

Polymerization of Alkyl Acrylates and Alkyl Methacrylates with Starch

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Synopsis

A series of C₄-C₁₂ alkyl acrylates and methacrylates was polymerized with starch by irradiating starch-monomer mixtures with ⁶⁰Co. Homopolymers were extracted with cyclohexane. The amounts of insoluble versus soluble synthetic polymer in polymerizations run with alkyl acrylates varied less with the chain length of the alkyl substituent than in the polymerizations run with alkyl methacrylates; and the poly(alkyl acrylate) contents of cyclohexane-insoluble fractions were all in the 38-45% range. Synthetic polymer contents of the products from butyl, hexyl, and decyl methacrylates were also close to this range. Octyl and lauryl methacrylate, however, gave high conversions to cyclohexane-soluble poly(alkyl methacrylate) along with little or no unextractable synthetic polymer in the starch-containing fractions. Poly(lauryl methacrylate) could be rendered insoluble by incorporating a small amount of tetramethylene glycol dimethacrylate in the polymerization mixture. In a series of polymerizations run with hexyl acrylate and hexyl methacrylate, lower irradiation doses led to more cyclohexane-soluble polymer and less synthetic polymer in the starch-containing fractions. Enzymatic digestion of starch-containing polymers gave synthetic polymer fractions that were largely insoluble in cyclohexane. Crosslinking is, therefore, probably taking place during these polymerizations; however, we could not eliminate the possibility that reduced solubility was caused by small amounts of residual carbohydrate in these polymer fractions. Ceric ammonium nitrate-initiated polymerizations of butyl acrylate, hexyl acrylate, and butyl methacrylate with starch gave cyclohexane-insoluble polymers that contained 33-39% synthetic polymer. The higher alkyl acrylates and methacrylates produced little or no polymer under these conditions. Starch-containing fractions were tested as absorbents for hydrocarbons. Products prepared from decyl acrylate and lauryl acrylate absorbed about 9 g of isooctane per 1 g of polymer, whereas the lower alkyl monomers gave polymers with lower absorbency.

INTRODUCTION

Although the literature contains reports on graft polymerizations of methyl methacrylate,¹ methyl acrylate,²⁻⁴ ethyl acrylate,^{2,5} and butyl acrylate^{2,5} onto starch, free-radical graft polymerizations of higher alkyl acrylates and methacrylates have not been described. Our interest in these materials comes from their potential use as absorbents for oils and other hydrocarbons. In this report, we will describe first the polymerization of several C₄ to C₁₂ acrylate and methacrylate esters with starch using both ⁶⁰Co and ceric ammonium nitrate initiation and then the evaluation of the resulting polymers as absorbents for isooctane.

EXPERIMENTAL

Materials*

Granular pearl cornstarch (Globe 3005), from CPC International, had a moisture content of about 12%.

Butyl acrylate was from Eastman; the other monomers were from Polysciences. Inhibitors were removed immediately before use by gently shaking small samples of monomers with 5% sodium hydroxide solution in a separatory funnel and then separating the aqueous layer.

Polymerizations with Starch

⁶⁰Co Initiation

The ⁶⁰Co source was a Gammacell 200 unit from Atomic Energy of Canada, Ltd. The dose rate at the center of the chamber varied from 0.53 to 0.46 Mrad/hr, as calculated from the initial dosimetry data provided by the manufacturer and the decay rate of ⁶⁰Co.

A 2-oz screw-cap bottle was charged with 4.0 g (dry basis) of starch, 4.0 g of monomer (inhibitor removed), and 1 ml of water; and the resulting mixture was thoroughly blended with a spatula. On blending, the mixture set up to a thick paste, similar to that found earlier for graft polymerizations using styrene.⁶ The paste was evacuated to 50 mm and repressured with nitrogen four times (to displace dissolved oxygen) and was then irradiated with ⁶⁰Co and allowed to stand at ambient temperature for 2 hr. The reaction mass was exhaustively extracted with cyclohexane, and the soluble and insoluble fractions were isolated by freeze drying. When residual monomer was observed in the freeze-dried soluble fractions (infrared), it was removed by ethanol extraction.

For the series of polymerizations with lauryl methacrylate and tetramethylene glycol dimethacrylate, the two monomers (inhibitors not removed, to avoid premature polymerization) were dissolved in 30 ml of cyclohexane and the solution was mixed with 40.0 g (dry basis) of starch. The resulting paste was let stand overnight at room temperature to allow the cyclohexane to evaporate, and 10 ml of water was then thoroughly blended into the solid. The solid was placed in a 4-oz screw-cap bottle, evacuated and repressured with nitrogen to displace oxygen, and irradiated with ⁶⁰Co to 0.5 Mrad. The reaction mass was allowed to stand at ambient temperature for 2 hr and was then washed with acetone and dried in a 60°C vacuum oven. Soluble synthetic polymer was then removed by cyclohexane extraction.

Ceric Ammonium Nitrate Initiation

A stirred suspension of 10.0 g (dry basis) of starch in 200 ml of water was sparged with a slow stream of nitrogen for 30 min at 25°C, and 15.0 g of monomer (inhibitor removed) was then added. After 5 min, a solution of 0.338 g of ceric ammonium nitrate in 3 ml of 1*N* nitric acid was added and the mixture was

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

stirred under nitrogen for 2 hr at 25°C. The reaction mixture was filtered and the solid was washed several times with methanol. The solid was allowed to air dry at room temperature and then was extracted with cyclohexane. These cyclohexane extractions apparently were not influenced to a large degree by water content of the sample,⁷ since extraction of the product from hexyl acrylate gave about the same results with 7% water as it did when 30% water was added.

Removal of Starch from Polymerization Products

A suspension of 5.0 g of starch-containing polymer in 200 ml of water was heated to 100°C and the hot mixture was subjected to high-speed stirring in a Waring Blendor to thoroughly disperse the solid. Then 1 ml of Thermamyl 60-*L* enzyme solution (Novo Enzyme Corp.) was added and the mixture was held at 95–100°C for 15–20 hr. The gummy polymer was collected on a spatula and rinsed several times with water. It was then dispersed in cyclohexane and isolated by freeze drying. The percentage of polymer soluble in cyclohexane was determined by stirring a known weight of polymer overnight in cyclohexane, centrifuging the dispersion, and freeze drying a known weight of the clear supernatant.

Infrared Spectra of Poly(hexyl acrylate)-Starch Blends

The gummy nature of poly(hexyl acrylate) made it necessary to use special methods to prepare known mixtures with starch and to obtain infrared spectra. Solutions of poly(hexyl acrylate) in benzene and acid-modified starch in water were prepared at concentration of 0.50 g/100 ml. The following volumes of poly(hexyl acrylate) solution and starch solution were then combined: 19.6:0.4 ml (2% starch), 19.0:1.0 ml (5% starch), 18.0:2.0 ml (10% starch). These mixtures were emulsified by high-speed stirring and then freeze dried. To obtain infrared spectra, a small portion of polymer was placed on a sodium chloride plate and a drop of Nujol was added. The plate was heated in a 60°C oven for 10 min and the Nujol-swollen polymer then was squeezed between two sodium chloride plates. Bands at 2.9 and 9.7 μm were used to estimate the amount of carbohydrate.

Determination of Isooctane Absorption

To a tared 40-ml centrifuge tube was added 0.50 g of polymer and 20 ml of isooctane. The mixture was allowed to stand for 24 hr at room temperature and then was centrifuged and the supernatant decanted. The tube was weighed to determine the weight of insoluble gel. Absorbency was calculated as grams of isooctane per gram of polymer.

RESULTS AND DISCUSSION

Initiation with ⁶⁰Co

Table I shows the results of ⁶⁰Co initiated polymerizations of some C₄-C₁₂ alkyl acrylates and methacrylates onto unmodified cornstarch. The procedure was one we used earlier to prepare starch-*g*-polystyrene,⁶ and products were extracted

TABLE I
 Polymerization of Alkyl Acrylates and Methacrylates onto Starch: ^{60}Co Initiation^a

Alkyl ester	Acrylate		Soluble in cyclohexane, g	Methacrylate		
	Insoluble in cyclohexane Poly(alkyl acrylate) content, % ^b	Wt., g		Insoluble in cyclohexane Poly(alkyl methacrylate) content, % ^b	Wt., g	Soluble in cyclohexane, g
Butyl	45	7.3	0.6	35	6.2	1.6
Hexyl	44	7.2	0.6	46	7.4	0.4
Heptyl	44	7.2	0.2	—	—	—
Octyl	39	6.6	1.0	5	4.2	3.4
Decyl	44	7.2	0.6	33	6.0	2.0
Lauryl	38	6.5	1.4	0	4.0	3.9

^a Amounts used: 4.0 g starch, 4.0 g monomer, 1 ml water, 1.0 Mrad.

^b Calculated from weight gain of starch.

with cyclohexane to remove soluble synthetic polymers. Homopolymers prepared from butyl acrylate, octyl acrylate, decyl acrylate, or butyl methacrylate, through ^{60}Co irradiation of 4–5% aqueous emulsions in the absence of starch, were soluble in cyclohexane. Wt % poly(alkyl acrylate) or poly(alkyl methacrylate) in cyclohexane-insoluble fractions was then calculated from the weight gain of starch.

Products of polymerizations in Table I, run with alkyl acrylates, varied less with the chain length of the alkyl substituent than products of those run with alkyl methacrylates; poly(alkyl acrylate) contents of cyclohexane-insoluble fractions were all in the 38–45% range. Synthetic polymer contents of the products from butyl, hexyl, and decyl methacrylate also were not far from this range. For some unknown reason, octyl and lauryl methacrylate behaved much differently under these polymerization conditions than the other monomers in Table I and gave high conversions to cyclohexane-soluble poly(alkyl methacrylate), along with little or no unextractable synthetic polymer in the starch-containing fractions.

Table II shows the effects of different irradiation doses on the products of hexyl acrylate and hexyl methacrylate polymerizations with starch. At a total dose of 0.1 Mrad, a 60% conversion of hexyl acrylate to cyclohexane-soluble polymer was realized, accompanied by only a negligible conversion to unextractable polymer. As the total dose was progressively raised, the amount of soluble polymer was reduced while unextractable polymer increased. With hexyl methacrylate, 0.1 Mrad produced only a 12% conversion of monomer to total polymer; however, comparison of polymerizations initiated with 0.5 and 1.0 Mrad showed a similar increase in unextractable polymer at the expense of cyclohexane-soluble polymer as the irradiation dose was raised.

Starch was removed from some randomly selected cyclohexane-insoluble products of Tables I and II by digestion with a starch-degrading enzyme. Enzyme was used rather than refluxing dilute hydrochloric acid to avoid ester hydrolysis in the synthetic polymer moiety. The synthetic polymer fractions isolated from enzyme treatment were only slightly soluble in cyclohexane. Hexyl and decyl acrylate fractions obtained by digestion of the products in Table I were 8 and 5% soluble, respectively; whereas cyclohexane solubilities were 8 and 6% for the poly(hexyl acrylate) and poly(hexyl methacrylate) fractions isolated from the products in Table II prepared with 0.5 Mrad.

The insolubility in cyclohexane of these synthetic polymers derived upon digesting the starch moiety with enzyme can be attributed to a crosslinking reaction taking place during the ^{60}Co initiated polymerizations. Our inability to separate synthetic polymers from starch through cyclohexane extraction could thus be due not only to their chemical attachment to the starch backbone (graft polymerization) but also to their crosslinking within the starch granule matrix (formation of a type of interpenetrating polymer network⁸). Therefore, the observed differences in extractability with cyclohexane between acrylate and methacrylate polymers might be due, at least in part, to differences in their ability to form polymer networks. The acrylate repeating unit has a hydrogen atom on the carbon α to the carbonyl, the removal of which gives a resonance-stabilized free radical and, thus, a site for branch formation. A stabilized free radical can also be formed in both acrylate and methacrylate polymers by abstraction of a hydrogen atom from the alkyl substituent carbon which is α to the oxygen.

TABLE II
 Polymerization of Hexyl Acrylate and Methacrylate onto Starch: Influence of ^{60}Co Dose^a

Dose, Mrad	Acrylate			Methacrylate		
	Wt, g	Insoluble in cyclohexane, Poly(alkyl acrylate) content, % ^b	Soluble in cyclohexane, g	Wt, g	Insoluble in cyclohexane Poly(alkyl methacrylate) content, % ^b	Soluble in cyclohexane, g
1.0	7.2	44	0.6	7.4	46	0.4
0.5	6.7	40	1.1	6.0	33	0.9
0.1	4.1	2	2.4	4.2	5	0.3

^a Amounts used: 4.0 g starch, 4.0 g hexyl acrylate or methacrylate, 1 ml water.

^b Calculated from weight gain of starch.

TABLE III
 Polymerization of Lauryl Methacrylate with Starch. Influence of Tetramethylene Glycol Dimethacrylate (TMGD)^a

TMGD, g	Insoluble in cyclohexane		Soluble in cyclohexane, g
	Wt, g	Synthetic polymer content, % ^b	
0	41.4	3	2.0
0.05	43.0	7	0.4
0.10	43.9	9	0.2
0.40	44.2	10	0.2

^a Amounts used: 40.0 g starch, 4.0 g lauryl methacrylate, 10 ml water, 0.5 Mrad.

^b Calculated from weight gain of starch.

Crosslinking of synthetic polymer within the starch matrix is substantiated by the results in Table II, since lower irradiation doses led to less synthetic polymer in the starch-containing fraction and to more cyclohexane-extractable homopolymer. Further evidence for crosslinking was obtained when hexyl acrylate was irradiated in the presence of water under graft polymerization conditions but in the absence of starch. A total dose of 0.1 Mrad afforded a 50% conversion to polymer that was 99% soluble in cyclohexane. At 1.0 Mrad, the conversion was 94%, and the polymer was only 21% soluble. Güven and Kocakanat⁹ have reported the crosslinking of alkyl methacrylate polymers under the influence of ⁶⁰Co and have found crosslinking to be markedly dependent on the molecular weight of the alkyl substituent. Under their conditions, poly(lauryl methacrylate) crosslinked more readily than poly(butyl methacrylate).

Comparison of infrared spectra of poly(hexyl acrylate) isolated from enzymatic digestions with spectra of poly(hexyl acrylate) homopolymer to which small amounts of carbohydrate were added showed an amount of residual carbohydrate in these products no greater than the detectable limit of about 5%. However, we cannot preclude the possibility that even these small amounts of residual carbohydrate could decrease solubility in a nonpolar solvent. This factor must, therefore, be considered along with crosslinking in explaining the limited solubility in cyclohexane of our polymers derived from enzymatic digestions.

We could easily show the marked effect of residual carbohydrate on solubility by examining the hydrolysis of starch-*g*-poly(methyl methacrylate). This model system was chosen because, unlike poly(methyl acrylate), poly(methyl methacrylate) is inert to refluxing 0.5*N* hydrochloric acid¹⁰: a hydrolysis method that will remove the starch moiety completely enough to give a polymer totally soluble in a nonpolar solvent such as benzene. Although the calculated synthetic polymer content of starch-*g*-poly(methyl methacrylate), determined from the weight loss of starch, was not greatly different for the enzyme method versus the hydrochloric acid method (51 vs. 47%), the enzyme-derived polymer was only 40% soluble in benzene, whereas hydrochloric acid hydrolysis led to complete polymer solubility. Infrared analysis showed no detectable carbohydrate in the soluble fraction (limit of detectability about 5%) and only about 10% carbohydrate in the insoluble fraction.

Polymers such as poly(lauryl methacrylate), which are readily extracted from the starch matrix with cyclohexane even at irradiation doses of 1.0 Mrad (Table I), may be rendered largely unextractable by incorporating small amounts of a

TABLE IV
 Polymerization of Alkyl Acrylates and Methacrylates onto Starch: Ceric Ammonium Nitrate Initiation^a

Alkyl ester	Acrylate		Soluble in cyclohexane, g	Methacrylate		
	Wt, g	Insoluble in cyclohexane Poly(alkyl acrylate) content, % ^b		Wt, g	Insoluble in cyclohexane Poly(alkyl methacrylate) content, % ^b	Soluble in cyclohexane, g
Butyl	16.3	39	2.3	15.0	33	1.4
Hexyl	15.1	34	1.8	10.1	1	0
Heptyl	11.4	12	0.3	10.1	1	0

^a Amounts used: 10.0 g starch, 15.0 g monomer, 200 ml water, 0.338 g ceric ammonium nitrate.

^b Calculated from weight gain of starch.

TABLE V
Absorption of Isooctane by Starch-Alkyl Acrylate and Starch-Alkyl Methacrylate Reaction Products^a

Alkyl ester	Absorbency, g isooctane/g polymer	
	Acrylate	Methacrylate
Butyl	1.6	0.6
Hexyl	6.4	2.2
Heptyl	5.5	—
Octyl	7.1	—
Decyl	9.0	7.1
Lauryl	9.3	—

^a These are the cyclohexane-insoluble products from Table I.

difunctional comonomer as a crosslinking agent in the polymerization mixture. Table III shows the results of such a series of reactions, in which a 10:1 ratio of starch:lauryl methacrylate was used. Addition of 50 mg of tetramethylene glycol dimethacrylate to 4 g of lauryl methacrylate decreased the amount of cyclohexane solubles by a factor of 5; larger amounts of difunctional monomer resulted in greater decreases in soluble polymer.

Initiation with Ceric Ammonium Nitrate

Table IV shows the results of some ceric ammonium nitrate-initiated polymerizations of alkyl acrylates and methacrylates with starch. Butyl and hexyl acrylate gave polymers that contained 39 and 34%, by weight, of synthetic polymer after removal of appreciable amounts of ungrafted poly(alkyl acrylate) by extraction with cyclohexane. Heptyl acrylate was converted to polymer in relatively low yield, and the conversions of octyl and lauryl acrylates under these conditions were negligible. Enzymatic hydrolysis of the starch-poly(hexyl acrylate) product gave a synthetic polymer fraction that was 27% soluble in cyclohexane.

Compared with the corresponding acrylate monomers, we observed lower conversions of alkyl methacrylates to polymer with ceric ammonium nitrate initiation. Butyl methacrylate afforded a polymer with starch that contained 33% poly(butyl methacrylate); however, conversions of hexyl and heptyl methacrylate to polymer were negligible. Similarly, lauryl methacrylate produced little or no polymer under these conditions.

The decrease in conversion of monomers to polymer with increased molecular weight of the alkyl substituent could reflect a dependence of these ceric-initiated polymerizations on the solubility of the monomer in our aqueous polymerization system. Increasing the polymerization temperature from 25 to 50°C did not produce polymer from either lauryl acrylate or lauryl methacrylate. Similarly, when acrylonitrile was added as a comonomer with lauryl methacrylate, we could detect only the polymerization of acrylonitrile; the infrared spectrum of the reaction product showed no ester carbonyl. Lauryl methacrylate was converted to polymer in low yield when the ceric-initiated polymerization with starch was run in 75:25 acetone water¹¹; however, virtually all of this polymer could be extracted from starch with cyclohexane.

Absorption of Isooctane

To get some estimate of the ability of these polymers to absorb hydrocarbons, we measured the number of grams of isooctane which 1 g of the cyclohexane-insoluble products of Table I would absorb on standing at room temperature for 24 hr (Table V). The acrylate polymers absorbed more isooctane than the corresponding methacrylates; and, as expected, absorbency increased with molecular weight of the alkyl substituent.

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