

Grafting of 2-Butenyl Acrylate onto Starch*

T. P. ABBOTT and C. JAMES, *Northern Regional Research Center, Agricultural Research, Science and Education Administration, U.S. Department of Agriculture, Peoria, Illinois 61604*

Synopsis

The monomer 2-butenyl acrylate was reacted with starch by exposure to either ^{60}Co irradiation or ceric ion initiation. Monomer conversion in the presence of starch is greater than in the absence of starch, indicating that a starch initiating mechanism takes place for ^{60}Co irradiated samples. Acetone extraction indicates little or no soluble homopolymer in the grafts. Portions of the samples soluble in dimethyl sulfoxide (DMSO) appear to be low-level 2-butenyl acrylate-grafted starch by infrared analysis. DMSO-insoluble portions (usually more than 50% of each sample) are somewhat more soluble in 1N NaOH at room temperature. This indicates that the 2-butenyl acrylate acts as an easily hydrolyzed crosslink for starch in samples containing as low as 5 wt % grafted poly(2-butenyl acrylate).

INTRODUCTION

Many monomers do not react by free-radical polymerization to produce high-molecular-weight homopolymers.¹ Formation of oligomers is often due to lack of free radical stability in the propagating species or, as in the case of allyl monomers, it is due to chain transfer reactions.¹ Although oligomer formation limits the achievement of high-strength homopolymers, it may be useful in graft copolymerization. Grafting of oligomer-forming monomers is more akin to derivatization of functional polymers than to normal graft copolymerization. Corn starch is a mixture of linear and branched hydroxy-functional, high-molecular-weight polymer. Several starch derivatives are made commercially with derivatization to change only slightly the physical properties of the homopolymer. Highly derivatized starch esters and ethers have drastically different properties from the homopolymer.² On the other hand, high molecular-weight grafts on starch are often submicroscopic two-phase systems and exhibit properties characteristic of a filled synthetic homopolymer unless the synthetic side chains are water soluble.³ A high frequency of grafted oligomers on a starch backbone would disrupt hydrogen bonding and should lead to new and interesting materials. Low-frequency oligomeric grafts should be similar to commercial starches that have been slightly derivatized.

2-Butenyl acrylate, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OCOCH}=\text{CH}_2$, was chosen for grafting studies because of the high reactivity of acrylate monomers toward ceric ion-starch and ^{60}Co initiation,⁴ the expected partial solubility of 2-butenyl acrylate in water based on the reactivity of butyl acrylate in starch-water systems,⁴ and the presence of allyl hydrogen functionality six bonds from the reactive acrylate double bond. Chain transfer via the allyl hydrogen is evidenced by the limited crosslinking in 2-butenyl acrylate and methyl acrylate copolymers when compared to other olefinic acrylate and methyl acrylate copolymers.⁵

* Presented at the 7th Annual Meeting of the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, Washington, DC, April 30-May 3, 1980.

EXPERIMENTAL

Materials

Pearl corn starch 3005 from CPC International was used. Other chemicals mentioned were reagent grade, used as received, and available from most chemical suppliers, except 2-butenyl acrylate.

Ceric ion solution was prepared by dissolving 39 g $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ in 98.2 g 1N HNO_3 .

2-Butenyl acrylate (crotyl acrylate) was made by the transesterification procedure described by Rehberg and Fisher.⁵

Procedures

Samples to be ^{60}Co irradiated typically were prepared by mixing 2 g dry corn starch (0.0123 mole anhydroglucose units) with 1.55 g (0.0123 mole) 2-butenyl acrylate and adding 1 ml water to make a viscous paste in a 23-ml Teflon-lined screw-cap vial. The loosely capped vial was evacuated and filled with N_2 six times, then capped tightly. The sample was irradiated with ^{60}Co in a gammacell 200 unit from Atomic Energy of Canada Ltd. Sample recovery weight was determined by ethanol precipitation and washing into a fritted crucible, followed by vacuum drying at 80°C for 4 hr.

Recovery weight, less the original dry starch weight, gave the weight of monomer converted to polymer. The polymer weight, as a percentage of the original monomer weight, is presented in the tables as "monomer conversion, percent." The polymer weight divided by the total recovered sample weight is designated "weight 2-butenyl acrylate, %, by recovery" in the tables. Relative amounts of starch and monomer and irradiation time were the variables investigated. Starch and 2-butenyl acrylate were treated separately by the same procedure to serve as controls in the resulting analyses.

Ceric ion-initiated samples were prepared by a procedure similar to that used by Fanta.⁴ Typically, 11.25 g dry starch (0.0694 mole anhydroglucose units) is added to 320 ml boiled, distilled water in a 500-ml resin flask and flushed with N_2 for 5 min. The resin flask is fitted with a stirrer, reflux condenser, thermometer, and N_2 source. Monomer, 3.1 g (0.0246 mole), is added, and then 25 ml of a $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ solution in 1N HNO_3 is added at the rate of 28 drops/min over a 30-min period. The mixture is heated to 40°C for 2 hr, and the product is recovered by centrifugation and water and ethanol washing. Recovered product is dried at 80°C under vacuum for 4 hr and weighed. Only initial monomer content was varied in the ceric ion-initiated samples.

RESULTS AND DISCUSSION

^{60}Co -Irradiated 2-butenyl acrylate will polymerize to as much as 77% conversion (Table I). However, irradiation for 4 hr (1.9 Mrad) leads to lower polymer recovery than irradiation for 2 hr. This is probably due to degradation of the already formed polymer on continued exposure to irradiation. Conversion of 2-butenyl acrylate in the presence of an equimolar amount of starch follows a similar pattern of conversion with time (Fig. 1). For the equimolar mixture, conversion of monomer to polymer is higher at 2 and 4 hr of irradiation time than

TABLE I
Poly(2-Butenyl Acrylate) by ^{60}Co Initiation

Irradiation time, hr	Dose, Mrad	Monomer conversion, %
4	1.90	60.1
2	0.95	76.9
2	0.95	84.1
1	0.48	53.6
0.5	0.24	21.2
0.25	0.12	7.28

in monomer alone; however, at lower levels of irradiation, this is not so. Even at equimolar amounts of starch and monomer, there may be large droplets of monomer in the paste made with water and exposed to the irradiation. Thus, the percentage of monomer exposed to starch surface is still probably low enough to not significantly differentiate between the polymerization in pure monomer and in the 1:1 starch-monomer mixture. Also, the water-soluble portion of monomer is a lower percentage of total monomer present in a 1:1 starch-monomer mix, where 1 ml H_2O is used to make the paste, than in a 10:1 starch-monomer mix, where more water per gram monomer is needed to make the mix into a paste.

As the starch is increased to a 10:1 and 18:1 ratio with 2-butenyl acrylate, a dramatic increase in monomer conversion takes place. After 15 min (0.24 Mrad) or more of irradiation, all of the monomer is converted to grafted polymer and recovered with the starch (sample 15 is the one exception). It is probable that monomer grafted onto starch at low irradiation levels is also short-chain-length grafts or crosslinks due to the monomer dilution and the higher relative concentration of starch radicals for chain termination.

^{60}Co -Initiated 2-butenyl acrylate starch grafts are difficult to characterize by the usual procedures for composition analysis. Starch removal by enzymatic treatment⁶ yields higher-than-actual percentages of synthetic add-on, as will be shown for ceric ion-initiated samples. Not all of the starch is removed in the enzyme treatment. The perchloric acid-acetic acid method⁷ tends to give low percentages of synthetic add-on (Table II). This is especially true because

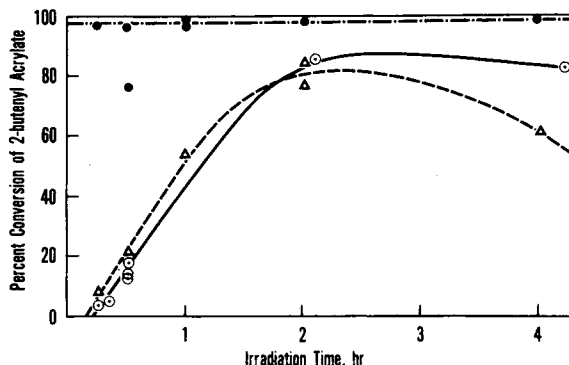


Fig. 1. Polymerization of 2-butenyl acrylate alone and in the presence of starch at various ^{60}Co irradiation doses: ($-\Delta-$) 2-butenyl acrylate; ($-\circ-$) 1:1 starch-to-monomer ratio; ($-\bullet-$) 10:1 starch-to-monomer ratio.

TABLE II
 Starch-*g*-2-butenyl Acrylates by ⁶⁰Co Initiation

Sample No.	Starch-to-monomer molar feed ratio	Irradiation time, hr	Monomer conversion, %	Weight 2-butenyl acrylate, %		Insoluble in DMSO, %
				by recovery	by HClO ₄ ^a	
1	1:1	4.2	82.4	39.4	29.4	85.4
2	1:1	2.1	85.3	39.3		86.5
3	1:1.2	1	36.5	25.6		95.5
4	1:1	0.5	13.7	9.2		17.2
5	1:1	0.5	13.4	5.2		
6	1:1	0.5	10.9	7.6		17.2
7	1:1	0.33	5.1	3.5		59.3
8	1:1	0.25	3.3	2.4		74.2
9	4.3:1	4.2	100	15.8	10.9	66.4
10	8:1	4.2	95.3	8.0	3.2	32.4
11	10:1	4	100	7.2 ^b	3.1	40.5
12	10:1	2	100	7.2 ^b	4.0	64.7
13	10:1	1	100	7.2	1.1	87.8
14	10:1	1	100	7.2		68.7
15	10:1	0.5	76.1	5.5		71.2
16	10:1	0.5	96	6.8		59.9
17	10:1	0.25	97	4.9		
18	16:1	0.25	98.2	2.9		71.4
19	16:1	0.25	97.8	2.4		
20	18:1	0.25	100	4.15 ^b		62.3
21	23:1	4	98.5	3.2		44.2
22	40:1	4	100	2 ^b		44
23	0:1	2	76.9	—	85.5, 90.2	
24	1:0	4	—	—	0	0

^a See ref. 7.

^b Maximum possible recovery weight. Actual recovery weight approximately 1% above maximum.

poly(2-butenyl acrylate) is somewhat solubilized in the procedure, as shown for the homopolymer in Table II, sample 23. For this reason, composition was determined from the sample recovery weight. Composition by recovery weight is sufficiently reproducible except at extremely low monomer concentrations. Samples 15 and 16 (Table II) may be extreme examples of the problem at low monomer concentrations.

Starch, unmodified, is soluble in dimethyl sulfoxide (DMSO) and aqueous 1*N* NaOH. Low-molecular-weight homopolymer and very slightly modified starch are probably also soluble in DMSO. For further characterization of the starch-2-butenyl acrylate products from ⁶⁰Co irradiation, their solubility in DMSO was determined by heating 1.5 g starch product in 100 ml DMSO to 50°C for 2 hr, diluting with 100 ml DMSO, and centrifuging. After three washes with DMSO and then three washes with H₂O, the sample was dried at 80°C under vacuum and weighed. The results are shown in Table II. A surprisingly high percentage of the graft is insoluble in DMSO even with only 2 to 3% 2-butenyl acrylate in the final product. The solubility of starch alone in DMSO is unchanged by irradiation in a water mixture (Table II, sample 24). One sample (sample 4, also it duplicates 5 and 6 in Table I) that stands out as unusual is the

TABLE III
 Starch-*g*-2-butenyl Acrylates by Ceric Ion Initiation

Sample No.	Starch-to-monomer molar feed ratio	Weight 2-butenyl acrylate, %			% Insoluble in	
		By recovery	HClO ₄ ^a	Enzyme ^b	DMSO	1 <i>N</i> NaOH
30	0.92:1	25	17.5	42.6	45.6, 47.2	
31	0.92:1	42.3	29.4, 30.7		52.0	41.3
32	1.67:1	27.4	18.0	32.7	44.5	
33	1.73:1	28.8	22	52		
34	1.67:1	21	11.8		55.2, 53.3	48.9
35	2.8:1	16.0	7.6	22.0	61.2	
36	2.9:1	17.0	15	29.7	50.8	34.0
37	4.9:1	13.5	8.6	10.8	57.7	27.5
38	5.1:1	13.1 ^c	9.6	32	56	
39	5.6:1	6.7	5.1, 5.1	8.0	73	24.4
40	8.4:1	8.5 ^c		13.1	54.2	8.8
41	10.3:1	6.7	7.6	23.3	72	
42	13.9:1	5.4		10.2	52.9	6.6
43	55:1	1.4 ^c	1.0		50.1	7.2
44	54:1	1.4 ^c	2.5	8.2	48.9	6.2
45	54:1	1.4 ^c	0.7		37.8	
46	100:1	0.8 ^c	0.3		15	
47	1:0		0	0.8	9.3	6.8

^a Ref. 7.

^b Ref. 6.

^c Based on maximum possible monomer conversion; actual recovery weight exceeded monomer plus starch weight.

equimolar mixture of starch and 2-butenyl acrylate irradiated for 30 min (0.24 Mrad). The low insolubility in DMSO is reproducible and anomalous. The presence of a small ester carbonyl at 1725 cm⁻¹ in the IR spectrum of the DMSO-soluble portion of several samples tested supports the earlier assumption that slightly grafted starch is soluble in DMSO unless crosslinked. Acetone extraction of the ⁶⁰Co-irradiated samples removed low-molecular-weight homopolymer prior to most DMSO solubility tests, although little or no extract was found. The acetone extracts were always below 0.4% by weight of the original graft.

In ceric ion-initiated reactions between starch and 2-butenyl acrylate, the compositions were again determined by recovery weight (Table III). As in the irradiated samples, the perchloric acid method gave consistently lower results than the recovery weight analysis for composition. But, far from being useless information, the low perchloric acid analysis results and the high results from the enzyme analysis bracketed the analysis based on the recovery weight, reassuring the appropriateness of the recovery weight method.

Like the ⁶⁰Co-irradiated samples, the solubility of starch in DMSO was reduced to 55% or less at all but the smallest levels of 2-butenyl acrylate addition (Table III).

In addition to the 2-butenyl acrylate crosslinking, starch was somewhat insolubilized by ceric ion oxidation even when no monomer was present (Table III, sample 47). Nonetheless, ceric ion-initiated samples are more soluble than ⁶⁰Co-initiated samples in DMSO at comparable compositions.

Room-temperature solubility in 1*N* NaOH differs from DMSO solubility,

especially below 13.5 wt % 2-butenyl acrylate in the graft (Table III, samples 37-46). The infrared spectrum of the 1N NaOH insolubles shows both ester and starch absorptions. Thus, the NaOH is not dissolving all of the originally added starch. It is most likely that even the mild treatment with 1N NaOH at room temperature hydrolyzes a few 2-butenyl acrylate crosslinks, altering what is a highly swollen gel in DMSO to a soluble structure in 1N NaOH.

Sample 47 contains 6.8% insolubles in 1N NaOH. Since samples 41 through 47 in Table III have similar solubilities in NaOH, it could be speculated that 2-butenyl acrylate crosslinks are totally hydrolyzed in these samples. Samples 40 through 46 may be pastable in dilute alkali in the same manner as some commercial modified starches. Stronger hydrolysis should solubilize the grafted samples completely, since all crosslinks would be hydrolyzable; even crosslinked poly(2-butenyl acrylate) is theoretically hydrolyzable to a water-soluble material. Little or no acetone-soluble homopolymer of 2-butenyl acrylate is present in the ceric ion-initiated samples. From samples containing 5% 2-butenyl acrylate to samples containing 42% 2-butenyl acrylate, only 0.3% acetone extract or less was obtained.

Neither the residue from perchloric acid treatment nor that from enzyme treatment was soluble in organic solvents for molecular weight determinations. Whether dilute monomer addition to starch by low-level irradiation achieved the expected oligomeric grafting is doubtful. The product is apparently a lightly crosslinked starch regardless of the method of initiation. Starch can be insolubilized in DMSO by grafted linear chains as well as crosslinks. Insolubilization in DMSO occurs at higher addition levels of DMSO-insoluble grafted side chains and not as low as 2%, as is observed for 2-butenyl acrylate starch.

The authors would like to acknowledge George Fanta of our laboratory for pioneering work in starch graft copolymers and helpful discussions.

References

1. H.-G. Elias, *Macromolecules*, Vol. II, Plenum, New York, 1977, Chap. 20.
2. H. J. Roberts, in *Starch: Chemistry and Technology*, Vol. II, R. L. Whistler and E. F. Paschall, Eds., Academic, New York, 1967, p. 296.
3. E. B. Bagley, G. F. Fanta, R. C. Burr, W. M. Doane, and C. R. Russell, *Polym. Eng. Sci.*, **17**, 311 (1977).
4. G. F. Fanta, in *Block and Graft Copolymerization*, Vol. I, R. J. Ceresa, Ed., Wiley, New York, 1973, p. 2.
5. C. E. Rehberg and C. H. Fisher, *J. Org. Chem.*, **12**, 226 (1947).
6. G. F. Fanta, R. C. Burr, and W. M. Doane, *J. Appl. Polym. Sci., Polym. Lett. Ed.*, **24**, 2015 (1979).
7. R. J. Dennenberg and T. P. Abbott, *J. Polym. Sci. Polym. Lett. Ed.*, **14**, 693 (1976).

Received May 19, 1980

Accepted May 28, 1980