Structure and Molecular Properties of Saponified Starch–Graft-Polyacrylonitrile*

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Synopsis

The Mn^{3+} initiation system has been used to prepare starch–g-polyacrylonitrile copolymers. Both granular native starch and water-swollen gelatinized starch have been used as substrate. Conversion of monomer, grafting ratio, and percent add-on tend to increase with increasing amounts of monomer charged. The amount of homopolymer formed is extremely low, approximately 1%. The efficiency, measured as conversion, is consistently higher with gelatinized starch as substrate. The molecular weight of the grafts on gelatinized starch is approximately eight times higher than those on granular starch. Granular starch has a correspondingly higher frequency of grafts. Solubility measurements of starch, polyacrylonitrile, and grafted starch were carried out in dimethylsulfoxide (DMSO) at 348 K. Starch and polyacrylonitrile were totally soluble in DMSO under the chosen conditions. The solubilities of grafted samples were independent of the state of the substrate before grafting and of molecular weights of the grafted chains, but were found to be correlated to percent add-on. Starch–g-polyacrylonitrile samples, with gelatinized starch as substrate, were saponified in aqueous sodium hydroxide solution. The water retention value increased linearly with increasing add-on. The saponified polyacrylonitrile branches alone had a water retention value that was three times higher than that of the original copolymer.

INTRODUCTION

In the past several decades, attention has been paid to the modification of native polymers. The alteration of structure and properties of polysaccharides by chemical and physical modification has been extensively reported. Polysaccharide graft copolymers have been prepared in order to add new properties to the polysaccharide with a minimum loss of native properties. Because naturally occurring polysaccharides are insoluble or have limited solubilities in most solvents, two-phase systems for grafting are usual. Free-radical initiation of the polymerization reaction is used in most processes.

Phosphate complexes of Mn^{3+} as initiators for grafting of vinyl monomers to cellulose and cellulose derivatives were first described in 1961.[1] Independently, a system for grafting of vinyl monomers onto starch using a manganic pyrophosphate complex was developed in these laboratories.[2-5] This system has also successfully been applied to cellulosic fibers.[6-9] The mechanism of the initiation has been studied using electron spin resonance (ESR) spin trapping techniques and ultraviolet–visible (UV-VIS) absorption spectroscopy. It has been concluded that both C1–C2 glycol end groups and

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C2–C3 glycol groups along the polysaccharide chains form reactive grafting sites.[10]

When the Mn^{3+} initiation system is used, acrylonitrile is very efficiently grafted to starch in the native granular and water-swollen gelatinized form, and also to starch derivatives. Starch–polyacrylonitrile graft copolymer can further be modified by alkaline hydrolysis to form a product with a high water absorption and retention capacity.[11] This material is similar to HSPAN, as first described by Weaver et al.[12]

As reported earlier by Gugliemelli et al.[13] alkaline hydrolysis of starch grafted with polyacrylonitrile destroys all nitrile functionality detectable by infrared (IR) absorption with formation of amide and carboxyl groups. Rogers[14] has reported a maximum of 70% conversion of nitrile to carboxyl groups. The remaining 30% are amide groups. The incomplete hydrolysis is interpreted as related to steric and polar factors due to hydrogen bonding between neighboring amide and carboxyl groups on the same chain or on adjacent chains. Weaver et al.[15] has suggested that condensation might also occur between acid and amide groups to form imide structures.

The conversion of nitrile groups to carboxyl groups is reported to be dependent on the base concentration. Higher base concentration gives higher carboxyl contents up to a certain concentration. Further increase of the base concentration actually gives lower carboxyl contents.[15] Raising the temperature from 353 K to 373 K during the hydrolysis also increases the carboxyl content in the final product.[15]

The main purpose of this work was to study the differences between granular and gelatinized starch as a substrate for grafting and to find evidence for assumed cross-linking during the grafting or saponification reactions.

EXPERIMENTAL

Materials

The chemicals used were the following: $MnSO_4 \cdot H_2O$, $KMnO_4$, $Na_4P_2O_7 \cdot 10\ H_2O$, and concentrated H_2SO_4 (all of pro analysi grade from Merck), acrylonitrile (synthetic grade from Merck), NaOH (purum grade from EKA, Sweden), N,N-dimethylformamide, dimethylsulfoxide, acetone, and methanol (all of purum grade from KEBO, Sweden). Native potato starch was supplied by Svenska Stärkelse Föreningen AB (SSF). Polyacrylonitrile was received from Polysciences, Inc. The chemicals were used as delivered, except for the acrylonitrile, which was purified by distillation at reduced pressure under a purified nitrogen atmosphere.

Graft Copolymerization

Starch–polyacrylonitrile graft copolymers were prepared under the following conditions.

Native potato starch (8.75 or 21.5 g dry weight) in the granular or gelatinized form, and different amounts of acrylonitrile were slurried in distilled water (185 or 465 mL) in a reaction vessel immersed in a thermostated water bath (303 K) (the water content in the moist starch is taken into

account). Gelatinized starch was prepared by raising the temperature to 338 K for 10 min. The reaction vessel was equipped with a stirrer, a condensor, a N_2 bubbler, and a dropping funnel. Initiator solution (25 or 62.5 mL), prepared to give an Mn^{3+} concentration of 1 mmol/L in the reaction vessel, and acidified water (25 or 62.5 mL), prepared to give a sulfuric acid concentration of 75 mmol/L in the reaction solution, were poured into the dropping funnel. After 30 min of N_2 bubbling, the solution in the dropping funnel was added to the reaction vessel. The reaction was carried out under an atmosphere of purified nitrogen at 303 K for 3 h.

The yield of the grafting experiment was calculated after drying the product overnight, and the water content and the amount of homopolymer formed were determined.

The amount of homopolymer formed was determined by extraction with dimethylformamide (DMF) for 24 h.

The molecular weights of the grafted polyacrylonitrile chains were determined after acid hydrolysis which removed the starch moiety. Viscosity measurements were conducted in DMF at 298 K and the $\overline{M}_n$ value was calculated from the relation:[16]

$$[\eta] = 3.92 \times 10^{-4} \times \overline{M}_n{}^{0.75}$$

Solubility in Dimethylsulfoxide (DMSO)

To determine the solubility in DMSO of starch, polyacrylonitrile, and graft copolymers of starch and polyacrylonitrile, and graft copolymers of starch and polyacrylonitrile, a moist sample of approximately 1 g was slurried in 100 mL DMSO and heated to 348 K. The samples were dried at 348 K for 24 h and then moistened at room temperature in a water-containing desiccator for 24 h. The moisture contents were 15–20% in the different samples. The bottle was sealed and allowed to stand at 348 K for 24 h with occasional stirring. After cooling to room temperature, the slurry was filtered, and 50 mL of the filtrate was precipitated by pouring into acetone. The solid was recovered and dried in air overnight. The percent solubility was calculated, after correcting for the initial moisture content.

Alkaline Hydrolysis of Nitrile Groups

The saponification was carried out at 363 K in a 1% aqueous sodium hydroxide solution directly after graft copolymerization. A deep-red color develops during the hydrolysis, due to intermediate formation of naphthyridine ring structures from adjacent nitrile groups.[17] The intermediate rings are subsequently hydrolyzed, causing a change in color from red to light yellow. This sharp color change was used as an indication to stop the hydrolysis. The product was recovered by precipitation in methanol and washed to neutrality.

Retention of Distilled Water

A weighed sample of modified starch was immersed in a weighed amount of distilled water in a weighed glass tube. After 30 min, the slurry was filtered and the amount of retained water calculated. Corrections were made

for the water retention of the filter paper. The water retention value (WRV) was calculated in grams per gram of dry modified starch charged.

RESULTS AND DISCUSSION

Graft Copolymerization

Grafting of acrylonitrile to granular starch with the Mn^{3+} initiation system and also, to some extent, to heat-pretreated starch has been reported previously.[2-4] While we were working on the saponification of acrylonitrile grafted starch and its water absorption capacity, we found that gelatination of starch prior to grafting increases the water absorption and retention of the final product.[11] Comparisons are herein reported between acrylonitrile–grafted starch products, with granular and with water-swollen starch as substrate.

The results of the grafting experiments are described with data defined on a weight basis as:

$$\text{Conversion of monomer (\%)} = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

$$\text{Grafting ratio (\%)} = \frac{\text{Polymer in grafts}}{\text{Weight of substrate}} \times 100$$

$$\text{Add-on (\%)} = \frac{\text{Polymer in grafts}}{\text{Total weight of grafted sample}} \times 100$$

A new definition is introduced:

Frequency of grafts =

   Number of grafted chains per 1000 anhydroglucose units (AGU)

In Table I, the results are shown for a series of graftings of native granular potato starch with different amounts of acrylonitrile. The amount of homopolymer formed during the grafting reaction is extremely low, below

TABLE I
Grafting of Acrylonitrile to 10 g Native Potato Starch (8.75 g dry weight) in Granular Form[a]

Starch (g)/ AN (mL)	Percent add-on		Grafting ratio (%)	Conversion of monomer (%)	Homopolymer formed (%)
	DMF[b]	Acid[b]			
10/2.5	8	6	8	38	(0.05)
10/5	19	18	24	52	0.5
10/10	36	35	57	61	0.7
10/20	59	50	141	77	0.7

[a] Conditions: Mn^{3+}, 1 mmol/L; $H_2P_2O_7{}^{2-}$, 3 mmol/L; H_2SO_4, 75 mmol/L; temperature, 303 K; time, 3 h.
[b] DMF, after DMF extraction; acid, after acidic hydrolysis.

1%. The conversion of monomer increases with increasing amounts of monomer charged. As expected, the grafting ratio and the add-on increase with increasing amounts of acrylonitrile charged. The add-on in grafted samples has been calculated both after extraction in DMF and after acid hydrolysis, and the agreement is satisfactory.

Grafting of different amounts of acrylonitrile to gelatinized starch is presented in Table II. Just as in the series with granular starch as substrate, add-on, grafting ratio, and conversion of monomer increase with increasing amounts of monomer. However, the efficiency of the grafting reaction, measured as conversion, is consistently higher with gelatinized starch as substrate. The amounts of homopolymer are slightly higher but still comparable with those from the grafting to granular starch.

The increased conversion with increasing amounts of monomer charged is expected, being a result of the concentration effect on the rate of propagation. If gelatinized starch is used as substrate, the accessibility of starch for grafting is enhanced, and this will cause increased conversion, as observed.

Molecular weights and frequency of grafts were determined for the granular and gelatinized starch samples (Table III). The molecular weights of the grafts on gelatinized starch are approximately eight times higher than that on granular starch. This is in good agreement with previous results reported by Mehrotra and Rånby[4] and Fanta.[18]

The frequency of grafts is about eight times higher when granular starch is used as substrate as compared with that of substrates in gelatinized form. With gelatinized starch as substrate, the molecular weight increases with monomer concentration. Above an acrylonitrile/starch ratio of one, the change is small.

When polymerization is performed in a nonsolvent for the polymer or in a viscous liquid medium or a gel, the mobility of propagating polymer radicals is restricted, and this will decrease the rate of termination. The rate of propagation is maintained because the diffusion rates of small molecules such as initiator and monomer are not affected much. This autoacceleration of polymerization, the "Trommsdorf–Norrish gel effect,"[19] is also apparently operative in the polymerization in gels such as the gelatinized starch–water system. When starch granules are grafted, the reaction may

TABLE II
Grafting of Acrylonitrile to 25 g Native Potato Starch (21.5 g dry weight)
in Gelatinized Form[a]

Starch (g)/ AN (mL)	Percent Add-on[b]	Grafting ratio (%)	Conversion of monomer (%)	Homopolymer formed (%)
10/2.5	16	19	72	5.3
10/5	23	30	64	1.2
10/10	45	82	88	1.0
10/20	63	173	93	1.0

[a] Conditions: Mn^{3+}, 1 mmol/L; $H_2P_2O_7^{2-}$, 3 mmol/L; H_2SO_4, 75 mmol/L; temperature, 303 K; time, 3 h.
[b] After DMF extraction.

TABLE III

Molecular weight ($\overline{M}_n$) of Grafted Polyacrylonitrile Chains and Frequency of Grafts

Starch pretreatment	Starch (g)/ AN (mL)	Molecular weight ($\overline{M}_n$)	Frequency of grafts (chains/1000 AGU)
None (granular)	10/10	80,000	1.7
Gelatinized	10/2.5	53,000	0.6
	10/5	254,500	0.2
	10/10	630,000	0.2
	10/20	703,000	0.4

occur mainly on the surface and in voids of the granules, where the mobility of the grafted chains is less restricted. This leads to a higher rate of termination as compared with the grafting to gelatinized starch, and thus to lower molecular weights of grafted chains.

Solubility Experiments

To study the possible cross-linking during the graft copolymerization with Mn^{3+} as initiator, solubility measurements in DMSO at 348 K were carried out. Because both starch and polyacrylonitrile are completely soluble in DMSO at that temperature, the assumption was made by Fanta et al.[20] that an uncross-linked starch–g-polyacrylonitrile would also be totally soluble. Cross-linking would decrease the solubility under the chosen conditions.

The results of solubility experiments with different starch samples and a sample of polyacrylonitrile (from Polyscience, Inc.) with a molecular weight of 150,000 are shown in Table IV. Fanta et al.[20] reported that the solubility of starch decreased after Ce^{4+} treatment. Here, the total solubility of starch is found to be essentially unaffected by the reaction with Mn^{3+} in acid solution. It seemed that dissolution was a little faster after the Mn^{3+} treatment. A sample treated only with aqueous sulfuric acid of the same concentration also dissolved faster than untreated starch, probably

TABLE IV

Solubility in DMSO for Native Potato Starch in Granular and Gelatinized Form and Starch Treated in the Mn^{3+} Initiator System, in Sulfuric Acid Solution, and in an Alkaline Solution of 1% and PAN

Sample	Solubility in DMSO (%)
Granular starch	97
Gelatinized starch	99
Granular starch treated with Mn^{3+} (1 mmol/L) and H_2SO_4 (75 mmol/L) for 3 h, 303 K	97
Gelatinized starch treated with Mn^{3+} (1 mmol/L) and H_2SO_4 (75 mmol/L) for 3 h, 303 K	100
Granular starch treated with H_2SO_4 (75 mmol/L) for 3 h, 303 K	100
PAN (MW 150,000)[a]	100

[a] Received from Polysciences Inc.

because of an expected small extent of hydrolysis in the acidic medium. The polyacrylonitrile sample received from Polyscience, Inc., was completely soluble in DMSO under these conditions.

Solubility measurements in DMSO were carried out on samples of granular and gelatinized starch grafted with polyacrylonitrile (Table V). Increasing the amount of acrylonitrile under the previously described reaction conditions decreased the solubility of the graft copolymer in DMSO. The solubilities were essentially independent of the state of the substrate before grafting and of the molecular weight of the grafted chains in the final product, but were found to be correlated to percent add-on. This is shown by comparison of the grafted copolymers obtained from granular and gelatinized starch. When the initial monomer/starch ratio is approximately one, add-ons of 36% and 45%, respectively, are obtained. The molecular weights differ by a factor of approximately 8. However, the solubilities of the graft copolymers in DMSO are essentially the same.

Figure 1 shows the correlation between solubility in DMSO at 348 K and percent add-on. The solubility of starch–g-polyacrylonitrile decreases with increasing content of synthetic polymer grafted and is independent of the molecular weight of the grafts and the state of the starch substrate. This property could be due partly to cross-links arising from chain combination between propagating polyacrylonitrile side chains. These cross-links are destroyed during the acid hydrolysis of the starch backbone, leaving a DMF-soluble polyacrylonitrile moiety. However, the rate of bimolecular termination is decreased considerably in heterogeneous polymerization of acrylonitrile.[21] Therefore, we assume that cross-links due to chain combination between propagating radical chain ends are not likely to occur to such an extent as to reduce the DMSO solubility as much as shown in Table V. Another possible explanation is the appearance of regions with dipole interactions between adjacent polyacrylonitrile chains (Fig. 2), leading to a "pseudo" (or physical) cross-linking effect in the graft copolymer. Nitrile groups have significant dipole moments and are highly associated in the liquid state. Entanglement of the polyacrylonitrile chains and association of stereoregular regions of the chains could be sufficient to decrease the

TABLE V
Solubility in Dimethyl Sulfoxide (DMSO) for Polyacrylonitrile–Grafted Granular and Gelatinized Starch

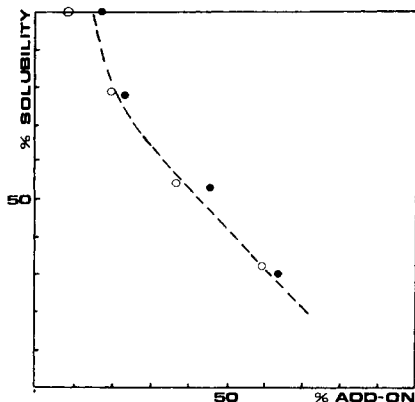| | Solubility in DMSO |
Starch (g)/AN (mL)	(%)
Granular starch	
10/2.5	100
10/5	79
10/10	54
10/20	32
Gelatinized starch	
10/2.5	100
10/5	78
10/10	53
10/20	30

Fig. 1.   The correlation between percent add-on and solubility in DMSO at 348 K for starch–graft-polyacrylonitrile. (○) Granular starch used as substrate; (●) gelatinized starch used as substrate.

solubility of the copolymer from that observed for starch and polyacrylonitrile separately. Hydrolysis of the starch backbone of the graft copolymer should disrupt this geometric preorientation. Dissolution in an appropriate solvent such as DMF or DMSO should therefore be possible. The possibility
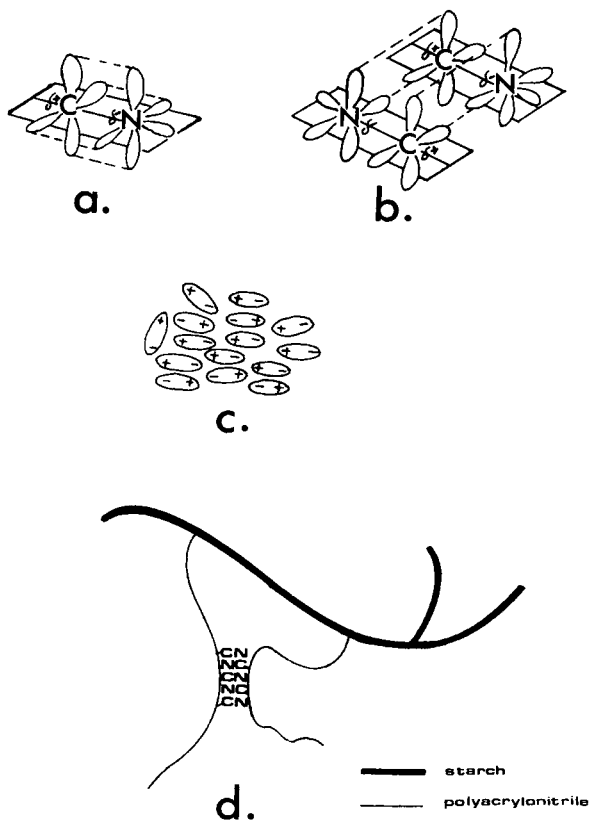

Fig. 2.   (a) Polarization in a single nitrile group. (b) Dipolar interaction between nitrile groups. (c) Ordinary structure of liquid resulting from dipole interactions. (d) Starch–g-polyacrylonitrile with regions of dipolar interactions between nitrile groups.

of hydrogen bonding between nitrile groups in side chains and hydroxyl groups in the substrate may also contribute to the decreasing solubility observed with increasing contents of synthetic polymer. This effect would likewise be disrupted by the hydrolysis of the starch backbone.

Alkaline Hydrolysis

Starch–g-polyacrylonitrile samples, with gelatinized starch as substrate, were saponified in 1% aqueous sodium hydroxide solution at 363 K. The sharp color change from red to light yellow after approximately 2 h was taken as an indication to stop the hydrolysis. The hydrolyzed starch–graft copolymer was precipitated by pouring into methanol, washed to neutrality, and dried at room temperature overnight. Essentially no nitrile functionality was detected in infrared (IR) absorption spectra. The retention of water was determined for samples with various percentages of add-on (Table VI). The water retention value increased linearly with increasing percent add-on.

If the starch moiety is hydrolyzed to glucose and other water-soluble carbohydrates, the water retention of the remaining saponified polyacrylonitrile branches increases by a factor of 3 (e.g., from 720 to 2300 for the sample with 45% add-on). This product was not soluble in water, although it should have been if it had been linear or branched. Polyacrylonitrile from Polysciences, Inc., was saponified under the same conditions as the graft copolymer. Most of the hydrolyzed product was totally water-soluble. The insoluble fraction did not swell at all in water. This indicates that the grafted branches on hydrolyzed starch–g-polyacrylonitrile are slightly cross-linked. These cross-links may arise from incompletely hydrolyzed structures between adjacent polyacrylonitrile chains formed during the saponification.
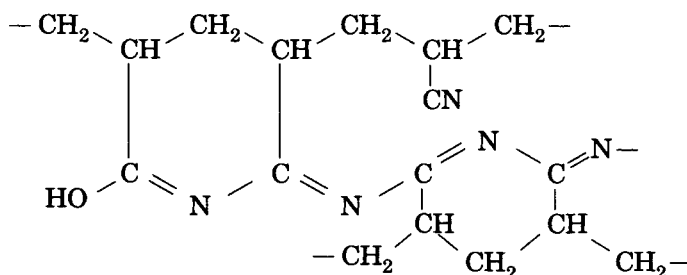

TABLE VI
Water retention (WRV) for Hydrolyzed Starch–Graft–Polyacrylonitrile with Gelatinized Starch as Substrate and Different Add-on Percentages

Starch (g) AN (mL)	Add-on (%)	Grafting ratio (%)	WRV[a] (g/g)
10/2.5	16	19	249
10/5	23	30	317
10/10	45	82	770
10/20	63	173	1061

[a] In grams of H_2O per gram dry modified starch.

The removal of the starch backbone, which has only a minor retention capacity, should result in a corresponding increase in retention capacity. For the sample with 45% add-on, the starch moiety is approximately 50% by weight of the total weight. The acid hydrolysis would thus result in an approximate twofold increase in the retention capacity. The observed increase was a factor of 3. Hydrogen bonds between carboxylate and amide groups in the side chains and hydroxyl groups on the starch backbone are likewise destroyed during the acid hydrolysis. The net effect of the acid hydrolysis would therefore probably be less restrictions and would give an expansion of the slightly cross-linked polymer network. This would also result in an increased retention capacity.

CONCLUSIONS

The increased conversion with increasing amounts of monomer charged, as observed in this work, is expected and is a result of the concentration effect on the rate of propagation. The accessibility of starch for grafting is enhanced when gelatinized starch is used as substrate. This explains the observed increase in conversion. Autoacceleration of the polymerization, the "Trommsdorf–Norrish gel effect," is operative for polymerization in gels such as the gelatinized starch–water system. This is the explanation for the higher molecular weight of the grafts on gelatinized starch as compared with that of the grafts on granular starch.

The solubility of starch–g-polyacrylonitrile in DMSO at 348 K decreases with increasing content of grafted synthetic polymer and is independent of the molecular weight of the grafts and the state of the starch substrate. There are three possible explanations, and these probably coexist in this system:

1. Cross-linking, due to a small extent of bimolecular termination between propagating chains
2. "Pseudo" cross-linking, due to regions of dipole interactions between adjacent polyacrylonitrile chains and entanglement of polyacrylonitrile side chains
3. Hydrogen bonding between nitrile groups in side chains and hydroxyl groups on the substrate

Saponification of the graft copolymer results in a product with a high water-retention capacity. Acid hydrolysis of the starch backbone, which has only a minor retention capacity, gives saponified polyacrylonitrile chains. These are not soluble in water as they should be if they were linear or branched. The retention capacity is increased by a factor of 3. The insolubility in water is probably due to cross-links of incompletely hydrolyzed structures between adjacent polyacrylonitrile chains formed during the saponification. The increased retention capacity is probably due not only to the removal of the "nonabsorbing" part of the copolymer, but also to fewer restrictions and an expansion of the slightly cross-linked polymer network.

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