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### Grafting of Preformed Polyethylene Oxide on Dialdehyde Starch by Acetal Formation

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## **Grafting of Preformed Polyethylene Oxide on Dialdehyde Starch by Acetal Formation**

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### **SUMMARY**

The acid-catalyzed reaction of dialdehyde starch with diethylene glycol and polyethylene oxide-400 under anhydrous conditions was studied as a new approach to the preparation of graft polymers of polyalkylene oxides on starch, the attachment of the side chains being through acetal linkages. The reaction was carried out in DMF in the presence of *p*-toluene sulfonic acid. It was found that increasing the reaction temperature, the diol concentration, or the reaction time led to an increase in the degree of grafting, as seen from the decrease in the dicarbonyl content of the products. Fusible graft polymers, soluble in water and in organic solvents, were obtained.

### **INTRODUCTION**

In continuation of our work on the grafting of alkylene oxides on starch [1, 2], we have examined a new approach to the preparation of such graft polymers based on the reaction of preformed and suitably activated polyalkylene oxides with starch. Such a method has the advantage that the molecular weights of the graft polymers are predetermined. Thus we have shown that the coupling reaction of the chloroformate derivative of

polyethylene oxide with starch alkoxide led to the formation of soluble graft polymers [3].

In the present work, we have studied the acid-catalyzed reaction of polyethylene oxide with dialdehyde starch to obtain graft polymers in which the side chains are attached to the starch by acetal linkages. Various factors affecting the graft polymerization were investigated.

Such a reaction has been investigated for the lower alcohols. Thus Goldstein and Smith [4, 5] have reported the preparation of the series methyl to n-butyl acetals of dialdehyde starch using alcoholic hydrogen chloride as catalyst. p-Toluene sulfonic acid was also used as catalyst [6] and other acetals were also prepared [7]. Polyvinyl alcohol films were insolubilized by reaction with dialdehyde starch [8].

## EXPERIMENTAL

### Materials

Diethylene glycol (digol) and polyethylene oxide ( $\bar{M}_n = 400$ ) from BDH were used. A stock solution of polyethylene oxide was prepared in toluene and was dried by azeotropic distillation. Benzene, toluene, and dimethyl formamide (DMF) were dried and distilled by known procedures. Dialdehyde starch was prepared according to Mehlretter [9].

Dicarbonyl analysis on dialdehyde starch and on the graft polymers was carried out on a micro scale according to the procedure reported by Hofreiter et al. [10].

### Grafting Procedure

Dialdehyde starch was suspended in DMF. Benzene or toluene were added and the dialdehyde was dried by azeotropic distillation. p-Toluene sulfonic acid and redistilled digol or a solution of polyethylene oxide in toluene were added, and the reaction mixture was heated as required under azeotropic distillation to remove the water formed in the reaction.

The reaction mixture was filtered from insoluble polymer, if present, which was washed with benzene. The graft polymer was precipitated from the filtrate with dry ether, washed with benzene to remove unreacted diol, and dried in vacuo over phosphorous pentoxide.

## RESULTS

The grafting reaction of digol and polyethylene oxide with dialdehyde starch in DMF was studied in the presence of *p*-toluene sulfonic acid. There were difficulties in the isolation of the products especially when polyethylene oxide was used as the reagent because the products were sticky and hygroscopic. The washup caused losses and the yields of the graft polymers isolated were low. The per cent decrease of the dicarbonyl content of dialdehyde starch was taken as a rough estimate of the degree of substitution of the grafted side chains.

### Grafting of Digol on Dialdehyde Starch (Table 1)

The effect of the amount of digol and the temperature of reaction (azeotropic distillation with benzene or toluene) on the degree of grafting and the properties of the graft polymers were investigated. Generally two fractions were isolated, one insoluble in the reaction medium and the other soluble. The soluble fraction was precipitated with ether. The fractions differed in their dicarbonyl content. With increasing amount of digol, the amount of soluble fraction increased (the insoluble decreased) and the dicarbonyl content of the soluble fraction also decreased. The amount of soluble fraction also increased with increase in the reaction time or temperature. When a relatively high amount of digol, a high reaction temperature, and a long reaction time was used, the soluble and no insoluble fraction was obtained.

The fraction insoluble in DMF was infusible and insoluble in water or other organic solvents. It had a high dicarbonyl content (77-80%), although less than that of the starting dialdehyde starch (85%), and did not change significantly under different reaction conditions. Blank experiments in which dialdehyde starch was heated for 7 hr in DMF under azeotropic conditions (toluene) in the presence of *p*-toluene sulfonic acid also gave an insoluble product. The dicarbonyl content of this material was lower than that of dialdehyde starch and similar to the insoluble fractions obtained in the reactions with digol. This indicates that the insoluble fraction is probably not a graft polymer.

The fractions soluble in the reaction mixture were also soluble in water (unlike dialdehyde starch) and insoluble in benzene (unlike digol); their melting range decreased with decreasing dicarbonyl content of the product, due to increased grafting.

Table 1. Grafting of Digol on Dialdehyde Starch<sup>a</sup>

Digol (g)	Digol (mmole)	Reaction time (hr)	Reaction time (g)	Product <sup>b</sup>		Dicarbonyl content <sup>c</sup> (%)
				Soluble fraction	Insoluble fraction	
				Dicarbonyl content <sup>c</sup> %	mp range (°C)	
8.9	84.0	1 <sup>d</sup>	0.70	76.3	Infusible	79.7
10.4	98.0	5 <sup>d</sup>	0.90	70.4	210-220	78.2
14.6	138.0	7 <sup>d</sup>	1.20	62.8	150-170	77.8
8.9	84.0	7 <sup>e</sup>	1.20	72.4	200-210	77.4
14.6	138.0	7 <sup>e</sup>	1.40	46.6	110-120	—

<sup>a</sup>Experimental conditions: Dialdehyde starch (1.5 g, 85% dicarbonyl) was suspended in DMF (40 ml), benzene or toluene was added, and the suspension was dried by azeotropic distillation. p-Toluene sulfonic acid (20 mg) and digol were added and the reaction mixture was heated under azeotropic distillation.

<sup>b</sup>The product of the reaction was composed of two fractions, one insoluble in the reaction mixture and infusible and the other soluble which is the graft polymer, recovered on precipitation by ether.

<sup>c</sup>100% dicarbonyl when all the C<sub>2</sub> and C<sub>3</sub> hydroxyl groups of the anhydroglucose units of the starch are oxidized to aldehyde groups.

<sup>d</sup>Azeotropic distillation with benzene.

<sup>e</sup>Azeotropic distillation with toluene.



Table 2. Grafting of Polyethylene Oxide-400 on Dialdehyde Starch<sup>a</sup>

Polyethylene oxide (g)	DMF (ml)	Graft polymer Dicarbonyl content <sup>b</sup> (%)	mp range (°C)
32.5	20	46.8	60-80
37.0	10	69.0	150-170
28.0	0	77.4	Infusible
37.0	20	40.3	55-75
28.0	20	51.6	70-90

<sup>a</sup>Experimental conditions: To a suspension of dialdehyde starch (1.5 g, 85% dicarbonyl content) in DMF, dried by azeotropic distillation with toluene, p-toluene sulfonic acid (20 mg) and a dry solution of polyethylene oxide-400 in toluene were added and the reaction mixture heated under azeotropic distillation. The graft polymers were recovered from the reaction mixture by precipitation with ether.

<sup>b</sup>100% dicarbonyl when all the C<sub>2</sub> and C<sub>3</sub> hydroxyl groups of the anhydroglucose units of the starch are oxidized to aldehyde groups.

hydroxyl group [11], or that cross-linked networks are formed by intermolecular hemiacetalization [12].

All the graft polymers obtained were soluble in water and organic solvents, showing that no cross-linking between the graft chains occurred, in spite of the difunctionality of the diols. This may be explained by the possibility that after one of the hydroxyl end groups has become attached to an aldehyde group on dialdehyde starch, the diffusion of the remaining hydroxyl group of the diol to the carbonyl group of the same or on different dialdehyde starch molecules becomes improbable because it is other end group of a high molecular-weight polymer.

In conclusion, the present method for the preparation of graft polymers of digol and polyethylene oxide-400 on dialdehyde starch may prove to be a method of general interest for the preparation of graft polymers of polyalkylene oxides having various molecular weights on starch and other carbohydrate dialdehydes.

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