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Graft polymerization of acrylonitrile onto spherocrystals formed from jet cooked cornstarch☆

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Abstract

Ceric ammonium nitrate-initiated graft polymerizations of acrylonitrile (AN) onto spherocrystals formed in slowly-cooled solutions of jet-cooked cornstarch yielded graft copolymers containing higher percentages of grafted polyacrylonitrile (PAN) than comparable polymers prepared from granular cornstarch. Weight percentages of PAN in grafted spherocrystals, prior to extraction with dimethylformamide to remove ungrafted PAN, were over 60% when 2.0 g of AN per gram of polysaccharide was used, and were about 55% with 1.5 g of AN. Copolymers prepared from the small (toroidal) and large (spherical) spherocrystals contained similar amounts of grafted PAN. Molecular weights of PAN in grafted spherocrystals were higher by about a factor of six than the PAN molecular weight in grafted granular cornstarch. The calculated number of anhydroglucose units separating each PAN graft was also higher for the spherocrystal graft copolymers, indicating that the higher percentage of grafted PAN in the spherocrystal polymers (relative to grafted granular cornstarch) was due to the higher molecular weight of grafted PAN and not to a greater number of grafts on the starch backbone. Gross morphologies of the cornstarch granules and spherocrystals used as starting materials were maintained after graft polymerization. Moreover, the PAN particles remaining after starch was removed by acid hydrolysis were similar in appearance to their respective graft copolymers. PAN-grafted cornstarch granules and PAN-grafted spherocrystals both exhibited birefringence patterns similar to those of the un-grafted starting materials, although the patterns were less clear. Birefringence patterns of PAN particles remaining after removal of the starch moiety were also similar. X-ray diffraction patterns of PAN-grafted spherocrystals were similar to those of the un-grafted starting materials; however, the major amylose reflections of the 6_1 V-helical pattern occurred at slightly higher angles, and the amylose peak intensities were smaller. When ethanol was used to wash the PAN-grafted large (spherical) particles, the 7_1 V-helical pattern was converted to the 6_1 V-helical pattern exhibited by the PAN-grafted small (toroidal) particles.

Keywords: Starch; Amylose; Polyacrylonitrile; Graft copolymer; Spherocrystal; Crystallite

1. Introduction

Steam jet cooking is a rapid and continuous process that has been used for decades to prepare aqueous starch solutions for industrial applications (Klem & Brogley, 1981). As part of a continuing research program on starch utilization, we are studying new starch-based compositions prepared by jet cooking mixtures of starch with non-starch materials, such as natural gums, fatty acids, polymers and lipids. In the course of these investigations, we have observed the formation of crystalline particles (spherocrystals or crystallites) in dilute solutions of jet cooked cornstarch, when these solutions were allowed to cool slowly. This particulate material is different in both size and morphology from retrograded amylose, and is not formed when jet cooked starch solutions are cooled rapidly.

Crystalline aggregates of this general type have been described previously by (Davies, Miller, and Procter (1980)). These authors used the term 'high temperature retrogradation' to describe these particles and have presented evidence that they result from crystallization of helical inclusion complexes formed from amylose

☆ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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and native lipid material normally present in cereal starch granules. In our earlier study (Fanta, Felker, & Shogren, 2002), we confirmed this conclusion and determined that the particulate material is actually a mixture of two birefringent species that are uniquely different in both size and morphology. Scanning electron microscopy (SEM) images showed that the smaller-sized particles were disc- or torus-shaped and often exhibited spiral surface striations. The larger particles were approximately spherical in shape, and had rough surface textures. X-ray powder diffraction patterns of the small particle fraction matched patterns previously reported for the 6_1 amylose V-helical complex in the hydrated form. In contrast, diffraction patterns for large particles suggested a 7_1 V-helical conformation for amylose. In a recent publication, Heinemann and coworkers (Heinemann, Escher, & Conde-Petit, 2003) described spherulites formed from potato starch-lactone inclusion complexes. Light micrographs published by these authors were similar in appearance to micrographs of our large-particle cornstarch-based material. Ziegler and coworkers have also studied spherocrystalline particles formed from heated starch dispersions (Nordmark & Ziegler, 2002a,b; Ziegler, Nordmark, & Woodling, 2003).

Graft polymerizations of acrylonitrile (AN) onto these crystalline particles were carried out as part of our investigation of possible end-use applications for these materials. AN was chosen for this study because it graft polymerizes efficiently onto both granular- and gelatinized starch with ceric ammonium nitrate (CAN) initiation (Fanta, 1996; Fanta and Doane, 1986). It was shown previously that graft polymerization does not lead to gross changes in the morphology of individual starch granules. The outward appearance of the grafted starch granules was also retained after the starch moiety was removed by acid hydrolysis (Brockway & Seaberg, 1967; Fanta, Baker, Burr, Doane, & Russell, 1973; 1977). In the present study, our major objective was to determine whether graft polymerizations of AN could be carried out on these spherocrystalline materials, despite their high levels of crystallinity and the presence of complexed native lipid. We also wished to determine whether the unique morphology and birefringence of these particles would be maintained after graft polymerization and after the starch component had been removed from the polyacrylonitrile (PAN)-grafted material by acid hydrolysis.

2. Materials and methods

2.1. Materials

Normal, unmodified food grade cornstarch was obtained from A.E. Staley Mfg. Co., Decatur, IL. Percent moisture was calculated from loss in weight after vacuum-drying accurately weighed starch samples at 100 °C. Starch weights are given on a dry weight basis. Acrylonitrile (99 + %, inhibited with 35–45 ppm monomethyl ether hydroquinone) was purchased from Aldrich Chemical Co., Inc., Milwaukee, WI, and was used as received. CAN (Certified A.C.S.) was purchased from Fisher Scientific, Fair Lawn, NJ, and was used as received. The PAN sample used for X-ray diffraction and birefringence (MW 485,000) was purchased from Polysciences, Inc., Warrington, PA.

2.2. Jet cooking of starch and isolation of spherocrystals

Spherocrystalline material was isolated from slowly-cooled solutions of jet cooked cornstarch as described earlier (Fanta et al., 2002). Undried mixtures of spherocrystals were fractionated with respect to particle size by allowing water dispersions to partially settle, leaving the smaller particles in suspension. Light microscopy was used to monitor the progress of this fractionation procedure. The small-particle fraction also contained minor amounts of endosperm protein fragments. The presence of this protein impurity was shown by infrared spectroscopy, selective staining with toluidine blue, and a nitrogen content of 1%. Commercial cornstarch normally contains traces of protein, and these small protein particles become concentrated in the small-particle spherocrystal fraction due to similarities in settling rates. Attempts to cleanly separate protein particles from spherocrystals were unsuccessful. Little or no protein was detected in the large-particle fraction.

2.3. Graft polymerization

One gram of freeze-dried spherocrystals in 25 ml of water was stirred and sparged with a slow stream of nitrogen for 1 h. Alternatively, an aqueous dispersion of spherocrystals of known concentration was diluted with water to give 1.00 g (dry basis) in 25 ml of water. The temperature was adjusted to 25 °C, and either 1.5 or 2.0 g of acrylonitrile was added. The mixture was stirred for 30 min to dissolve acrylonitrile, and a solution of 0.0337 g of CAN in 0.9 ml of 1 N nitric acid was added. This weight of CAN corresponds to one mole of Ce^{+4} per 100 glucopyranose units of starch. The mixture was stirred for 2 h, and the graft copolymer was separated by filtration. The polymer was washed with water and dried at 50 °C under vacuum.

Ungrafted PAN was extracted from graft copolymers by stirring about 0.25 g of polymer with excess dimethylformamide (DMF) overnight at room temperature. Three extractions with DMF were carried out. Extracted graft copolymers were washed with 95% ethanol to remove DMF, and the polymers were then vacuum-dried.

Percent PAN, by weight, in graft copolymer samples was calculated from the gain in weight of starch after graft polymerization. PAN content was also calculated from percent nitrogen, as determined on a Perkin Elmer 2400 Series II Dumas-type elemental analyzer. Approximately 2 mg of material was used for each nitrogen analysis, and the instrument was calibrated with an acetanilide standard.

Nitrogen analyses were carried out in duplicate, and the results were averaged. Standard deviations of replicate determinations varied from 0.01 to 0.21% N.

2.4. Isolation of PAN grafts and determination of intrinsic viscosity

A stirred mixture of 1 g of graft copolymer in 50 ml of 0.5 N hydrochloric acid was heated under reflux for 3 h. Grafted PAN remaining after acid hydrolysis was separated by filtration, washed with water and ethanol, and dried at 50 °C under vacuum. FTIR spectra showed no residual starch. Intrinsic viscosities of PAN samples were measured in DMF solution at 25 °C with a Schott (Hofheim, Germany) AVS 360 automated intrinsic viscosity measurement instrument. Molecular weights were calculated from the equation: $[\eta]$ (dl/g) $= 3.92 \times 10^{-4}\ M_n^{0.75}$ (Onyon, 1959).

2.5. Scanning electron microscopy

PAN-grafted samples used for SEM were not extracted with DMF. Aqueous dispersions of polymer (about 20 μl) were added to 20 ml of absolute ethanol, and the polymers were allowed to settle. Settled solids were washed with ethanol and then critical point dried on aluminum stubs using supercritical CO_2. Dried specimens were sputter coated with gold–palladium and examined and photographed with a JEOL 6400 V scanning electron microscope.

2.6. Birefringence

Samples were dispersed in water, placed on a glass slide, and a coverslip applied. Birefringence images were photographed with Polaroid #57 film using crossed polarizing filters and a Zeiss bright field light microscope (Carl Zeiss, Inc., Thornwood, NY). PAN-grafted samples used for birefringence studies were not extracted with DMF.

2.7. X-ray diffraction

X-ray diffraction was carried out as described previously (Fanta et al., 1999). Samples were equilibrated at 23 °C and 45% relative humidity for 2 days prior to analysis. PAN-grafted samples used for X-ray diffraction studies were not extracted with DMF.

3. Results and discussion

3.1. Synthesis and characterization of graft copolymers

Results of CAN-initiated graft polymerizations of acrylonitrile onto an un-fractionated mixture of large- and small-particle spherocrystals, isolated from jet cooked, normal dent cornstarch, are illustrated in Table 1. Results obtained from similar graft polymerizations onto granular, uncooked cornstarch are also shown for comparison. The amount of AN used was either 2.0 or 1.5 g per gram of polysaccharide. Graft polymerizations onto spherocrystals were carried out with aqueous dispersions that had never been dried and also with freeze-dried material. Weight percent PAN in these graft copolymers was calculated from the weight gain of the polysaccharide after graft polymerization and also from the percent nitrogen in the polymer. Values for % PAN obtained by these two methods agreed to within ±2%.

A portion of each graft copolymer was extracted with DMF at room temperature to remove ungrafted PAN homopolymer. These extractions removed 3.7–15.4% of the total polymer, by weight. FTIR spectra showed that some polysaccharide was also extracted along with ungrafted PAN, and calculations from nitrogen analyses showed that the PAN content of these DMF-soluble fractions was 80.8–89.5%. Due to the small amounts of sample extracted, relative amounts of ungrafted PAN versus DMF-soluble starch-*g*-PAN in these fractions was not determined.

Table 1
Graft polymerization of acrylonitrile onto an unfractionated mixture of spherocrystals comparison with granular cornstarch

No.	Starting material	g AN[a]	Wt % PAN, before DMF extraction		DMF insoluble fraction		DMF soluble fraction	
			From wt.gain	From % N	% of Total	Wt % PAN[b]	% of Total	Wt % PAN[b]
1	Granular cornstarch	2.0	51.2	49.7	96.3	49.2	3.7	– [c]
2	Spherocrystals, not dried	2.0	63.0	63.3	84.6	58.0	15.4	80.8
3	Spherocrystals, freeze dried	2.0	61.8	64.5	88.6	61.6	11.4	89.5
4	Granular cornstarch	1.5	44.4	43.8	96.2	41.5	3.8	– [c]
5	Spherocrystals, not dried	1.5	55.5	55.5	89.7	50.4	10.3	86.3
6	Spherocrystals, freeze dried	1.5	54.3	57.7	91.8	51.3	8.2	88.6

[a] Grams of acrylonitrile per gram of polysaccharide.
[b] Calculated from % nitrogen.
[c] Not determined.

Weight percentages of PAN in grafted spherocrystals prior to DMF extraction were over 60% when 2.0 g of AN per gram of polysaccharide was used, and were about 55% with 1.5 g of AN. As expected, PAN contents were somewhat lower after PAN homopolymer was removed. With both 2.0 and 1.5 g of AN, the spherocrystals yielded graft copolymers with higher PAN contents than granular cornstarch.

Large- and small-particle spherocrystals could be separated by taking advantage of their differences in settling rates from water dispersions. Graft polymerizations were then carried out on the individual freeze-dried fractions (Experiments 1 and 2, Table 2). Graft copolymers obtained from the two spherocrystal fractions had similar PAN contents, and values for weight % PAN were not greatly different than those observed for the spherocrystal mixtures in Table 1. For entries 3 and 4 in Table 2, graft polymerization was first carried out with an unfractionated mixture of spherocrystals, and the resulting graft copolymer was then separated into its two component fractions after the polymerization was complete. PAN contents of the two graft copolymer fractions were also similar in this experiment, where the two types of spherocrystals were allowed to compete in the same reaction vessel for monomer and initiator. DMF extractions were not carried out in these latter two experiments because of the small quantities of graft copolymer fractions isolated.

Hydrolysis with refluxing HCl was used to remove starch from graft copolymers prepared from granular cornstarch (No. 4, Table 1), small (toroidal) spherocrystals (No. 2, Table 2) and large (spherical) spherocrystals (No. 1, Table 2), and the molecular weights of PAN grafts were then calculated from intrinsic viscosities in DMF solution. The results are shown in Table 3. Graft copolymers not extracted with DMF were used for acid hydrolyses, because DMF-extracted polymers were not available in sufficient quantities. Grafting frequencies, expressed as the average number of anhydroglucose (i.e. glucopyranose) units per PAN graft, were then calculated from the weight percentages of PAN in these graft copolymers and the molecular weights of grafted PAN. Table 3 shows that the molecular weights of PAN in graft copolymers obtained from the two types of spherocrystals were not greatly different, and were higher by about a factor of six than the molecular weight of grafted PAN in granular cornstarch. Also, the calculated number of anhydroglucose units per PAN graft was higher for the two spherocrystal graft copolymers, indicating that the PAN grafts were more widely separated on the starch backbone in these two polymers. The higher percentage of grafted PAN observed in grafted spherocrystals, compared to grafted granular cornstarch, is therefore due to the higher molecular weight of grafted PAN and not to the formation of a greater number of free radical graft sites. The reduced number of graft sites in these spherocrystal products, relative to granular cornstarch, could be due to the high levels of crystallinity in these spherocrystals as well as to the presence of complexed native lipid.

Table 2
Graft polymerization of acrylonitrile (AN) onto spherocrystal fractions (1.5 g AN per g polysaccharide)

No.	Spherocrystal fraction	Wt. % PAN[a] before DMF extraction	DMF insoluble fraction	
			% of Total	Wt. % PAN[a]
Graft polymerization carried out on freeze dried spherocrystal fractions				
1	Large (spherical)	62.2	91.6	58.3
2	Small (toroidal)	58.8	90.6	55.5
Graft copolymer fractionated after polymerization				
3	Large (spherical)	56.8	–[b]	–[b]
4	Small (toroidal)	54.1	–[b]	–[b]

[a] Calculated from % nitrogen.
[b] Not determined, due to insufficient material.

Table 3
Molecular weights of grafted PAN, and calculated grafting frequencies of graft copolymers

Starch-g-PAN sample[a]	Grafted PAN remaining after starch hydrolysis		Grafting frequency, AGU/graft[c]
	[η], dl/g	MW[b]	
From granular cornstarch (No. 4, Table 1)	1.63	67,000	530
From small toroidal spherocrystals (No. 2, Table 2)	6.38	413,000	1790
From large spherical spherocrystals (No. 1, Table 2)	6.07	386,000	1450

[a] Samples not extracted with DMF.
[b] Calculated from: $[\eta]$ (dl/g, DMF, 25 °C) $= 3.92 \times 10^{-4} M_n^{0.75}$ (Onyon, 1959).
[c] Average number of anhydroglucose (i.e. glucopyranose) units per PAN graft.

3.2. SEM

Fig. 1 shows SEM images of (A) cornstarch granules, (D) a mixture of small (toroidal) and large (spherical) spherocrystals used in graft polymerization studies, polysaccharide-*g*-PAN copolymers prepared from the above two starting materials (B and E, respectively), and the PAN particles remaining after removal of starch from the two graft copolymers by acid hydrolysis (C and F, respectively). Although images of graft copolymers clearly showed the deposition of PAN on particle surfaces, the gross morphologies of both cornstarch granules and the two types of spherocrystals used as starting materials were maintained after graft polymerization. Moreover, the PAN particles remaining after acid hydrolysis were similar in appearance to their respective graft copolymers, even though the starch moiety was completely removed.

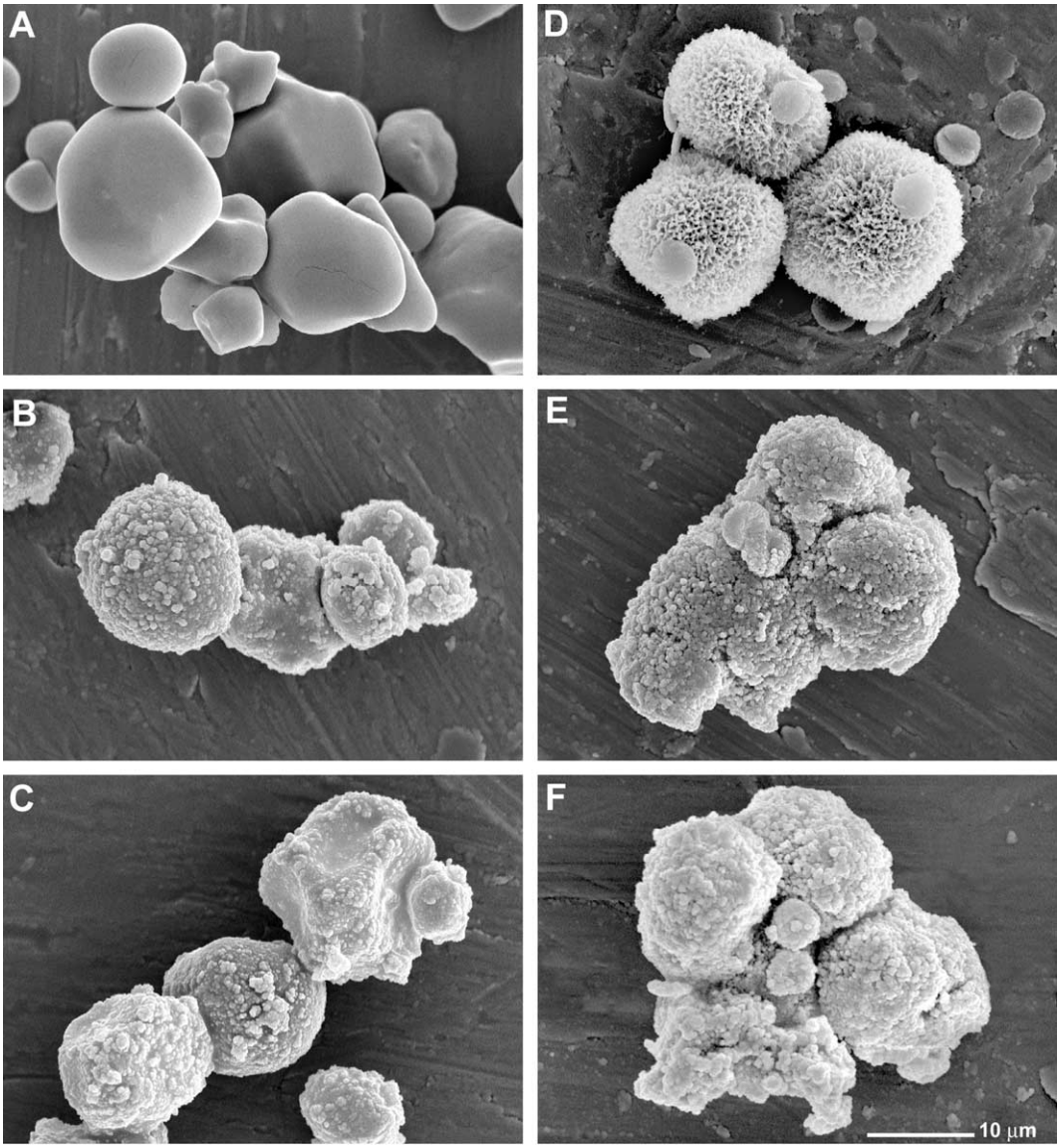

Fig. 1. SEM images of samples critical point-dried from ethanol. (A) Un-grafted cornstarch granules. (B) PAN-grafted cornstarch granules (No. 4, Table 1). (C) PAN remaining after removal of starch by HCl hydrolysis from a vacuum-dried sample of graft copolymer (B), above. (D) Un-dried spherocrystals used as starting materials in Table 1. (E) PAN-grafted product, prepared from undried spherocrystals under the same conditions as No. 5, Table 1. (F) PAN remaining after removal of starch by HCl hydrolysis from an undried sample of graft copolymer (E), above.

3.3. Birefringence

Images showing the birefringence of cornstarch, PAN-grafted cornstarch (product No. 4, Table 1), and the PAN particles remaining after removal of starch from the graft copolymer by acid hydrolysis are shown in Fig. 2. Ungrafted, granular cornstarch (A) showed the familiar 'Maltese cross' pattern. PAN-grafted cornstarch granules (B) and the granules of PAN isolated after acid hydrolysis (C) were also birefringent, and some of these granules showed similar Maltese cross patterns. In contrast to PAN granules isolated from starch graft copolymers, particles of PAN obtained from a commercial source were uniform in brightness and exhibited no distinct birefringence patterns (Fig. 2D).

Images showing the birefringence of large (spherical) spherocrystals, the same spherocrystals after graft polymerization of PAN (product No. 1, Table 2) and the PAN particles remaining after acid hydrolysis of the graft copolymer are shown in Fig. 3A–C, respectively. As observed with granular cornstarch, birefringence was retained after graft polymerization and also after removal of the starch moiety by acid hydrolysis. The clarity of the birefringence patterns of the graft copolymer particles (3B) was consistently less than that of the ungrafted spherocrystals (3A) or the PAN remaining after acid hydrolysis (3C). This suggests that addition of PAN to the spherocrysytal structure interferes with light transmission, which is restored when the starch moiety is removed. Images of PAN-grafted toroidal spherocrystals are not shown, because

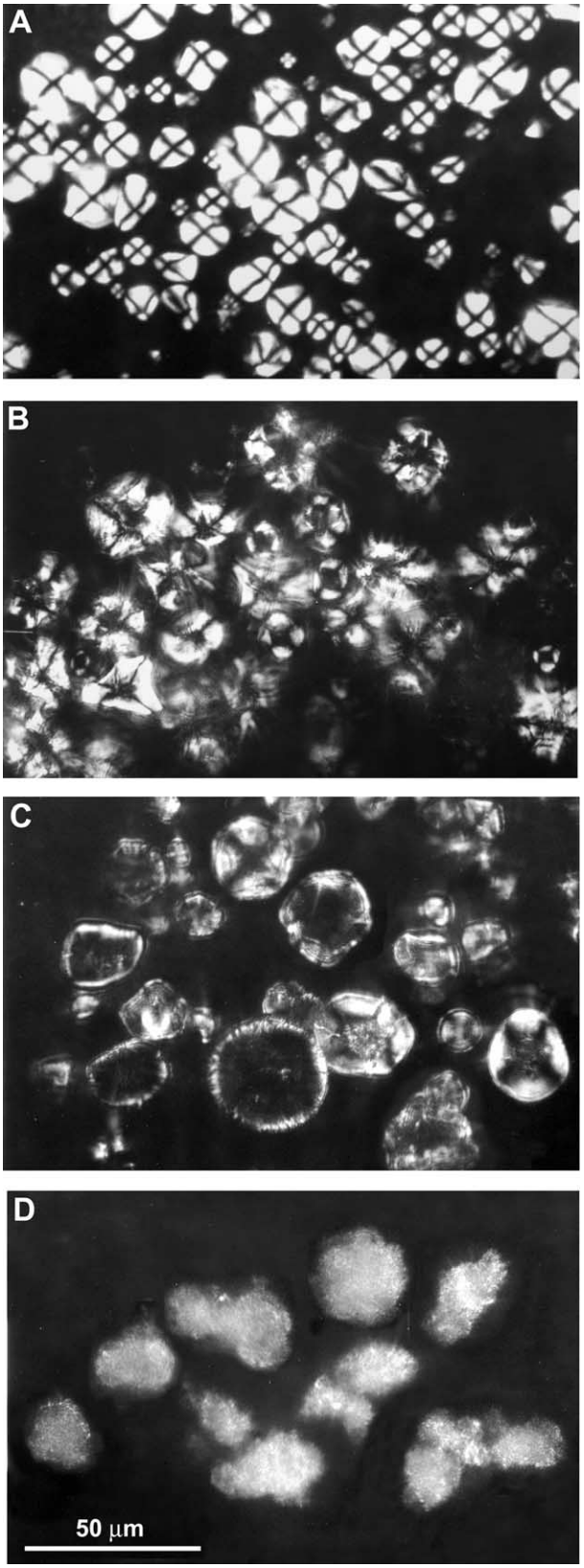

Fig. 2. Birefringence images photographed using crossed polarizing filters. (A) ungrafted cornstarch. (B) PAN-grafted cornstarch (No. 4, Table 1). (C) PAN grafts remaining after removal of starch from sample No. 4, Table 1, by acid hydrolysis. (D) PAN, MW 485,000 (from Polysciences, Inc.).

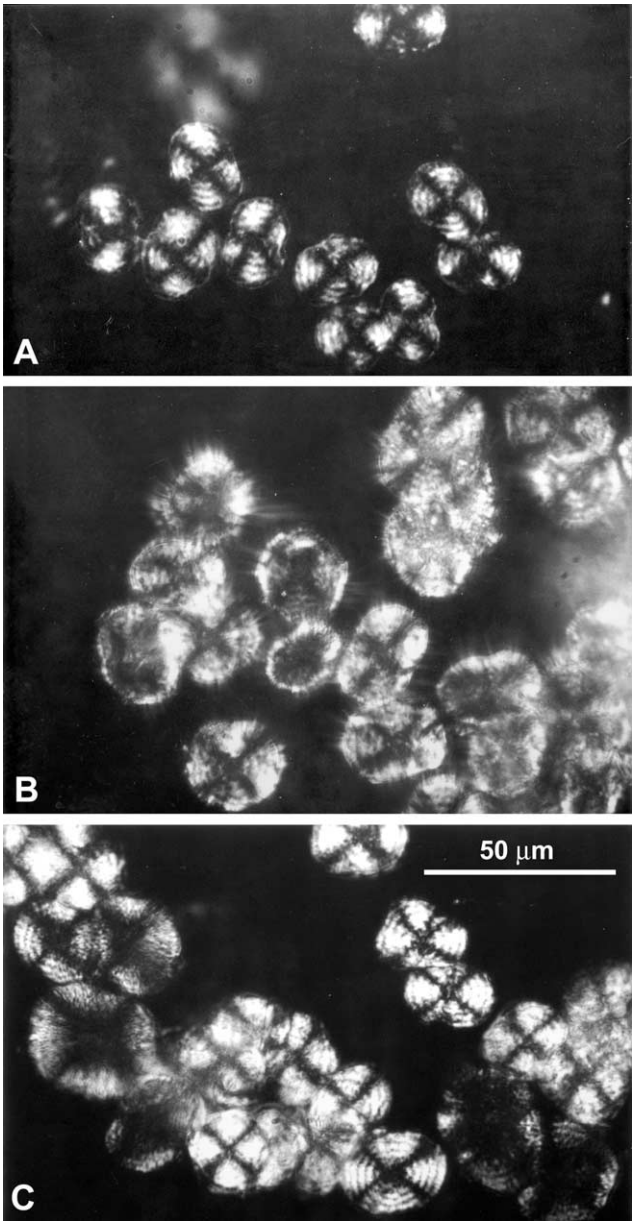

Fig. 3. Birefringence images photographed using crossed polarizing filters. (A) Freeze-dried sample of large (spherical) spherocrystals. (B) PAN-grafted sample of large (spherical) spherical spherocrystals (No. 1, Table 2). (C) PAN grafts remaining after removal of starch from sample No. 1, Table 2, by acid hydrolysis.

the details of their birefringence patterns are difficult to see due to the small particle size.

The fact that PAN-grafted starch granules and PAN-grafted spherocrystals exhibit birefringence patterns similar to those of the ungrafted starting materials indicates that graft polymerization does not completely disrupt the orientation of individual starch chains within the granule or spherocrystal. Furthermore, starch apparently acts as a template for grafted PAN on a molecular-scale as well as on a macro-scale; since the PAN particles that remain after removal of the starch moiety by acid hydrolysis also exhibit

similar birefringence patterns. Further studies will be needed to determine what factors are responsible for the variations in birefringence patterns exhibited by individual particles of PAN-grafted polymer and the PAN particles isolated after acid hydrolysis of starch.

3.4. X-Ray diffraction

X-ray powder diffraction scans for large (spherical)- and small (toroidal) spherocrystals and the PAN graft copolymers prepared from these materials are shown in Fig. 4. Freeze dried small (toroidal) particles prior to grafting (Fig. 4A) had major reflections at 7.4, 12.9, 19.8 and 22.4° two theta, indicative of the 6_1 V-helical complex in the hydrated form (Fanta et al., 2002). The X-ray pattern for these spherocrystals after grafting (Fig. 4C) was similar, except for a reflection for PAN (Fig. 4F) at 16.9° 2θ scattering angle. Also, the major amylose reflections occurred at slightly higher angles (7.7, 13.3 and 20.6° 2θ) and the amylose peak intensities were smaller. These scattering angles correspond to d spacings of 11.5, 6.6 and 4.3 Å and are close to those reported for the amylose 6_1 dehydrate structure (11.3, 6.5, and 4.3 Å) (Zobel, 1988). This contraction of the helix may be due to the dehydrating effect of the ethanol used to wash the material after grafting and a constricting effect of the PAN which may prevent the amylose helix from re-expanding on exposure to humid air. The X-ray pattern for freeze-dried large (spherical) particles prior to grafting (Fig. 4B) was similar to that seen previously (6.8, 11.8, 13.0, 18.1 and 20.5° 2θ) and was assigned the 7_1 amylose V-helical structure (Fanta et al., 2002). The diffraction pattern for the PAN-grafted large (spherical) particles, isolated by freeze drying (Fig. 1E) was similar except for the presence of the PAN peak and less intense amylose diffraction maxima. This suggests that the process of graft polymerization somehow reduces the crystallinity of the amylose complex. If ethanol is used to wash the PAN-grafted large particles before drying, the X-ray pattern is converted to that exhibited by the PAN grafted small particles, i.e. the 6_1 V-helical complex (Fig. 4D). This suggests that ethanol is able to penetrate the grafted amylose crystals and displace the native lipids which form the 7_1 helical complex. The 6_1 V-helical complex is then formed due to the small size and linearity of the ethanol molecule. Future research will address the finer details of where the PAN grafting occurs within the spherocrystals and native starch, the ease of extraction of native lipids from the amylose helix, and whether polymerization of AN can occur within the amylose helix.

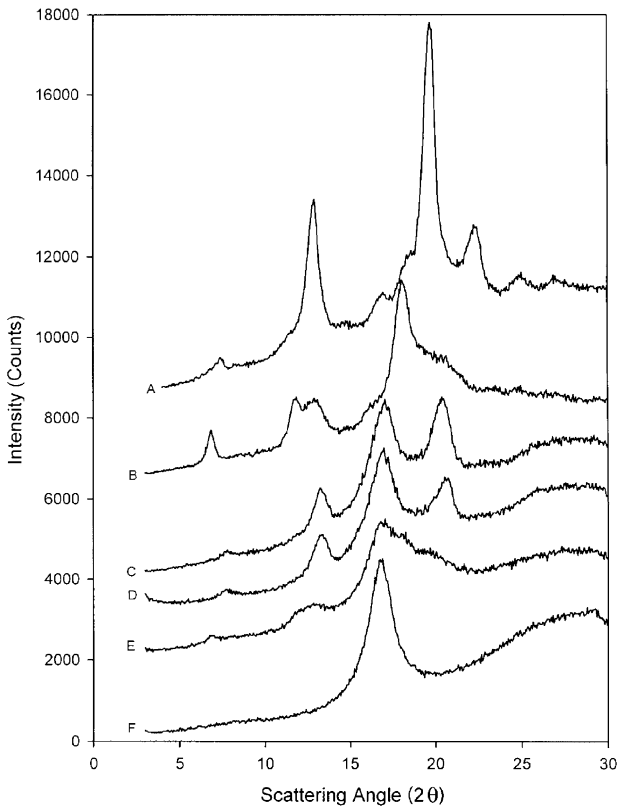

Fig. 4. X-ray powder diffraction scans of spherocrystals and their PAN-grafted copolymers. (A) Freeze-dried sample of small toroidal spherocrystals. (B) Freeze-dried sample of large (spherical) spherocrystals. (C) PAN-grafted sample of small (toroidal) spherocrystals (No.2, Table 2). Sample washed with ethanol and air-dried. (D) PAN-grafted sample of large (spherical) spherocrystals (No. 1, Table 2). Sample washed with ethanol and air-dried. (E) Freeze dried sample of PAN-grafted large (spherical) spherocrystals (No. 3, Table 2). (F) PAN, MW 485,000 (from Polysciences, Inc.).

4. Summary and conclusions

Ceric ammonium nitrate-initiated graft polymerizations of AN onto the small (toroidal)- and large (spherical) spherocrystals formed in slowly-cooled solutions of jet-cooked cornstarch yielded graft copolymers containing higher percentages of grafted PAN than comparable polymers prepared from granular cornstarch. Freeze dried as well as un-dried mixtures of spherocrystals were used, and graft polymerizations were also carried out using the two separated spherocrystal fractions. Weight percentages of PAN in grafted spherocrystals, prior to extraction with DMF to remove ungrafted PAN, were over 60% when 2.0 g of AN per gram of polysaccharide was used and were about 55% with 1.5 g of AN. Copolymers prepared from the small (toroidal)- and large (spherical) spherocrystals contained similar amounts of grafted PAN.

Molecular weights of PAN in grafted spherocrystals were higher by about a factor of six than the PAN molecular weight in grafted granular cornstarch. The calculated number of anhydroglucose units separating each PAN graft was also higher for the spherocrystal graft copolymers, indicating that the higher percentage of grafted PAN in the spherocrystal polymers (relative to grafted granular cornstarch) is due to the higher molecular weight of grafted

PAN and not to a greater number of grafts on the starch backbone. Fewer graft sites in these copolymers could be due to the highly crystalline nature of the spherocrystals, as well as to the presence of complexed native lipid.

SEM images of graft copolymers showed the deposition of PAN on particle surfaces; however, gross morphologies of the cornstarch granules and spherocrystals used as starting materials were maintained after graft polymerization. Moreover, the PAN particles remaining after starch was removed by acid hydrolysis were similar in appearance to their respective graft copolymers. PAN-grafted cornstarch granules and PAN-grafted spherocrystals both exhibited birefringence patterns similar to those of the un-grafted starting materials, indicating that graft polymerization does not completely disrupt the orientation of individual starch molecules within the granule or spherocrystal. Individual molecules of starch apparently act as templates for grafted PAN, since the PAN particles remaining after removal of the starch by acid hydrolysis exhibit similar birefringence patterns. Further studies are needed to identify factors responsible for the different birefringence patterns shown by the individual particles of PAN-grafted polymer and the PAN remaining after acid hydrolysis of starch.

X-ray diffraction patterns of PAN-grafted spherocrystals were similar to those of the un-grafted starting materials; however, the major amylose reflections of the 6_1 V-helical pattern occurred at slightly higher angles, and the amylose peak intensities were smaller. When ethanol was used to wash the PAN-grafted large (spherical) particles, the 7_1 V-helical pattern was converted to the 6_1 V-helical pattern exhibited by the PAN-grafted small (toroidal) particles.

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