Behavior of Cyanoethylated Cotton Towards Gamma Radiation

A. Hebeish, A. H. Zahran,* and A. M. Kh. El-Naggar,* *National Research Centre, Textile Research Division, Dokki, Cairo, Egypt*

Synopsis

Unmodified cotton fabric, cyanoethylated cottons having 0.12, 0.55, 0.77, and 1.24% N as well as cotton treated with NaOH under conditions similar to those of cyanoethylation but in absence of acrylonitrile were exposed to gamma radiation doses (3.199–31.199 Mrads). The six substrates before and after irradiation were assessed for copper number, carboxyl content, degree of polymerization, tensile strength, and elongation at break to determine the extent of degradation of these substrates. The effect of radiation dose on the nitrogen content of cyanoethylated cottons was also examined. It was found that degradation is higher the higher the radiation dose irrespective of the substrate used. Nevertheless, the extent of degradation is determined by nature of the substrate. Introduction of cyanoethyl groups in the molecular structure of cotton cellulose impart certain resistance to radiation degradation of cotton provided that these groups are present in appreciable amounts (0.55% N and above). The cyanoethyl groups seems to impede oxidation of the cellulose hydroxyls and/or glucosidic bonds against radiolysis. On the other hand, when present in smaller amounts, the cyanoethyl groups are not able to outweigh the increased accessibility of cotton cellulose brought about by the alkaline environment of the cyanoethylation reaction. Hence, substrates containing lower cyanoethyl contents are more susceptible to degradation than the modified cotton, and in this respect they are similar to alkali-treated cotton.

INTRODUCTION

Cyanoethylation is one of the most common processes for chemical modification of cotton. Cyanoethylated cottons are prepared by treatment of cotton cellulose with acrylonitrile in presence of sodium hydroxide as a catalyst.[1] The reaction between cellulose hydroxyls and acrylonitrile is

$$\text{Cell}-\text{OH} + \text{CH}_2=\text{CHCN} \xrightarrow{\text{NaOH}} \text{Cell}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CN}$$

Cyanoethylated cottons aquire improved resistance to rot, heat, and damage by acids and abrasion.[2,3] They are more receptive than cotton to some dyes in all classes of dyestuffs and require more work than untreated cotton for rupture tension. Furthermore, the dielectric constant of cyanoethylated cellulose is increased proportionally to the extent of reaction. The cyanoethylated cotton can be hydrolyzed to carboxyethyl cellulose. Susceptibility of cyanoethylated cotton towards thermal treatments has also been reported.[4] Furthermore, soiling and soil release properties of cyanoethylated cotton have been examined.[5]

* National Centre for Radiation Research and Technology, Nasr City, Cairo, Egypt.

Journal of Applied Polymer Science, Vol. 30, 4057–4067 (1985)
 CCC 0021-8995/85/104057-11$04.00

Literature dealing with the effect of high energy radiation on cotton in absence of vinyl monomer (oxidation) and in its presence (grafting) is voluminous.[6] The reverse is the case with cyanoethylated cotton. To the authors' knowledge, only very few studies has dealt with radiation-induced interaction of acrylonitrile with cyanoethylated cottons that have different cyanoethyl contents.[7,8]

This work is undertaken with a view of studying the effect of structural changes of cotton brought about by cyanoethylation on the susceptibility of cotton towards oxidation by gamma radiation

EXPERIMENTAL

Cotton Fabrics

Mill, desized, scoured, bleached, and mercerized plain weave (31 picks and 36 ends/cm) was supplied by El-Nasr Spinning, Weaving, and Knitting Co. (Shourbagi). For sampling the cotton fabric was cut into strips (6 × 20 cm) in the warp and weft directions.

Cyanoethylated Cotton

Cyanoethylated cotton (CEC) was prepared according to a method described by Compton et al.[9] The cotton fabric was impregnated in an aqueous solution of sodium hydroxide 5% (w/v) for 15 min followed by squeesing to ca. 100% wet pickup. After being batched for 10 min, the alkali-treated fabric was padded with acrylonitrile and stored in a polyethylene cover. The fabric was then washed thoroughly with water, neutralized with acetic acid (1%), washed again, and dried at ambient conditions. Cyanoethylated cotton of different degree of cyanoethylation, expressed as % N, were obtained by using different reaction time.

A control sample, namely, sodium-hydroxide-treated cotton, was prepared under conditions identical to those of cyanoethylation except that treatment with acrylonitrile was omitted and the treatment was allowed for 15 min.

Radiation Treatment

Irradiation to the required radiation doses has been carried out in the cobalt-60 gamma ray sources 220 type 3600 Ci installed at the National Centre for Radiation Research and Technology (dose rate ranged between 25–20 rads/s and the cobalt-60 gamma ray source 220 type 8000 Ci installed at the Middle Eastern Regional Radioisotope Centre (dose rate ranged between 38 and 37 rads/s).

Analysis

The copper number was determined using the procedure of Heyes.[10] The carboxyl content was estimated according to a reported method.[11] The nitrogen content was estimated according to the Kjeldahl method. The degree of polymerization was determined using the cuprammonium hydroxide method.[12] Breaking strength and elongation at break were measured by the

strip method.[13] The Instron Machine type 1195 was employed throughout this investigation.

RESULTS AND DISCUSSION

Cotton cellulose in fabric form was cyanoethylated via reaction with acrylonitrile in the presence of sodium hydroxide in a way that cellulose having different amounts of cyanoethyl groups could be obtained. The cyanoethylated cottons and the unmodified cotton were exposed to varying doses of high energy gamma radiation. They were then analyzed for copper number, carboxyl content, and degree of polymerization. In addition, the tensile strength and elongation at break of the modified cottons before and after irradiation were monitored.

Copper Number

When the unmodified cotton and the modified cottons having different degree of cyanoethylation were analyzed for copper number, the difference in the values of the latter were not that striking. The unmodified cotton showed a copper number value of 0.028 whereas the cyanoethylated cottons exhibited a copper number value of ca. 0.033 irrespective of their degree of cyanoethylation. This is rather in accordance with previous reports,[4] which ascribed this to oxidation of some of the cellulose hydroxyls to aldehydic groups under the influence of alkali (used as catalyst for cyanoethylation) in the presence of atmospheric and/or occluded oxygen. On the other hand, considerable differences between the copper number of the cyanoethylated cottons and the unmodified cotton as well as among the cyanoethylated cottons themselves were observed after irradiation as shown in Figure 1.

Figure 1 shows the effect of gamma radiation at different doses on the copper number of cotton cellulose before and after cyanoethylation to different degrees. The degree of cyanoethylation is expressed as nitrogen percent. It is seen that the copper number of cotton enhances significantly upon increasing the radiation dose from 3.199 to 31.144 Mrads. The same holds true for cyanoethylated cottons irrespective of their degree of cyanoethylation. Nevertheless, the copper number is determined by the magnitudes of radiation dose and degree of cyanoethylation. The copper number for cotton is higher the higher the radiation dose. On the other hand, the copper number increases by introducing a small amount of cyanoethyl groups in the molecular structure of cotton cellulose but decreases upon increasing the degree of cyanoethylation.

It is logical that the enhancement in copper number is due to conversion of some of the cellulose hydroxyls to reducing aldehydic groups and/or glucosidic bond scission of the cellulose chains during irradiation. Hence, the higher copper number observed with cyanoethylated cotton having low cyanoethyl content (ca. 0.15% N) as compared with the unmodified cotton suggests that this degree of cyanoethylation makes cotton more susceptible to degradation by gamma radiation. The opposite holds true for cyanoethylated cottons having higher cyanoethyl contents (0.3% N and above). These modified cottons show lower copper number and, therefore, undergo

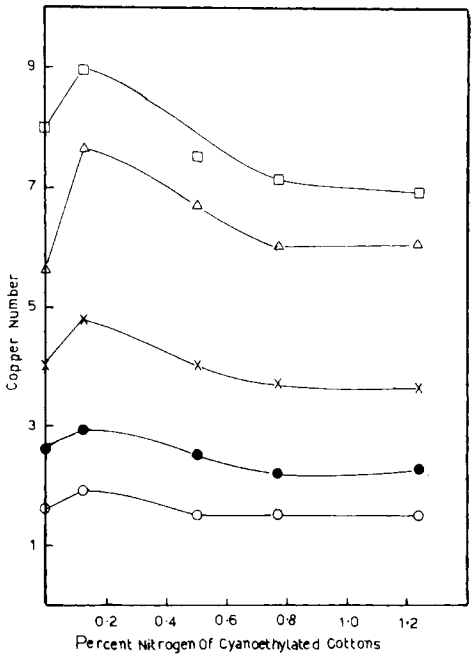

Fig. 1. Effect of gamma radiation (Mrads) on the copper number of cotton before and after cyanoethylation: (○) 3.199; (●) 6.399; (×) 12.797; (△) 25.595; (□) 31.114.

lower degradation than the unmodified cotton. Furthermore, the copper number is lower the higher the cyanoethyl content, though it tends to be almost constant after a nitrogen percent of ca. 0.75%.

It follows from the above that when present in appreciable amounts along the cellulose chains the cyanoethyl groups impart to the cotton certain resistance to gamma radiation. The cyanoethyl groups seem to impede oxidation of the cellulose molecule during irradiation via protection of some of the cellulose hydroxyls and/or glucosidic bonds against radiolysis. On the other hand, when present in small amounts in the molecular structure of cotton, the cyanoethyl groups are not able to outweigh the increased accessibility of cotton brought about by the alkaline environment of the cyanoethylation reaction. It is understandable that cotton with higher accessibility would undergo higher degradation.

Carboxyl Content

Determination of the carboxyl contents of the unmodified cotton and cyanoethylated cottons having 0.12, 0.55, 0.77, and 1.24% N showed values of 0.59, 1.2, 1.4, 1.6, and 1.8 meq —COOH/100 g cellulose, respectively. This is rather in accordance with previous reports.[4]

Figure 2 shows the effect of gamma radiation at different doses on the carboxyl content of the unmodified cotton and cyanoethylated cottons. It is seen that the carboxyl content increases by increasing the radiation dose irrespective of the substrate used. Nevertheless, the carboxyl content is higher the higher the radiation dose. Furthermore, the carboxyl content of

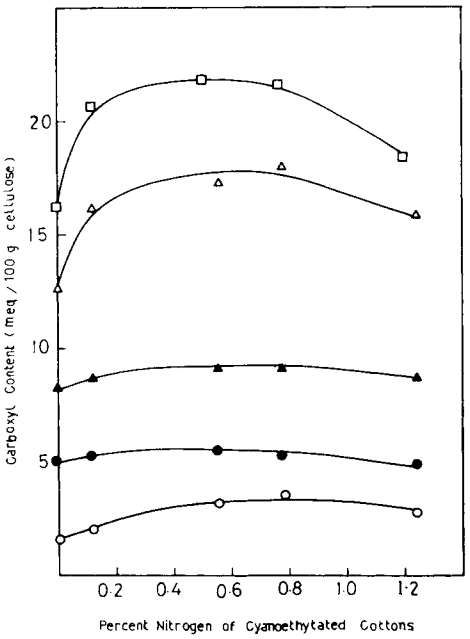

Fig. 2. Effect of gamma radiation (Mrads) on the carboxyl content of cotton before and after cyanoethylation: (○) 3.199; (●) 6.399; (▲) 12.797; (△) 25.595; (□) 31.114.

cyanoethylated cotton increases by increasing the degree of cyanoethylation up to a certain limit then tends to decrease particularly at higher radiation doses (i.e., ca. 25 and 31 Mrads). At any event, however, the carboxyl contents of cyanoethylated cottons are higher than those of the unmodified cotton, indicating higher degradation, a point which appears in contrast with the data of copper number particularly those for cyanoethylated cotton with higher cyanoethyl content. This suggests that (a) oxidation of the aldehydic groups—already existing and/or newly formed in cyanoethylated cotton under the influence of irradiation—is more difficult as compared with their mate in the unmodified cotton and (b) the cyanoethyl group are partly converted to carboxylic groups during irradiation. If this is accepted, it would account for the contradiction between the indications of the copper number and carboxyl content.

Nitrogen Content

Figure 3 shows the effect of gamma radiation at different doses on the nitrogen contents of cyanoethylated cottons. It is observed that increasing the radiation dose is accompanied by a marginal decrease in nitrogen content. This is observed regardless of the degree of cyanoethylation of the modified cotton. The decrement in nitrogen content, though slight, suggests that some of the cyanoethyl groups are converted to carboxyethyl groups or that some of these groups are split off under the influence of irradiation. Indeed, the finding—given above—that irradiated cyanoethylated cottons, particularly those having higher cyanoethyl content, acquire higher carboxyl content than the corresponding unmodified cotton substantiates the

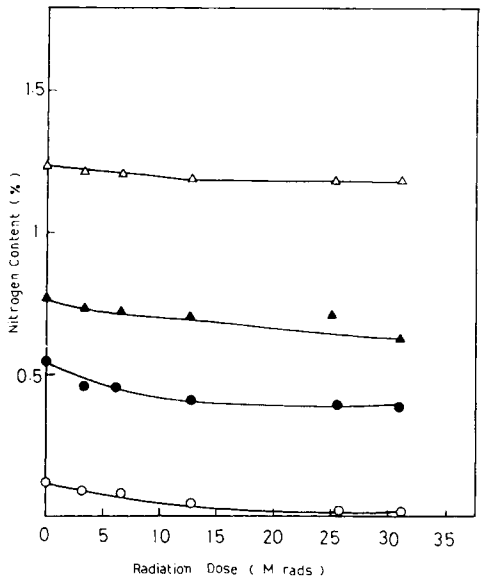

Fig. 3. Effect of gamma radiation on the nitrogen content of cyanoethylated cottons. Nitrogen (%): (○) 0.12; (●) 0.55; (▲) 0.773; (△) 1.238.

argument that some of the cyanoethyl groups are converted to carboxyethyl groups.

Degree of Polymerization (DP)

It has been reported[14,15] that when cellulosic materials are irradiated in the solid state by high energy radiation, energy transfer effects leads to localization of the energy within the molecule. These energy transfer effects are generally considered to be dependent on the mechanism of energy loss by the incident radiation to the chemical molecule, and initial random nonlocalized deposition (and subsequent dissipation) of the energy within the molecule and the rapid localization of the energy within the molecule. The localization of the energy in the molecule results in physical and chemical changes depending on nature of the matter irradiated, such as degradation, activation of long-lived excited sites, degradation of the molecule, or depolymerization.

Figure 4 shows the effect of gamma radiation on the DP of unmodified cotton and cyanoethylated cottons as well as on alkali-treated cotton. The latter was prepared under conditions similar to those cyanoethylation but in absence of acrylonitrile. For convenience, the unmodified cotton will be referred to as substrate I, alkali-treated cotton as substrate II, and cyanoethylated cottons having 0.12, 0.55, 0.77 and 1.24% N as substrates III, IV, V and VI, respectively.

It is clear (Fig. 4) that, before irradiation, the untreated cotton (substrate I) and the highly cyanoethylated cotton (substrate VI) show the highest DP while alkali-treated cotton (substrate II) shows the lowest. DPs of other

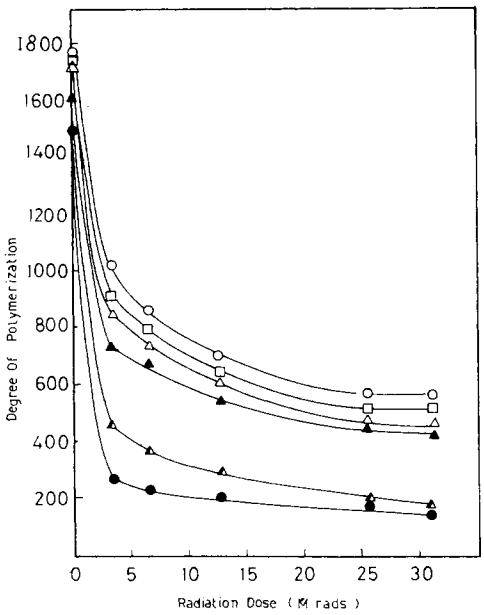

Fig. 4. Effect of gamma radiation on the degree of polymerization: (○) unmodified cotton; (●) alkali-treated cotton; cyanoethylated cottons. Nitrogen (%): (◭) 0.12; (▲) 0.55; (△) 0.773; (□) 1.238.

cyanoethylated cottons (substrates III, IV, and V) lie in between. The DP follows the order:

substrate I > substrate VI > substrate V > substrate III
> substrate IV > substrate II

The above order implies that cotton cellulose undergoes depolymerization during the alkali treatment via oxidation degradation in the presence of atmospheric and occluded oxygen. It further indicates that occurrence of cyanoethylation during alkali treatment reduces the extent of depolymerization. It is likely that presence of acrylonitrile impedes oxidation degradation of cellulose during alkali treatment, in accordance with previous reports.[4]

Figure 4 reveals that exposing the six substrates in question to gamma radiation causes a significant decrease in the DP particulary upon using a radiation dose of 3.199 Mrads. Increasing the radiation dose up to 31.194 Mrads is also accompanied by decrement in the DP but to a much lower extent. At any event, however, the decrement in DP depends upon the nature of substrate. Alkali-treated cotton and cyanoethylated cotton having the lowest cyanoethyl content undergo the highest depolymerization whereas the untreated cotton and cyanoethylated cotton having the highest cyanoethyl content undergo the lowest depolymerization, and the above order still presists after irradiation.

The higher susceptibility of alkali-treated cotton (substrate II) towards depolymerization (degradation) as compared with the unmodified cotton (substrate I) is unequivocally due to greater accessibility. The same holds true for cyanoethylated cotton with the lowest cyanoethyl content (substrate III). Increasing the cyanoethyl content in the molecular structure of cotton cellulose seems to compensate for the increased accessibility and indeed irradiated cyanoethylated cotton samples having 1.24% N (substrate VI) exhibit DPs, which are comparable with those of the unmodified cotton (substrate I). The cyanoethyl groups perhaps provide radiation protection of the glucosidic bonds of the cellulose chains through affecting energy transfer, particularly localization of energy. By virtue of their resonance stabilization, the —CN groups in cyanoethylated cotton would favor abstraction from the carbon atom next to the —CN groups. That is, the cyanoethyl groups offer a good position for radiation interaction. Meanwhile they are attached to cellulose via stable linkage as evidenced by the slight decrease in nitrogen content of cyanoethylated cottons after irradiation as shown above.

Tensile Strength

Table I shows the effect of gamma radiation at different doses on the tensile strength of unmodified cotton (substrate I), alkali-treated cotton (substrate II), and cyanoethylated cottons (substrates III, IV, V, and VI). It is observed that before irradiation the tensile strength of substrate II is lower than that of substrate I. This is rather expected since the alkali treatment was carried out without tension, and, therefore, substrate II would acquire a lower degree of crystallinity and orientation than substrate I. In addition, the DP of substrate II is lower than that of substrate I as previously indicated. It is understandable that crystallinity, orientation, and DP are the essential parameters which determine the tensile strength. On the other hand, tensile strength of cyanoethylated cottons (substrates III, IV, V, and VI) are generally comparable with that of unmodified cotton (substrate I).

Exposing the six substrates to gamma radiation brings about significant losses in tensile strength, being dependent on the radiation dose and nature of substrate. The loss in tensile strength is higher the higher the radiation dose. There is a tendency that cyanoethylated cottons retain higher strengths than the unmodified cotton. Alkali-treated cotton, on the other hand, stands in a midway position between cyanoethylated cottons and the untreated cotton. Differences in strength losses observed between the six substrates could be associated with differences in microstructural features of these substrates as well as the differences in their copper number, carboxyl content, and DP given above.

Elongation at Break

Table II shows the elongation at break of the six substrates under investigation before and after exposure to gamma radiation at different doses. It is obvious that alkali treatment causes a twofold increase in the elongation at break. The elongation at break of substrate II is almost double

TABLE I
Effect of High Energy Gamma Radiation on The Tensile Strength of Cotton (Substrate I), Alkali-Treated Cotton (Substrate II), and Cyanoethylated Cottons (Substrates III–VI) at Different Radiation Doses

Radiation dose (Mrads)	Tensile strength (kg)											
	Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI	
	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
0	55.76	43.52	50.47	40.6	55.5	45.5	53.9	44.77	54.0	42.67	54.65	47.9
3.199	43.33	36.92	43.37	31.67	48.42	37.83	48.75	40.5	44.66	33.33	48.31	44.75
6.399	39.1	33.13	38.67	30.91	39.73	33.8	39.23	35.25	37.46	30.37	41.73	31.93
12.797	29.83	23.66	27.14	15.24	31.03	22.5	32.75	23.17	33.93	19.87	34.46	24.85
25.595	21.98	16.65	21.51	11.05	22.83	12.57	24.22	14.93	23.46	11.73	25.2	18.75
31.194	20.5	13.17	19.54	9.47	20.56	10.33	20.25	13.42	21.58	11	23.17	16.1

TABLE II
Effect of High Energy Gamma Radiation on The Elongation at Break of Cotton (Substrate I), Alkali-Treated Cotton (Substrate II), and Cyanoethylated Cottons (Substrates III–VI) at Different Radiation Doses

Radiation dose (Mrads)	Elongation at break (%)											
	Substrate I		Substrate II		Substrate III		Substrate IV		Substrate V		Substrate VI	
	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
0	10.16	20.79	17.33	40.23	14.0	35.58	15.58	35.92	14.17	34.42	12.31	34.37
3.199	9.17	20.83	16.5	40.17	13.5	34.5	14.17	34.5	13.67	31.33	12.87	34
6.399	9.83	20.83	16	34.5	15.5	33.5	16.17	33.25	12.67	35	12.17	31.5
12.797	9.83	20.83	14.43	33.19	14	34	15	39.33	13	36.37	11.64	31
25.595	7.5	16.33	14.3	29.5	11.5	28	11.5	30.17	12.25	33.33	11.25	29.25
31.194	7.17	14.17	13.72	29	10.12	23.75	11.67	25.33	10.17	27.83	10	25.83

that of substrate I. The same situation is encountered with cyanoethylation, but the enhancement in elongation at break brought about by cyanoethylation is less than alkali treatment. That is, the elongation at break generally follows the order:

alkali-treated cotton > cyanoethylated cottons > unmodified cotton

This order persists after irradiation, but the latter causes substantial losses in elongation at break particularly upon using high radiation doses.

References

1. G. C. Daul, R. M. Reinhardt, and J. D. Reid, *Text. Res. J.*, **23**, 719 (1953).
2. R. M. Reinhardt, A. H. Markazich, H. D. Moore, and J. D. Reid, *Text. Res. J.*, **26**, 423 (1958).
3. J. Compton, *Am. Dyestuff Rep.*, **43**, 103 (1954).
4. M. H. El-Rafie, E. M. Khalil, S. A. Abdel-Hafiz, and A. Hebeish, *J. Appl. Polym. Sci.*, **28**, 311 (1983).
5. A. Hebeish, M. H. El-Rafie, A. T. El-Aref, and M. M. Kamel, *Acta Polym.*, **35**(1), 93 (1984).
6. (a) J. C. Jr. Arthur, F. A. Blouin, and R. J. Demint, *Am. Dyestuff Rep.*, **49**, 383 (1960); (b) J. C. Jr. Arthur and O. Hinojosa, *J. Polym. Sci., C*, **36**, 53 (1971); (c) I. Sakurada, T. Okada, and Y. Akiyama, *Doitai to Hoshasan*, **3**, 35 (1960); (d) A. Chapiro and V. Stannett, *Int. J. Appl. Radiation Isotopes*, **5**, 164 (1960); (e) A. Hebeish and J. T. Guthrie, *The Chemistry and Technology of Cellulosic Copolymers* Springer-Verlag, New York, 1981.
7. R. J. Demint, J. C. Arthur, and W. F. Mc Sherry, *Text. Res. J.*, **31**, 821 (1961).
8. J. C. Arthur, Jr. and F. A. Blouin, *J. Appl. Polym. Sci.*, **8**, 2813–2824 (1964).
9. J. Compton, W. H. Martin, and D. M. Gagarine, *Text. Res. J.*, **40**, 813 (1970).
10. T. H. Heyes, *J. Soc. Chem. Ind.*, **47**, T 90 (1928).
11. O. Samuelson and A. Wennerblau, *Svens. Paepperstidn*, **58**, 713 (1955).
12. A. Kantouch and I. Geczy, *Eur. Polym. J.*, **1**, 207 (1965).
13. ASTM Test Methods D-1682, in *Book of Standards*, Am. Soc. for Testing and Mater. Philadelphia, 1972, part 24.
14. J. Weiss, J. Polym. Sci., **29**, 425 (1958).
15. J. F. Saeman, M. P. Millett, and E. J. Lawton, *Ind. Eng. Chem.*, **44**, 2848 (1952).

Received January 7, 1985
Accepted January 24, 1985