

## Grafting of Preformed Polyethylene Oxide on Starch

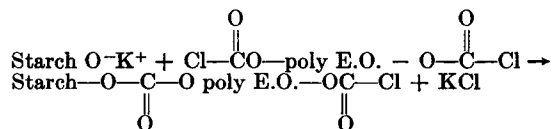
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### Synopsis

Polymer-polymer interaction was used for the preparation of graft polymers of polyethylene oxide on starch. Preformed polyethylene oxide having hydroxyl end groups was converted to the chloroformate derivative and reacted with starch alkoxide. Water-soluble graft polymers were obtained free of cross linking. The efficiency of the coupling process decreased with increasing the  $\overline{DP}_n$  of the polyethylene oxide.

### INTRODUCTION

We have recently investigated in detail the preparation of graft polymers of polyethylene oxide (poly-E.O.) on starch utilizing the alkoxide derivative of starch as initiator of the graft polymerization of ethylene oxide.<sup>1</sup> We wish here to report another approach to the preparation of such graft polymers which has not been investigated before. This consists of directly linking preformed polyethylene oxides, suitably activated, to the starch. Polymer-polymer interactions for the formation of graft polymers have the advantage in that the molecular weight of the grafted side chains is known and can be controlled. In general, this approach has received only limited attention.<sup>2</sup> The process that was developed for the preparation of the graft polymers consisted of the conversion of polyethylene oxide having hydroxyl end groups to the chloroformate derivative and its subsequent reaction with starch alkoxide, as follows:



### EXPERIMENTAL

#### Materials

Polyethylene oxide ( $M_n = 400$ ) (BDH) and ( $M_n = 4000$ ) (Koch-Light) were used. Stock solutions of polyethylene oxide in toluene were dried by azeotropic distillation. Potassium naphthalene and dry THF were prepared as previously described.<sup>3</sup>

A solution of phosgene (12.5%) in toluene (BDH) was used. Stock solutions of soluble starch in DMSO were dried by azeotropic distillation. All solvents and stock solutions were kept under anhydrous conditions in pure argon atmosphere.

**Grafting of polyethylene oxide on starch.** The reaction was carried out under argon. To a solution of poly-E.O. in toluene, potassium naphthalene, equivalent to the hydroxyl end groups, was added at 30°C with stirring to form the alkoxide derivative which was obtained as a gel. The reaction mixture was cooled to 10°C and a solution of phosgene in toluene (excess) was added. The reaction was fast, as seen from the disappearance of the gel. The reaction mixture was stirred for 1 hr, and excess phosgene was evaporated completely in vacuo with stirring. To the resulting solution of the chloroformate derivative, a suspension of potassium starch alkoxide in dry THF was added under argon and the mixture was stirred at room temperature for 30 hr. The starch alkoxide suspension was prepared by adding potassium naphthalene in THF to starch dissolved in DMSO, and replacing the DMSO by THF. The reaction cannot be carried out directly in DMSO since the chloroformate, similar to phosgene, reacts with DMSO.<sup>4</sup>

Dry ether was added to precipitate the crude graft contaminated with homopolymer and potassium chloride. This was suspended in THF and the alkoxide groups which did not react were neutralized with acetic acid. The mixture was centrifuged at 30°C to separate homopoly-E.O. which is soluble in THF. The residue was suspended in absolute ethanol and centrifuged. The ethanol dissolved the potassium acetate besides some graft polymer. The insoluble fraction contained graft polymer contaminated with potassium chloride from which it was purified by dialysis of its aqueous solution. The pure graft polymer was recovered from solution by lyophilization.

The starch content of the graft polymers was determined by acid hydrolysis and titration of the glucose.<sup>5</sup>

## RESULTS AND DISCUSSION

The chloroformate derivative of polyethylene oxide was prepared by reaction of the potassium alkoxide derivative of polyethylene oxide, obtained by metallation with potassium naphthalene, with phosgene in toluene.

The effect of varying the chloroformate and the potassium starch alkoxide concentrations on the yield and properties of the graft polymers was determined. Generally it was found that the yields, the composition of the graft polymers, the distribution of the side chains, and the properties of the graft polymers were dependent on the starch alkoxide and poly-E.O. chloroformate concentrations (Table I). The yield of the pure graft polymers was not high, probably due to the heterogeneous nature of the reaction mixture, and it increased with increasing the chloroformate con-

TABLE I  
Reaction of Poly-E.O. Chloroformate with Starch Alkoxide<sup>a</sup>

Starch alkoxide introduced		Poly-E.O. chloroformate introduced,	Pure graft polymer		D.S. <sup>c</sup>	No. of glucose <sup>d</sup> units per Poly-E.O. side-chain
mmole	D.S.	mmole	Yield, <sup>b</sup> g	Starch content, %	calculated	
5.25	1.06	4.30	1.2	60.0	0.027	37.0
8.50	1.72	4.30	1.1	54.0	0.035	28.6
7.80 <sup>e</sup>	1.72	3.45	1.0	63.0	0.024	41.5
8.50	1.72	5.15	1.4	41.0	0.060	16.6
8.50	1.72	4.75	1.4	45.5	0.049	20.2
5.25	1.06	2.05	1.2	65.5	0.022	45.5
5.25	1.06	3.10	1.2	63.0	0.024	41.5
8.50	1.72	4.30	1.1	50.5	0.040	25.0
4.23	0.85	4.30	1.1	68.0	0.019	52.5
8.5 <sup>f</sup>	1.72	5.15	1.0	70.0	0.175	5.7

<sup>a</sup> Experimental conditions: The starch potassium alkoxide was prepared in DMSO (25 ml) from starch (0.8 g, 4.95 mmole anhydro glucose). Four triturations with THF (each 60 ml) under argon, followed by centrifugation, were carried out to replace the DMSO. A suspension of the alkoxide in THF was added to the chloroformate of poly-E.O. 4000.

<sup>b</sup> After purification by dialysis.

<sup>c</sup> Calculated from the composition of the graft polymer (mole poly-E.O./mole glucose).

<sup>d</sup> Calculated from the D.S.<sup>e</sup>

<sup>e</sup> Starch (0.65 g) was used.

<sup>f</sup> Poly-E.O. 400 was used.

centrations especially at the high alkoxide concentration (D.S. of alkoxide 1.72).

From the composition of the graft polymers (Table I), and the known molecular weights of the side chains, it was possible to calculate the grafting degree of substitution, i.e., the distribution of the side chains on the starch backbone. This D.S. was found to increase with increase of the alkoxide or the chloroformate concentrations as expected (Table I). Graft polymers having 1 poly-E.O. side chain per 16.6–52.5 anhydro glucose units were formed.

To find out the effect of the molecular weight of poly-E.O. on the grafting, comparable experiments were carried out using poly-E.O. having molecular weights of 400 and 4000. In the former case (poly-E.O. 400) the D.S. was 0.175 and in the latter only 0.06. This shows that the chloroformate derivative of the shorter polymer was 2.5–3 times more reactive than that of the higher molecular weight polymer toward the starch alkoxide groups, probably due to easier diffusion of the short polymer. It may be noted that the hydroxyl groups at C<sub>2</sub> and C<sub>3</sub> of the chair conformation of the anhydro glucose unit are equatorial and are not so far from each other,<sup>6,7</sup> and steric effects involved in the reaction of alkoxide groups at these positions with the chloroformate groups may be more pronounced toward longer poly-

mers. Avny and Schwenker<sup>8</sup> have found similar results in the reaction of preformed polystyrene having acid chloride end groups with cellulose in the presence of base. Thus, the grafting degree of substitution was found to be mainly dependent on the molecular size of the reacting preformed polymer, whereby high molecular-weight preformed polymers led to low degrees of substitution.

All the graft polymers obtained were soluble in water, showing that no cross linking between the chains occurred even though the poly-E.O. contained two chloroformate end groups. This may be explained by the possibility that after that one of the chloroformate groups has become attached to an insoluble starch molecule, the diffusion of the remaining group becomes much more limited, so that the possibility of reaction with an alkoxide group on the same or on a different starch chain becomes much smaller, taking into account the low efficiency of the coupling process.

The graft polymers having a higher content of poly-E.O. were more soluble in water than those having a smaller content, besides the former melted at 170–185°C while the latter melted partially only at about 200°C. Generally, the graft polymers can be cast into films on evaporation of their aqueous solutions. The graft polymers having side chains of poly-E.O. 400 were more soluble in water than those having side chains of poly-E.O. 4000, having the same poly-E.O. content, due in part to the larger number of grafted side chains. The former graft polymers were even soluble in methanol.

The present method developed for the preparation of graft polymers of poly-E.O. on starch may prove of general interest for the preparation of graft polymers of other alkylene oxides on starch and similar polyhydroxy polymers, especially in the case of alkylene oxides which are difficult to polymerize on starch alkoxide, using preformed polymers prepared by convenient methods.

Research Support from the United States Department of Agriculture, Grant No. FG-Is-166.

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Received February 26, 1969