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Influence of Swelling and Disruption of the Starch Granule on the Composition of the Starch-Polyacrylonitrile Copolymer

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LETTER TO THE EDITOR

Influence of Swelling and Disruption of the Starch Granule on the Composition of the Starch–Polyacrylonitrile Copolymer

Grafting acrylonitrile (AN) to gelatinized wheat starch has afforded products with grafted chains, few in number, but high in molecular weight (about 800,000) (*1*). Simultaneously with our studies on gelatinized starch, Reyes and co-workers (2) examined the grafting of AN to ungelatinized starch. In contrast to our results, they obtained a more frequently grafted copolymer whose grafted chains had molecular weights on the order of 150,000. Our study was therefore made to determine accurately how the degree of swelling and the extent of granule disruption would influence the composition of graft copolymers prepared under constant experimental conditions.

EXPERIMENTAL

Purification of the monomer and preparation of the ceric ammonium nitrate catalyst solution have been described (3). The starch used was Supergel wheat starch from Industrial Grain Products Ltd. Suspensions of starch (21.9 g, dry basis) in 500 ml of water were sparged with a nitrogen stream for 1 hr at either 25, 60, or 85°C. Starch with its granule structure completely disrupted was prepared by dissolving it in warm dimethyl sulfoxide (DMSO) followed by precipitation with methanol (*4*). Oxygen was displaced in the aqueous suspension of the methanol-wet product by sparging with nitrogen at 85°C. This treatment also removed methanol and gave a nearly clear solution. (Supernatant after centrifugation at 1600 × gravity for 35 min contained 97% of the original solid, and this 4% solution showed 91% transmission at 650 mμ as compared with 100% for water.) Acrylonitrile (31.8 g) was added to the aqueous dispersions, followed after 5 min by the catalyst solution to

give a ceric ion concentration of 1.5×10^{-3} mole/liter. The mixture was allowed to react under a nitrogen atmosphere for 3 hr at 25–28°C. The reaction mixture with DMSO-pretreated starch was difficult to cool, owing to its high viscosity, and reached a maximum temperature of about 35°C.

The crude graft copolymer was extracted with dimethylformamide (DMF), and the material insoluble in DMF was further extracted with DMSO to yield an insoluble fraction and a DMSO solution. The solution was concentrated and blended with water to yield a precipitate and an aqueous solution from which a third fraction was obtained by concentration and addition of ethanol. A detailed description of the fractionation procedure is given elsewhere (*3*). Starch was removed from the graft copolymer by the periodate-base method (*5*) and the molecular weight of the grafted polyacrylonitrile (PAN) determined by viscosity as previously described (*3*).

Aqueous starch slurries were examined microscopically to determine the effect of pretreatment at 25, 60, and 85°C on the granule. After stirring for 1 hr at 25°C, all granules showed birefringence. One hour at 60°C caused a loss of birefringence and roughly a twofold increase in granule size. The slurry was not viscous, and the supernatant after centrifugation contained only 2% of the original solid. After stirring an aqueous starch slurry for 1 hr at 85°C, the granules swelled to about three times the diameter of those in the unheated slurry. A heavy-bodied mixture resulted, and the supernatant after centrifugation contained 16% of the original starch. We will refer to the starch pretreated at 60°C as swollen, and, as in the previous papers, we will use the term gelatinized to describe the starch pretreated at 85°C.

RESULTS AND DISCUSSION

The effect of swelling and disruption of the starch granule on the composition of the graft copolymer is shown in Table 1. In run 1, the starch-water slurry was held at 25°C while sparging with nitrogen. In runs 2 and 3, the slurry was sparged at 60 and 85°C, respectively. This series of reactions shows that copolymers with a wide range of molecular weights and grafting frequencies may be obtained by varying the pretreatment temperature and consequently

TABLE 1

Influence of Swelling and Disruption of the Starch Granule

Run[a]	Fraction[b]	Wt., g	% PAN[c] in fraction	Molecular weight of graft	AGU[d]/ graft
1	DMSO[e] sol., ppt. by H_2O	1.2	58.3	76,500	337
	DMSO insol.	46.0	52.8	116,000	640
2	DMSO sol., ppt. by H_2O	2.6	53.4	400,000	2170
	DMSO insol.	44.0	55.6	566,000	2770
3	DMSO sol., ppt. by H_2O	3.2	64.7	418,000	1400
	DMSO insol.	38.6	56.4	810,000	3880
4	Water sol.	10.6	48.6	304,000	1980
	DMF[f] sol.	12.5	85.5	280,000	294
	DMSO sol., ppt. by H_2O	21.3	44.8	480,000	3650
	DMSO sol., not ppt. by H_2O	4.5	49.2	306,000	1950

[a] In runs 1, 2, and 3, starch pretreated at 25, 60, and 85°C, respectively; in run 4, granule structure completely disrupted by DMSO pretreatment.

[b] The following additional fractions were obtained for runs 1, 2, and 3, respectively. Recovered AN: 3.8, 1.4, 4.0 g; water-soluble: 0.2, 1.5, 4.8 g; DMF-soluble: 1.4, 2.3, 2.1 g (infrared showed starch in all fractions); DMSO-soluble but not precipitated by water: 0.4, 1.3, 1.0 g. In run 4, there was 2.0 g recovered AN and no DMSO-insoluble material.

[c] Polyacrylonitrile.

[d] Anhydroglucose unit.

[e] Dimethyl sulfoxide.

[f] Dimethylformamide.

the degree of swelling of the starch. Shorter and more frequent grafts are produced if granules are unswollen. In the 85, 60, and 25°C runs, 78, 85, and 94% of the total isolated solid, respectively, was in the DMSO-insoluble fraction.

In run 4, an aqueous dispersion of starch was used in which the granule structure was completely disrupted (see Experimental). A copolymer with increased solubility was produced under these conditions. Although DMSO did not give a true solution, the insoluble copolymer was so highly swollen that separation of the two phases could not be achieved by centrifugation at 1600 × gravity

for 35 min. It is noteworthy that an appreciable amount of copolymer could be extracted by water at room temperature in the form of a milky dispersion. The DMF-soluble fraction was also larger than in the other reactions.

Fractional precipitation of the grafted PAN from runs 1 and 3, after removal of the starch moiety, showed that the higher molecular weight for PAN grafted to gelatinized starch was real and not an artifact due to an overweighting of viscosity data by a small amount of exceptionally high molecular weight PAN.

Evidence that the molecular weight and frequency of the grafts was not influenced by variations in the amount of oxygen remaining in starch because of sparging at different temperatures was obtained from two reactions (not included in Table 1). In the first reaction, acrylonitrile and untreated starch (as a powder) were added in that order to a nitrogen-sparged solution of catalyst in 500 ml of water at 25°C. The DMSO-insoluble fraction comprised 92% of the isolated solid and had a molecular weight for grafted PAN of 137,000 and a grafting frequency of 750 anhydroglucose units per graft, a result not greatly different from that found for run 1. In a second reaction, a copolymer was prepared at 25°C from starch which had been repeatedly pumped under vacuum and repressured with nitrogen. This copolymer was also similar to that obtained in run 1. If subtle variations in oxygen concentration were responsible for changes in the copolymer due to the temperature of starch pretreatment, these two reactions should have yielded significantly different results.

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