Swelling and Rheology of Saponified Starch–g–Polyacrylonitrile Copolymers. Effect of Starch Granule Pretreatment and Grafted Chain Length

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Synopsis

A series of well-characterized starch–g–polyacrylonitrile (PAN) graft copolymers was prepared from corn starch which had been heated in water at temperatures up to 94°C to vary the extent of starch granule swelling and disruption. Graft polymerization onto gelatinized starch gave less frequent grafting of higher molecular weight PAN than comparable graft polymerizations onto ungelatinized starch. A graft copolymer was also prepared from gelatinized starch under high dilution conditions to give lower molecular weight grafted PAN and more frequent grafting. Graft copolymers were then saponified with sodium hydroxide to convert nitrile substituents to a mixture of carboxamide and sodium carboxylate. Saponified graft copolymers were only partially water soluble and consisted largely of highly swollen, insoluble gel, which was separated from solubles for the study of physical properties. Saponification mixtures were also dried to yield highly absorbent polymer films. With the exception of the graft copolymer prepared under high dilution conditions, the physical properties of saponified graft copolymers depended on whether or not the granules of starch were gelatinized before graft polymerization. Compared with saponified graft copolymers derived from ungelatinized starch, those prepared from gelatinized starch gave films that absorbed larger amounts of aqueous fluids. Also, the gel fractions from these saponified gelatinized polymers exhibited higher water swelling, lower shear modulus, and a lower reduced viscosity function (η/cQ). The saponified graft copolymer prepared from gelatinized starch under high dilution conditions more closely resembled those prepared from ungelatinized starch, suggesting that molecular weight of grafted PAN and the grafting frequency rather than starch granule pretreatment might be the most important factor which influences properties.

INTRODUCTION

Water-dispersible polyelectrolytes can be made from starch–g–polyacrylonitrile (PAN) copolymers by converting the nitrile groups to a mixture of carboxamide and carboxylate functionalities through alkaline saponification. The ratio of carboxamide to carboxylate may vary with saponification conditions but is typically[1] in the range of 1:1 to 1:2. The saponified graft copolymers are excellent thickening agents.[1] Moreover, aqueous polymer dispersions dry under ambient conditions to form films that will absorb several hundred times their weight of deionized water.[2] Water absorption level and rheological properties may be varied over fairly broad ranges to suit the end use application. Some of the variables that affect these properties are examined in this report.

The molecular weight of the grafted chains of starch–g–PAN copolymers depends on the physical state of the starch granules used in the grafting reaction. Copolymers made with gelatinized starch have grafted chains of higher molecular weight and lower grafting frequency than those made with granular starch.[3] The solvent swelling and rheological properties of the saponified starch–g–PAN co-

polymers might be expected to depend on these structural parameters, i.e., graft molecular weight and physical state of the starch. To date, no detailed study of these parameters has been made.

Saponified graft copolymers are largely in the form of an insoluble gel, and soluble polymer is a minor component of the mixture.[4] These polymers dispersed in water consist primarily of highly swollen gel particles, and when closely packed, with no free solvent present, they are highly viscous. A measure of how much the system can be diluted and still retain the closely packed state is the reduced concentration cQ, where c is the weight concentration of saponified graft copolymer in the suspension and Q is the swelling weight ratio in excess solvent of the same ionic strength μ. Swelling is strongly influenced by ionic strength in the gel. If cQ is equal to or greater than 1, the system is closely packed.

The viscosity η of the pastes depends on both c and μ. Empirical correlations have disclosed that a reduced viscosity function, η/cQ, is nearly constant, independent of both c and μ, if cQ is greater than 2, that is, if the gel particles are not too near their maximum swelling limit for the ionic strength of the system.[4] Values of η/cQ are greater for polymer gels with higher modulus, that is, more apparent crosslinking.

The number of apparent crosslinks in these gels is much too low to be determined analytically. In an ideal swollen rubber, the crosslink density can be estimated from the shear modulus.[5] Since saponified starch–g–PAN copolymers are elastic gels, we have also used shear modulus as a measure of apparent crosslink density. The modulus as obtained from rheology of their pastes correlated well with swelling and viscous properties in a previous series of saponified polymers differing in crosslink density.[6] The actual density of crosslinks in the gel may differ from the apparent density deduced from the modulus because of the two different components—starch and synthetic polymer—and the numerous free ends in the grafted PAN.

EXPERIMENTAL

Materials

Unmodified corn starch was Globe 3005 from CPC International. Acrylonitrile (Eastman practical grade) was fractionated at atmospheric pressure through a 15-in. Vigreux column, and a center cut was collected and stored in amber glass at 5°C. Ceric ammonium nitrate was Fisher Certified ACS grade.

Graft Polymerization

Ceric Initiation, Normal Concentration. A 500-ml resin flask was charged with 10.0 g (dry basis) starch and 167 ml water. The slurry was stirred and purged with a slow stream of nitrogen for 1 hr at 25°C. For the series of graft polymerizations employing swollen or gelatinized starch, starch slurries were purged with nitrogen for 30 min at 60°, 70°, or 87°–88°C or for 1 hr at 92°–94°C and were then cooled to 25°C. A solution of 0.338 g (6.17×10^{-4} mole) ceric ammonium nitrate in 3 ml $1N$ nitric acid was added; and after the mixture had stirred for about 10 sec, addition of 15.0 g (0.283 mole) acrylonitrile was made. Since the solubility of acrylonitrile in water under these conditions is slightly

over 7%, a small fraction of the monomer will initially be insoluble. However, this second organic phase will be rapidly depleted as soluble monomer is polymerized. The mixture was stirred under nitrogen for 2 hr and was then added to 7800 ml water. The resulting suspension was stirred for 2 hr, the pH was adjusted to 4, and the crude graft copolymer was isolated by centrifugation or filtration, washed with water and ethanol, and dried at 60°C in vacuo. Ungrafted PAN was removed from starch–*g*–PAN by repeated extraction with dimethylformamide (DMF) at room temperature.

Ceric Initiation, Highest Dilution. A 12-l. flask was charged with 7666 ml water and 7.5 ml concentrated nitric acid. The solution was purged with a slow stream of nitrogen, heated to 96°C over a period of 2.3 hr, and finally allowed to cool under nitrogen to 25°C. Acrylonitrile (50.0 g, 0.942 mole) was then added. A 500-ml resin flask was charged with 10.0 g (dry basis) starch (0.0617 mole anhydroglucose unit, MW 162), and 334 ml water. The stirred slurry was purged with a slow stream of nitrogen, heated for 30 min at 87°–90°C, and cooled to 25°C. A solution of 1.356 g (0.00247 mole) ceric ammonium nitrate in 20 ml 1*N* nitric acid was then added to the gelatinized starch slurry. After the mixture had stirred for 10 sec, the contents of the flask was added to the dilute acidified acrylonitrile solution and the resulting mixture stirred under nitrogen at 25°–30°C for 6.5 hr. The pH of the mixture was adjusted to 4.0 with dilute sodium hydroxide and the solid separated by centrifugation, washed with water and ethanol, and dried in a vacuum oven at 60°C. The yield of crude product was 21.9 g. Exhaustive extraction of this product with DMF gave 18.7 g DMF-insoluble starch–*g*–PAN, and 2.8 g ungrafted PAN was isolated from the DMF extract.

Cobalt-60 Initiation. A mixture of 8.0 g (dry basis) starch (0.0494 mole AGU), 12 g acrylonitrile, and 2 ml water in a 2-oz screw cap bottle was blended with a spatula and the resulting paste evacuated to 100 mm and repressured with nitrogen a total of four times. Assuming that the loss in weight due to evacuation was all acrylonitrile, the acrylonitrile remaining in the bottle now amounted to 11.68 g (0.220 mole). The bottle was placed in an ice bath for 30 min and was then irradiated with cobalt 60 to a total dose of 0.25 Mrad in a Gammacell 200 unit (Atomic Energy of Canada, Ltd.) having a dose rate of 0.796 Mrad/hr. During the irradiation time of 1131 sec, the temperature of the reaction mass reached a maximum of 77°C. After irradiation, the mixture was allowed to stand at ambient temperature for 2 hr and was then blended with water, diluted with water to a volume of 6 l., and stirred for 2 hr. The crude product was isolated by filtration, washed with water and ethanol, and dried in vacuo at 60°C. The yield was 17.0 g. Exhaustive extraction with DMF afforded 15.76 g starch–*g*–PAN and 0.98 g ungrafted PAN.

Graft Copolymer Characterization

A stirred suspension of 2.00 g starch graft copolymer in 150 ml 0.5*N* hydrochloric acid was heated under reflux for 1 hr, cooled, and filtered. The solid was suspended in fresh 0.5*N* hydrochloric acid and heated under reflux for 2 hr to complete the hydrolysis. The water-insoluble grafted PAN was separated by filtration, washed with water and ethanol, and dried in vacuo at 60°C. Carbohydrate content was less than 5%, by infrared. The weight per cent PAN in the graft copolymer (% add-on) was calculated from the loss in weight of the graft copolymer after removal of starch by acid hydrolysis.

The intrinsic viscosity of grafted PAN was determined in DMF solution using Cannon Fenske viscometers, and a molecular weight was then calculated from the equation

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

We recognize, of course, that values of $\overline{M}_n$ will be only approximate due to the polydispersity of our PAN samples. Grafting frequency, expressed as the average number of AGU per grafted PAN chain, was calculated from the % add-on and the molecular weight of grafted PAN.

Samples of grafted PAN were also dissolved in DMF containing 200 ppm lithium bromide and analyzed by gel permeation chromatography on a Waters Anaprep unit. Two 4 ft × $^3/_8$ in. columns packed with Styragel (10^7 and 10^4 Å) were used, the pumping rate was 1 ml/min, and the column temperature was 70°C. Molecular weights for PAN were calculated with the assumption that fractionation in the column, or count number, is directly related to the product of intrinsic viscosity and molecular weight for both the polystyrene standards and the PAN unknowns.[8]

Alkaline Saponification

A suspension of 1.00 g starch–g–PAN in 20 ml 0.5N sodium hydroxide in a 125-ml Erlenmeyer flask was heated on a steam bath until the mixture assumed a red color and thickened sufficiently to preclude settling on standing. The flask (loosely stoppered to permit escape of ammonia) was then placed in a 95°–100°C oven for 2 hr to complete the saponification. The mixture was dispersed in 400 ml water and the viscous dispersion dialyzed against distilled water for seven days, with frequent changes of water. Final pH of the dispersion was about 5.5–6.0, and the per cent solids was determined by freeze drying an accurately weighed sample. About 200 ml of the dispersion was poured onto a Teflon-coated sheet and dried to a film in a forced-air oven at about 35°C.

To prepare a saponified starch–g–PAN sample for rheological measurements at 0.76% solids, the graft copolymer was treated with 0.5N sodium hydroxide as described above. The saponification mixture was transferred with minimal dilution to a small dialysis bag and dialyzed against distilled water for seven days. The pH of the dialyzed dispersion was adjusted to 7.6 with 0.1N sodium hydroxide and the per cent solids determined by freeze drying a weighed portion of dispersion. The final polymer concentration was adjusted to 0.76% by addition of deionized water.

To determine percent solubles in the saponified and dialyzed dispersion, a weighed portion was diluted with water to 0.014% solids and the mixture shaken overnight at room temperature. The dilute dispersion was then filtered twice through fluted Whatman 54 paper and a weighed portion of clear filtrate freeze dried to determine its per cent solids. This value was then divided by 0.014 to give per cent solubles.

To determine what percentage of the dried film was water soluble, sufficient water was added to a weighed portion of film to give 0.014% solids. The mixture was shaken overnight at room temperature and then filtered twice through fluted Whatman 54 paper. per cent solids in the filtrate was determined by freeze drying, and this value was divided by 0.014 to give per cent solubles.

Fluid Absorbency

To determine water absorbency of the dried saponified graft copolymer film, an accurately weighed 20-mg sample of film was allowed to soak for 30 min in 50 ml deionized water. The swollen polymer was then separated from unabsorbed water by screening through a tared 325-mesh sieve which was 4.8 cm in diameter. The polymer on the sieve was allowed to drain for 20–30 min, and the sieve was then weighed to determine the weight of water-swollen gel. No correction for moisture content of the film (about 10–15%) was applied. Absorbency was calculated as grams water per gram polymer. A similar absorbency test was run in simulated urine (0.64 g $CaCl_2$, 1.14 g $MgSO_4 \cdot 7H_2O$, 8.20 g NaCl, 20.0 g urea, 1000 g deionized water) with about 75 mg polymer film.

Solubility and Swelling Power[9] of Starch

Dispersions of 10.0 g (dry basis) starch in 167 ml water were prepared in centrifuge bottles and stirred for either 1 hr at 25°C or for 30 min at 40°–41°C, 60°–61°C, or 70°–71°C. Dispersions were cooled to 25°C and centrifuged for 30 min at 3000 rpm (1800 × g). Supernatants were decanted and filtered through fluted Whatman 54 paper, and a weighed portion of each filtrate was freeze dried to determine per cent solubles. The water-swollen insoluble starch was weighed and the swelling power calculated from the following equation:

$$\text{swelling power} = \frac{\text{wt of swollen starch}}{10.0 - \text{wt of dissolved starch}}$$

Due to the high viscosity of the starch dispersion heated at 87°–89°C, swelling power and solubility at this temperature were determined with 5.0 g (dry basis) starch in 167 ml water.

Isolation of Gel Fraction of Saponified Graft Copolymers

The gel fraction was isolated by adding NaCl to the dialyzed saponified graft copolymer dispersion, to make 500 ml 1M NaCl per g polymer, and centrifuging for 20 min at 2500 rpm (1400 × g). The supernatant fluid containing soluble material was removed and the gel again suspended in 1M NaCl and centrifuged. The gel was then recovered as the acid form by resuspending in 0.3M HCl and centrifuging. Five more centrifugations, in HCl concentrations diminishing to 0.001M, washed the NaCl from the gel, which was then titrated with NaOH (to pH 7.6) to convert it to the sodium salt form and to determine titer of the gel material. A portion of this gel dispersion was dried (110°C, 18 hr) to determine weight of dry polymer and concentration for use in swelling and rheological tests.

Swelling Ratio of Gel

Swelling ratios Q of the gel fractions of saponified graft copolymers were determined in a Servall table centrifuge with type A (angle) head. Small clear plastic tubes containing suspensions of isolated gel (at pH 7.6) in water or appropriate NaCl solution were centrifuged for 90 min at 3600 rpm (1300 × g, approximately at the center of the suspension). Concentration of polymer gel was

adjusted to bring the volume of hydrated gel in the range of $\frac{1}{3}$ to $\frac{2}{3}$ of the suspension volume. The boundary between gel and supernatant fluid was detected by adding a drop of an ethanol suspension of corn starch into the tubes. In a few minutes, the starch grains outlined the slanted boundary between gel and fluid.

Rheological Characterization

Viscosity η and primary normal force, $P_{11} - P_{22}$, were determined in a Rheometrics Mechanical Spectrometer (Union, N.J.) with a cone-and-plate fixture of 36 mm radius.

RESULTS AND DISCUSSION

Synthesis and Characterization of Starch–g–PAN

Graft copolymers of starch and polyacrylonitrile were prepared by established procedures[3] (Table I); and in each preparation ungrafted PAN was removed from the graft copolymer by exhaustive extraction with DMF. A portion of each starch–g–PAN was then treated with refluxing 0.5N hydrochloric acid to depolymerize the starch moiety to glucose and other low molecular weight sugars, and the water-insoluble grafted PAN was then washed with water and dried. The weight per cent PAN present in starch–g–PAN (% add-on) could then be calculated from the loss in weight of the graft copolymer on acid hydrolysis. The acidic conditions used to hydrolyze starch have no effect on PAN.

The intrinsic viscosity of grafted PAN, which contained less than 5% carbohydrate by infrared analysis, was determined in DMF solution, and these values were used to calculate the molecular weights given in Table I. Grafting frequency, expressed as the average number of anhydroglucose units (AGU) per grafted PAN chain, was then calculated from % add-on and PAN molecular weight.

Although the molecular weights for grafted PAN calculated from intrinsic viscosities are useful for comparing polymers within a given series, the absolute values must obviously be considered as only approximations. Number-average molecular weights determined by gel permeation chromatography were significantly higher than those calculated from intrinsic viscosity, particularly for product 6. Reasons for these differences might lie in the nonroutine nature of molecular weight determinations of PAN in DMF solution[10,11] or in the uncertainty in $\overline{M}_n$ of a polydisperse polymer as determined by the Mark-Houwink relation. Molecular weight distributions ($\overline{M}_w/\overline{M}_n$) of the higher molecular weight PAN samples (700,000–800,000) were in the range of 3–4, whereas broader distributions (7–12) were found for lower molecular weight PAN.

Graft polymerizations were initiated by the reaction of starch with ceric ammonium nitrate, with the exception of product 2, which was prepared by the simultaneous cobalt-60 irradiation of starch and acrylonitrile in the presence of water.[12] The granules of starch, which are virtually insoluble in water at ambient temperatures, were subjected to varying degrees of swelling and gelatinization before graft polymerization. When heated in water, starch granules reversibly imbibe water with limited swelling until the gelatinization temperature, about

TABLE I
Synthesis and Characterization of Starch Graft Copolymers

Product no.	Starting materials					DMF[b] solubles, g	Wt, g	% Add-on[c]	Graft copolymer	
	Starch, g	Starch pretreatment	AN,[a] g	Water, ml	Initiator				Graft, MW[d]	Grafting frequency, AGU[e]/graft
1	10.0	none (25°C)	15.0	167	CAN[f] (0.338 g)	0.6	22.6	55	100,000 (120,000)	500
2	8.0	none (25°C)	11.7	2	60Co (0.25 Mrad)	1.0	15.8	48	130,000 (220,000)	870
3	10.0	60°C, 30 min	15.0	167	CAN (0.338 g)	0.7	23.8	57	170,000	800
4	10.0	70°C, 30 min	15.0	167	CAN (0.338 g)	1.5	21.9	56	820,000	4,000
5	10.0	87°–88°C, 30 min	15.0	167	CAN (0.338 g)	2.7	19.3	55	700,000 (930,000)	3,500
6	10.0	87°–90°C, 30 min	50.0	8,000	CAN (1.356 g)	2.8	18.7	52	74,000 (270,000)	420
7	10.0	92°–94°C, 1 hr	15.0	167	CAN (0.338 g)	3.6	19.4	52	760,000	4,200

[a] AN = Acrylonitrile.
[b] DMF = Dimethylformamide.
[c] Calculated from weight loss on acid hydrolysis.
[d] Calculated from intrinsic viscosity in DMF. Values in parentheses are $\overline{M}_n$ determined by GPC.
[e] AGU = Anhydroglucose unit.
[f] CAN = Ceric ammonium nitrate.

60°C, is reached. At this temperature, granules lose their birefringence, hydrogen bonds are broken, and the granules undergo an irreversible rapid swelling. As the temperature is further increased, granules become more swollen and disrupted, and a significant percentage of the starch is solubilized (Fig. 1). Swelling power, or the amount of water imbibed per gram of starch, has been used as a measure of granule swelling,[9] and a plot of swelling power versus temperature is shown in Figure 1.

Gelatinization of starch granules led to a large increase in the molecular weight of grafted PAN and a corresponding decrease in the frequency of grafting (larger number of AGU per graft) as compared with granular starch. This molecular weight increase did not occur gradually with an increase in starch pretreatment temperature but took place within a relatively narrow temperature range, which roughly corresponds to the gelatinization temperature, or the temperature in Figure 1 where swelling power and starch solubility begin to show a sharp increase (60°–70°C). Gelatinization of starch at temperatures higher than 70°C did not further increase the molecular weight of grafted PAN.

More frequent grafting of lower molecular weight PAN results when graft polymerizations are run under highly dilute conditions.[13] The sixth reaction of Table I was therefore run to obtain a graft copolymer with a degree of starch gelatinization identical to that of product 5 but with a significantly different length and spacing of grafted branches.

Properties of Unfractionated Saponified Starch-g-PAN

Graft copolymers (1.0 g) were heated with 20 ml 0.5N sodium hydroxide solution to saponify the nitrile groups of PAN. The method used to work up saponification mixtures was governed by the particular physical property to be examined. For the fluid absorbency measurements given in Table II, saponified polymer dispersions were first dialyzed at about 0.2% solids and then dried on Teflon sheets to form thin films. After exhaustive dialysis, dispersions generally had a pH of 5.5–6.0; however, absorbency values of polymer 5, Table II, were not significantly changed when a film was prepared from a dispersion at pH 7.7. Absorbencies, expressed in grams of absorbed fluid per gram of polymer film, were not greatly different for saponified polymers prepared from unswollen
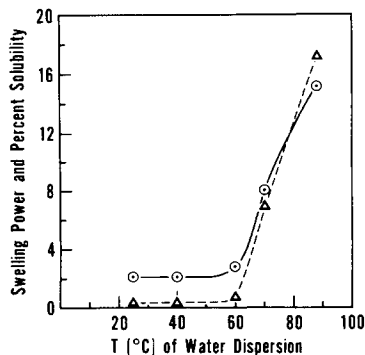

Fig. 1. Relation of swelling power and solubility of starch to water dispersion temperature: (⊙—⊙) swelling power; (△ - - - △) % solubility.

TABLE II
Properties of Saponified Graft Copolymers

Starch-g-PAN no.[a]	% Solubles (by filtration)		Absorbency, g/g		Viscosity,[b] cp		Modulus,[b] dynes/cm²	
	In undried dispersion	In dry film	Water	Simulated urine	10 sec⁻¹	100 sec⁻¹	10 sec⁻¹	100 sec⁻¹
1	22	—[c]	300	31	7,200	2,320	—	9,000
2	33	—	270	28	2,500	830	—	—
3	17	—	360	29	10,200	3,280	3,400	13,000
4	25	—	720	40	10,200	2,140	2,500	3,700
5	36	25	870	38	7,600	1,790	1,300	1,900
5A[d]	36	—	810	42	7,300	1,800	900	1,400
6	22	—	230	25	4,700	1,200	1,800	3,100
7	50	24	1,205	51	8,800	1,920	1,200	1,700

a Numbers refer to products in Table I; PAN = polyacrylonitrile.
b Determined at 0.76% solids, pH 7.6.
c Not determined.
d Product 5 (Table I) was treated with sufficient ceric ammonium nitrate to give the same ceric:starch ratio as product 6.

starch (ceric or ^{60}Co initiation, polymers 1 and 2) and a saponified polymer prepared from starch which was pretreated at 60°C (polymer 3). Starch pretreatment at 70°C (polymer 4) produced a sharp rise in absorbency, and further increases were observed with pretreatment temperatures of 87°–88°C and 92°–94°C. However, polymer 6, which was prepared under high dilution conditions from 87°–90°C pretreated starch, resembled in absorbency the polymers prepared from ungelatinized starch. The highest values and the greatest differences in absorbency between the various saponified polymer samples were observed in deionized water. Since the polymers are polyelectrolytes, absorbencies are reduced and differences between individual polymer samples are minimized in the presence of inorganic salts, e.g., in simulated urine.

Values in Table II for per cent solubles in undried dispersions were obtained by diluting dialyzed dispersions to 0.014% solids, allowing the dispersion to gravity filter, and then freeze drying a weighed portion of each clear filtrate. With ceric initiation and starch pretreatment temperatures of 25°, 60°, and 70°C, the amount of solubles in saponified polymers (i.e., polymer not retained on the filter paper) was in the range of 17%–25%. Cobalt-60 initiation of graft polymerization led to 33% solubles on saponification. With the exception of high-dilution polymer 6, which more closely resembled polymers derived from ungelatinized starch, pretreatment temperatures above 70°C gave a higher percentage of solubles. When starch was heated at 92°–94°C for 1 hr before graft polymerization, half of the saponified polymer was water soluble. Dried films were less soluble than the corresponding undried polymers.

To indicate their potential end use application as thickeners, viscosity and modulus measurements at 0.76% solids (Table II) were obtained on saponification mixtures which had been dialyzed against distilled water in small diameter tubing with minimal dilution of polymer samples.

Properties of the Gel Fraction of Saponified Starch-g-PAN

A series of physical measurements was next made on the insoluble gel fraction in each saponified starch-g-PAN (Table III). Soluble polymer was removed by extraction with dilute sodium chloride solution, which reduced the swelling of the polyelectrolyte gel sufficiently to permit its separation by centrifugation. Successive washings with increasingly dilute hydrochloric acid solution removed sodium chloride and further reduced gel swelling through conversion of sodium carboxylate groups in saponified starch-g-PAN to the carboxylic acid form. Titration of the gel fraction to pH 7.6 reformed the sodium carboxylate salt and gave the titer values in Table III. Gel recovery values in Table III were calculated from the initial weight of starch-g-PAN and the dry weight of the gel fraction, as determined from the per cent solids of the titrated dispersion. These values are consistently higher than the corresponding values calculated by difference from % solubles by filtration and reported in Table II. This might indicate a lower solubility of the polymer in dilute sodium chloride solution than in water; however, it is also possible that in the procedure used in Table II, some of the microgel was not retained by the filter paper. Although a significant percentage of some saponified graft copolymers was removed as solubles, we have assumed that no significant solvent fractionation has occurred, i.e., that differences in % add-on, graft MW, and grafting frequency observed in starch-g-PAN samples will also be present in the saponified gel fractions.

TABLE III
Physical Properties of Isolated Gel Fractions of Saponified Graft Copolymers

Starch–g-PAN no.[a]	Gel recovery,[b] %	Titer,[c] meq/g	$Q_{0.01}$[d]	Q_{H_2O}[d]	$[\eta_{100}/cQ]_{P}$,[e] poises	$[G_{100}/c^{1/3}]_{P}$,[f] dynes/cm^2 × 10^{-3}	cQ of 0.76% suspension[g]
1	84	4.43	260	390	23	25	2.0
1A	75	4.62	240	390	24	26	—
1B	72	4.73	290	490	25	30	—
1C	50	5.98	410	670	13	14	—
2	74	4.36	200	340	32	50	1.5
3	94	4.20	220	460	25	24	1.9
4	89	4.67	440	1,200	13	14	3.3
5	—	4.63	620	6,000	7	10	5.4
5A	—	4.88	510	4,400	11	11	4.7
6	—	4.08	300	1,300	20	28	2.4
7	78	4.38	620	2,400	6	8	4.7

[a] Numbers refer to products in Table I.
[b] Fraction of initial weight recovered as gel. Initial weight = wt of starch–g–PAN saponified × 1.24, except for 1B and 1C. For these two entries, initial weight = initial dry wt of saponified starch–g–PAN.
[c] Milliequivalents of NaOH to prepare 1 g (Na form) at pH 7.6.
[d] Weight ratio of swollen gel to dry weights, in 0.01 μ salt or water, respectively.
[e] Plateau value of viscosity function for a shear rate of 100 sec^{-1}.
[f] Plateau value of modulus function.
[g] Assuming polymer is all gel.

For convenience, the swelling ratios Q of the isolated gel fractions in excess solvent were determined in a small angle-head centrifuge rather than by our earlier procedure in the ultracentrifuge.[4] Comparable results can be obtained by suitable choice of conditions. Results at three ionic strengths are linear in Figure 2, as were previous results in the ultracentrifuge. The value of Q, determined with the same gel in the ultracentrifuge (Fig. 2), agrees with these data.

Swelling curves for all gels in Table III were determined as in Figure 2. Q^{-1} was essentially linear with $\mu^{1/2}$ for each. Values of $Q_{0.01}$ (Table III) were taken from the curves, and Q_{H_2O} was determined from the centrifuge data directly by an average of two tests.

Gel fractions 1 and 1A (Table III) are the same and were obtained by duplicate saponifications. Since the swelling ratio of a saponified starch–g–PAN used in an earlier study[5] could be increased by further treatment with alkali, gel fraction 1A was dried to a film, the film suspended in $4M$ sodium hydroxide for 20 hr at 27°C, and the resulting product purified like the other gel fractions by washing with sodium chloride solution and dilute hydrochloric acid. The properties of the resulting gel fraction 1B were not significantly different from those of 1 or 1A. Treatment with $5M$ sodium hydroxide at 60°C for 20 hr produced a gel fraction (1C) with a higher Q value and a higher titer but gave a gel recovery of only 50%.

Swelling ratios Q_{H_2O} for the gel fractions in Table III are higher than the absorbency values given in Table II, possibly because the gel fractions had never been dried, and also because of the differences in the two methods of determination. Both sets of data, however, show similar trends. Gel fractions 4, 5, 5A, and 7, having the largest Q values, were obtained from starch that had been pretreated at 70°C or higher. Gel fraction 6, prepared from high-dilution starch–g–PAN, was low in $Q_{0.01}$ value compared to other gel fractions made with gelatinized starch. All swelling curves are linear in Q^{-1} versus $\mu^{1/2}$ and radiate from the origin such as shown by gel fraction 5 in Figure 2. The $Q_{0.01}$ values in Table III thus represent the relative values of Q at any given value of μ. The curve for fraction 6 was in the low Q region throughout the measured range of μ. However, we were surprised to find that in water, fraction 6 had a Q value about equal to that of fraction 4 derived from the 70°C pretreated starch.

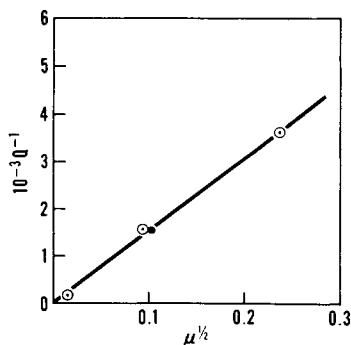The high viscosities of saponified gel fractions are interpreted in terms of

Fig. 2. Relation of reciprocal of swelling ratio, Q^{-1}, for gel fraction 5 to square root of ionic strength, $\mu^{1/2}$, in the gel after different centrifuge treatments: (⊙) 3600 rpm (1300 × g) for 90 min in Servall angle head; (●) 2600 rpm (490 × g) in an ultracentrifuge, extrapolated to infinite running time.

systems of closely packed gel particles.[4]   The viscosity η of such a gel system depends not only on structure and constitution of the gel itself but also on system conditions, i.e., the shear rate in the rheometer,[4] the ionic strength of the medium, μ, and the concentration c of gel material.   Shear rate was held constant at 100 sec^{-1}, and the plateau value of η/cQ at $cQ > 2$, that is, $[\eta_{100}/cQ]_p$, was then determined for each gel in Table III.

The shear modulus G of the gel fractions was determined by first measuring the primary normal force, $P_{11} - P_{22}$, and then applying the equation

$$G = 2\tau^2/P_{11} - P_{22}$$

where τ is shear stress. G depends on c, but a reduced modulus, $G/c^{1/3}$, is approximately constant in rubbery network theory as well as in closely packed gel systems when $cQ > 2$.   The plateau values at a shear rate of 100 sec^{-1}, $[G_{100}/c^{1/3}]_p$, are given in Table III.

The function $[G_{100}/c^{1/3}]_p$ is the important measure of gel structure.   In an ideal rubbery network, $G/c^{1/3}$ defines the average molecular weight between crosslinks, M_c, by the equation[6]

$$M_c = \rho^{2/3}RT/(G/c^{1/3})$$

where ρ is polymer density, R is the gas constant, and T is the absolute temperature.   In the saponified gels, we assume that $[G_{100}/c^{1/3}]_p$ is an indication of an effective crosslink density without defining the chemical nature of the crosslink points.

The values of $Q_{0.01}$ (Table III) are correlated with $[G_{100}/c^{1/3}]_p$ in Figure 3.   The gel fractions with lower values of $Q_{0.01}$ have higher values of $[G_{100}/c^{1/3}]_p$, and the data appear nearly linear on this double logarithmic plot.   The data points can arbitrarily be divided into two groups having higher and lower Q values.   Gels 4, 5, 5A, and 7, made with 70°C or higher starch pretreatment have higher Q values and lower values of $[G_{100}/c^{1/3}]_p$.   The gels made with starch pretreated at 60°C or lower have distinctly higher $[G_{100}/c^{1/3}]_p$ values and are correspondingly lower in $Q_{0.01}$.   That is, these gels are lower in Q mainly because they have a high modulus and are apparently more highly crosslinked.   The data in Figure 3 do lie somewhat lower than our earlier series of samples differing in crosslink density.[5]   The two series were prepared differently, and the polymers may have different structures that affect Q and $[G_{100}/c^{1/3}]_p$.
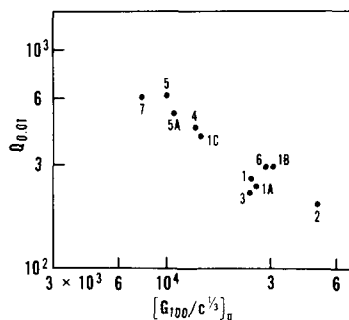

Fig. 3. Relation of swelling ratio at $\mu = 0.01$, $Q_{0.01}$, to modulus function $[G_{100}/c^{1/3}]_p$ for saponified starch–g–PAN gel fractions.   Numbers refer to preparations in Table I.   Values plotted are given in Table III.

The relation of the function $[\eta_{100}/cQ]_p$ to $[G_{100}/c^{1/3}]_p$ is shown in Figure 4. The gel fractions can again be classed in the same two groups as for $Q_{0.01}$, with saponified starch–g–PAN polymers having long grafted chains in one group and those having short chains in the other. Gel 1C, however, is lowered in $[\eta_{100}/cQ]_p$ as well as in $[G_{100}/c^{1/3}]_p$.

CONCLUSIONS

In absorbency, swelling, and rheological properties, the saponified starch–g–PAN copolymers can be divided into two groups. Saponified polymers prepared from starch pretreated at 60°C or below tend to have relatively low fluid absorbency and give low-swelling, high-modulus gel fractions as compared with those prepared from starch pretreated at 70°C or higher. The one exception was saponified starch–g–PAN number 6, which was prepared from starch pretreated at 87°–90°C but under high dilution conditions to give polydisperse, low molecular weight grafted PAN chains similar to the grafted PAN obtained at lower starch pretreatment temperatures. The properties of the saponified polymer resembled those prepared with low starch pretreatment temperatures, suggesting that the determining factors that govern properties might be the molecular weight of the grafted PAN and the grafting frequency rather than the degree of swelling and disruption of the starch granule. We recognize, however, that the high dilution method used to synthesize polymer 6 may have introduced other variables that also influence physical properties. The higher ratio of ceric ammonium nitrate to starch used to prepare starch–g–PAN number 6 is apparently not an important variable, since treatment of starch–g–PAN number 5 with sufficient ceric ammonium nitrate to give the same ceric:starch ratio as number 6 gave, on saponification, a product (5A) that was not greatly different from 5.

Approximate values of cQ are given in Table III for the unfractionated 0.76% dispersions presented earlier in Table II. These values were calculated from the swelling curves of the gel fractions assuming that all polymer was gel. Actual cQ values would thus be lower, since a portion of the saponified polymer is soluble. Table III shows relatively low cQ values for the short graft chain polymers 1–3 and 6, some of which show relatively low viscosities in Table II. These low cQ values indicate that gel particles in these four dispersions might not be closely
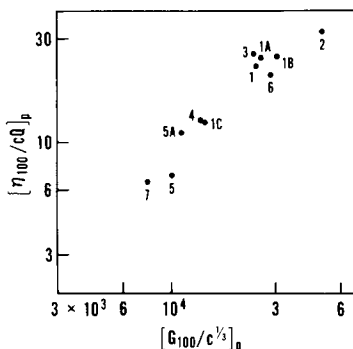

Fig. 4. Relation between plateau values of viscosity function $[\eta_{100}/cQ]_p$ and modulus function $[G_{100}/c^{1/3}]_p$ for saponified starch–g–PAN gel fractions.

packed but might instead be separated by some interstitial water. At higher c, where interstitial water is absent, these polymers would have higher viscosities than the others (as shown in the $[\eta_{100}/cQ]_p$ column of Table III) due to their higher modulus and higher apparent crosslink density. We thus conclude that although viscosity gives some measure of thickening ability, it is dangerous to rely on viscosity alone when comparing the properties of a series of closely packed gel thickeners; and having too low a value of cQ has probably been a common error in the gathering of data on these systems.

References

1. L. A. Gugliemelli, M. O. Weaver, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.,* **13,** 2007 (1969).

2. G. F. Fanta, M. O. Weaver, and W. M. Doane, *Chem. Technol.,* **4,** 675 (1974).

3. G. F. Fanta, in *Block and Graft Copolymerization,* Vol. I, R. J. Ceresa, Ed., Wiley, London, 1973, p. 5.

4. N. W. Taylor and E. B. Bagley, *J. Appl. Polym. Sci.,* **18,** 2747 (1974).

5. L. R. G. Treloar, *The Physics of Rubber Elasticity,* Oxford University Press, Oxford, 1958.

6. N. W. Taylor and E. B. Bagley, *J. Appl. Polym. Sci.,* **21,** 113 (1977).

7. P. F. Onyon, *J. Polym. Sci.,* **37,** 315 (1959).

8. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci. B,* **5,** 753 (1967).

9. H. W. Leach, in *Starch, Chemistry, and Technology,* Vol. I, R. L. Whistler and E. F. Paschall, Eds., Academic Press, New York, 1965, p. 294.

10. G. Coppola, P. Fabbri, B. Pallesi, and U. Bianchi, *J. Appl. Polym. Sci.,* **16,** 2829 (1972).

11. A. S. Kenyon and E. H. Mottus, *Am. Chem. Soc., Div. Polym. Chem., Prepr.,* **14**(2), 652 (1973).

12. G. F. Fanta, R. C. Burr, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.,* **21,** 425 (1977).

13. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.,* **13,** 133 (1969).