Preparation and Characterization of Hydrogels Obtained by Grafting of Acrylonitrile onto Cassava Starch by Ceric Ion Initiation

M. VERA-PACHECO, H. VÁZQUEZ-TORRES,* and G. CANCHÉ-ESCAMILLA

Centro de Investigación Científica de Yucatán, A.C., División de Química, Departamento de Polímeros, Apdo. Postal 87, Cordemex. Mérida, Yucatán, México, C.P. 97310

SYNOPSIS

Graft starch-polyacrylonitrile copolymers have been obtained from cassava starch (yucca starch or tapioca), which was pre-heated at 65 and 95°C for different lengths of time. The copolymerization was carried out by using ceric ion as initiator at different concentrations (2.0 to 8.0 mmol/L) and also varying both the length of time of copolymerization and the ratio of monomer to starch. The composition, or grafting parameters, of all the obtained copolymers was determined by weight difference after they were extracted with dimethylformamide and hydrolyzed with an acidic solution. Samples of these copolymers were also hydrolyzed with an aqueous solution of potasium bydroxide to produce the corresponding hydrogels, and its absorbency in water was determined. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Hydrogels, absorbent materials having the capacity of absorbing high amounts of water, have currently been obtained by alkaline hydrolysis of starch-g-polyacrylonitrile (SPAN) graft copolymer. The starches most commonly used to prepare this copolymer are those from maize, wheat, and potato.[1-4] The copolymerization is usually initiated with a redox-type initiator such as the ions Ce(IV) or Mn(III), among others, which oxidize both the C1—C2 and the C2—C3 glycol groups of some glucopyranosyl units, resulting in the formation of free radicals along the polysacharide chains.[3,4] The most important variables that determine the absorbency of the H-SPAN are both the content of carboxylate and amide groups, which are generated by saponification of the nitrile groups, and the cross-linking degree, which appears to occur during both the graft polymerization and the alkaline hydrolysis of SPAN.[4,5] Absorbency and cross-linking degree strongly depend, in turn, on the weight percent and the molecular weight of grafted PAN, as well as on its graft frequency.[6] All these variables are also affected, though in a lesser extent, by both the type of starch used[6] and the thermal pretreatment applied to gelatinize the starch.[7] In regard to the type of starch, it has been reported that the higher the content of amylopectin in starch, like potato starch, the higher the absorbency of the obtained starch-based hydrogels.[6]

In this work, the experimental conditions to obtain a superslurper from the starch of yucca (Cassava, Manihot esculenta), or tapioca, are presented. This starch was used in these studies because of its similarity in composition to potato starch[8] and because it is a subutilized product widely distributed in tropical regions.[9] The influence of the temperature and the time of starch pretreatment, as well as the concentration of Ce(IV) as initiator and the monomer/starch ratio, on the copolymer composition was studied. The results of composition characterization of the obtained copolymer SPAN and the absorbency of the final hydrolyzed product H-SPAN are reported.

EXPERIMENTAL

Materials

The yucca starch was obtained from Calotmul (Yucatán, Mexico). Native granular starch was purified by suspending in water and stirring for 2 h, then centrifuging and recovering by decantation. After drying at 60°C, it was extracted with 95% ethanol in a Soxhlet extractor for 12 h and dried at 60°C overnight. Acrylonitrile (AN; Aldrich, U.S.A.), ceric ammonium nitrate (E. Merck, Germany), potas-

---

Table I   Influence of Time and Temperature of Starch Pretreatment on Both the Grafting Parameters of SPAN and the Water Retention of H-SPAN[a]

T (°C)	Time (min)	Mc (%)	Gr (%)	Gef (%)	Ad (%)	Hp (%)	Wr
65	15	64	65	90	39	4.2	533
65	30	61	62	91	38	3.7	553
65	45	57	60	96	37	1.6	512
65	60	69	63	81	39	1.9	444
95	15	40	42	99	30	0.3	625
95	30	67	61	87	38	5.2	737
95	45	56	57	95	36	9.5	523
95	60	60	58	98	38	9.5	625

[a] T = Temperature; Mc = monomer conversion; Gr = grafting ratio; Gef = grafting efficiency; Ad = add-on; Hp = homopolymer formed; Wr = water retention in gram per gram of dried H-SPAN. Experimental conditions: 9.5 g of dried starch gelatinized in 136 mL of water and reacted with 12 mL of AN, 4 mmol/L of Ce (IV), at 30–33°C for 2.5 h.

sium hydroxide, and acetic acid (J. T. Baker, Mexico), and N,N-dimethylformamide (E. Merck, Germany) were used without any further treatment. All these chemicals were reagent grade. Distilled technical-grade ethanol was used to precipitate the copolymer SPAN and the hydrogel H-SPAN.

Graft Copolymerization

The graft copolymer, SPAN, was prepared following the procedure reported by Weaver et al.[10] Dried starch (9.5 g) was gelatinized in distilled water (136.0 mL) by heating at two different temperatures for different lengths of time (Table I) in a 500 mL four-necked glass kettle, which was equipped with a stirrer, condenser, thermometer, and nitrogen inlet tube. After this pretreatment, the slurry was cooled to 30°C and a brisk stream of oxygen-free nitrogen was bubbled for 1 h. After this time, variable quantities of AN were added from an dropping funnel to obtain different weight ratios of AN to starch into the reactor, as indicated in Table II. Five minutes later, the freshly prepared solution of 0.303 g of ceric ammonium nitrate [or the amount required for at-

taining different concentrations of ion Ce(IV), as indicated in Table III] in 0.1N HNO₃ (5.5 mL) was added. The slurry was kept between 30 and 33°C for 2.5 h (or between 1.5 and 3.0 h to study the effect of time on this reaction) under an oxygen-free nitrogen atmosphere and stirring. The whole volume of the resulting mixture was divided into two equal portions. One of them was reserved to be hydrolyzed as described below and the other one was precipitated with 100 mL of 95% ethanol. The precipitate was separated by filtration under vacuum, using a coarse glass filter, washed with 95% ethanol, and dried under vacuum at 60°C. The yield of the product was calculated and this product was characterized by the following procedures.

Graft Copolymer Characterization

Homopolymer Content

The amount of homopolymer formed was determined on product samples (2 g) by extraction with 100 mL of dimethylformamide (DMF) in a glass-stopped Erlenmeyer flask at room temperature and

Table II   Influence of the Monomer/Starch (M/S) Ratio on Both The Grafting Parameters of SPAN and the Water Retention of H-SPAN[a]

M/S	Mc (%)	Gr (%)	Gef (%)	Ad (%)	Hp (%)	Wr
0.5	32	20	62	17	9.5	Soluble
1.0	53	38	72	27	9.3	508
1.5	56	53	83	35	6.5	620
2.0	60	62	81	38	8.2	664
5.0	79	151	88	60	7.8	494

[a] Experimental conditions: 9.5 g of dried starch gelatinized in 136 mL of water (at 95°C for 30 min) and reacted with AN (4.25, 9.50, 13.75, 19.00, or 42.50 g, respectively) and 4.0 mmol/L of Ce(IV), during 2.5 h. Nomenclature as in Table I.

Table III Influence of the Ion Ce(IV) Concentration on the Grafting Parameters of SPAN[a]

[Ce(IV)] (mmol/L)	Mc (%)	Gr (%)	Gef (%)	Ad (%)	Hp (%)
2.0	48	39	72	28	10.0
4.0	65	62	92	38	2.1
6.0	68	64	95	39	2.8
8.0	69	65	96	40	3.0

[a] Experimental conditions: 9.5 g of dried starch gelatinized in 136 mL of water (at 95°C for 30 min) and reacted with 12 mL of AN, at 30–33°C for 2.5 h. Nomenclature as in Table I.

stirring for 24 h.[11] After this time, the suspension was centrifuged at 2000 rpm for 40 min. The liquid was decanted and filtered through a porous glass (40-C) filter, previously dried at 105°C to constant weight. The residue was quantitatively poured into an Erlenmeyer flask containing 50 mL of ethanol at room temperature, and after stirring for 1 h, the copolymer dispersion was filtered through the same 40-C filter. The extracted homopolymer was calculated by the weight difference after drying the recovered copolymer at 60°C under vacuum for 12 h.

Grafted Polyacrylonitrile (PAN)

The content of PAN in the copolymer was determined by acidic hydrolysis: Two grams of the extracted copolymer was dispersed in 125 mL of an aqueous $0.5N$ HCl solution and refluxed for 2 h, left to cool, and filtered through a porous glass (40-F) filter. After washing with water until neutral pH was attained, the recovered precipitate was dried at 60°C under vacuum for 12 h.

Alkaline Hydrolysis of SPAN

The other portion (80 g approximately) of the mixture containing the graft copolymer was warmed up to 60°C, in a 250 mL three-necked glass reactor, and 20 mL of an aqueous 25 wt % KOH solution was added with slow stirring. The slurry was kept boiling. After 15 min had elapsed since the change in color from deep red to light yellow, the heating was stopped. The solution was left to cool, its pH adjusted to 8.0 with concentrated acetic acid, and poured into an excess of ethanol. The precipitate (H-SPAN) was washed with ethanol to neutrality and dried under vacuum at 60°C.

Determination of Water Retention (Wr)

Samples of powdered H-SPAN (0.1 g) were immersed in distilled water (100 mL) in a beaker at room temperature. After 30 min, the slurry was filtered through a weighed porous glass (40-C) filter with vacuum pump for 10 min. The amount of ab-

sorbed water was calculated in grams per gram of dried H-SPAN after weighing the swollen hydrogel retained in the filter.

RESULTS AND DISCUSSION

Graft Copolymerization

Copolymer yield varied between 75 and 80%. The compositional parameters of this type of copolymer are usually expressed on a weight basis as follows[3,12]:

Monomer conversion (%)

$$= \left(\frac{\text{Wt of PAN formed}}{\text{Wt of AN charged}} \right) \times 100$$

Grafting ratio (%)

$$= \left(\frac{\text{Wt of PAN in grafts}}{\text{Wt of starch}} \right) \times 100$$

Grafting efficiency (%)

$$= \left(\frac{\text{Wt of grafted PAN}}{\text{Wt of grafted PAN} + \text{Wt of homopolymer PAN}} \right) \times 100$$

Add-on (%)

$$= \left(\frac{\text{Wt of PAN in grafts}}{\text{Total wt of copolymer sample}} \right) \times 100$$

Homopolymer (%)

$$= \left(\frac{\text{Wt of nongrafted PAN}}{\text{Total wt of formed PAN}} \right) \times 100$$

Influence of Temperature and Time Pretreatment

The results of the grafting experiments using preheated starch at different conditions are shown in Table I and Figures 1–3. Monomer conversion, as well as grafting ratio and add-on, were higher in value for short times of starch pretreatment at preheating temperature of 65°C than that at 95°C. However, as the preheating time was higher than 30 min, these parameters tended to be similar in value, showing only a slight dependence on the preheating temperature. In contrast, the value of grafting effi-
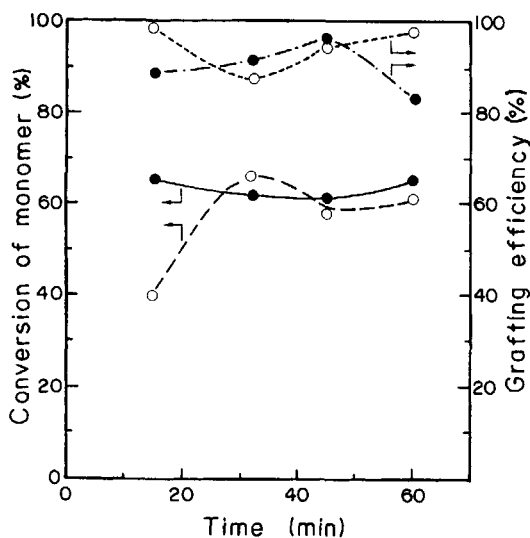
Figure 1 Influence of the starch preheating time on both the conversion of monomer and the grafting efficiency: (O) starch preheated at 65°C; (●) starch preheated at 95°C. Copolymerization of dried starch (9.5 g) with 12 mL of AN and 4.0 mmol/L of Ce(IV) at 30–33°C for 2.5 h.

ciency was higher (99%) for starch preheated at 95°C than that at 65°C (90%) for a short time of pretreatment. This difference tended to be negligible when the preheating time was longer than 25 min. In general, the best values of the parameters in Table I were obtained with the starch preheated at 95°C during a time between 30 and 40 min. Then, it is
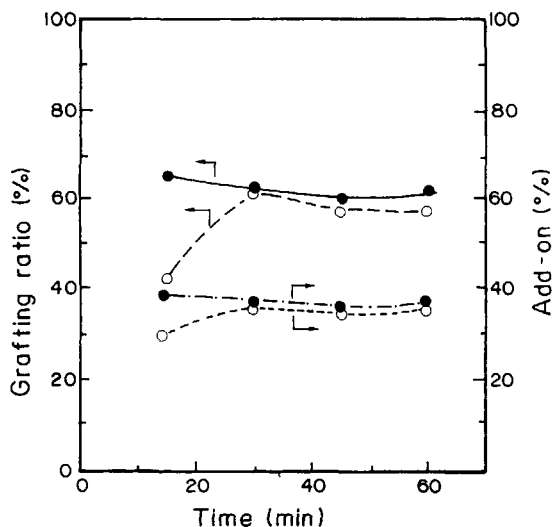

Figure 2 Dependence of both the grafting ratio and the add-on of copolymer SPAN on the starch preheating time: (O) starch preheated at 65°C; (●) starch preheated at 95°C. Experimental conditions as in Figure 1.
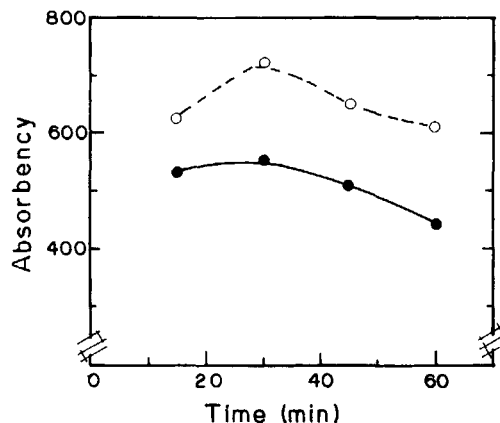

Figure 3 Effect of the starch preheating time on the absorbency (water retention) of H-SPAN: (●) starch preheated at 65°C; (O) starch preheated at 95°C. Experimental conditions as in Figure 1.

expected that, at these conditions, the accessibility of starch to both the monomer and the initiator be high enough to render a less heterogeneous copolymer. Thus, 95°C and 30 min can be considered as convenient conditions to preheat the starch to obtain better values for compositional parameters of SPAN, as well as a higher absorbency of the H-SPAN. Since the gelatinization temperature of Cassava starch is in the range between 60 and 70°C,[13] these results refute the earlier suggestion made by Smith[14] that the preheating had to be up to the corresponding gelatinization temperature of the starch used to obtain the best results. Indeed, Mehrotra and Ranby[7] reported good results for grafting experiments of AN onto potato starch by ion Mn(III) initiation, although this starch was preheated at a temperature higher than the corresponding gelatinization temperature.

Influence of the Monomer/Starch Ratio

In general, compositional parameters of the copolymer SPAN were increased to higher values with the monomer/starch ratio, as expected (Table II and Figs. 4–6). Though the value of 5 of this ratio was used only to explore qualitatively this tendency, it is evident that this increasing was more notorious in the parameters such as grafting ratio, grafting efficiency, and add-on, when the monomer/starch ratio was varied from 0.5 to approximately 2.0. Then, taking into account that absorbency obtained a maximum value at a monomer/starch ratio of 2.0 approximately, one can consider this value as the most adequate to prepare hydrogels, at least under
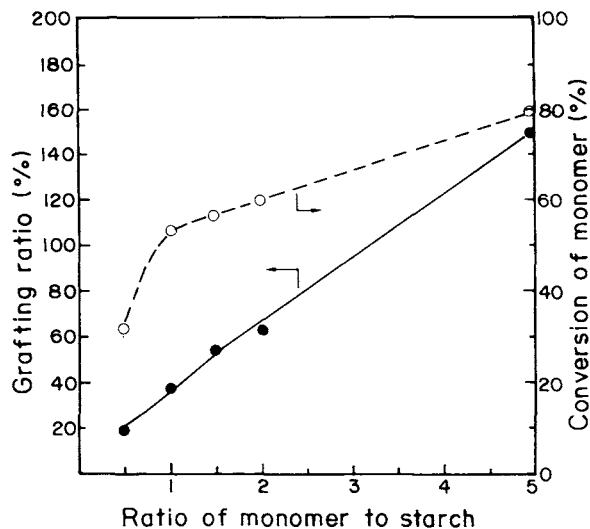
Figure 4 Influence of the monomer/starch ratio (weight basis) on both the grafting ratio (●) and the conversion of monomer (○). Experimental conditions as in Table II.

Figure 6 Effect of the monomer/starch ratio (weight basis) on the absorbency (water retention) of H-SPAN. Experimental conditions as in Table II.

Influence of the Initiator Concentration

All the grafting parameters of SPAN (Table III and Fig. 7) were increased in value with the concentration of ion Ce(IV). However, this increasing was very low for concentrations ranging from 4.0 to 8.0 mmol/L. Similar results were reported by Reyes et al.[15] after grafting experiments onto wheat starch. To explain these results, one could assume that diffusive factors are involved here, but this is a matter that requires further, specific studies. Nevertheless, from a practical point of view, 4.0 mmol/L is an adequate concentration of Ce(IV) to graft AN onto gelatinized cassava starch.

the experimental conditions used in this study. Indeed, with the basis on the results reported by Castel et al.,[6] absorbency values shown in Table II would be higher the lower the concentration of copolymer SPAN during the hydrolysis step, because the crosslinking reaction between PAN chains, which was suggested by Grassie and McNeill,[5] would occur in a lesser extent the higher the dilution of copolymer during the hydrolysis step.
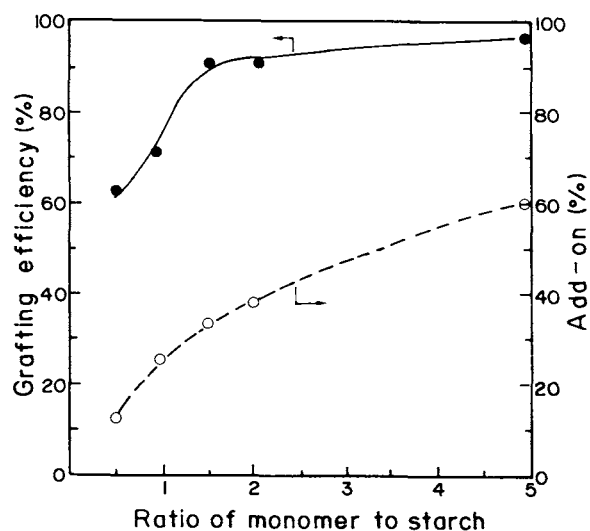

Figure 5 Effect of the monomer/starch ratio (weight basis) on both the grafting efficiency (●) and the add-on (○). Experimental conditions as in Table II.
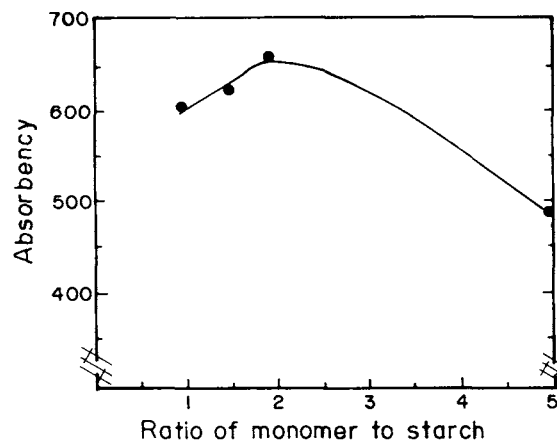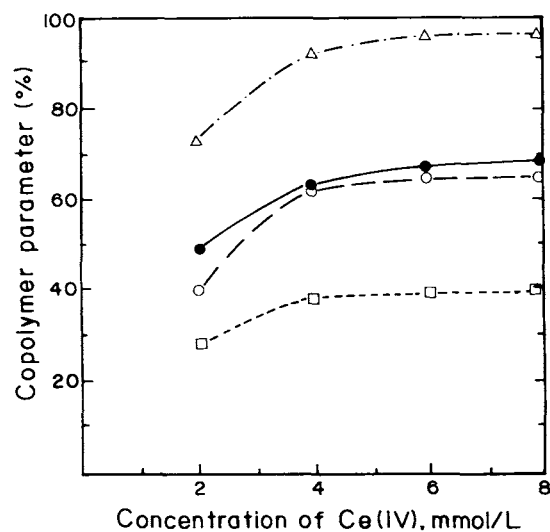

Figure 7 Influence of the concentration of ion Ce(IV) on the composition parameters of SPAN: (●) conversion of monomer; (○) grafting ratio; (△) grafting efficiency; (□) add-on. Experimental conditions as in Table III.

Table IV   Influence of the Reaction Time on Both the Grafting Parameters of SPAN and the Water Retention of H-SPAN[a]

Time (h)	Mc (%)	Gr (%)	Gef (%)	Ad (%)	Hp (%)	Wr
1.5	55	57	79	35	8.6	730
2.0	63	60	86	36	5.0	750
2.5	66	63	91	37	4.5	620
3.0	67	64	91	37	4.0	675

[a] Experimental conditions: 9.5 g of dried starch gelatinized in 136 mL of water (at 95°C for 30 min) and reacted with 2 mL of AN and 4.0 mmol/L of Ce(IV), at 30–33°C. Nomenclature as in Table I.

Influence of the Time of Grafting Copolymerization

The results of characterization of copolymers SPAN, which were prepared varying the time of grafting, are shown in Table IV and Figure 8. As expected, monomer conversion and grafting ratio, as well as grafting efficiency and add-on, were increased in value with the time of reaction, in the interval between 1.5 and 2.5 h. However, reaction time higher than 2.5 h did not improve these values, but they appeared to reach a limit. This behavior has been reported for similar experiments, in which the starch used was from maize,[1] potato,[2] and wheat.[15]

Remarks

When the cassava starch (yucca starch or tapioca) was preheated at 95°C, the grafting parameters of

Figure 8   Influence of copolymerization time on the composition parameters of copolymer SPAN: (●) conversion of monomer; (○) grafting ratio; (△) grafting efficiency; (□) add-on. Experimental conditions as in Table IV.

the obtained copolymer SPAN, as well as the absorbency of H-SPAN, were higher in value than those of copolymer based on starch preheated at its gelatinization temperature (65°C). The most convenient preheating time was nearly 30 min.

Higher values of grafting parameters of SPAN were obtained the higher the time of reaction, as well as the higher the concentration of ion Ce(IV) and the monomer/starch ratio, during the grafting copolymerization of AN onto cassava starch. However, the most convenient conditions to effect this reaction, from a practical point of view, were the following: 4.0 mmol/L of Ce(IV), a monomer/starch ratio of 2, and a reaction time between 2.5 and 3.0 h. Indeed, these experimental conditions promoted the highest value of absorbency (750) of the H-SPAN, though this value might be increased by applying other conditions of alkaline hydrolysis of SPAN. Absorbency values of H-SPAN obtained in this study were similar to those based on wheat or maize starch.

Finally, it is worthy of mention that a reliable determination for the molecular weight of the PAN released from the copolymer SPAN has not been obtained, due to two problems: (a) Some sort of chemical modification appeared to occur on the PAN, as revealed from its infrared spectrum, in spite of two different methods (acidic hydrolysis and oxidation with sodium periodate) being applied to release it from SPAN. This fact impedes the use of the corresponding values of Mark–Houwink constants for viscometric experiments. (b) A high portion of this PAN was insoluble in DMF, but swelled in this solvent. Since the amount of this portion appeared to depend on the AN-to-starch ratio used in the copolymerization experiments, the soluble portion cannot be considered as representative of the whole sample of PAN. This behavior of PAN might be addressed to some sort of cross-linking that might take place in the grafted PAN during copolymerization or when the starch was eliminated from the SPAN. At first sight, this result appears to be
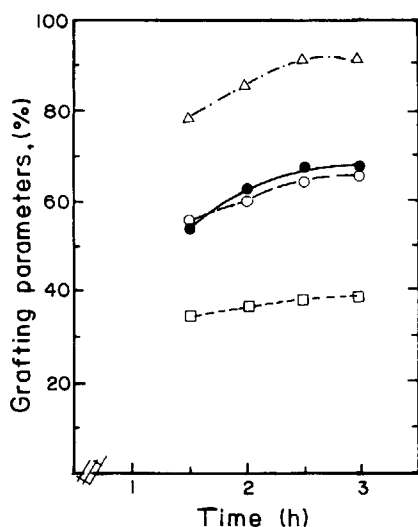
an anomalous behavior of PAN because it has not been mentioned in reports of similar experiments, and, at present, we are pursuing studies on this interesting phenomenon.

REFERENCES

1. L. A. Gugliemelli, M. O. Weaver, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.,* **13,** 2007 (1969).
2. R. Mehrotra and B. Ranby, *J. Appl. Polym. Sci.,* **21,** 3407 (1977).
3. G. F. Fanta and E. B. Bagley, in *Encyclopedia of Polymer Science and Technology, Supplement* Wiley, New York, 1977, Vol. 2, pp. 665–699.
4. G. F. Fanta and W. M. Doane, in *Modified Starches: Properties and Uses,* O. B. Wurzburg, Ed., CRC Press, Boca Raton, FL, 1986, Chap. 10, pp. 149–178.
5. N. Grassie and I. C. McNeill, *J. Polym. Sci.,* **56,** 189 (1962).
6. D. Castel, A. Ricard, and R. Audebert, *J. Appl. Polym. Sci.,* **39,** 11 (1990).
7. R. Mehrotra and B. Ranby, *J. Appl. Polym. Sci.,* **22,** 2991 (1978).
8. D. M. W. Anderson, C. T. Greenwood, and E. L. Hirst, *J. Am. Chem. Soc.,* 225 (1955).
9. J. H. Cock, *Cassava,* Westview Press, Boulder, CO, 1985, Chap. 1, pp. 3–22.
10. M. O. Weaver, L. A. Gugliemelli, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.,* **15,** 3015 (1971).
11. R. Mehrotra and B. Ranby, *J. Appl. Polym. Sci.,* **21,** 1647 (1977).
12. C. Rodehed and B. Ranby, *J. Appl. Polym. Sci.,* **32,** 3323 (1986).
13. T. J. Schoch and E. C. Maywald, *Anal. Chem.,* **28,** 328 (1956).
14. T. Smith, U.S. Pat. 3,661,815 (May 9, 1972).
15. Z. Reyes, C. E. Rist, and C. R. Russell, *J. Polym. Sci. Part A-1,* **4,** 1031 (1966).