amylose graft polymers were measured with a Brookfield Model LVF viscometer at 25°C.

Number-average molecular weights of polyacrylamide were measured with a Melabs CSM-2 osmometer. A B-19 membrane was made by Schleicher and Schuell Co.

An Ana-Prep (Analytical-preparative) gel permeation chromatographic unit, manufactured by Waters Associates, Inc., was used for determinations of molecular weight distribution. Analytical columns (4 ft × ⅜ in. O.D.) were filled with deactivated Porasil B and E. The solvent was 0.01*M* Na_2SO_4.

A Lourdes Beta-fuge Model A (Series 400) with slant-head (28°) rotor, accommodating six 250-ml high-density polypropylene bottles, was run at 10,000 rpm (16,500 *G*) to separate precipitates of amylose graft polymers following nonsolvent additions to aqueous reaction media. The rotor chamber was refrigerated to maintain constant temperature.

Graft Polymer Preparation

Amylose was slurried in water, heated (60°C), and stirred for about 20 min. The solution was filtered while hot through sintered glass to remove any undissolved amylose. Acrylamide was added and dissolved, and the solution was degassed under partial vacuum before being blanketed with nitrogen. Amylose was 2% concentration, and the temperature was kept above 50°C until irradiation. Temperature of the solutions during radiation was 50°C.

After irradiation the solutions were diluted with water to 1.0% amylose basis, methyl alcohol was added to give a 25% concentration (v/v), and each solution was cooled to 15°C. The syrupy precipitates were separated by high-speed centrifugation. The amylose graft polymers were redissolved in water, precipitated with methyl alcohol (25%) at 15°C, and recovered by freeze drying. Add-on of polyacrylamide was calculated from nitrogen contents of the graft polymers.

Isolation of Grafts

Graft polymer solutions at 2% concentration and buffered at pH 4.0 were digested with an amylolytic enzyme (Diazyme L30) for at least 72 hr at 60°C. The hydrolyzates were dialyzed, and grafts were recovered by freeze drying. On the basis of nitrogen contents, it was determined that about 6% of recovered material was undigested carbohydrate residue.

Materials

High molecular weight amylose of 95% purity was fractionated from commercial tapioca starch by a method based on that of Schoch.[14] A steam jet cooker[15] was used to disperse 20% aqueous slurries of the tapioca starch. The dispersions were diluted to 2.7% concentration and maintained at 75°C during additions of *n*-butyl alcohol to 8.5% concentration (v/v). The solutions were stirred and allowed to cool slowly, more than 24 hr, to room temperature. The

separated amylose complex was washed in absolute ethyl alcohol, vacuum dried over calcium chloride, and equilibrated at ambient laboratory conditions. Its intrinsic viscosity was 2.00 (90% DMSO), and its nitrogen content was 0.004%.

Acrylamide was purchased from Eastman Organic Chemicals, mp 83–85°C.

Polyacrylamide was prepared by polymerization of 4% solutions of acrylamide irradiated under nitrogen at room temperature to an absorbed dose of 0.057 Mrad at a dose rate of 1.19 Mrad/hr. Polyacrylamide was recovered by dialysis and freeze drying.

The amylolytic enzyme that hydrolyzed the amylose graft polymers (Diazyme L30, Miles Laboratories) had an activity of 30 DU/ml (80 DU convert 454 g starch in 72 to 96 hr at 60°C).

Hydroquinone, purified grade, from the J. T. Baker Chemical Co., was used in dilute aqueous solution to terminate polymerizations following irradiations.

The contributions of Miss M. I. Schulte for chemical analyses, R. C. Burr for molecular weight determinations (osmometer), C. L. Swanson for GPC data, and R. G. Fecht for general assistance are gratefully acknowledged. The mention of firm names or trade products does not constitute an endorsement by the U.S. Department of Agriculture over other firms or similar products not mentioned.

References

1. N. Geacintov, V. T. Stannett, E. W. Abrahamson, and J. J. Hermans, *J. Appl. Polym. Sci.*, **3,** 54 (1960).
2. R. L. Whistler and H. J. Roberts, *J. Org. Chem.*, **26,** 2458 (1961).
3. S. K. Patra, S. Ghosh, B. K. Patnaik, and R. T. Thampy, *Chem. Soc.* (London), Special Publication **No. 23,** 233 (1968).
4. S. Kimura and M. Imoto, *Makromol. Chem.*, **42,** 140 (1960).
5. C. M. Patel and V. M. Patel, *Staerke,* **25**(1), 12 (1973).
6. A. Mishina and Z. Nikuni, *Nature* (London), **184,** 1867 (1959).
7. A. Mishina, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, **18,** 93 (1961).
8. A. Mishina, *Nippon Nogei Kagaku Kaishi,* **36**(7), 617 (1962).
9. H. W. Leach and T. J. Schoch, *Cereal Chem.*, **39,** 318 (1962).
10. B. T. Hofreiter, *J. Polym. Sci.*, **12,** 2755 (1974).
11. E. Collinson, F. S. Dainton, and G. S. McNaughton, *Trans. Faraday Soc.*, **53,** 489 (1957).
12. A Chapiro, *Radiation Chemistry of Polymeric Systems,* Interscience, New York and London, 1962, p. 140.
13. W. Banks and C. T. Greenwood, *Carbohydr. Res.*, **7,** 414 (1968).
14. T. J. Schoch, *Cereal Chem.*, **18,** 121 (1941).
15. J. C. Rankin, E. B. Lancaster, and J. C. McClenden, *Staerke,* **25**(3), 95 (1973).

Received January 26, 1976
Revised March 8, 1976