# Cross-linking in Saponified Starch-g-Polyacrylonitrile

GEORGE F. FANTA, ROBERT C. BURR, and WILLIAM M. DOANE

Northern Regional Research Center, Agricultural Research Service,
U.S. Department of Agriculture, Peoria, IL 61604

Evidence, based on solubility data in DMSO, was obtained for crosslinking during the graft polymerization of acrylonitrile onto starch, and this crosslinking apparently occurs by way of chain combination of growing PAN macroradicals. Crosslinking also occurs between starch and PAN during alkaline saponification. Soluble (and thus uncrosslinked) starch-g-PAN polymers were rendered partially insoluble by alkaline saponification, as was a synthetic mixture of starch and PAN. Although PAN will crosslink with itself if saponifications are carried out in ethanol-water systems containing predominantly ethanol, PAN:PAN crosslinking does not take place during aqueous saponifications. Since the individual grafted granules of starch are crosslinked, these granules maintain their integrity after alkaline saponification and exist in the saponificate as highly swollen gel particles. When the saponificate is dried, these gel particles coalesce into either films or macroparticles which will not redisperse back into gel when placed in water. These properties are analogous to those of crosslinked rubber latexes and may be similarly explained by assuming interdiffusion of polymer chain ends on the surfaces of individual gel particles, followed by hydrogen bonding between these polymer chains. If dry saponified starch-g-PAN is heated, its ability to absorb water is reduced; however, this absorbency loss is not related to loss of hydrogen-bonded water from the graft copolymer.

Acrylonitrile graft polymerizes readily with either granular or pasted starch to yield starch-g-polyacrylonitrile (PAN), and reactions are generally carried out in water with ceric ammonium nitrate as the initiating system (1). Reaction of starch-g-PAN with alkali at elevated temperatures converts the nitrile substituents of PAN to a mixture of carboxamide

© 1982 American Chemical Society

and alkali metal carboxylate and yields a family of final
products that are useful as thickeners (2) and as water
absorbents (3, 4). Although saponified (hydrolyzed) starch-g-
PAN (HSPAN) is hydrophilic and exhibits extensive swelling in
aqueous systems, Taylor and Bagley (5) have shown that it exists
largely as insoluble gel particles. We later showed by scanning
electron microscopy (6) that these particles maintain the
outward appearance of the original PAN-grafted starch granules.
Since both starch and saponified PAN are soluble in aqueous
alkali, the fact that a copolymer of the two components is not
only insoluble but still bears some physical resemblance to the
original starch-g-PAN precursor, as it swells and imbibes water,
is indicative of crosslinking in the final saponified product.
The purpose of this research was to gain some insight as to how
this crosslinking might take place, and also to explain some
of the properties of HSPAN films and particles. Although
gelatinized starch gives thickening agents and water absorbents
with superior properties, we used granular, unpasted starch in
nearly all of this study because final products are easier to
handle. Any conclusions based on results obtained with granular
starch would certainly be applicable to gelatinized starch.

## Results and Discussion

Crosslinking During Graft Polymerization. Perhaps the
most obvious reaction path leading to crosslinking in HSPAN
is the combination of two growing PAN macroradicals during the
graft polymerization step. Combination of a PAN and a starch
macroradical would give the same final results. Since the
high degree of swelling of HSPAN in water indicates a low
crosslink density, only a few such chain combinations would be
sufficient to produce the observed physical properties. Ceric-
initiated aqueous polymerizations of acrylonitrile in the
presence of polyols have been studied, and evidence has been
presented for termination by chain combination at low ceric
ion concentrations (7, 8).

To gain some insight into whether crosslinking by free
radical combination indeed takes place during graft polymeri-
zation reactions with starch, a number of these polymerizations
were run under carefully controlled conditions, and the
solubilities in dimethylsulfoxide (DMSO) of the resulting
starch graft copolymers were determined at 75°C. Since starch
and PAN are individually soluble under these conditions, we
assumed that a totally uncrosslinked graft copolymer of the
two components would be soluble also, and that the solubility
of a particular polymer would thus decrease as its crosslink
density increased. Polymers prepared with ceric ammonium
nitrate initiation (Ce$^{+4}$:starch anhydroglucose unit [AGU] molar
ratio of 1:100) and their respective solubilities in DMSO are
shown in Table I. When corn starch was allowed to react with

TABLE I

Polymer Solubilities in Dimethylsulfoxide at 75°C. Ceric Initiation

| No. | Polymer | Add-on,[a] % | $\bar{M}_v$ of grafted PAN[b] | Grafting frequency, AGU[c]/graft | Solubility, % |
|---|---|---|---|---|---|
| 1 | Starch | -- | --- | | 100 |
| 2 | Ce[+4]-Treated starch | -- | --- | | 36 |
| 3 | Starch-g-PAN | 52 | 83,000 | 473 | 8 |
| 4 | Starch-g-PAN ($C_6H_{13}SH$) | 50 | 17,000 | 100 | 34 |
| 5 | Ce[+4]-Treated starch ($C_6H_{13}SH$) | -- | --- | | 28 |

[a] Determined by weight loss on acid hydrolysis.

[b] Calculated from intrinsic viscosity in dimethylformamide.

[c] Anhydroglucose unit.

ceric ammonium nitrate in the absence of acrylonitrile (No. 2),
its solubility was reduced from 100% to 36%:  a result which
parallels an earlier study with wheat starch (9).  Although
starch can thus be rendered partially insoluble by reaction
with ceric ion, we will later show that by allowing ceric-
treated starch to react with alkali under the conditions of
saponification, we obtain a product that is highly soluble in
water.  Therefore, any crosslinks introduced by reaction with
$Ce^{+4}$ apparently have no large bearing on the final properties
of HSPAN.
    When starch was graft polymerized with acrylonitrile to
give a product containing 52% grafted PAN, the solubility of
the resulting starch-g-PAN in DMSO was only 8% (No. 3, Table I),
a result which immediately suggests crosslinking during the
polymerization reaction.  If this crosslinking is indeed due
to termination of growing PAN macroradicals by chain combina-
tion, graft polymerization in the presence of a chain transfer
agent should not only lower the molecular weight of grafted
PAN but should increase solubility in DMSO as well.  Exactly
this effect was observed when the graft polymerization was
repeated in the presence of 1-hexanethiol (No. 4).  Graft
molecular weight was decreased by about a factor of 5, while
solubility in DMSO increased approximately fourfold.  When
1-hexanethiol was included in the reaction mixture when starch
was allowed to react with $Ce^{+4}$ in the absence of acrylonitrile,
we obtained a starch product that was only 28% soluble in
DMSO (No. 5).
    Since the partial insolubility of the starch-ceric
ammonium nitrate reaction product complicates the interpretation
of solubility data, we ran a second series of graft
polymerizations using cobalt-60 as an initiator in an attempt
to remove this variable (Table II).  If combination of PAN
macroradicals is occuring during graft polymerization, it
should occur during cobalt-60 initiated polymerizations as
well as in those initiated by ceric ammonium nitrate.  In
the first four reactions of Table II, starch was irradiated
as a water slurry under graft polymerization conditions, but
in the absence of acrylonitrile, to determine the influence
of different doses of irradiation on starch solubility.
An effect of total dose on starch solubility was indeed
observed, and this can perhaps be ascribed to competing
radiation-induced degradation and crosslinking (10, 11).  One
path leading to crosslinking might be acetal and hemiacetal
formation through carbonyl groups formed by irradiation (12).
Since maximum solubility (95%) was observed at 0.1 Mrad, this
total dose was used in subsequent graft polymerizations with
acrylonitrile.

TABLE II

Polymer Solubilities in Dimethylsulfoxide at 75°C.  Cobalt-60 Initiation

| No. | Polymer | Dose, Mrad | AN,[a] g | Add-on,[b] % | $\bar{M}_v$ of grafted PAN[c] | Grafting frequency, AGU[d]/graft | Solubility, % |
|-----|---------|-----------|----------|--------------|-------------------------------|----------------------------------|---------------|
| 1 | Starch | 0 | -- | -- | -- | | 100 |
| 2 | Starch | 0.05 | -- | -- | -- | | 62 |
| 3 | Starch | 0.1 | -- | -- | -- | | 95 |
| 4 | Starch | 0.2 | -- | -- | -- | | 80 |
| 5 | Starch-g-PAN | 0.1 | 5 | 13 | 30,000 | 1,200 | 34 |
| 6 | Starch-g-PAN | 0.1 | 10 | 27 | 110,000 | 1,800 | 29 |
| 7 | Starch-g-PAN | 0.1 | 15 | 38 | 180,000 | 1,800 | 26 |
| 8 | Starch-g-PAN ($C_6H_{13}SH$) | 0.1 | 15 | 28 | 30,000 | 480 | 45 |
| 9 | Starch-g-PAN ($HOCH_2CH_2SH$) | 0.1 | 15 | 17 | 29,000 | 870 | 53 |

[a] AN = acrylonitrile.
[b] Determined by weight loss on acid hydrolysis.
[c] Calculated from intrinsic viscosity in dimethylformamide.
[d] Anhydroglucose unit.

In numbers 5-7 of Table II, starch-g-PAN copolymers containing different amounts of grafted PAN were prepared by the mutual irradiation of starch and varying amounts of acrylonitrile in water. Although values for % add-on in these three reactions ranged from 13-38%, and graft molecular weights varied from 30,000 to 180,000, solubilities in DMSO were not greatly different (26-34%). The roughly threefold reduction in solubility observed by the incorporation of as little as 13% PAN into the starch matrix is a good indication that graft polymerization had led to crosslinking. Although complete DMSO solubility was not achieved when graft polymerizations were run in the presence of 1-hexanethiol (No. 8) or 2-mercaptoethanol (No. 9), both of these chain transfer agents enhanced solubility. Numbers 5 and 9 of Table II make an especially good comparison to show the effect of a chain transfer agent on solubility, since both PAN content and graft $\bar{M}_v$ in the two polymers are similar.

Crosslinking During Alkaline Saponification. Although granules of starch-g-PAN are apparently crosslinked, the PAN moiety is not itself a network polymer, since removal of the starch component gives a material that is readily soluble (e.g., in DMF, for $\bar{M}_v$ determination). We, therefore, needed to know initially whether the saponified PAN moiety was likewise soluble or whether aqueous alkaline saponification causes the PAN portion of starch-g-PAN to crosslink with itself. A ceric-initiated starch-g-PAN containing 50% PAN ($\bar{M}_v$:64,000) was thus prepared and saponified in aqueous alkali, and the resulting HSPAN was isolated by methanol precipitation and dried. Enzymatic hydrolysis of this product removed the starch component and afforded saponified PAN with $\bar{M}_n$ = 44,000, as determined by membrane osmometry. Since saponification of the PAN moiety gives soluble polymer with a molecular weight not greatly different from its PAN precursor, PAN:PAN crosslinking is apparently not occurring to a large extent during alkaline saponification in water.

We next examined the effect of running the saponfications in aqueous ethanol instead of in water, since alcohol-containing solvent systems are also being used for some saponified starch-g-PAN preparations (13). Contrary to aqueous saponfications, we found evidence that crosslinking of the PAN moiety does take place in this solvent system, although it is highly dependent on the ethanol:water ratio. Initially, we examined the saponification of PAN homopolymer in solvent combinations ranging from 95% ethanol to a 1:1 mixture of 95% ethanol and water (Table III). Crosslinking in the different solvents was compared by determining percent soluble polymer in the undried saponification reaction mixtures after exhaustive dialysis against distilled water. Brookfield viscosities of these water dispersions also served as an

Table III. Influence of Ethanol:Water Ratio on Alkaline Saponification[a]

| 95% EtOH (ml) | $H_2O$ (ml) | Saponified PAN[b] dispersion | | Saponified starch-g-PAN[d] dispersion | |
| | | Solubles (%) | Viscosity cp[c] (% solids) | Solubles (%) | Absorbency of insoluble gel[e] |
|---|---|---|---|---|---|
| 8.9 | 0 | 64 | 4,600 (0.25) | 31 | 150 |
| 8.0 | 0.88 | 84 | 300 (0.27) | 27 | 140 |
| 7.56 | 1.32 | 71 | 200 (0.26) | -- | -- |
| 4.44 | 4.44 | 100 | 19 (0.24) | 28 | 310 |

[a]2.00 g of 50% NaOH added to each solvent system.  0.50 g poly-acrylonitril (PAN) or 1.00 g starch-g-PAN added, and dispersion heated under reflux for 3 h.  Saponified dispersions were dialyzed against distilled water.

[b]$M$  of PAN:  49,000.

[c]Brookfield viscosity at 30 rpm.

[d]No. 3, Table I.

[e]Expressed as grams of water-swollen gel per gram of dry polymer.

indicator for crosslinking; since the viscosity of a crosslinked, partially soluble, swollen gel network would be higher than the corresponding uncrosslinked polymer solution. Although crosslinking clearly occurs in 95% ethanol, as indicated by a water solubility of only 64% for saponified PAN and a Brookfield viscosity of 4600 cp for the aqueous reaction mixture at 0.25% solids, solubilities progressively increase and Brookfield viscosities decrease with increasing water contents of the solvent systems.  When saponified in a 1:1 solution of 95% ethanol and water, PAN apparently does not crosslink to a significant extent, since the resulting saponified PAN is 100% water soluble, and the Brookfield viscosity of the solution is only 19 cp.

The saponification of a ceric-initiated starch-g-PAN was likewise examined at the different ethanol-water ratios, and these results are also shown in Table III.  Once again, solubilities were determined for undried water dispersions after exhaustive dialysis.  Brookfield viscosity was not used as a measure of crosslinking for these HSPAN preparations, because individual gel particles could not absorb all of the available water at 0.22% solids and thus could not exist in

the closely packed state which is necessary for the attainment
of meaningful viscosities (5).  To more reliably estimate the
extent of crosslinking, the insoluble gel was separated from
excess solution by filtration and freeze dried.  The weight of
freeze-dried solid was determined, and water absorbency was then
expressed as grams of swollen gel per gram of dry polymer.  Low
crosslink densities would thus give highly water-swollen gels
and high absorbency numbers.  Although the percent solubles did
not vary greatly with the ethanol content of the saponification
mixture, 1:1 ethanol (95%)-water produced an insoluble HSPAN
gel fraction with about twice the absorbency of those prepared
at higher ethanol contents.  We can therefore assume that some
PAN:PAN crosslinking likewise has taken place at high ethanol
concentrations, as was observed for PAN homopolymer.

Although the formation of PAN:PAN crosslinks during alkaline
saponification of starch-g-PAN takes place to a significant
extent only when alcohol is the major component of the
saponification solvent system, some crosslinking between starch
and PAN occurs even when saponifications are carried out in
water or in 1:1 ethanol (95%)-water (Table IV).  Evidence for
this starch:PAN crosslinking was obtained by saponifying two
totally DMSO-soluble (and thus not crosslinked) starch-g-PAN
polymers and then showing that:  (1) The resulting saponified
polymers had only a partial solubility in water, and (2) they
gave viscous aqueous dispersions of gel at low concentrations
(about 0.25% solids).  The first soluble starch-g-PAN (No. 2,
Table IV) was prepared by dispersing starch graft copolymer
No. 1 in hot DMSO and then subjecting the dispersion to treatment
with ultrasound to mechanically degrade the polymer. Residual
gel was removed from the DMSO solution by filtration, and the
soluble polymer was then isolated by alcohol precipitation.
The second soluble starch-g-PAN (No. 3) was prepared by
subjecting another starch graft copolymer to a mild acid
hydrolysis to partially depolymerize the starch moiety.  The
ethanol-water solvent system apparently promotes a greater
number of starch:PAN crosslinks than water, as evidenced by the
lower solubilities (45 vs. 71% and 42 vs. 65%) and the higher
viscosities for water dispersions (2400 vs. 920 cp and 690 vs.
220 cp).

The next logical step to prove crosslinking between starch
and PAN was to saponify a 1:1 physical mixture of starch and
PAN and to show that the resulting saponificate had solubility
and viscosity properties different than those of the saponificate
of the individual components.  Numbers 4, 5, and 6 (Table IV)
show the results of saponifying starch, ceric-treated starch,
and PAN homopolymer.  Saponifications in water and in ethanol-
water gave complete or nearly complete solubilities as well as
low viscosities for the dialyzed solutions.  Although
saponification of the physical mixture (No. 7) in water gave
about the same results as the individual components,

Table IV.  Alkaline Saponifications.  Properties of Saponified Dispersions

| No. | Polymer | Saponified in water[a] | | | Saponified in EtOH-H$_2$O[d] | | |
|---|---|---|---|---|---|---|---|
| | | Solubles, (%) | Viscosity, cp[b] (% solids) | Absorbency of insoluble gel[c] | Solubles, (%) | Viscosity, cp[c] (% solids) | Absorbency of insoluble gel[c] |
| 1 | Starch-g-PAN (Ce$^{+4}$)[e] | 26 | --- | 270 | 28 | --- | 310 |
| 2 | Sonified starch-g-PAN (Ce$^{+4}$)[f] | 71 | 920 (0.25) | --- | 45 | 2400 (0.25) | --- |
| 3 | Acid-treated starch-g-PAN (Ce$^{+4}$)[g] | 65 | 220 (0.23) | --- | 42 | 690 (0.25) | 340 |
| 4 | Starch | 99 | 2.4 (0.25) | --- | 100 | 3.0 (0.28) | --- |
| 5 | Ce$^{+4}$-treated starch | 100 | 3.0 (0.25) | --- | 94 | 2.8 (0.25) | --- |
| 6 | PAN ($\overline{M}_v$: 49,000) | 100 | 16 (0.25) | --- | 100 | 19 (0.24) | --- |
| 7 | Starch-PAN phys. mixture | 100 | 22 (0.31) | --- | 85 | 1000 (0.25) | --- |
| 8 | Starch-g-PAN ($^{60}$Co)[h] | --- | --- | --- | 28 | 3900 (0.23) | 480 |
| 9 | Sonified starch-g-PAN ($^{60}$Co)[i] | --- | --- | --- | 51 | 2900 (0.25) | --- |
| 10 | Sonified starch-g-poly-acrylamide ($^{60}$Co)[j] | --- | --- | --- | 100 | 11 (0.25) | --- |

[a] Either 1.0 g starch graft copolymer or 0.5 g homopolymer (starch or PAN) saponified in 9.0 ml 0.7 N NaOH for 3 h at 95-100°C.

[b] Brookfield viscosity at 30 rpm.

[c] Expressed as g water-swollen gel/g dry polymer.

[d] Polymers (same quantities as footnote a) saponified for 3 h at reflux in a solution of 2.0 g 50% NaOH, 4.44 ml water, and 4.44 ml EtOH.

[e] Prepared under the same conditions as No. 3, Table I, PAN content: 51%; $\overline{M}_v$ of PAN: 64,000.

[f] PAN content: 53%; $\overline{M}_v$ of PAN: 36,000.

[g] PAN content: 46%; $\overline{M}_v$ of PAN: 35,000.

[h] No. 7, Table II.

[i] PAN content: 37%; $\overline{M}_v$ of PAN: 100,000.

[j] Polyacrylamide content: 35%.

saponification in ethanol-water gave a product that was 85% soluble and that had a Brookfield viscosity of 1000 cp at 0.25% solids in water.

Although the number of starch:PAN crosslinks in HSPAN is too low to permit their identification by spectroscopy, we can propose a reasonable crosslinking mechanism based on the known reactions of PAN and starch with alkali. When PAN is heated with alkali, a deep red-brown color is produced due to nucleophilic-initiated polymerization through the nitrile groups to yield a polyimine type of conjugated ring structure (14, 15). This conjugated ladder-type polymer is then opened in a second reaction to give a polyacrylamide, which is then further hydrolyzed to the observed poly(acrylic acid salt-co-acrylamide). Under the conditions of Table IV, a crosslinked final product is not observed in the absence of starch, since $^{\ominus}$OH (and to a lesser extent, $^{\ominus}$OC$_2$H$_5$) is the nucleophile that initiates the nitrile polymerization and then reacts to open the conjugated ring structure. In the presence of starch, however, starch alkoxide can also serve as the nucleophile, thus leading to the observed crosslinking. The close proximity of starch and PAN, when the two polymers are chemically bonded through graft polymerization, would favor these reactions.

The role of the conjugated polyimine intermediate in the observed crosslinking can be seen by comparing the saponification of a starch-g-PAN (No. 9, Table IV) with that of a starch-g-polyacrylamide prepared under the same conditions (No. 10). Although polyacrylamide is an intermediate in the conversion of PAN to poly(acrylic acid salt-co-acrylamide), the polyimine structure is of course not formed during its saponification. Both starch-g-PAN and starch-g-polyacrylamide were prepared by cobalt-60 initiation, since acrylamide does not graft efficiently in the presence of ceric ammonium nitrate (16). Both graft copolymers were irradiated with ultrasound to give totally soluble products; the ultrasonic treatment of starch-g-PAN was carried out in DMSO, while that of starch-g-polyacrylamide was run in water.

Saponifications of these graft copolymers were carried out in 1:1 ethanol (95%)-water (Table IV). Reaction No. 8 shows the saponification results for starch-g-PAN before treatment with ultrasound; and although the insoluble gel fraction was more highly swollen, the % solubles was the same as for starch-g-PAN prepared with ceric initiation (No. 1). After solubilization by treatment with ultrasound, starch-g-PAN gave a saponification product that was only 51% water-soluble and that showed a Brookfield viscosity of 2900 cp at 0.25% solids in water. The corresponding starch-g-polyacrylamide, however, gave a totally water-soluble saponification product with low viscosity, indicating that crosslinking did not occur.

Film Formation.  From our first studies of HSPAN, it was
apparent that continuous films can be formed by simply allowing
water dispersions of the polymer to evaporate to dryness (17).
These films are unique in that they do not revert back to the
original gel particles when placed in water.  Rather, the
entire film swells as a continuous entity as it imbibes water;
and within a few minutes, a highly swollen sheet of gel is
formed that has enough tensile strength to allow it to be
carefully manipulated without breaking.  If these films are
redispersed in water with rapid stirring (e.g., Waring Blendor
for short periods of time), the resulting dispersion will again
form a film with similar properties if it is allowed to
evaporate to dryness.  Swollen films derived from gelatinized
starch graft copolymers possess more strength and continuity
than similar films prepared from granular starch.
      Bonding of individual gel particles with each other to
give larger conglomerates of highly absorbent polymer is also
observed when other isolation techniques are used, e.g.,
alcohol precipitation or drum drying (4).  However, if alcohol
precipitation is carried out by slow addition of alcohol to the
water dispersion, HSPAN tends to precipitate as individual gel
particles rather than as larger chunks, and the resulting dried
polymer therefore gives very smooth water dispersions when
hydrated (18).
      To verify that these film- and conglomerate-forming
properties of HSPAN were not related to the sticking together
of individual gel particles by the minor amount of soluble
polymer present in saponification mixtures, films were cast
from water dispersions of HSPAN polymers, prepared from either
granular or gelatinized starch, from which the solubles had
been extracted with water.  These films were indeed continuous,
and they absorbed water to form continuous gel sheets.  We also
observed that addition of 10% of either saponified PAN or
soluble starch to HSPAN prepared from granular starch did not
outwardly alter film properties.
      To explain the fact that HSPAN swells in water to form
gel sheets or macroparticles rather than disintegrating into a
gel dispersion, we initially felt that chemical bonding must
take place between individual particles of water-swollen gel
as water evaporates.  Although we cannot totally eliminate this
possibility, the proposal of primary chemical bonding is not
necessary to explain the behavior of these films and
conglomerates.  For example, Voyutskii (19) has reviewed the
formation of films from vulcanized rubber latexes and concludes
that film formation in these systems is observed because of
interdiffusion of ends of individual macromolecules in adjacent
latex particles.  This diffusion can take place even though
individual latex particles are crosslinked, 3-dimensional
networks; and the continuity of the resulting films, even when

partially swollen in a hydrocarbon solvent, can be ascribed
to Van der Waals forces between interwoven polymer ends.
Bradford and Vanderhoff (20) have also prepared films from
crosslinked latex particles.  These authors studied a 65:35
styrene-butadiene copolymer crosslinked with varying amounts of
divinylbenzene and found that although the incorporation of
divinylbenzene retarded the coalescence of latex particles,
these particles did indeed coalesce, presumably due to a
similar interdiffusion of polymer chain ends.

    The analogy between crosslinked latex particles and the
particles of water-swollen HSPAN is obvious.  In addition to
Van der Waals forces, hydrogen bonding between the hydrophilic
polymer chains can also take place, and some of these
hydrogen bonds could be quite strong, as evidenced by the well-
known phenomenon of amylose retrogradation (21) and the
resistance of retrograded amylose to water solution.  An analogy
to the vulcanized rubber latexes can also be seen in the facile
conversion of HSPAN film to gel particles by a short period of
high-speed stirring in water, followed by the reformation of
a film similar to the original by simply drying the water
dispersion.  Voyutskii (22) found that a film prepared from
vulcanized latex gave a continuous rubber sheet on cold milling,
presumably because the absence of primary chemical bonding
between individual particles allows them to easily slide with
respect to each other; the same type of secondary (Van der
Waals) bonds can then readily reform.  In contrast, a rubber
film that was vulcanized after it had been prepared, and was
thus crosslinked throughout the entire polymer matrix, was
converted to a rubber crumb on milling.

    If the formation of continuous films from HSPAN gel is
indeed largely due to hydrogen bonding and Van der Waals forces
between interdiffused polymer chains, rather than to the
formation of primary chemical bonds, this property should not
be unique to the starch graft copolymers but should be
exhibited, at least to some extent, by other water-swollen,
hydrophilic gels as well.  This probability was verified
experimentally for a commercial thickening agent (Carbopol 941)
and a commercial water absorbent (Permasorb 10).  Water
dispersions of both of these polymers (neither of which contain
starch) formed films when dried; and although the water-swollen
films were more easily disintegrated than those from HSPAN,
they did remain intact if they were not agitated.  Carbopol is
a particularly good polymer for comparison, since Taylor and
Bagley (5, 23) have studied its rheology and gel content and
in these respects have found it to be quite similar to HSPAN.

    Heat-Induced Crosslinking of Dry Polymer.  When a dry
sample of HSPAN is heated, the polymer gradually loses its
capacity to absorb water (24), and this absorbency loss

increases with both temperature and the duration of the heat
treatment.  Physical mixtures of starch and saponified PAN
also crosslink when heated (25).   An increase in hydrogen
bonding between polymer chains (e.g., through starch hydroxyls)
due to removal of bound water molecules at the higher
temperatures could explain these findings; however, if this
mechanism were operating, loss of absorbency should parallel
the loss of water when HSPAN is heated.  This is not what we
observed experimentally (Table V).  When samples of polymer,

Table V. Influence of Water Loss on Absorbency
of Saponified Starch-g-PAN[a]

| Heating conditions | | | |
|---|---|---|---|
| Temp.,°C | Time, h | Weight Loss, % | Absorbency[b], g/g |
| 25 (control) | = | --- | 730 |
| 60 | 1 | 2.4 | 680 |
| 80 | 1 | 6.8 | 700 |
| 100 | 1 | 10.4 | 680 |
| 120 | 1 | 12.8 | 680 |
| 140 | 1 | 14.8 | 480 |
| 100 | 3 | 12.4 | 700 |
| 100 (vacuum) | 3 | 14.1 | 680 |

[a]A commercial sample prepared from gelatininzed starch (SGP 502S,
Henkel Corp., screened to 100-200 mesh, water content:  14.2%.

[b]Distilled water.

containing 14.2% water, were heated in an oven for 1 hr at
temperatures ranging from 60 to 120°C, absorbencies of the
heated polymers were not greatly affected, even though nearly
all of the water had been driven off at 100-120°C, as
evidenced by weight loss of the samples.  The fact that, even
at these temperatures, a small amount of water was still
retained by the polymer was apparently not the reason that
absorbency did not decrease.  When two separate polymer samples
were heated in the oven for 3 hr at 100°C, the first at
atmospheric pressure and the second under a vacuum of about
3 mm Hg, both polymers showed about the same absorbency, even

though the vacuum-heated polymer had virtually all of its
water removed.

When a sample of HSPAN was heated for 1 hr at 140°C
(Table V), its weight loss was actually slightly greater than
the original water content of 14.2%, and there was also a
significant decrease in water absorbency.  A condensation type
of crosslinking reaction with loss of volatiles might account
for these observations, and either hydroxyl, carboxamide, or
carboxyl substituents could participate in such reactions at
this high temperature.  A choice among the several mechanistic
pathways must await further research.

Conclusions

There are a number of factors which simultaneously
contribute to give HSPAN its unique properties.  First of all,
crosslinking occurs during the graft polymerization reaction of
acrylonitrile with starch, probably by combination of PAN
macroradicals.  Further crosslinking within the granule
structure takes place during alkaline saponification.
Crosslinking of PAN with itself can occur when saponifications
are carried out in systems composed predominantly of alcohol;
however, starch:PAN crosslinking is the major reaction in
solvents which contain mainly water.  As a result of these
crosslinking reactions, individual granules of starch-g-PAN
do not disintegrate when saponified with hot alkali, but retain
their integrity and exist in water as highly swollen gel
particles.  Aqueous dispersions of these gels thus have high
viscosity, when all the free water has been absorbed and the
gel particles are in a closely packed state.

When viscous aqueous dispersions of HSPAN are spread onto
a Teflon-coated tray and allowed to dry, individual gel
particles knit together to form continuous films. Gel particles
also coalesce to form larger conglomerates when the polymer
is isolated from water by other techniques, such as alcohol
precipitation or drum drying.  Dry HSPAN does not redisperse
back into gel particles when placed in water but swells as
either a continuous film or as macroparticles as it imbibes
water.  The formation of primary chemical bonds between
individual gel particles need not be proposed to account for
these properties.  The behavior of HSPAN is similar in many
respects to the published behavior of crosslinked rubber
latexes, and HSPAN properties may be similarly explained by
assuming interdiffusion of polymer chain ends on the surfaces
of gel particles, followed by hydrogen bonding between these
polymer chains.

When dry HSPAN is heated, its ability to absorb water is
diminished.  This loss of absorbency is not related to loss
of bound water and therefore cannot be due to additional

hydrogen bonding.  A condensation type of crosslinking reaction is probably occurring between hydroxyl, carboxamide, or carboxyl substituents at high temperatures.

Experimental

Materials.  Granular Globe Pearl corn starch (Globe 3005; water content about 10%) was from CPC International. Acrylonitrile (Eastman practical grade) was fractionated at atmospheric pressure through a 15-in. Vigreux column, and a center cut was collected.  Ceric ammonium nitrate was Fisher certified ACS grade.  PAN homopolymer was Polymeric Acrylonitrile Type A from DuPont.

Graft Polymerization.  Ceric Initiation.  A stirred slurry of 10 g of starch in 200 ml of water was sparged with a slow stream of nitrogen for 1 hr at room temperature; 15 g of acrylonitrile was then added, followed after 5 min by a solution of 0.338 g of ceric ammonium nitrate in 3 ml of 1N nitric acid.  In the reaction run with 1-hexanethiol, ceric ammonium nitrate solution was added first, followed after 5 min by a solution of 1.0 g of mercaptan in 15 g of acrylonitrile.  The resulting mixture was allowed to stir for 2 hr at 25-27°C (temperature maintained with ice-water) and then was diluted with 200 ml of ethanol. The pH was adjusted to 6-7 with sodium hydroxide solution, and the polymer was isolated by filtration, washed with water and ethanol, and vacuum dried at 60°C.  Ungrafted PAN was removed by repeated extraction of the polymer with dimethylformamide (DMF) at room temperature.

Graft Polymerization.  Cobalt-60 Initiation.  The cobalt-60 source was a Gammacel 200 unit from Atomic Energy of Canada, Ltd.  Dose rate at the center of the chamber was 0.44-0.42 Mrad/hr, as calculated from the original dosimetry data provided by the manufacturer and the decay rate of cobalt-60.
    A stirred slurry of 10 g of starch in 100 ml of water was sparged with a slow stream of nitrogen for 30 min at room temperature, and acrylonitrile (5, 10, or 15 g) was added. In reactions run with mercaptans, either 1.0 g of 1-hexanethiol or 0.1 g of 2-mercaptoethanol was dissolved in 15 g of acrylonitrile.  The reaction mixture was stirred magnetically and irradiated with cobalt-60 to a total dose of 0.1 Mrad. The reaction mass thickened with the onset of polymerization, and most reaction mixtures were too thick to stir by the end of the irradiation period.  Reaction temperature reached 40-50°C due to the exothermic polymerizations.  The reaction mass was allowed to stand for 2 hr at ambient temperature, and the polymer was isolated by filtration, washed with water and with ethanol, and vacuum dried at 60°C.  Ungrafted PAN was

removed from the polymer by repeated extraction with DMF
at room temperature.

A similar procedure was used to prepare starch-g-
polyacrylamide, and 15 g of acrylamide (97%, Polysciences) was
used in the polymerization. After irradiation, the reaction
mass was extracted several times with water to remove ungrafted
polyacrylamide, and the graft copolymer was washed with ethanol
and vacuum dried at 60°C. Weight percent polyacrylamide in
the graft copolymer (% add-on) was 35%, based on the weight
gain of starch.

Characterization of Graft Copolymers. Starch was removed
from starch-g-PAN by heating 2 g of graft copolymer in 150 ml
of 0.5N hydrochloric acid for 1.5 hr under reflux. The
residual PAN was separated by filtration, washed with water
and with ethanol, and dried. Infrared analysis showed the
amount of carbohydrate remaining to be near the limit of
detectability of about 5%. Percent add-on was calculated by
weight loss on acid hydrolysis, and the molecular weight of
PAN ($\bar{M}_v$) was determined from its intrinsic viscosity in DMF
solution (26). Grafting frequency, expressed as the average
number of anhydroglucose units (AGU) per grafted PAN chain,
was calculated from % add-on and $\bar{M}_v$ of PAN.

Solubility Determination in Dimethylsulfoxide (DMSO).
About 2-2.5 g of polymer, which had been previously oven
dried, was allowed to stand overnight at room temperature
over water in a closed container. Water contents of these
moistened polymers ranged from 13-22%, depending on
PAN content. About 1.2 g (accurately weighed) of moistened
polymer was dispersed in 200.0 g of DMSO, and the resulting
mixture was stirred and heated to 75°C. The flask was
stoppered, and the dispersion was heated with occasional
stirring in a 75°C oven for 22 hr and then was cooled to
room temperature. The mixture was centrifuged, and the
supernatant was gravity filtered through fluted Whatman 54
paper. A weighed portion of filtrate was evaporated to near
dryness, and the polymer was precipitated with 95% ethanol,
washed with 95% ethanol, and dried. Percent solubility
was calculated from the weight of dry soluble polymer and
the initial weight of polymer used, after correcting for %
moisture.

Preparation of DMSO-Soluble Starch-g-PAN Samples and
Water-Soluble Starch-g-Polyacrylamide. Five grams of starch-
g-PAN (prepared by either ceric- or cobalt-60 initiation) was
dispersed in 333 g of DMSO, and the dispersion was heated for
2 hr at 115°C. The cooled dispersion was then treated with
ultrasound for 10 min to mechanically rupture gel particles and
to render the polymer soluble (Branson Sonifier, Model S 125;

set for maximum output) the treated dispersion then was allowed to filter through fluted Whatman 54 paper.  The filtrate was concentrated, and the polymer was precipitated with 95% ethanol. The polymer was removed by filtration, washed with 95% ethanol, and dried under vacuum at 60°C.  A portion of sonified starch-g-PAN was subjected to acid hydrolysis, and % add-on by weight loss and $\bar{M}_v$ of grafted PAN were determined.  Total solubility in DMSO at 75°C was confirmed for the ceric-initiated starch-g-PAN preparation.

Starch-g-PAN with 40% add-on ($\bar{M}_v$ of PAN:35,000) was prepared by ceric initiation as described above, with the exception that only 10 g of acrylonitrile was used.  Five grams of this graft copolymer was dispersed in 200 ml of water, and concentrated hydrochloric acid was added to give a pH of 2.0.  The mixture was heated under reflux for 15 min, and the polymer was isolated by filtration.  The polymer was suspended in water, the pH was adjusted to 6.5 with sodium hydroxide solution, and the polymer was again separated by filtration.  The polymer was washed with water and with ethanol and dried under vacuum at 60°C.  The yield was 4.357 g of starch-g-PAN, which was 99% soluble in DMSO at 75°C.  The % add-on was 46%, as calculated from the original 40% add-on and the loss of 0.643 g of starch by acid hydrolysis.

Five grams of starch-g-polyacrylamide was dispersed in 333 ml of water and the mixture was heated for 4.5 hr at 95-100°C.  The cooled dispersion was then treated with ultrasound, as described for starch-g-PAN in DMSO.  The resulting solution was gravity-filtered through fluted Whatman 54 paper, and the filtrate was freeze-dried to give 4.4 g of polymer.  To give a denser, more compact product, which might more closely resemble soluble starch-g-PAN, the freeze-dried polymer was dispersed in 20 ml of water, and the polymer was precipitated from the thick paste by addition of ethanol.  The polymer was separated by filtration, washed with ethanol, and vacuum dried at 60°C.

**Preparation of Starch-PAN Synthetic Mixture.**  Solutions of both starch and PAN homopolymer were prepared in DMSO at 1% solids.  Equal weights of the two solutions were combined and then concentrated under vacuum. The polymer mixture was precipitated with ethanol, and the precipitated solid was washed with ethanol and dried under vacuum at 60°C.  PAN content of the mixture was 45%, as determined by weight loss on acid hydrolysis.

**Alkaline Saponifications in Water.**  A suspension of 1.0 g of starch-g-PAN or starch-PAN physical mixture in 9 ml of 0.7N sodium hydroxide (in a 25 ml Erlenmeyer flask) was heated on a steam bath for 5-10 min until the mixture thickened sufficiently to preclude settling.  Reactions with either starch or PAN

homopolymer were run with 0.5 g of polymer. The flask was
loosely stoppered (to permit escape of ammonia) and heated for
3 hr in a 95-100°C oven. The reaction mass was then diluted
with water (75 or 150 ml, depending on the weight of polymer
saponified) and dialyzed against distilled water. A known
weight of the dialyzed dispersion (pH about 7) was freeze
dried to determine % solids. The dispersion was diluted with
water to 0.25% solids, and the Brookfield viscosity was
obtained at 30 rpm. With some dispersions, a well-drained
insoluble gel fraction could be isolated by gravity filtration
through fluted Whatman 54 paper. A weighed portion of this
insoluble gel was freeze-dried, and the absorbency (expressed
as grams of water-swollen gel per gram of dry polymer) was
calculated from the weight of freeze-dried solid. To reduce
viscosity and polymer swelling, the dispersion was acidified
with hydrochloric acid to pH 4.5, and a portion of this
dispersion was allowed to gravity filter through fluted
Whatman 54 paper. The percent soluble polymer was calculated
from the % solids in both the filtrate and the unfiltered
dispersion, as determined by freeze-drying.

   Alkaline Saponifications in Aqueous Ethanol. A solution
of 2 g of 50% sodium hydroxide in 4.44 ml of water and 4.44 ml
of 95% ethanol was prepared, and 1 g of either starch-g-PAN
or starch-PAN physical mixture was added. Reactions with starch
or PAN homopolymer were run with 0.5 g of polymer. The mixture
was heated under reflux for 3 hr, and the resulting reaction
mass was dispersed in water, dialyzed, and analyzed as described
for saponifications in water. Saponifications run at higher
ethanol:water ratios were carried out in a similar manner.

   Enzymatic Hydrolysis of HSPAN. HSPAN for this particular
experiment was prepared as follows. Five grams of starch-g-PAN
(prepared from granular starch, 50% add-on, $\bar{M}_v$ of PAN:64,000)
in 45 ml of 0.7$\underline{N}$ sodium hydroxide solution was heated for 3 hr
at 95-100°C. The reaction mass was added to 500 ml of methanol,
and the mixture was subjected to high-shear stirring (Waring
Blendor) for 1 min. HSPAN was separated by filtration, washed
with methanol, and vacuum dried at 60°C.
   Two grams of HSPAN was added to 500 ml of water, the
pH was adjusted from 9 to 6.5 with dilute hydrochloric acid,
and 0.1 ml of Thermamyl 60L enzyme solution (Novo Enzyme Corp.)
was added. The resulting mixture was heated at 95°C for 21 hr,
and the clear yellow solution was exhaustively dialyzed against
distilled water. Freeze drying yielded 1.235 g of polymer,
which contained only about 5% residual carbohydrate (by
infrared analysis). The number average molecular weight of
this polymer was 44,000, as determined in 0.15$\underline{N}$ sodium chloride
solution on a Melabs Model CSM-2 membrane osmometer equipped
with a B-19 membrane (Schleicher and Schuell Co.).

Film Formation. Starch–g–PAN samples used for this study
were prepared as described above, except that the small amounts
of PAN homopolymer were not removed by DMF extraction. For the
graft polymerization with gelatinized starch, the starch–water
slurry was heated for 30 min at 85°C before reaction at room
temperature with acrylonitrile and ceric ammonium nitrate.
Saponifications in these experiments were carried out by
stirring 55 g of graft copolymer with 450 ml of 0.7N sodium
hydroxide solution in a sigma mixer for 2 hr at 90–100°C.
The reaction mass was stirred with 3 l. of methanol, and
HSPAN was isolated by filtration. The polymer was washed
with 90:10 methanol–water, dried under vacuum at 40°C, and
ground to pass 40 mesh (yield: 63–64 g).

Either 1.0 g of HSPAN from granular starch or 0.5 g of
the polymer derived from gelatinized starch was added to
800 ml of water, and the dispersion was slowly stirred
overnight at room temperature. The mixture was centrifuged
(1500 X $g$) and the supernatant decanted. The gel fraction
was subjected to three more water extractions and was then
spread onto a Teflon-coated tray and dried in a forced air
oven at about 40°C.

HSPAN films containing 10% by weight of either
saponified PAN or soluble starch were prepared by separately
saponifying starch–g–PAN (prepared from granular starch by
ceric-initiation) and PAN homopolymer and then dialyzing
the saponificates. Starch solution was prepared by dissolving
an acid-modified starch (Clinton 290B) in water. Solutions/
dispersions were then combined in the desired ratios (after
determining concentrations by freeze drying) and were dried
on Teflon-coated trays.

A film from Carbopol 941 (B. F. Goodrich) was prepared
by dispersing 0.5 g of polymer in 200 ml of water. Sodium
hydroxide solution was added to adjust the pH to 7.5, and
the dispersion was then dried on a Teflon-coated tray.

A film from Permasorb 10 (National Starch & Chemical
Corp.) was prepared by dispersing 0.50 g of polymer in 200 ml
of water and drying the dispersion on a Teflon-coated tray.

Influence of Heating on Absorbency and Moisture Loss.
The HSPAN used in this study was a commercial sample prepared
from gelatinized starch (SGP 502 S, Henkel Corp.), which we
screened to give a fraction that passed 100 mesh but was
retained by 200 mesh. The water content was 14.2%, as determined
by drying in an Abderhalden drying apparatus for 4 hr under
vacuum (1 mm Hg) at 100°C over $P_2O_5$.

Duplicate 0.5 g samples of HSPAN were accurately weighed
into small glass-stoppered vials, and the open vials were
kept for 1 hr in an oven heated to the desired temperature.
The vials were stoppered, allowed to cool in a desiccator,
and then weighed to determine the percentage of the original
sample weight lost through volatilization. Percent weight

loss of two duplicate samples generally did not differ by more than 0.2.

To determine water absorbency, an accurately weighed 5 mg sample of HSPAN was allowed to soak for 30 min in 50 ml of distilled water.  The swollen polymer was then separated from unabsorbed water by screening through a tared 280 mesh sieve, which was 4.8 cm in diameter.  The polymer on the sieve was allowed to drain for 20 min, and the sieve was then weighed to determine the weight of water-swollen gel. Absorbency was calculated as grams of water per gram of polymer.  No correction for residual moisture in the polymer was applied.  Absorbencies were run in duplicate, and results agreed to within 10%.

Literature Cited

1.    Fanta, G. F.; Bagley, E. B.  Encyclopedia of Polymer Science and Technology, Supplement, Vol. 2, N. M. Bikales, Ed., Wiley, New York, 1977, p. 669.
2.    Gugliemelli, L. A.; Weaver, M. O.; Russell, C. R.; Rist, C. E.  J. Appl. Polym. Sci. 1969, 13, 2007.
3.    Fanta, G. F.; Weaver, M. O.; Doane, W. M.  Chem. Technol. 1974, 4, 675.
4.    Weaver, M. O.; Montgomery, R. R., Miller, L. D.; Sohns, V. E.; Fanta, G. F.; Doane, W. M.  Staerke, 1977, 29, 413.
5.    Taylor, N. W.; Bagley, E. B.  J. Appl. Polym. Sci. 1974, 18, 2747.
6.    Fanta, G. F.; Baker, F. L.; Burr, R. C.; Doane, W. M.; Russell, C. R.  Staerke 1977, 29, 386.
7.    Rout, A.; Rout, S. P.; Singh, B. C.; Santappa, M. Makromol. Chem. 1977, 178, 639.
8.    Mohanty, N.; Pradhan, B.; Mahanta, M. C.  Eur. Polym. J. 1980, 16, 451.
9.    Fanta, G. F.; Burr, R. C.; Russell, C. R.; Rist, C. E. Cereal Chem. 1970, 47, 85.
10.   Hofreiter, B. T.  J. Polym. Sci., Polym. Chem. Ed. 1974, 12, 2755.
11.   Whistler, R. L.; Ingle, T. R.  Starch: Chemistry and Technology, Vol. 1, R. L. Whistler and E. F. Paschall, Eds., Academic Press, New York, 1965, p. 414.
12.   Hofreiter, B. T.; Russell, C. R.  Staerke 1974, 26, 18.
13.   Smith, T.  U.S. Patent 3,661,815, May 9, 1972.
14.   Peebles, L. H., Jr.  Encyclopedia of Polymer Science and Technology, Supplement, Vol. 1, H. F. Mark and N. M. Bikales, Eds., Wiley, New York, 1977, p. 2.
15.   Takata, T.; Hiroi, I.; Taniyama, M.  J. Polym. Sci. A, 1964, 2, 1567.

16. Fanta, G. F.; Burr, R. C.; Doane, W. M.; Russell, C. R. J. Appl. Polym. Sci. 1971, 15, 2651.

17. Weaver, M. O.; Bagley, E. B.; Fanta, G. F.; Doane, W. M. Appl. Polym. Symp. 1974, No. 25, 97.

18. Antholz, P.; Swarthout, E. J. U.S. Patent 4,221,684, Sept. 9, 1980.

19. Voyutskii, S. S. Autohesion and Adhesion of High Polymers, Polymer Reviews, Vol. 4, H. F. Mark and E. H. Immergut, Eds., Wiley, New York, 1963, p. 80.

20. Bradford, E. B.; Vanderhoff, J. W. J. Macromol. Chem. 1966, 1, 335.

21. Foster, J. F., Starch, Chemistry and Technology, Vol. 1, R. L. Whistler and E. F. Paschall, Eds., Academic Press, New York, 1965, p. 350.

22. Voyutskii, S. S. Autohesion and Adhesion of High Polymers, Polymer Reviews, Vol. 4, H. F. Mark and E. H. Immergut, Eds., Wiley, New York, 1963, p. 87.

23. Taylor, N. W.; Bagley, E. B. J. Polym. Sci., Polym. Phys. Ed. 1975, 13, 1133.

24. Bagley, E. B.; Taylor, N. W. Ind. Eng. Chem., Prod. Res. Dev. 1975, 14, 105.

25. Fanta, G. F.; Doane, W. M. U.S. Patent 4,116,899, Sept. 26, 1978.

26. Onyon, P. F. J. Polym. Sci. 1959, 37, 315.