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Copolymers of Starch and Polyacrylonitrile. Influence of Granule Swelling on Copolymer Composition under Various Reaction Conditions

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SUMMARY

Molecular weights and grafting frequencies of graft copolymers prepared with ferrous ammonium sulfate-hydrogen peroxide initiation showed a dependence on granule swelling similar to that found with ceric ammonium nitrate (increased swelling of starch granules decreased the number of grafted polyacrylonitrile chains and increased their average molecular weight). As with unswollen starch, the composition of the copolymer prepared from swollen starch was not influenced by granule size. Molecular weights of polyacrylonitrile branches grafted to swollen and unswollen starch were independent of reaction time; however, grafting frequencies with swollen and unswollen starch tended to converge toward a common value with increased reaction time and increased dilution. Data suggest that the influence of granule swelling on copolymer composition is due to a faster termination rate for growing polyacrylonitrile chains in unswollen starch.

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INTRODUCTION

We described earlier the influence that starch granule swelling has on the composition of the starch-polyacrylonitrile (PAN) copolymer, prepared through ceric ammonium nitrate initiation [1]. Increased swelling of the starch granules, brought about by preparing aqueous starch slurries at 25, 60, and 85°C before reaction with monomer and initiator, led to an increase in the average molecular weight of grafted PAN chains and a decrease in the number of PAN chains grafted to starch. Although this early work permitted us to vary grafting frequencies and molecular weights of grafted PAN in our copolymer syntheses, factors affecting the influence of granule swelling on molecular weight and frequency of grafted branches remained undetermined. In this report, starch-PAN copolymers prepared under various reaction conditions from swollen and unswollen starch are compared. Based on these data, an explanation for the influence of granule swelling on copolymer composition is suggested.

EXPERIMENTAL

Materials

The starch used was unmodified wheat starch (Supergel) from Industrial Grain Products, Ltd.

Ferrous ammonium sulfate hexahydrate and 30% hydrogen peroxide were Baker Analyzed Reagent grade.

Acrylonitrile (Eastman Kodak, practical grade) was fractionated at atmospheric pressure through a 15-in. Vigreux column. A center cut was collected and stored in amber glass at 5°C.

Ceric ammonium nitrate initiator solution was prepared by dissolving 13.9 g of ceric ammonium nitrate (Fisher Certified Reagent) in 250 ml of 1 N nitric acid.

Graft Polymerization

For reactions with ferrous ammonium sulfate-hydrogen peroxide as initiator, a stirred suspension of 21.9 g, dry basis, of starch (0.135 mole anhydroglucose unit, AGU) in 500 ml of water was purged with a nitrogen stream for 1 hr at 25, 60, or 85°C. The suspension was cooled to 25°C and 31.8 g of acrylonitrile (0.60 mole) added. After 5 min, 1.0 g of 30% hydrogen peroxide (8.8×10^{-3} mole) was added followed by 0.2 g of

ferrous ammonium sulfate hexahydrate (5.1×10^{-4} mole) dissolved in about 2 ml of water. The mixture was stirred under nitrogen at 25°C for 3 3/4 hr and 0.5 g of hydroquinone added. The insoluble reaction product was separated by filtration, then washed, and dried.

For ceric ammonium nitrate-initiated reactions, the conditions were: (1) High dilution [2]—a slurry of 3.0 g of starch, dry basis, (0.0185 mole) in 800 ml of water was purged with nitrogen for 1 hr at 25 or 60°C. Ten grams of acrylonitrile (0.189 mole) was added to the suspension at room temperature followed after 5 min by 12 ml of initiator solution (1.22×10^{-3} moles Ce^{+4}). (2) Highest dilution—a starch slurry identical to that used for the high dilution conditions was prepared (3.0 g of starch, dry basis, in 800 ml of water). Initiator solution (12 ml) was added to the slurry (to obtain the same ceric ion-to-starch ratio used under high dilution conditions) followed after 5 min by 10.0 g of acrylonitrile dissolved in 1600 ml of nitrogen-sparged water. For both dilutions, reaction mixtures were stirred under nitrogen at 25°C for the chosen reaction time, hydroquinone was added, and the crude polymer was separated by filtration, washed, and dried.

Each of the insoluble reaction products was exhaustively extracted at room temperature with dimethylformamide (DMF) to remove ungrafted PAN. In general, as the pretreatment temperature for starch was raised, swelling of the copolymers in DMF increased; this made them difficult to handle and also resulted in the solution of some carbohydrate-containing polymer in addition to ungrafted PAN. A sharper fractionation of ungrafted PAN and starch-PAN copolymer was therefore achieved when starch was pretreated at 25 or 60°C rather than 85°C. The graft copolymer (insoluble in DMF) was analyzed for nitrogen and the starch moiety then removed by acid hydrolysis (0.5 hr reflux in 0.5 N HCl) followed by the periodate-base method [3]. The molecular weight of grafted PAN was determined from its intrinsic viscosity [4], and the grafting frequency was then calculated.

RESULTS AND DISCUSSION

In our earlier work on ceric ammonium nitrate-initiated graft polymerization [1], an increase in the pretreatment temperature of an aqueous starch slurry from 25 to 60°C and from 25 to 85°C caused the average molecular weight of grafted PAN to increase by factors of 4.9 and 7.0 and the number of grafted chains to decrease by factors of 4.3 and 6.1,

respectively. To determine whether granule swelling influences copolymer composition only with ceric ion initiation (where a carbohydrate-ceric complex is first formed which then yields free radicals [5]) or whether another method of initiation would show a similar trend, we prepared starch slurries at 25, 60, or 85°C and initiated grafting at room temperature with hydrogen peroxide-ferrous ammonium sulfate (Table 1). For this initiating system, no complex with starch is formed. Rather, hydroxyl

Table 1. Influence of Granule Swelling on Copolymer Composition. Hydrogen Peroxide-Ferrous Ammonium Sulfate Initiation^a

Starch pretreatment, ^b °C	DMF sol., g	DMF insoluble			
		Wt., g	% PAN in copolymer	Mol. wt. of grafted PAN	Grafting frequency, AGU/graft
25	5.6	31.0	28.7	84,200	1,290
60	12.8	24.8	11.1	240,000	11,800
85	14.4	23.3	14.8	449,000	15,900

^aPolymerization recipe given in Experimental. Reaction time was 3 3/4 hr.

^bAqueous starch slurry stirred for 1 hr at this temperature while sparging with a nitrogen stream.

radicals are produced [6] which abstract hydrogen atoms from starch. The molecular weights and grafting frequencies in Table 1 showed a dependence on granule swelling similar to that found for ceric ion initiation, although the ferrous ammonium sulfate-hydrogen peroxide system gave a product having fewer grafted PAN chains which were of lower molecular weight.

In another study in which ceric ammonium nitrate initiation was used [2], we showed that reduced amounts of starch and acrylonitrile in an increased volume of water (high dilution conditions; see Experimental) led to a greater number of grafted PAN chains which were of lower average molecular weight than was found previously [1]. In addition, evidence was presented that grafting of PAN to unswollen starch under these conditions occurred internally rather than merely on the surface of the granule. It was recognized that swollen granules, contrary to unswollen starch, might be predominantly surface grafted. This possibility was tested

by the same technique used earlier [2] for unswollen starch; namely, a comparison of grafting frequencies of copolymers derived from swollen starch granules of two different diameters, obtained through classification of whole wheat starch. The average diameters of the granules before swelling were 4.6 and 18.0 μ (as determined on a 12-channel Coulter Counter); microscopic examination showed that granules swollen at 60°C maintained approximately the same relative diameters. Because of the reduced surface area per unit weight of starch, the larger granules would be less frequently grafted if surface grafting predominated. The two classified starches, however, gave similar grafting frequencies under high dilution conditions (Table 2), and

Table 2. Influence of Granule Size on Copolymer Composition. Swollen Starch. High Dilution.^a Ceric Ammonium Nitrate Initiation

Starch	DMF sol., g	DMF insoluble			Grafting frequency, AGU/graft
		Wt., g	% PAN in copolymer	Mol. wt. of grafted PAN	
Unclassified	0.7	6.7	55.4	230,000	1,140
4.6 μ	0.5	7.6	59.6	238,000	994
18.0 μ	0.8	7.1	58.2	190,000	843

^aPolymerization recipe given in Experimental. Aqueous starch slurries sparged with nitrogen for 1 hr at 60°C before room temperature reaction with monomer and catalyst. Reaction time was 3 hr.

slightly fewer chains were actually grafted to the smaller diameter granules. The influence of granule swelling on molecular weight and frequency of grafted branches is therefore not affected by granule size.

We next studied the influence of reaction time on the frequency and molecular weight of grafted PAN chains for swollen and unswollen starch (Table 3). High dilution conditions were employed with reaction times of 20, 40, and 90 min, as well as 3 and 22 hr. Although grafting frequencies varied with time, the average molecular weights of grafted PAN within each series (swollen or unswollen starch) were relatively time-independent. For each reaction time in Table 3 the unswollen starch gave a more frequently grafted copolymer than the swollen starch; however, the two grafting frequencies tended to converge toward a common value as the reaction time was increased. This convergence is readily seen from the quotients

Table 3. Influence of Reaction Time and Dilution on Grafting Frequency, Molecular Weight of Grafted PAN, and Percent Conversion of Acrylonitrile to PAN for Swollen and Unswollen Starches. Ceric Ammonium Nitrate Initiation

Reaction time, min	Granule state ^a	DMF sol., g	Wt., g	%PAN in copolymer	Mol. wt. of grafted PAN	DMF insoluble			% conversion of AN to PAN ^c
						Grafting frequency, AGU/graft	Grafting frequency, quotient ^b	Mol. wt. of grafted PAN	
20	Unswollen	0.1	3.4	10.4	24,000	1,300	12	4.5	
20	Swollen	Trace	3.2	9.4	266,000	15,800		3.0	
40	Unswollen	0.1	3.9	22.3	31,600	677	5.9	9.7	
40	Swollen	0.1	3.6	21.1	172,000	3,980		8.6	
90	Unswollen	0.1	4.7	36.8	28,300	300	5.4	18	
90	Swollen	0.4	5.1	44.0	205,000	1,610		26	

High Dilution^d

180	Unswollen	0.3	5.4	44.7	36,700	281	4.1	27
180	Swollen	0.7	6.7	55.4	230,000	1,140		44
1320 (22 hr)	Unswollen	0.3	5.9	48.9	34,000	219	2.8	32
1320	Swollen	1.0	9.1	70.6	240,000	616		74
Highest Dilution ^d								
1320	Unswollen	0.3	4.1	25.0	10,800	200	1.7	13
1320	Swollen	0.5	4.6	37.9	34,200	346		22

^aUnswollen: Aqueous starch slurry sparged with nitrogen for 1 hr at 25°C. Swollen: Aqueous starch slurry sparged with nitrogen for 1 hr at 60°C. Reactions with unswollen starch at high dilution are taken from Ref. 2.

^bAGU/graft for swollen starch divided by AGU/graft for unswollen starch. It was shown in Ref. 2 that reproducible grafting frequencies are obtained.

^cTotal conversion. DMF-soluble fraction assumed to be 100% PAN.

^dPolymerization recipes given in Experimental.

obtained by dividing the grafting frequency for swollen starch by that for unswollen starch at each reaction time, and is apparently due to the grafting of new PAN chains onto swollen starch at a significant rate long after initiation of grafting onto unswollen starch has diminished.

Table 3 shows that the grafting frequency quotient is also reduced by increased dilution. For unswollen starch the grafting frequency does not change appreciably (219 vs 200 AGU/graft) on going from high to highest dilution (high dilution concentrations further reduced by a factor of three), whereas the same change in dilution almost doubles the number of chains grafted to swollen starch (616 vs 346 AGU/graft).

On the basis of the data presented, certain explanations first considered for the influence of granule swelling on molecular weight and frequency of grafted branches now appear less probable. First, similar trends with two initiators (Ce^{4+} and $\text{Fe}^{2+}-\text{H}_2\text{O}_2$), which produce starch free radicals by different mechanisms, suggest that changes in copolymer composition with differences in granule swelling are not associated with some special characteristic of ceric ion, such as complex-forming ability or decomposition rates of starch-ceric complexes. Second, a study of graft polymerization onto different size granules indicates that surface grafting is not a likely explanation for the less frequent grafting onto swollen starch. Finally, the data in Table 3 show that if graft polymerizations are run with a sufficiently low concentration of reactants and for a long enough time, the grafting frequencies for swollen and unswollen starch converge toward a common value. Therefore, large differences in grafting frequencies between swollen and unswollen starch observed under certain conditions [1] are probably not due to a large difference in the number of free radical sites produced in swollen and unswollen granules through reaction with ceric ammonium nitrate.

One explanation for the swelling effect, which is consistent with our data, is a faster rate of termination of growing PAN chains in unswollen starch granules, possibly because the closer packing of starch macromolecules permits more efficient chain transfer to carbohydrate. In a system which allows rapid termination of growing PAN (unswollen starch), the number of PAN radicals is reduced, reaction of monomer with starch radicals is therefore favored, and the result is a relatively rapid initiation of a large number of grafted branches. The data in Table 3 on conversion of acrylonitrile to PAN are consistent with this explanation. Early in the reaction, the rapid termination of growing PAN in unswollen starch is offset by the rapid initiation of new grafts, an effect making the total conversion to PAN roughly the same for swollen and unswollen starch. However, when the

number of PAN chains grafted to swollen starch approaches more closely the number grafted to unswollen starch, then the conversion of acrylonitrile exceeds that for unswollen starch due to the higher average molecular weight attained by PAN grafted to the swollen granule.

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Mention of trade names should not be construed as recommendation or endorsement by the U.S. Department of Agriculture over those not mentioned.

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