

GRAFTING OF ACRYLONITRILE ONTO POTATO STARCH (PS) USING CERIC AMMONIUM NITRATE AS INITIATOR

A Rasheed Khan^{*a}, Kausar Ali Syed^b, Khalil Ahmed^b, A F K Ifrahim^b

^aFuel Research Centre, PCSIR Karachi-75280, Pakistan

^bPolymer Research Centre, PCSIR Laboratories Complex, Karachi-75280, Pakistan

(Received 4 July 2000; accepted 25 October 2000)

Graft copolymerization of acrylonitrile (AN) onto potato starch (PS) using ceric ammonium nitrate as initiator was accomplished. Before grafting starch was gelatinized in two ways; one is dispersing PS in water and other in aqueous butanol. The results show that PS gelatinized in aqueous iso-butanol facilitates the grafting of growing polymer chain of AN onto backbone slightly better than PS gelatinized in water. The effects of monomer, backbone and catalyst concentration on rate of conversion of monomer, rate of graft copolymerization, rate of homopolymerization, grafting efficiency and grafting rate are discussed in detail. The absorbency of saponified products of each sample was determined in distilled water, tap water and aqueous solution of NaCl and KCl and discussed thoroughly.

Key words: Graft copolymerization, Acrylonitrile, Potato starch (PS)

Introduction

Graft copolymerization is very important from the technological point of view. It helps in modifying a polymer product with specially desired properties. Starch may be modified by grafting with vinyl monomers like acrylonitrile, acrylamide, acrylates etc. One of the useful end product of these graft copolymer is super absorbent polymer. They possess remarkable property of absorbing (within a few minutes) and retaining water several hundred times its weight (Fanta *et al* 1982). In the agriculture area, seeds are being coated with this product to hold water on the seed surface and thus enhance germination process (Chaudry *et al* 1995). Also plant-roots are being dipped into HSPAN-water (hydrolysed poly acrylonitrile-water) before transplanting to help prevent transplant shock. In our earlier papers grafting of onto AN maize and rice starches were reported (Khan *et al* 1999, 2000b). These graft copolymers on saponification give products which absorb and retain water about 175-250 times its weight (ww^{-1}). This paper deals with graft copolymerization of AN onto potato starch (PS) using ceric ammonium nitrate (CAN) as initiator. Before grafting starch was first gelatinized. This is done in two different ways; one is dispersing starch in water and other in iso-butanol to find out its effect on yield and other parameters. Besides, grafting rate (GR), grafting efficiency (GE), rate of conversion of monomer (Rp), rate of grafting (Rg) and absorbency in water obtained from different sources were studied.

Experimental

Material. CAN (Riedel-dattaen), GR grade NaCl, KCl and NaOH, KOH (Merck) and PS (Commercial grade) were used without further purification. Pure grade AN was fractionally distilled at their respective boiling points before use.

Procedure of graft copolymerization. Grafting of AN onto starch was carried out in flanged flask with nitrogen outlet/inlet by two methods. In one method, starch was gelatinized in water whereas in other method starch was gelatinized in aqueous iso-butanol.

Method-1. Required quantity of starch was added in the reaction flask containing 100 ml water. It was stirred at 80°C for 1h. A slow stream of nitrogen was allowed to bubble through the slurry. The whole content were then cooled to room temperature. Freshly prepared solution of CAN in 5.0 ml of 1N HNO₃ as shown in respective Table was added. The resulting mixture was stirred under nitrogen for 1h at 30-35°C. Thereafter ethanol was added and pH was adjusted at 6-6.5 with aqueous NaOH solution. The polymer was separated by filtration, washed with 50% aqueous ethanol and then with ethanol. It was finally dried under vacuum. Homopolymer (PAN) was removed by several extractions with DMF at room temperature and the percentage of grafted product was determined.

Method-2. In this method, starch was gelatinized in iso-butanol following the procedure given elsewhere (Khan *et al* 1999). Required quantity of starch was added in the flask containing 200 ml water and 20 ml butanol. A slow stream of

* Author for correspondence

nitrogen was allowed to bubble through the reaction contents while refluxing for 4-5 h. It was cooled and alcohol was distilled off along with some quantity of water (30 ml). CAN (0.3 g) was added followed by a required quantity of AN. The whole contents were heated at 58-60°C under nitrogen for 4 h. At the end of which it was cooled, ethanol was added and pH was adjusted to 6.5. The polymer was separated by filtration. It

was first washed with 50% aqueous ethanol and then with ethanol. Finally the product was dried under vacuum and kept in a desiccator.

Homopolymer was removed by several extractions with DMF at room temperature and the percentage of ungrafted product was determined as shown in the Tables. It was about 1-1.8%. Since the grafted starch contained a very small amount of

Table 1

Effect of monomer concentration on graft copolymerization of acrylonitrile (AN) onto potato starch (PS) using ceric ammonium nitrate (CAN) in HNO₃ as catalyst. The (PS) was gelatinized in aqueous butanol

Expt No	AN (g)	Total conversion of AN		Elemental analysis %N	Grafted AN (g)	GR %	GE %	Rate of polymerization x 10 ⁵ mole sec ⁻¹			Absorbency g H ₂ Og ⁻¹			
		(g)	%					Rp	Rg	Rh	D.W	T.W	*NaCl	*KCl
												1 %	1 %	
1	12.0	7.15	59.6	14.80	6.9	276	96.5	9.3684	9.0409	0.3275	224	167	58	74
2	16.0	9.63	60.2	15.90	9.32	373	96.8	12.6179	12.2117	0.4062	183	165	27	19
3	20.0	12.62	63.1	16.80	12.25	484	97.6	16.5356	16.0508	0.4848	164	159	13	11
4	28.0	17.98	64.2	19.42	17.5	700	97.3	23.5587	22.2997	0.6290	201	193	49	56

PS, 2.5g; Time, 4h; CAN, 5.5x10⁻⁴ mole; Temp, 60°C; *aqueous NaCl and KCl

Table 2

Effect of backbone concentration on grafting acrylonitrile (AN) onto potato starch (PS) using ceric ammonium nitrate (CAN) in HNO₃ as catalyst. The (PS) was gelatinized in aqueous butanol

Expt No	PS (g)	Total conversion of AN		Elemental analysis %N	Grafted AN (g)	GR %	GE %	Rate of polymerization x 10 ⁵ mole sec ⁻¹			Absorbency g H ₂ Og ⁻¹			
		(g)	%					Rp	Rg	Rh	D.W	T.W	*NaCl	*KCl
												1 %	1 %	
5	2.0	7.86	49.1	16.1	7.60	380	96.7	10.2987	9.9581	0.3406	188	183	26	24
6	2.5	9.63	60.2	15.9	9.32	373	96.8	12.6179	12.2117	0.4062	183	165	27	19
7	3.0	9.94	62.1	18.8	9.70	323	97.6	13.0241	12.7096	0.3145	183	165	23	20
8	4.0	11.63	72.7	19.0	11.35	283	97.6	15.2384	14.8715	0.3669	213	193	58	47

AN, 16g; Time, 4h; CAN, 5.5x10⁻⁴ mole; Temp, 60°C; *aqueous NaCl and KCl

Table 3

Effect of catalyst concentration on grafting acrylonitrile (AN) onto potato starch (PS) using ceric ammonium nitrate (CAN) in HNO₃ as catalyst. The (PS) was gelatinized in aqueous butanol

Expt No	PS (g)	Total conversion of AN		Elemental analysis %N	Grafted AN (g)	GR %	GE %	Rate of polymerization x 10 ⁵ mole sec ⁻¹			Absorbency g H ₂ Og ⁻¹			
		(g)	%					Rp	Rg	Rh	D.W	T.W	*NaCl	*KCl
												1 %	1 %	
9	5.00	7.58	47.4	15.35	7.4	370	97.6	9.9319	9.6960	0.2359	205	184	24	17
10	5.47	7.86	49.1	13.90	7.6	380	96.7	10.2987	9.9581	0.3406	200	190	23	18
11	6.39	9.72	60.8	12.90	9.5	475	97.2	12.7358	12.4475	0.2883	188	181	21	19
12	7.30	11.12	69.5	12.46	10.8	540	97.1	14.5702	14.1509	0.4193	192	180	29	21

PS, 2.5g; AN, 16 g; Time, 4h; Temp, 60°C; *aqueous NaCl and KCl

homopolymer the product was saponified without its DMF extraction.

Saponification of graft copolymer. The graft product was saponified with 8% alcoholic solution of KOH at 70°C for

2h. The saponified product was initially washed with 50% aqueous alcohol (95%) and then with ethanol to remove excess KOH and dried under vacuum. It was crushed and kept in air tight bottle.

Table 4

Effect of monomer concentration on grafting acrylonitrile (AN) onto potato starch (PS) using ceric ammonium nitrate (CAN) in HNO₃ as catalyst. The (PS) was gelatinized in aqueous medium

Expt No	PS (g)	Total conversion of AN		Elemental analysis %N	Grafted AN (g)	GR %	GE %	Rate of polymerization x 10 ⁵ mole sec ⁻¹			Absorbency g H ₂ Og ⁻¹			
		(g)	%					Rp	Rg	Rh	D.W	T.W	*NaCl	*KCl
													1 %	1 %
13	12.0	9.24	77	15.38	9.08	182	98.3	4.7589	4.7589	0.0839	244	167	58	74
14	16.0	13.92	87	15.76	13.70	274	98.4	7.2956	7.1803	0.1153	183	165	23	21
15	20.0	17.20	86	11.23	16.91	338	98.3	9.0147	8.8627	0.1520	160	172	33	32
16	28.0	25.00	89	16.30	24.72	494	98.9	13.1027	12.9559	0.5032	188	178	48	66

PS, 5.0 g; CAN (in 1 N HNO₃), 0.274 g; Time, 1h; Temp, 30-35°C; *aqueous NaCl and KCl

Table 5

Effect of backbone concentration on grafting acrylonitrile (AN) onto potato starch (PS) using ceric ammonium nitrate (CAN) in HNO₃ as catalyst. The (PS) was gelatinized in aqueous medium

Expt No	PS (g)	Total conversion of AN		Elemental analysis %N	Grafted AN (g)	GR %	GE %	Rate of polymerization x 10 ⁵ mole sec ⁻¹			Absorbency g H ₂ Og ⁻¹			
		(g)	%					Rp	Rg	Rh	D.W	T.W	*NaCl	*KCl
													1 %	1 %
17	1.5	7.47	46.7	19.00	7.36	491	98.5	3.9151	3.8574	0.0577	181	168	25	20
18	2.5	12.39	77.4	15.76	12.20	488	98.5	6.4937	6.3941	0.0996	148	124	21	14
19	5.0	13.92	87.0	15.76	13.70	274	98.4	7.2956	7.1803	0.1153	183	165	23	21
20	8.0	14.17	88.6	15.90	13.93	174	98.3	7.4266	7.3008	0.1258	180	170	21	17
21	10.0	12.96	81.0	16.10	12.70	127	98.0	6.7924	6.6562	0.1362	188	178	23	20

AN, 16 g; CAN (in 1N HNO₃), 0.274 g; Time, 1 h; Temp, 30-35°C; *aqueous NaCl and KCl

Table 6

Effect of catalyst concentration on grafting acrylonitrile (AN) onto potato starch (PS) using ceric ammonium nitrate (CAN) in HNO₃ as catalyst. The (PS) was gelatinized in aqueous medium

Expt No	PS (g)	Total conversion of AN		Elemental analysis %N	Grafted AN (g)	GR %	GE %	Rate of polymerization x 10 ⁵ mole sec ⁻¹			Absorbency g H ₂ Og ⁻¹			
		(g)	%					Rp	Rg	Rh	D.W	T.W	*NaCl	*KCl
													1 %	1 %
22	5.00	17.20	86	15.0	16.91	338	98.3	9.0147	8.8627	0.1520	181	175	21	19
23	5.47	17.40	87	17.2	17.10	342	98.2	9.1195	8.9623	0.1572	190	176	27	23
24	6.39	17.60	88	14.7	17.38	348	98.7	9.2243	9.1090	0.1153	201	190	25	23
25	7.30	18.00	90	11.2	17.75	355	98.6	9.4340	9.3029	0.1311	190	178	58	45

PS, 5.0 g; AN, 20 g; Time, 1 h; Temp, 30-35°C; *aqueous NaCl and KCl

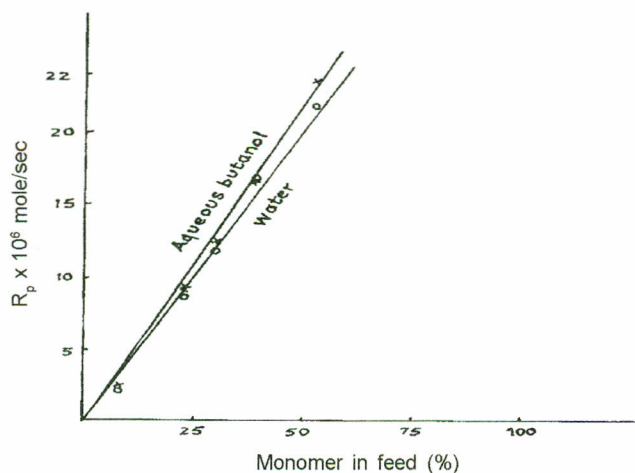


Fig 1. Effect of PS gelatinised in aqueous butanol (x) and water (o) on rate of polymerization of AN

Infrared spectra of graft copolymer and starch were recorded for the identification of grafted PAN chains on the backbone of PS. The products were estimated for nitrogen. Absorbency of saponified materials was determined in different source of water, e.g. tap water, distilled water and aqueous solution of KCl and NaCl at room temperature for 24 h.

Results and Discussion

Table 1-3 illustrate the results of graft copolymerization of AN onto PS gelatinized in aqueous iso-butanol whereas Table 4-6 show the data obtained from graft copolymerization of AN on to PS gelatinized in water. Effects of water obtained from different sources and of aqueous solutions of NaCl on the absorbency of saponified products of graft copolymers are also summarized in Table 1-6.

There are several methods which may indicate that the products obtained by interaction of AN and PS are indeed graft copolymer and not merely physical mixtures of starch and PAN. For this purpose, the products samples were estimated for nitrogen. The analysis of PAN gave 26.3 % nitrogen whilst the 21 products estimated gave 11.2-19.4 % nitrogen. This difference in the percentage of nitrogen may be due to the branching of growing polymer chains of AN onto the backbone of PS. The nitrogen contents of the products samples are different and do not show any regular decrement or increment. It clearly evidences the formation of graft copolymers. PAN is soluble in cold/hot DMF whilst the products samples only get swollen in hot DMF with high solvent uptake. This change also supports the above assumption that the products are graft copolymers. The separation of PAN by the hydrolysis of DMF-extracted PS-g-PAN in 0.5N HCl is an additional proof of grafting of PAN onto PS. The PAN so obtained

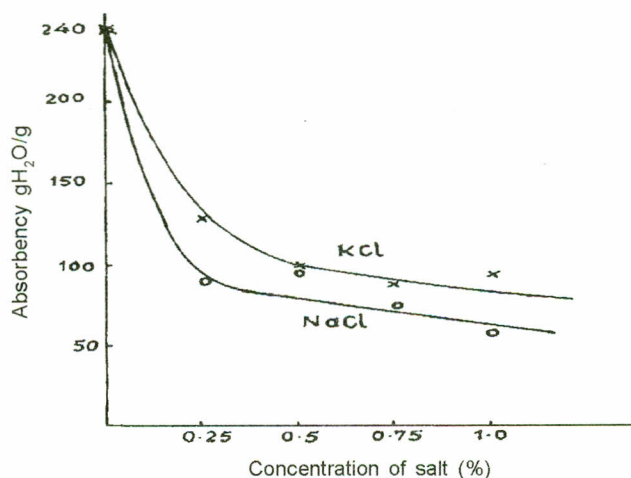


Fig 2. Effects of Na⁺ and K⁺ on absorbency of saponified graft copolymer PS-g-AN.

was estimated for nitrogen as 25.9 % IR spectral studies also support the above observations. The spectrum of PS was compared with the spectrum of PS-g-PAN. The presence of nitrile band at 2240 cm⁻¹ -OH band at 3400 cm⁻¹ and carbonyl band at 1660-1630 cm⁻¹ indicate the coupling of growing polymer chains onto PS.

The effect of monomer concentration on the grafting of AN onto PS is shown in Table 1 (gelatinized in aqueous iso-butanol) and Table 4 (gelatinized in water). The results shown in both tables indicate that with the increment of AN concentration in feed, the values of Rp, Rg, Rh, GR and GE get increased though increase in GE is not appreciable. A similar trend was also observed in the graft copolymer of AN onto maize and rice starches (Khan *et al* 1999). This could be attributed to the higher availability of AN molecules in the close proximity of activated sites of PS at higher monomer concentration. Starch macroradicals (activated sites of PS) are almost immobile and for grafting to occur, the monomer molecules should be in the close vicinity of starch radicals. Growing polymer chains of AN available in the vicinity of starch radicals attach onto the activated sites of starch resulting more grafting. The Rp is greater than Rg since at the early stage of reaction homopolymerization of AN also occurs though it is very low. The monomer propagation species are utilized in the homopolymer of AN which directly influence the GE. Since Rp of AN into homopolymer is very low (2.6-3.4 % in aqueous butanol and 1.4 - 1.6 % in aqueous medium) the value of GE remains the same. Data also show that GR is higher (276 - 700 %) when the PS is gelatinized in aqueous butanol whereas it is on lower side (182 - 494 %) when the starch is gelatinized in water. But the value of GE remains near about the same in both cases.

Table 2 and 5 summarize the effect of backbone concentration on the graft copolymerization of PAN on starch when the starch is gelatinized respectively in aqueous iso-butanol and water respectively. It is very interesting to note that the value of GE was found to be same at all concentrations of starch but GR showed a decrement. On the other hand the values of Rp and Rg increase with increase in concentration of PS. The increment in Rp and Rg and same value of GE at all concentration of backbone may be attributed to the fact that the monomer and initiator are more easily accessible to the surface of starch. The increase in concentration of starch produce large number of grafting sites along the backbone resulting in increases of Rp and Rg. The value of GE does not show any change. On the other hand, the decrease in GR might be due to the decrease of the monomer to starch concentration ratio (AN/PS). It means that the number of grafting sites onto starch are more than the number of growing polymer chains of AN which make use of the grafting sites of starch partially and some unbound starch propagating radicals are left behind and cause mutual termination between starch and propagating species (Mohan *et al* 1989; Khan *et al* 1999).

Tables 3 and 6 include the results of effect of catalyst concentration on the graft copolymerization of AN onto PS when the starch is gelatinized in aqueous butanol and water respectively. These results indicate that GP, Rp, Rg and Rh increased regularly with increase in concentration of catalyst whilst the values of GE remain the same at all concentration of initiator. It is due to more available active centers produced by different medium and the reach of initiating radicals ($-Ce^{+4}$ ions) to PS is facilitated. The value of Rh (homopolymerization of AN) is low which makes the value of GE maximum (98 %) and constant at all concentration of CAN.

In Fig 1, AN (in feed) is plotted against $R_p \times 10^6$ mole sec^{-1} for the graft copolymerization of AN onto the backbone of the PS. It comprises the data for gelatinized PS in aqueous iso-butanol (X) and water (O). These results show that PS gelatinized in aqueous iso-butanol facilitate the grafting of growing polymer chain of AN onto PS better though not to higher side.

Twenty one products of graft copolymers were saponified with 8% alcoholic solution of KOH. The absorbency of these saponified materials was determined in distilled water, tap water and aqueous solutions of NaCl and KCl as shown in Tables 1-6. These results indicate that the absorbency in distilled water ranges 148-244 $g H_2Og^{-1}$ whereas absorbency in tap water ranges 124-193 $g H_2Og^{-1}$. On the other hand absorbency in aqueous solutions of NaCl and KCl respectively is observed as 13-58 $g H_2Og^{-1}$ and 11-74 $g H_2Og^{-1}$ respectively. The absorbency of sample 13 was also determined at different concentration of aqueous solutions of NaCl and KCl which found to be de-

crease with increasing concentration of NaCl and KCl (see Fig 2). Saponification of graft copolymer in alcoholic alkali converts the nitrile substituents of PAN to a mixture of metal carboxylate and carboxamide and affords a polymer that exists in water as a highly swollen but largely insoluble gel. This conversion into carboxylate and carboxamide results in the formation of carboxylic anions in the polymer network which produce electrostatic forces. When the saponified product is placed in water it starts to expand for dissolution in water. Concurrently, the hydrophilic group ($-COO^-$) which are negative ions repel each other, helping the polymer expand further. The polymer has a three dimensional structure which allows it to expand only to a certain extent and the electrostatic forces make the product highly swollen but largely insoluble gel (Khan *et al* 1999, 2000b). The strong electrostatic network is also effected by dissolved CO_2 in distilled water, the presence of Na^+ and K^+ (cations) in tap water including other soluble salts and aqueous solution of NaCl and KCl. It seems that the network becomes too narrow and does not accept excess water. It might be due to the adsorption of various ions including Na^+ and K^+ cations on the surface of saponified polymer. This assumption is supported by the observations shown in Fig 2 and respective tables. Similar results were also obtained in the studies of hydrogels based on PVA-acrylic acid using methylene-bis-acrylamide as crosslinking agent (Khan *et al* 2000a). Furthermore the saponified product of maize AN and rice starch-g-AN show the same tendency towards water.

References

- Chaudry M A, Tahira Ahmad, Khan M F A 1995 Effect of polymer on germination plant weight and permanent wilting point of maize (*Zea Mays*) and soybean (*Glycine*) Max. *Pak J Sci Ind Res* **38** 308-311.
- Fanta G E, Burr R C, Doane W F 1982 Saponified starch-g-polyacrylonitrile. Variables in the Ce^{+4} initiation of graft polymerization. *J Appd Polymer Sci* **27** 2731-2237.
- Khan A Rasheed, Shabiul Hasan, Kausar Ali Syed, Khalil Ahmed 1999 Preparation of graft copolymer maize starch-e-AN and its saponification. *Pak J Sci Ind Res* **42** (1) 74.
- Khan A Rasheed, Farooqi Z H, Shabiul Hasan, Asif Imran 2000a Preparation of hydrogels based on PVA-acrylic acid using methylene-bis-acrylamide as crosslinking agent. *Pak J Sci Ind Res* **43** (1) 60-64.
- Khan A Raheed, Tehzeeb Akhter, Kausar Ali Syed, Ifrahim AFK 2000b Grafting of Acrylonitrile onto rice starch-super absorbent polymer. *Pak J Sci Ind Res* **43** (3) 150-155.
- Mohan D, Radhakrishan G, Rajdurai S, Venkata Rao, Cameran G 1989 Graft copolymerization of acrylamide onto casein. *J Polymer Sci Par A Polymer Chemistry* **27** 2123.