

## Hydrolyzed Starch-Polyacrylonitrile Graft Copolymers: Effect of Structure on Properties\*

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### Synopsis

Three starch-polyacrylonitrile (S-PAN) graft copolymers containing ratios of S: PAN of 1:1.90, 1:1.16, and 1:0.64 were prepared by graft polymerization of acrylonitrile onto gelatinized starch. A fourth graft, made from granular starch, had an S: PAN ratio of 1:2.16. These grafts were hydrolyzed in potassium hydroxide under various conditions to give a series of products with varying amounts of carboxylic acid and amide groups. Maximum conversion of nitrile to carboxyl was 65%. Aqueous dispersions of the hydrolyzed S-PAN's at pH 7-8.5 were viscous, and, in general, their viscosities reflected the amount of PAN add-on, with the highest add-on giving the highest viscosity. Plots of the  $\eta/C$  versus  $C$  show that hydrolyzed S-PAN's from gelatinized starch behave as normal polyelectrolytes on dilution to low concentration but that S-PAN from granular starch does not.

### INTRODUCTION

A previous report<sup>1</sup> described the preparation and hydrolysis of a starch-polyacrylonitrile (S-PAN) graft copolymer consisting of one part PAN of molecular weight  $7.9 \times 10^5$  and one part starch. Hydrolysis under various conditions converted the 1:1 S: PAN preparation into a series of water-soluble polymers that varied in carboxyl and amide content. Aqueous dispersions of the hydrolyzed S-PAN's were highly viscous, with viscosity values ranging from 15,000 to 26,500 cp for 1% dispersions. The 1% dispersions retained considerable viscosity (e.g., 5000 cp) on addition of KCl to a level of 8%. These solution properties suggest that hydrolyzed S-PAN polymers have potential as industrial thickeners in various end-use applications.

To further exploit hydrolyzed S-PAN polymers and to gain insight into how their composition influences solution properties, S-PAN copolymers were prepared that contained different proportions of starch and PAN and PAN side chains of different average molecular weight. Each S-PAN was then subjected to a set of hydrolysis conditions to introduce various proportions of carboxyl and amide functionalities.

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Graft polymerization of acrylonitrile onto both granular and gelatinized starch was performed to assess how the physical state of the starch influenced solution properties of the hydrolyzed S-PAN.

## EXPERIMENTAL

### Preparation of S-PAN

Materials and methods of graft polymerization of acrylonitrile onto gelatinized wheat starch were as described previously<sup>1</sup> except for amounts of reagents (Table I). For the preparation with granular starch (graft D), starch was first swollen by stirring in water at 50°C for 1 hr and then cooled to 25°C before the reaction.

The crude graft copolymers were extracted with hot water and dimethylformamide (DMF) as described previously<sup>1</sup> to yield purified products from which PAN contents were determined.

### Isolation of PAN Side Chains

A portion of each S-PAN listed in Table I was treated by either one or both of the following methods to remove the starch portion.

**Acid Hydrolysis.** A 1–5% slurry of S-PAN graft copolymer in 1*N* HCl or H<sub>2</sub>SO<sub>4</sub> was heated under reflux conditions for 2 hr. The residue was isolated by filtration, washed thoroughly with water, and finally washed with methanol.

**Periodate.** This method of Gugliemelli et al.<sup>2</sup> consists of periodate oxidation of the starch followed by alkaline degradation.

Intrinsic viscosities (Table II) of the isolated PAN side chains were determined in DMF using a 25°C constant temperature bath and Cannon-Fenske tubes.

TABLE I  
Preparation of Starch-Polyacrylonitrile (S-PAN) Copolymers

Graft	Starch per 400 ml H <sub>2</sub> O, g	0.1 <i>M</i> Ce <sup>+4</sup> solution, ml	Acrylo- nitrile, ml	Yield, g		Ratio S: PAN <sup>b</sup>
				Crude	Purified <sup>a</sup>	
A <sup>c</sup>	28.8	14	95	90	70	1:1.90
B <sup>d</sup>	42.4	14.6	77.3	71	53	1:1.16
C	18	6.4 <sup>e</sup>	18.5	—	24.4	1:0.64
D <sup>f</sup>	28.8	14	95	92	81	1:2.16

<sup>a</sup> Crude grafts were extracted with 80°–90°C water and then with dimethylformamide.

<sup>b</sup> Calculated from nitrogen content of purified samples.

<sup>c</sup> Data reported in part before Division of Carbohydrate Chemistry at the 156th ACS Meeting, Atlantic City, N. J., 1968.

<sup>d</sup> Reference 1.

<sup>e</sup> Here 0.05*M* Ce<sup>+4</sup> was used.

<sup>f</sup> This preparation used granular starch, whereas the others used gelatinized starch.

## Alkaline Hydrolysis of S-PAN

Alkaline hydrolysis of the four grafts in Table I was carried out as reported earlier<sup>1</sup> under conditions which varied base concentration, temperature, and time. Each S-PAN was hydrolyzed under four sets of conditions to yield a series of products that varied in carboxyl and nitrogen contents (Table III).

TABLE II  
Isolation of PAN Chains

Graft	Method of starch removal <sup>a</sup>	Yield <sup>b</sup> , g		[ $\eta$ ]
		Found	Theory	
A	H	6.4	6.5	10.3
B	H	5.1	5.4	10.0
C	H	3.2	3.9	9.0
D	H	6.2	6.8	4.8
D	P	6.2	6.8	4.8

<sup>a</sup> H is acid hydrolysis method, and P is periodate method.

<sup>b</sup> Based on 10 g S-PAN.

TABLE III  
Alkaline Hydrolysis of S-PAN

Prepr.	KOH, wt-%	KOH: PAN	Temp., °C	Time, hr	Yield, <sup>a</sup> g	N, %	Carboxyl, %
Graft A							
A1	8.6	3.6	100	2	92	5.34	27.4
A2	8.6	3.6	80	3	95	6.10	26.6
A3	17.2	7.2	80	2	87	6.33	24.8
A4	3.4	1.4	80	2	113	7.97	20.2
Graft B							
B1	8.6	5.0	100	2	82	4.40	26.6
B2	17.3	10.0	100	2	86	4.81	22.2
B3	8.6	5.0	80	2	85	5.90	23.0
B4	4.3	2.5	80	3	88	6.06	21.1
Graft C							
C1	17.2	13.3	100	2	98	2.86	16.9
C2	8.6	6.7	100	2	110	3.53	18.2
C3	4.3	3.3	80	3	104	4.17	17.8
C4	8.6	6.7	80	2	104	4.52	17.6
Graft D							
D1	2.2	3.2	100	2	89	5.63	28.8
D2	17.2	6.6	80	2	90	5.78	25.2
D3	8.6	3.3	80	2	101	6.45	23.8
D4	4.3	1.6	80	2	104	7.10	21.4

<sup>a</sup> Expressed in grams per 100 g S-PAN; theory: graft A, 123; B, 119; C, 114; D, 124.

TABLE IV  
Viscosities of Hydrolyzed S-PAN Dispersions\*

Dispersion, % KCl, %	Viscosity, cp											
	A3	B2	C1	D2	A1	B1	C2	D3	A4	B4	C3	D4
1	26,000 <sup>b</sup>	15,000	9,200	15,500	34,000 <sup>b</sup>	19,000	11,900	16,600	58,000 <sup>b</sup>	26,500 <sup>b</sup>	16,200	25,000 <sup>b</sup>
1	12,000	9,400	5,400	—	17,800	11,000	5,500	—	2,000	9,800	5,800	—
2	10,000	5,800	3,000	1,240	12,720	8,900	3,600	600	600	6,800	4,000	115
4	7,200	4,800	2,300	660	6,300	7,000	2,500	360	270	2,400	2,600	ppt
0.5	15,000	7,500	4,800	9,900	17,800	10,900	6,600	8,600	28,500 <sup>b</sup>	15,000	9,000	10,100
0.25	7,000	4,200	2,800	3,900	10,200	5,450	3,800	3,300	15,400	9,400	5,200	1,600

\* Viscosity measurements were made at 30 rpm; dispersions had a pH of 7-8.5. See Table III for hydrolysis conditions (KOH concentration), and Table VI for composition of hydrolyzed S-PAN's.

<sup>b</sup> Extrapolated value.

The isolated side chains from grafts A through D were hydrolyzed in a manner closely resembling that used for the whole grafts. Carboxyl contents of the hydrolyzed PAN's ranged from 31% to 36%, and nitrogen contents ranged from 6% to 8%.

### Hydrolyzed S-PAN Dispersions

The hydrolyzed graft polymers are insoluble in water when isolated in their "free acid" state at pH 3 but are soluble in dilute base.

A convenient method for preparing a 1% dispersion is to weigh 1.0 g hydrolyzed S-PAN, suitably corrected for volatiles,<sup>1</sup> into an appropriate tared container. Fifty grams of water is added, and after slurring thoroughly, 1*N* KOH is added with stirring until the pH is 7-8.5. Sometimes it is necessary for the mixture to stand overnight before becoming completely dispersed. The pH is again checked and adjusted if necessary, and dilution is completed to bring final weight to 100 g. Lower concentrations are easily obtained by weighed dilutions of this 1% dispersion.

The effect of inorganic salts on the dispersions was determined by adding the appropriate weight of solid salt and observing changes in pH, phase, and viscosity.

### Viscosity Measurements

A Brookfield Synchro-Lectric Viscometer was used to make viscosity measurements of the various dispersions at 25°C and 30 rpm. Tables IV and V give viscosities of some hydrolyzed S-PAN and PAN dispersions at several concentrations with varying amounts of KCl.

## RESULTS AND DISCUSSION

### Preparation of S-PAN

The grafting of PAN onto starch using ceric ammonium nitrate for site initiation has been reported by several workers,<sup>3-5</sup> and the grafting reac-

TABLE V  
Viscosities of Hydrolyzed PAN Side Chain Dispersions\*

Dispersion, %	KCl, %	Viscosity, cp			
		A	B	C	D
1	0	18,400	13,200	6,200	1,920
	1	7,200	7,400		
	2	5,300	5,600		
	4	3,900	4,100		
0.5	0	7,800	5,400	2,400	920
0.25	0	3,600	2,700	1,000	472

\* Viscosity measurements were made at 30 rpm; dispersions had a pH 7-8.5. PAN'S hydrolyzed with 8.6% KOH.

tion need not be detailed here. Reaction conditions were selected to give copolymers with approximate S: PAN ratios of 1:2, 1:1, and 1:0.5. Use of starch-to-monomer proportions of 1:2.6, 1:1.45, and 1:0.83 afforded copolymers with S: PAN ratios of 1:1.90 (A), 1:1.16 (B), and 1:0.64 (C), respectively (see Table I). Crude products were extracted with hot water to remove any ungrafted starch and then with DMF to remove homopolymer. The DMF solubles constituted only 5–10% of the crude product, and their analysis indicated that they contained about 10% starch as well as PAN.

The three S–PAN grafts A, B, and C were prepared with gelatinized starch. The highly viscous polymerization media gave rise to high molecular weight grafted chains, most probably via the so-called "gel effect."<sup>6</sup> The polymerization medium for graft D was much less viscous because the starch was in granular form; consequently, this copolymer had lower molecular weight PAN chains as reflected by their lower intrinsic viscosity (see Table II).

### Alkaline Hydrolysis of S–PAN

As reported earlier,<sup>1</sup> alkaline hydrolysis of S–PAN grafts destroys all nitrile functionality detectable by infrared adsorption and gives rise to carboxylic acid and amide groups. Hydrolysis of each S–PAN under variable conditions afforded a range of products that differed in nitrogen and carboxyl contents (Table III). Assuming that PAN of the original grafts yields only poly(acrylic acid–acrylamide), the composition of each hydrolyzed S–PAN was calculated from carboxyl and nitrogen values (Table VI). The starch content of the hydrolyzed graft was obtained by adding acrylic acid and acrylamide percentages and subtracting the sum from 100. Comparison of this value with the theoretical starch content as calculated from the original S–PAN composition shows close agreement.

From Table VI it is readily seen that the maximum conversion of nitrile to carboxyl was only approximately 65%. This percentage agrees with a report<sup>7</sup> that cites cessation of hydrolysis of PAN at 70% conversion to carboxyl. The explanation proposed in the report was: "incomplete hydrolysis is believed due to steric and polar factors caused by hydrogen bonding between amide and neighboring carboxyl ions or between amide and neighboring carboxyl ions of different molecules." For hydrolyzed S–PAN's, the lowest conversion to carboxyl occurs when potassium hydroxide concentration is 3–4%. Increasing the concentration of base to 8.6% gives a higher conversion to carboxyl; however, further increases in the concentration of base do not increase carboxyl but actually lower values. Raising the temperature from 80° to 100°C at the 8.6% potassium hydroxide concentration increases conversion to carboxyl somewhat.

When starch was removed from the S–PAN's and the isolated side chains were hydrolyzed and analyzed for carboxyl and nitrogen, the PAN from graft A gave a product with 50% acrylic acid and 33% acrylamide;

TABLE VI  
Composition of Hydrolyzed Grafts

Hydrolyzed S-PAN	Acrylic acid, %	Acrylamide, %	Starch, <sup>a</sup> %	Amide/acid	Acrylic acid in side chain, %
Graft A (S: PAN 1:1.90)					
A1	44	27	29	0.61	62
A2	42	31	27	0.74	58
A3	40	32	28	0.80	55
A4	32	40	28	1.25	44
Graft B (S: PAN 1:1.16)					
B1	43	22	35	0.51	66
B2	36	24	40	0.67	59
B3	37	30	33	0.81	55
B4	34	31	35	0.91	52
Graft C (S: PAN 1:0.64)					
C1	27	16	57	0.59	65
C2	29	18	53	0.62	62
C3	29	21	50	0.72	57
C4	28	23	49	0.82	55
Graft D (S: PAN 1:2.16)					
D1	46	29	25	0.63	62
D2	40	29	31	0.72	58
D3	38	33	29	0.87	54
D4	34	36	30	1.06	49

<sup>a</sup> Starch was determined by difference; theory: A, 28%; B, 39%; C, 54%; D, 25%.

graft B, 58% acrylic acid and 35% acrylamide; graft C, 57% acrylic acid and 32% acrylamide; and graft D, 50% acrylic acid and 41% acrylamide. Thus only about 83–93% of the hydrolyzed PAN's can be accounted for on the acrylic acid–acrylamide basis. Since infrared studies clearly show no residual starch and no nitrile after hydrolysis, an additional explanation is required. A plausible explanation is that condensation occurs between acid and amide groups or two amide groups to form imide structures. The work of others<sup>8</sup> and preliminary spectral data of the hydrolyzed PAN's suggest that such groups are present. If one assumes that the nitrogen content of hydrolyzed PAN from graft B (6.87%) is derived from 26 wt-% acrylamide and 16 wt-% imide, 100% of the polymer can be accounted for. Further research is required to establish the existence of such structures and, if present, to determine what their effect is on solution behavior.

### Solution Behavior

Since aqueous dispersions of hydrolyzed S-PAN's are extremely viscous and since our studies required a large number of viscometric measure-

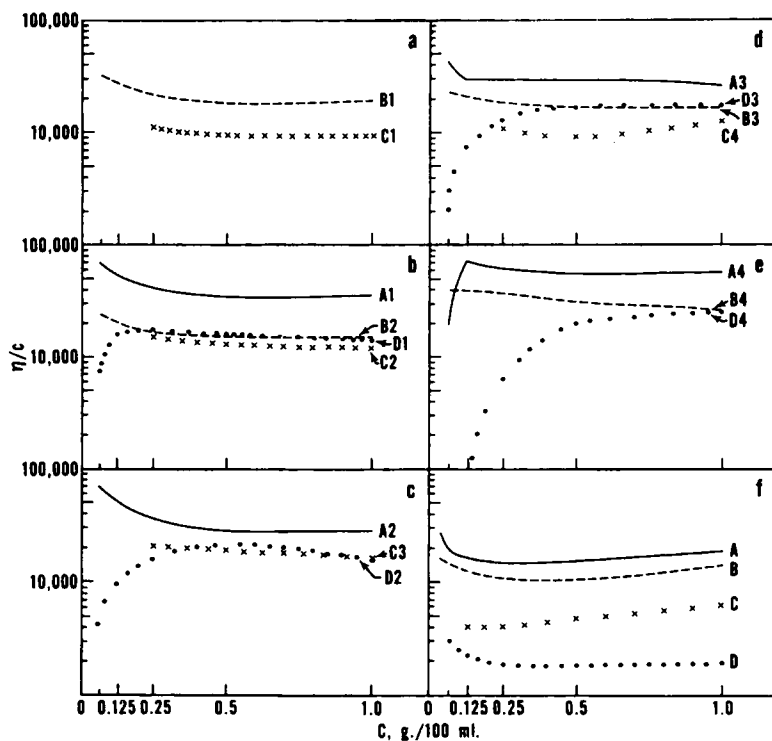


Fig. 1. Dilute solution viscosity for hydrolyzed starch-polyacrylonitrile (S-PAN) and for hydrolyzed side chains in aqueous solution. Composition of A1, B2, C3, etc. given in Table VI: (—) hydrolyzed S-PAN A, (---) hydrolyzed S-PAN B; (XXXX) hydrolyzed S-PAN C; (·····) hydrolyzed S-PAN D. Amide/acid range: (a) 0.51 to 0.59; (b) 0.61 to 0.67; (c) 0.72 to 0.74; (d) 0.80 to 0.87; (e) 0.91 to 1.25; (f) hydrolyzed side chains.

ments, a Brookfield viscometer was selected to expedite this work. Although such an instrument is intended for relative measurement only, plotting the viscosities, measured at 30 rpm, of the hydrolyzates of an individual graft and of the several grafts provided appropriate comparisons. Since the measured Brookfield viscosities were high, these values divided by concentration  $C$  were taken to be reasonable approximations of reduced viscosity ( $\eta/C$ ).

Plots of  $\eta/C$  versus  $C$  of hydrolyzed S-PAN's dispersed in dilute base show that in general they behave as typical polyelectrolytes<sup>9</sup> giving higher values at low concentration (Fig. 1a-e). Hydrolyzed PAN's give similar curves (Fig. 1f). Solutions of nonelectrolyte polymers give linear plots or gradually decreasing reduced viscosity on dilution. The behavior of polyelectrolytes has been attributed to changes in the volume of the polymer-solvent complex and to changes in the way polymer molecules coil because of change in repulsion of charges. With dilution, the screening effect of electrolytes diminishes and the repulsion between polymer



charges increases;<sup>10</sup> these changes result in greater extension of the molecule, which increases viscosity. Starch grafts with polyelectrolyte side chains may be doubly affected. The side chains themselves are extended by charge effects, and because the chains are attached to starch, repulsion between chains extends the starch molecule.

Although the hydrolyzed side chain from graft D behaves like those from grafts A, B, and C, the hydrolyzed S-PAN's from graft D (dotted lines) differ from the other hydrolyzed S-PAN's. The curves for graft D hydrolyzed S-PAN's show a downward slope unlike typical polyelectrolytes, even though there are a large number of charged side chains. This dissimilarity leads us to propose that graft D, prepared from granular starch, has its side chains highly localized. These charged side chains are locked so closely together in one area of the starch molecule that comparatively large segments of starch are left ungrafted. In a simple polyelectrolyte, dilution increases ionization which increases molecular extension. In a starch with polyelectrolyte grafts distributed over the starch molecule, dilution can be accomplished in the sense of chains moving away from each other by extension of the starch molecule. However, when starch is grafted so that the side chains are highly localized, dilution in effect cannot be accomplished; therefore, the increase in  $\eta/C$  at low concentration does not occur.

The curves in Figure 1 are grouped so that they have similar amide:acid ratios and so that the acrylic acid content of the side chains is similar. Comparison of the nearly linear part of curves of A1, A2, and A3 reveals that  $\eta/C$  decreases as acid content decreases. A similar observation is made for B1, B2, and B3. However, grafts A4 and B4, which have the least amount of acrylic acid in their respective series, exhibit the highest  $\eta/C$ . Perhaps the high level of amide in these two polymers serves to space the acid groups more efficiently.

The curves for hydrolyzed side chains arrange themselves in order of decreasing molecular weight of the original PAN chains. It is not known at this time whether the PAN chains suffer any change in size due to degradation or crosslinking during hydrolysis.

Comparison of the Brookfield viscosities of hydrolyzed S-PAN's A, B, and C at 1.0, 0.5, and 0.25% concentration (Table IV) reveals a good correlation between viscosity and percent PAN add-on. For hydrolyzed S-PAN's prepared under similar conditions of hydrolysis, graft A hydrolyzed S-PAN's have approximately three times the viscosity of C hydrolyzed S-PAN's, and B hydrolyzed S-PAN's have approximately twice the viscosity of C hydrolyzed S-PAN's, at any one concentration. Hydrolyzed S-PAN grafts prepared from gelatinized starch retain considerable viscosity when 1, 2, or 4% salt is added. The amount of viscosity retained correlates with per cent add-on as observed in the absence of salt. An exception is observed when 3-4% KOH is used for hydrolysis. But here, conversion to carboxyl for A is very low. Hydrolyzed graft D, which has short-chain localized grafts, was poor in salt tolerance.

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The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

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