

Hydrolysis of Poly(acrylamide)–Starch Graft Copolymer

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SYNOPSIS

Poly(acrylamide)–starch graft copolymer was treated independently with sodium hydroxide and different acid solutions. The different acids include phosphoric, hydrochloric, and sulphuric acid. The treatment was carried out under a variety of conditions including sodium hydroxide concentration, time, and duration of hydrolysis as well as type of acid used. The extent of hydrolysis was assessed by estimating amide and carboxyl content as well as the acrylate and starch content before and after treatment. It was found that the increment in carboxyl content is equal to the decrement in amide on using sodium hydroxide concentration up to 1*N*, while using higher concentration than 1*N* leads to a difference in formed carboxyl and decreased amide groups. The magnitude of this difference depends on sodium hydroxide concentration as well as temperature and duration of hydrolysis. The maximum value of carboxyl content obtained was 593 meq/100 g sample. The acidic treatment of the starch copolymer does not affect the conversion of amide groups to carboxyl groups, and the sole effect was hydrolysis of starch component of the copolymer. Evaluation of the alkali-treated copolymer as cation exchanger was carried out. The absorption efficiency % of different cations depends on the associated anions and follow the order: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Mg}^{2+}$. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Previous reports^{1–6} have dealt with carboxyl-containing polymers and the ability of the latter to bind heavy metals. It has also been reported^{7–10} that introduction of reactive functional groups in the backbone of highly crosslinked starches brings about products that were capable of removing heavy metal ions from industrial waste water. Thus, anionic starch was prepared by reacting crosslinked starch with monochloroacetic acid.^{11–13} Cation exchange starch could also be prepared by saponification of poly(acrylonitrile)–starch graft copolymers^{14,15} and cyanoethylated starch¹⁵ under the influence of alkali. It was found¹⁵ that beside conversion of the cyanide groups to carboxyl groups, alkaline hydrolysis brings about cleavage of ether linkage of the copolymer and cyanoethyl starch. Cleavage of the ether linkage is greater with cyanoethyl starch than the poly(acrylamide)–starch graft copolymer. The maxi-

imum conversion of cyanide groups into carboxyl groups at the optimum conditions was 43.2%.

The present work is undertaken with a view of studying the hydrolysis of crosslinked poly(acrylamide)–starch graft copolymer in both alkaline and acidic medium. Hydrolysis was carried out under a variety of conditions including sodium hydroxide concentration, acid type, and concentration as well as treatment temperature and duration. This was done to find out the most appropriate conditions for converting the amide groups in the copolymer to carboxyl as a prerequisite for preparing anionic starch. The evaluation of the hydrolysis product as ion exchange is also studied.

EXPERIMENTAL

Materials

Maize starch, acrylamide, potassium persulphate, and sodium hydroxide were of pure grade chemicals. Hydrochloric acid, sulphuric acid, and phosphoric acid were of laboratory grade chemicals. Also, the

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acetate, chloride, and sulphate of zinc, cobalt, copper, and magnesium were of pure grade.

Preparation of Poly(acrylamide)–Starch Graft Copolymers

Maize starch (500 g) was slurried into (5000 mL) of solution containing (1000 g) acrylamide and potassium persulphate (60 mmol/L) and purged for 15 min with nitrogen to remove oxygen. The reaction mixture was heated in an oven at 100°C for 4 h. The reaction product was Soxhlet, extracted with a mixture of ethanol : water (80 : 20) and dried. The prepared poly(acrylamide)–starch graft copolymer was analyzed for nitrogen and carboxyl contents according to reported methods.^{16,17} The prepared poly(acrylamide)–starch graft copolymer contained 785 mmol amide group and 125 mmol carboxyl group/100 g sample.

Alkaline Hydrolysis

Saponification of the aforementioned starch copolymer was performed as follows: 4 g of poly(acrylamide)–starch graft copolymer was added to 30 mL of sodium hydroxide solution (0.5–2.5*N*) in 100 mL stoppered flask. This mixture was placed in thermostated water bath at specified temperature (60–100°C) for different times (15–120 min). At the end of the required reaction time the content of the flask was poured into 400 mL ethyl alcohol containing the necessary amount of H₂SO₄ to adjust the pH to 3. The product was filtered and washed with ethanol : water mixture (70 : 30) and finally with ethanol and dried. The reaction product was analyzed for amide and carboxyl contents.

Acid Hydrolysis

Acid hydrolysis of starch copolymer was performed as follows: 4 g of poly(acrylamide)–starch graft copolymer was added to 50 mL of acid (1*N*) in 100 mL stoppered flask. This mixture was placed in thermostated water bath at specified temperatures (80–100°C) for different times (15–120 min). At the end of the required reaction time, the content was poured into 300 mL ethanol. The product was washed several times with ethanol : water (70 : 30) and finally with ethanol and dried. The product was analyzed for amide and carboxyl contents.

Heavy Metal Ions Removal

A solution (50 mL) of metal ion (0.01 mol) was treated with the prepared sample (0.25 g) added as

solid. After 24 h contact time, the solution were filtered and the residual metal ions concentration in the filtrate were measured.

RESULTS AND DISCUSSION

It is known that amides undergo hydrolysis to carboxylic acids in alkaline or acidic medium.¹⁸ Cross-linked poly(acrylamide)–starch graft copolymer was saponified under alkaline and acidic medium to study the validity of preparing cation exchange starch.

Alkaline Hydrolysis of Starch Copolymer

On treating poly(acrylamide)–starch graft copolymer with sodium hydroxide solution the following reactions were expected: (1) saponification of amide groups to carboxyl groups;¹⁵ (2) deetherification and depolymerization reactions of the polyacrylate component of the copolymer.^{15,19–21} The extent of these reactions depend on the treatment conditions.

Crosslinked poly(acrylamide)–starch graft copolymer with 785 mmol amide and 125 mmol carboxyl group/100 g was subjected to the action of sodium hydroxide of different concentrations (0.5–2.5*N*) at various temperatures (60–100°C) for different times (15–90 min). The hydrolytic effect of the alkali was assessed by monitoring the amide content as well as the carboxyl content of the copolymer before and after hydrolysis. The results obtained are set out in Tables I–III.

Amide Content

The results (Tables I–III) signify that alkaline hydrolysis is accompanied by a decrement in the amide content of the copolymer, irrespective to the conditions used. However, the magnitude of this decrement is determined by sodium hydroxide concentration as well as temperature and duration of hydrolysis, being higher the higher the magnitude of these parameters.

It is further noted that the decrement in the amide content during the first 15 min hydrolysis was relatively high, particularly at a sodium hydroxide concentration higher than 0.5*N*. The decrement in the amide content of the copolymer amount to 3.8%, 10.2%, 16.6%, 41.5%, 50.1%, and 53% when hydrolysis was carried out using 0.50, 0.75, 1.0, 1.5, 2.0, and 2.5*N* sodium hydroxide, respectively, at 60°C: this against 14.6%, 27.4%, 43.3%, 55%, 66%, and 65% at 80°C and 30.6%, 36.3%, 49.7%, 58.1%, 61.5%,

Table I The Amide and Carboxyl Contents of Alkali-Treated Poly(acrylamide)-Starch Graft Copolymer (Expressed as mmol/100 g Sample) at 60°C Using Different Durations and Sodium Hydroxide Concentrations

Reaction Time (min)	[NaOH]																	
	0.5N			0.75N			1.0N			1.5N			2.0N			2.5N		
	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total
0	785	125	910	785	125	910	785	125	910	785	125	910	785	125	910	785	125	910
15	755	155	910	705	205	910	655	255	910	517	388	905	497	390	887	485	350	835
30	715	195	910	670	240	910	625	285	910	438	420	858	422	405	775	333	380	713
45	675	235	910	635	275	910	595	315	910	400	436	836	338	425	763	313	375	688
60	635	275	910	600	310	910	565	345	910	367	455	822	295	430	725	280	383	663
120	595	315	910	575	335	910	550	360	910	310	465	775	280	378	658	208	335	543

Table II The Amide and Carboxyl Contents of Alkali-Treated Poly(acrylamide)-Starch Graft Copolymer (Expressed as mmol/100 g Sample) at 80°C Using Different Durations and Sodium Hydroxide Concentrations

Reaction Time (min)	[NaOH]																	
	0.5N			0.75N			1.0N			1.5N			2.0N			2.5N		
	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total
0	785	125	910	785	125	910	785	125	910	785	125	910	785	125	910	785	125	910
15	670	240	910	570	340	910	445	465	910	405	475	880	383	475	858	284	446	730
30	630	280	910	535	375	910	415	495	910	341	480	821	306	460	766	230	400	630
45	590	320	910	500	410	910	385	525	910	288	483	771	243	461	704	209	383	592
60	555	355	910	465	445	910	355	555	910	257	495	752	215	475	690	198	367	565
120	540	370	910	430	480	910	335	575	910	217	511	728	200	447	647	198	344	542

Table III The Amide and Carboxyl Contents of Alkali-Treated Poly(acrylamide)-Starch Graft Copolymer (Expressed as mmol/100 g Sample) at 100°C Using Different Durations and Sodium Hydroxide Concentrations

Reaction Time (min)	[NaOH]																	
	0.5N			0.75N			1.0N			1.5N			2.0N			2.5N		
	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total	-CONH ₂ Content	-COOH Content	Total
0	785	125	910	785	125	910	785	125	910	785	125	910	785	125	910	785	125	910
15	545	365	910	500	410	910	395	515	910	300	563	863	302	540	842	240	465	705
30	540	370	910	483	427	910	380	530	910	270	508	778	240	465	705	180	396	576
45	535	375	910	465	445	910	360	550	910	265	468	733	223	430	653	150	351	501
60	530	380	910	450	460	910	345	565	910	250	435	685	209	405	614	135	335	470
120	520	390	910	430	480	910	317	593	910	240	395	635	180	350	530	116	320	436

and 67% at 100°C. Beyond 15 min hydrolysis, the decrement in amide content continues but in a regular manner.

Carboxyl Content

Tables I-III show the carboxyl content of the prepared copolymer before and after alkaline hydrolysis under different conditions. The data show that:

1. The carboxyl content of the hydrolyzed poly(acrylamide)-starch graft copolymer samples depends on sodium hydroxide concentration as well as duration and temperature of the treatment.
2. The carboxyl content increases on increasing reaction duration and/or reaction temperature within sodium hydroxide concentration 0.5-1.5N and 0.5-1.0N at 60-80°C and 100°C, respectively. On the other hand, the

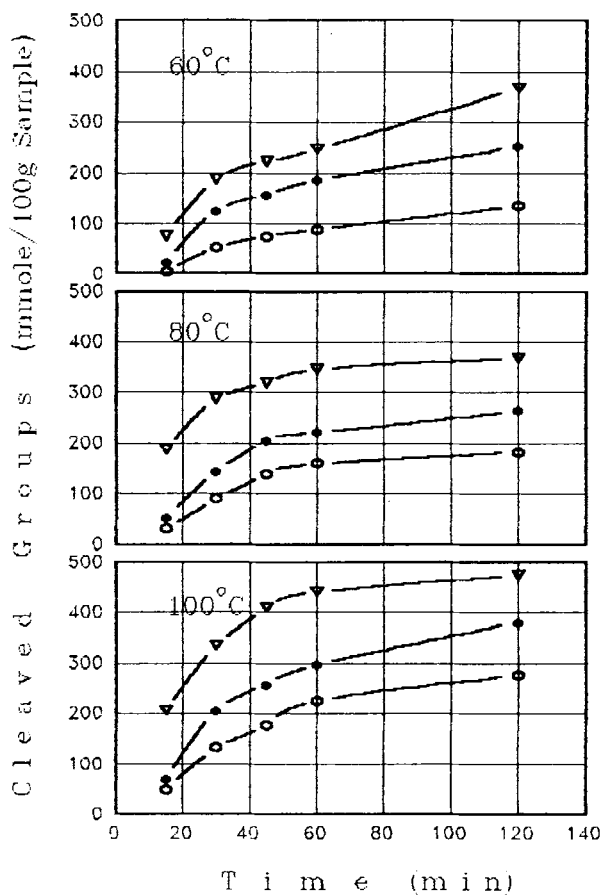


Figure 1 Cleaved groups (expressed as m.mol/100 g sample) under the influence of sodium hydroxide on poly(acrylamide)-starch graft copolymers at different conditions. O, 1.5N; ●, 2N; ▽, 2.5N.

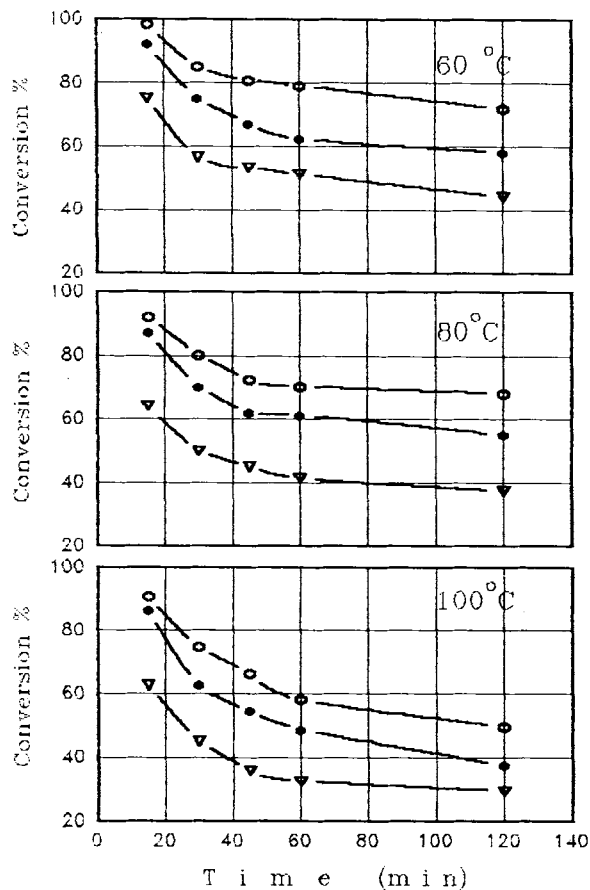


Figure 2 Conversion (%) of amide groups into carboxyl groups through alkali treatment of poly(acrylamide)-starch graft copolymers at different conditions. O, 1.5N; ●, 2N; ▽, 2.5N.

carboxyl content increases with reaction duration to reach a maximum and then decreases on using sodium hydroxide concentration higher than 1.5N.

- The values of these maxima depend on sodium hydroxide concentration as well as temperature, i.e., at 60°C the maxima occur after 45 min and 15 min on using 2.0N and 2.5N sodium hydroxide, respectively, and at 80-100°C, the maxima occur after 15 min on using sodium hydroxide concentration higher than 1.5N.
- The increment in the carboxyl content during the first 15 min hydrolysis is higher compared to those formed during the next equal periods of hydrolysis. This is particularly observed on using all sodium hydroxide concentration at 80-100°C and 0.75N upward at 60°C. The increment in carboxyl content within the first 15 min on using 1.5N were 33.5%, 44.6%, and

Table IV Amid and Carboxyl Contents of Acid-Treated Poly(acrylamide)-Starch Graft Copolymer (Expressed as meq/100 g Sample) at 60 and 80°C Under Different Duration

Time (min)	60°C			80°C		
	H ₃ PO ₄	H ₂ SO ₄	HCl	H ₃ PO ₄	H ₂ SO ₄	HCl
	Amide Content	Carboxyl Content	Total	Amide Content	Carboxyl Content	Total
0	785	125	910	785	125	910
15	800	125	925	881	190	1071
30	810	128	938	885	195	1080
45	815	132	947	890	200	1090
60	820	135	955	895	205	1100
90	825	137	962	905	205	1110
120	830	140	970	917	205	1122

Reaction conditions: crosslinked poly(acrylamide)-starch graft copolymer, 4 g; acid (1.0N), 50 mL.

Table V The Polymer (%) within Different Periods Using Different Acids at 60°C and 80°C

Time (min)	60°C						80°C					
	H ₃ PO ₄		H ₂ SO ₄		HCl		H ₃ PO ₄		H ₂ SO ₄		HCl	
	Polymer %	Starch %	Polymer %	Starch %	Polymer %	Starch %	Polymer %	Starch %	Polymer %	Starch %	Polymer %	Starch %
0	64.61	35.39	64.61	35.39	64.61	35.39	64.61	35.39	64.61	35.39	64.61	35.39
15	65.68	34.32	68.50	31.50	69.90	30.10	71.82	28.18	76.10	23.90	76.75	23.25
30	66.60	33.40	69.23	30.78	71.00	29.00	72.42	27.58	79.17	20.83	82.90	17.10
45	67.24	32.76	70.29	29.71	71.10	27.90	73.13	26.87	80.23	19.77	83.50	16.50
60	67.80	32.20	71.36	28.64	73.10	26.90	73.84	26.16	81.29	18.71	84.40	15.60
90	68.30	31.70	72.10	27.90	73.84	26.16	74.90	25.10	85.77	14.23	88.04	11.96
120	68.90	31.10	72.80	27.20	74.55	25.45	76.50	23.50	87.19	12.81	89.50	10.50

Reaction conditions: crosslinked poly(acrylamide)-starch graft copolymer, 4 g, acid (1.0N), 50 mL.

55.8% of the original amide groups at 60, 80, and 100°C respectively, while the increment within 120 min under the same conditions were 43.3%, 49.2%, and 34.4%, respectively.

- The carboxyl content increases with increasing sodium hydroxide concentration to reach a maximum and then decreases. The value of this maximum depends on reaction temperature and duration, i.e., on using reaction duration of 15 min, the maxima occur at 2.5N, and 1.5N sodium hydroxide for 60°C, and 80–100°C, respectively.
- It is further noted (Tables I–III) that the increase in carboxyl content is equal to the decrease in amide content at all temperatures on using sodium hydroxide concentration 0.5–1.0N. On the other hand, on using a sodium hydroxide concentration higher than 1.0N, the formed carboxyl groups is much less than the corresponding decrement in amide content, a point that calls for substituents cleavage. Cleavage of substituents was also observed when poly(acrylonitrile)-starch graft copolymer was treated with alkali.¹⁵
- The difference between the increment in carboxyl content and the decrement in amide content increases with increasing sodium hydroxide concentration as well as reaction temperature and/or duration.
- The maximum value of carboxyl content obtained by alkali treatment of poly(acrylamide)-starch graft copolymer was 593 meq COOH/100 g sample. This was achieved on carrying out the saponification reaction at 100°C with sodium hydroxide (1.0N) for 2 h. The increase in carboxyl content is equal to 59.6% from the original amide content.

Cleavage of Substituent

The sum of carboxyl and amide contents of poly(acrylamide)-starch graft copolymer before and after alkali treatment (using NaOH concentration more than 1.0N) were calculated. It reveals a large difference, indicating cleavage of some substituent groups. The dependence of this cleavage on the condition of alkali treatment is shown in Figure 1. It is obvious that the amount of cleaved groups increases with increasing sodium hydroxide concentration, treatment duration and temperature.

Table VI Absorption Behavior of Saponified Poly(acrylamide)-Starch Graft Copolymer for Different Metal Cations

Exchanger's Capacity meq 100 g	Mg ²⁺			Co ²⁺			Zn ²⁺			Cu ²⁺		
	Cl ⁻	SO ₄ ⁻	Ac ⁻	Cl ⁻	SO ₄ ⁻	Ac ⁻	Cl ⁻	SO ₄ ⁻	Ac ⁻	Cl ⁻	SO ₄ ⁻	Ac ⁻
340	3.5	3.5	48.5	6.2	6.2	56.5	7.6	7.6	76.0	17.2	17.2	83.0
445	4.0	4.0	50.6	6.7	6.7	58.0	8.1	8.1	77.0	23.6	23.6	84.3
575	7.8	7.8	52.2	10.4	10.4	60.0	12.0	12.0	78.3	25.0	25.0	86.1

Conversion Percent

The conversion % of amide groups of the starch copolymer after treatment with sodium hydroxide was calculated as follows:

$$\text{Conversion \%} = \frac{\text{formed carboxyl groups}}{\text{decrement in amide groups}} \times 100.$$

The conversion % of amide groups to carboxyl groups during alkali treatment were set out in Figure 2. The data show that:

1. The conversion % depends on sodium hydroxide concentration, i.e., the conversion % was 100% on using sodium hydroxide concentration, up to 1.0*N*, while it decreases on using higher concentrations and the magnitude of the decrement is higher, the higher concentration used.
2. The conversion % decreases in general with increasing either reaction duration or temperature specially at higher sodium hydroxide concentration. The decrement in conversion can be attributed to the deetherification, depolymerization, and cyclization reactions.^{15,19-22}

From the above findings, it is shown that on using sodium hydroxide concentration up to 1.0*N* the saponification reaction (conversion of —CONH₂ group into —COOH) is the lonely reaction, while on using higher concentration, the deetherification and depolymerization reactions occur simultaneously with the saponification reaction.

Acid Hydrolysis of Starch Copolymer

Crosslinked poly(acrylamide)-starch graft copolymer (785 mmol amide and 125 mmol carboxyl group/100 g sample) was subjected to acid hydrolysis at 80°C and 100°C using 1.0*N* solutions of different acids. These acids were phosphoric, hydrochloric, and sulphuric acids. The hydrolytic effect

of acid solutions was assessed by monitoring the amide as well as the carboxyl contents of the copolymer before and after hydrolysis. The results obtained were set out in Tables IV and V. The data show that:

1. The amide content depends on the acid type and/or the temperature used.
2. The amide content increases with increasing the treatment temperature as well as duration on the contrary of alkaline treatment.
3. The increment in amide content follow the order: HCl ≥ H₂SO₄ > H₃PO₄.
4. The carboxyl content has the same behaviour as the amide content.
5. The sum of amide and carboxyl content increases with increasing treatment temperature and/or duration.
6. The acrylate content of the poly(acrylamide)-starch graft copolymer increases with acid treatment while the starch component decreases.

From these data it is obvious that the hydrolysis of amide group to carboxyl group does not occur, and the main effect is the hydrolytic effect of these mineral acids on the starch component of the poly(acrylamide)-starch graft copolymer, as shown in Tables IV and V. The same phenomenon occurs on hydrolysis of polyacrylonitrile in the presence of sulphuric acid, which shows that the reaction ceased at the amide group step and not to the carboxyl step.²²

Heavy Metal Absorption

The alkali treated poly(acrylamide)-starch graft copolymer were evaluated as a cation exchanger. Saponified copolymers having different capacities were treated with solutions containing cations of Mg²⁺, Co²⁺, Zn²⁺, and Cu²⁺. The cations were in the form of acetate, chloride, and sulphate. The ab-

sorption values of these cations are shown in Table VI. The data show that:

1. The absorption % increases with increasing the capacity of exchanger used.
2. The absorption % of the different cations follow the order: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Mg}^{2+}$.
3. This is in accordance with Irving-Williams series.²³ The difference in absorbancy % of these different metals is due to the difference in (a) their ability to form covalent bonds with the carboxyl group; (b) ion potential of these metals.

The absorption % of any cation depends on the associated anion and follow the order; acetate > chloride, and sulphate. This difference is attributed to the difference in ionization values (pK_a) of these anions and its effect on the salt formed after sorption of the cation on the cation exchanger.

REFERENCES

1. R. Kunin and D. G. Dowing, *Chem. Eng. Progr., Symp. Ser.*, **67**, 575 (1971).
2. H. Nichiguchi and X. Harui, *Jpn. Pat.* 7695, 492 (1976).
3. P. Monjol, *Bull. Soc. Chem. Fr.*, **215**, 1319 (1972).
4. J. A. Marinsky and W. M. Anspach, *J. Phys. Chem.*, **79**, 435 (1975).
5. J. A. Marinsky, N. Imai, and M. C. Lim, *Isr. J. Chem.*, **11**, 435 (1973).
6. C. Travers and J. A. Marinsky, *J. Polym. Sci., Symp.* **47**, 285 (1974).
7. R. E. Wing, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **19**, 847 (1975).
8. R. E. Wing, *Ind. Wastes (Chicago)*, **21**, 26 (1975).
9. R. E. Wing and W. M. Doane, U.S. Pat. 3,979,286 (1976).
10. M. I. Khalil, A. Waly, S. Farag, and A. Hebeish, *J. Appl. Polym. Sci.*, **43**, 2303 (1991).
11. I. Kuniak, and R. Marchessault, *Can. Pat.* 960,652 (1975), C.A. **82**, 141948 (1975).
12. A. L. Bullock and J. D. Guthrie, U.S. Pat. 3,065,222 (1962).
13. A. L. Bullock and J. D. Guthrie, U.S. Pat. 2,992,215 (1961), C.A. **55** 228278 (1961).
14. W. E. Rayford, R. E. Wing, and W. M. Doane, *J. Appl. Polym. Sci.*, **24**, 105 (1979).
15. M. I. Khalil, S. Farag, and A. Hebeish, *Starch/Stärke*, **43**, (2), 254 (1991).
16. A. I. Vogel, *Elementary Practical Organic Chemistry, Part 3: Quantitative Organic Analysis*, 2nd Ed., Longman Group Ltd., London, 1975, p. 625.
17. G. Daul, R. M. Reinhardt, and J. D. Reid, *Textile Res. J.* **23**, 719 (1953).
18. R. T. Morison and R. N. Boyd, *Organic Chemistry*, 7th Ed., Allyn and Bacon Inc., Boston, 1975, p. 671.
19. M. I. Khalil, A. Bayazeed, S. Farag, and A. Hebeish, *Starch/Starke*, **39**, 311 (1987).
20. A. Hebeish and M. I. Khalil, *Starch/Stärke*, **40**, 104 (1988).
21. J. R. McCartney, *Modern Plast.* **30**, 118-124, 179-181 (1953).
22. A. Strepikheyev, V. Derevitskaya, and G. Slonimsky, *A First Course in Polymer Chemistry*, Chapt. XII, Mir Publication, Moscow, 1971, p. 259.
23. H. Irving and R. J. P. Williams, *Nature*, **162**, 746 (1948); *J. Chem. Soc.*, 3192 (1953).

Received October 3, 1994

Accepted January 10, 1995