

Study on the Decrystallization of Cotton*

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Received April 23, 1966

It was found that cotton cellulose was remarkably decrystallized by treating with acrylonitrile after padding with 18% aqueous solution of sodium hydroxide. By this reaction a little quantity of cyanoethyl unit was introduced into cellulose chains in the amorphous region which was widened by the alkali swelling. It was presumed that the recrystallization during water washing and drying was prevented by the introduction of cyanoethyl groups, and permanent effect of decrystallization was obtained. The decrease of degree of crystallinity was ascertained by acid hydrolysis, X-ray diffraction and infrared spectroscopy. The cotton fiber thus decrystallized has greater deal of moisture and dyestuff absorbency than untreated or mercerized cotton.

INTRODUCTION

It was reported that cellulose could be obtained in amorphous form by grinding in a vibratory ball mill^{1,2)}, or by saponification of cellulose acetate in a non-aqueous medium³⁾. Amorphous cellulose thus obtained was known to recrystallize on immersion in water.

Since 1950 interesting works have been made in America⁴⁾. In those works cotton was treated with lower alkyl amines such as ethyl amine, which were then extracted with nonaqueous solvent such as hexane or chloroform. By this way the degree of crystallization of cotton was remarkably decreased. The fiber tenacity was not lowered and elongation, elasticity, water absorbency, dyeability, chemical reactivity and luster of fabric were improved⁵⁾.

It seems, however, that this method has some difficult points for practical use. Ethyl amine has low boiling point, so cotton has to be immersed in it at low temperature ($-40\sim 0^{\circ}\text{C}$), and it is high cost and poisonous. Extraction of amine needs hexane, chloroform or acetone. Moreover, cotton thus decrystallized easily recrystallizes on immersion in water, especially in hot water^{6,7)}.

Under these circumstances, we originated a plan to decrystallize cotton cellulose stably by more practical method. The principle of our method is to treat with acrylonitrile the cotton which contains 18% caustic soda solution. In this reaction a little quantity of cyanoethyl unit is introduced into cellulose chains in the amorphous region which was widened by the alkali swelling. It is presumed that this cyanoethyl groups play a role to prevent the recrystallization during water washing and drying.

Previously in our joint research on the chemical treatment of cotton, S. Okamura found a similar effect of decrystallization using acetic anhydride in stead

* The major part of this paper was reported in *Report of the Institute for Chemical Fiber, Kyoto Univ.*, 20, 9 (1963).

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of acrylonitrile. In this case a little quantity of acetyl unit was introduced into cellulose molecules. But it seemed that this method had some difficulties for practical use, such as loss of acetic anhydride by the water contained in cotton, and unevenness of the reaction. Therefore, the method using acrylonitrile was adopted by us as more effective and practical mean and detailed work was carried out.

Recently, two papers were presented on the decrystallization of cellulose. Cotton fiber was decrystallized by swelling in aqueous solutions of caustic soda, ethylene diamine and zinc chloride⁸⁾. Degree of crystallinity and crystallite size were evaluated by X-ray method and optimal decrystallizing conditions were given. In another paper⁹⁾ it was reported that amorphous cellulose prepared by saponification of cellulose triacetate in a non-aqueous medium easily recrystallized on wetting, but if it was crosslinked with formaldehyde under anhydrous condition, its amorphous X-ray pattern was retained even after the prolonged aqueous treatment.

EXPERIMENTAL AND DISCUSSION

1. Treating Method of Cotton and Properties of the Treated Cotton

Scoured and bleached cotton fabric (30'S) was used as raw material. Cotton fabric was immersed in slack condition in 18% aqueous solution of sodium hydroxide at room temperature and squeezed. Then it was immersed in acrylonitrile, neutralized with dilute acetic acid after squeezing, and water rinsed. Typical treating condition was shown in Table 1. (AN-Dec-I). For comparison, another cases were also shown in which cotton fabrics were immersed in 4% caustic soda solution at room temperature after immersion in 18% caustic, then reacted with acrylonitrile at 40°C for 10 or 20 min. (AN-Dec-II (a) and (b)).

The values of nitrogen content of the treated cotton found by micro-Kjeldahl method were shown in Table 2. The values of the degree of cyanoethylation shown

Table 1. Typical condition of decrystallization of cotton.

Sample NO.	Treating condition
AN-Dec-I	Immersion in 18% caustic soda aqueous solution (15°C, 30 min.), squeezing, immersion in acrylonitrile (room temp., 15 min.), squeezing, neutralizing with 0.2% acetic acid (room temp., 30 min.), Water rinse (30 min.), room drying.
AN-Dec-II	Immersion in 18% caustic soda aqueous solution (15°C, 30 min.), squeezing, immersion in 4% caustic soda solution (room temp., 30 min), squeezing, then (a) immersion in acrylonitrile (40°C, 10 min.) (sample no. AN-Dec-II-a), (b) immersion in acrylonitrile (40°C, 20 min.) (sample no. AN-Dec-II-b). Both (a) and (b) were then squeezed, neutralized with 0.2% acetic acid (30 min), water rinsed (30 min.), and room dried.

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Table 2. Moisture and nitrogen contents of the decrystallized cotton.

Sample	Moisture content (%) ^{b)}		N (%)	Degree of cyanoethylation ^{a), b)} (mole %)
	Exp. 1	Exp. 2		
Untreated	7.69	7.39	—	—
Mercedized (with 18% NaOH)	11.93	12.06	—	—
Decrystallized				
AN-Dec-I	14.67	14.39	1.61	6.59
AN-Dec-II-a	12.10	11.66	4.09	18.6
AN-Dec-II-b	8.72	7.96	6.97	36.5

^{a)} Calculated assuming that nitrogen atoms were introduced into cotton cellulose as cyanoethyl units.

^{b)} The moisture contents of cottons cyanoethylated to the degrees of about 1.6, 4.1 and 7 mole % by ordinary method using 3~4% caustic soda aqueous solution, were found by M. Negishi to be about 7.3, 5 and 4.5% respectively.

in Table 2 were calculated assuming that the nitrogen atoms were introduced into cellulose in the form of cyanoethyl unit. This fact was ascertained by infrared spectroscopy as described later. When the same cotton fabrics were immersed into 4% caustic soda without previous immersion in 18% caustic and reacted with acrylonitrile at 40°C for 10 or 20 min. as typical method of liquid phase cyanoethylation, the values of the degree of cyanoethylation were about 5 and 10 mole %, respectively. So it is known that the previous immersion of cotton in 18% caustic soda solution remarkably accelerates the reaction of cyanoethylation.

Table 3 shows tensile properties of the fibers taken from the warp yarns. The high value of dry tenacity of decrystallized cotton may be probably attributed to

Table 3. Tensile property of fibers taken from warp yarn.

Sample	Dry		Wet	
	Tenacity (g)	Elongation (%)	Tenacity (g)	Elongation (%)
Untreated	5.04	4.8	5.26	11.4
Mercedized (18% NaOH, 18°C, 30 min.)	5.27	10.5	5.73	13.5
Decrystallized (AN-Dec-I)	6.59	7.5	4.68	15.9

the deviation of experimental values, but in many experimental results not described here it was shown that dry tenacity was not decreased, but somewhat increased by this treatment. Tearing strength of fabric also tended to somewhat increase in many examples. It is interesting to see that the wet tenacity of the decrystallized cotton fiber is lower than the dry tenacity in contrast with untreated or mercedized cotton.

Table 4 shows the values of crease recovery of fabrics. Dry crease recovery is not increased by the decrystallization, but wet crease recovery is fairly improved

as in the case of dichloropropanol treatment which is used in Belfast wash and wear finishing of cotton fabric. This fact implies that wet crease recovery of cotton fabric can be improved without covalent cross-linking.

Table 4 Crease recovery of various chemically treated cotton fabrics.

Sample	Treating method	Crease recovery (warp) ^{a)} (%)	
		Dry	Wet
Untreated		36	41
Mercerized	18% NaOH, 18°C, 30 min.	32	44
Carboxymethylated	25% monochlor acetic acid, 33% NaOH	36	49
Decrystallized	18% NaOH, acrylonitrile (room temp.)	32	54
1,3-dichloro-2-propanol	Immersed at room temp., squeezed, then immersed in 15% NaOH at room temp.	23	66

^{a)} 500g load for 5 min., 2 min. after unloading.

2. Evaluation of the degree of decrystallization

Some experimental results are given below to show the decrease of crystallinity by this treatment.

a) Moisture Absorption

As shown in Table 2, moisture absorption of the decrystallized cotton is much more than untreated or mercerized cotton, and, moreover, than cotton cyanoethylated by ordinary method without preliminary immersion in 18% caustic soda solution.

b) Specific Gravity

Specific gravity was measured by submerged-float method using carbon tetrachloride-xylene mixture. The decrease of specific gravity is evident as shown in Table 5.

Table 5. Specific gravity.

Sample	Specific gravity (30°C)
Untreated	1.529
Mercerized	1.517
Decrystallized ^{a)}	1.417

^{a)} Degree of cyanoethylation 8~10 mole %; treated in jigger.

c) Dyeability

In detailed experiments it was found that the decrystallized cotton by our method had much more dyeability for various kinds of dyes especially for cotton dyes than untreated, mercerized or ordinary cyanoethylated cotton. These results will be reported in other paper.

d) Determination of Crystallinity by Acid Hydrolysis

0.5g of fiber sample, dried at 105~110°C for 2 hrs, was hydrolysed with 2.5 N hydrochloric acid at 100°C for 2 hrs. The residue was washed with 0.5% acetic acid and water. The ratio of the dry weights measured after and before the hy-

drolysis was adopted as an index of degree of crystallinity. In this calculation it was assumed that all cyanoethyl units were introduced into cellulose chains in amorphous region, and the dry weight before hydrolysis was calculated assuming that all cyanoethyl units were transformed into hydroxyl units.

The decrease of the degree of crystallinity of the fibers obtained by immersion into acrylonitrile at 20~50°C for various times after immersion into 18% caustic soda solution at 23°C for 30 min. was as shown in Fig. 1.

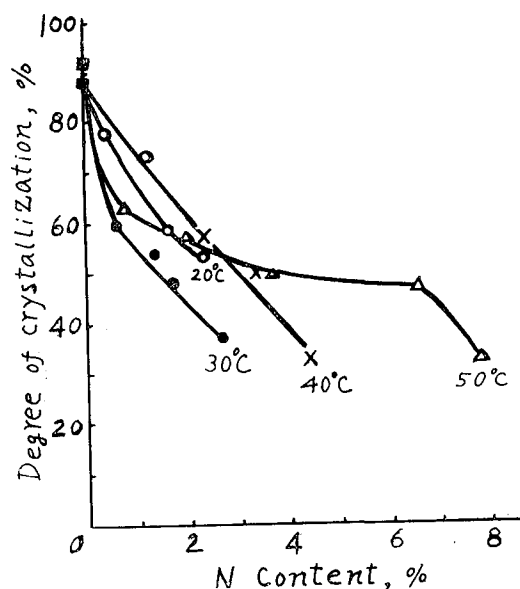


Fig. 1. Effect of the immersion temperature in acrylonitrile on the degree of crystallization determined by acid hydrolysis method (immersed in 18% caustic soda solution at 23°C for 30 min., then immersed in acrylonitrile at 20, 30, 40, 50°C for 5, 10, 20, 30 min. at each temperature).

It is interesting that by proper selection of the reaction conditions samples having various degrees of crystallinity and cyanoethylation are obtained. The properties of those fiber samples are now being examined in detail.

e) X-ray Diffraction

The X-ray diffraction pattern of the decrystallized cotton fiber (N 1.53%), obtained by treating with 18% caustic soda (18°C, 30 min.) and acrylonitrile (28~30°C, 30 min.), was shown in Fig. 2, comparing with those of untreated and mercerized cotton fibers.

Further, intensity curves of X-ray diffraction for the same samples were obtained using Geiger counter X-ray diffractometer (Fig. 3). The values of degree of crystallinity thus obtained were shown in Table 6, together with the values obtained by acid hydrolysis method.

f) Infrared spectroscopy

Infrared spectra of untreated, mercerized and decrystallized (AN-Dec-1 in Table 1 and 2) cottons were taken using KBr powder method. Fig. 4 shows the results. O'Conner et al.¹⁰⁾, who had made the detailed study on infrared spectra of various chemically modified cottons, found that on cotton decrystallized by

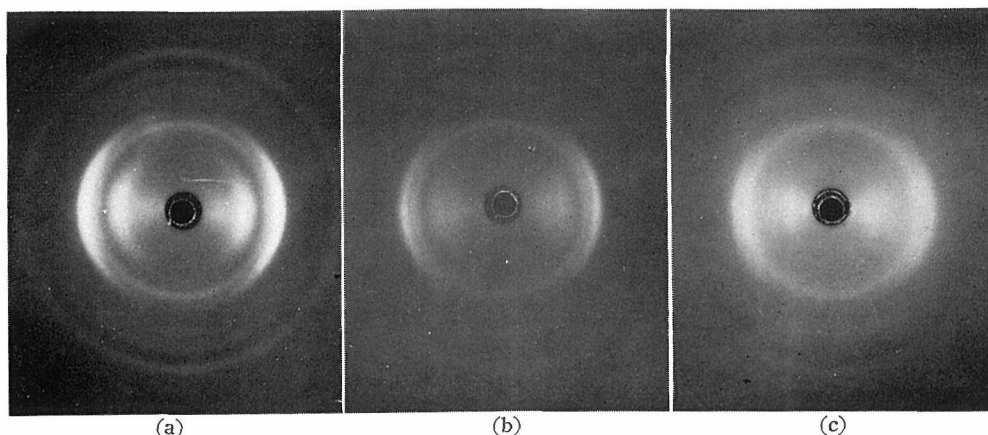


Fig. 2. X-ray diffraction photographs.
 (a) Untreated cotton, (b) Mercerized cotton, (c) Decrystallized cotton

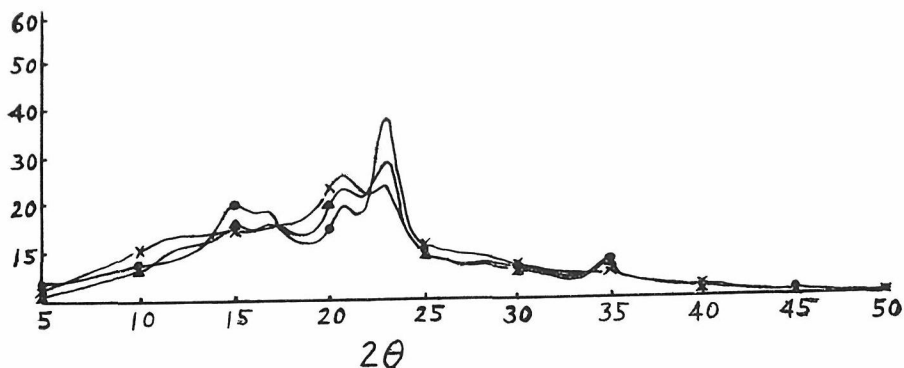


Fig. 3. Intensity curves of X-ray diffraction.
 ● : Untreated cotton, ▲ : Mercerized cotton, × : Decrystallized cotton.

Table 6. Degree of crystallinity.

Sample	Degree of crystallinity (%)	
	X-ray	Acid hydrolysis
Untreated	62	92.6
Mercerized	49	87.9
Decrystallized	44	50~55

ethyl amine treatment, the absorption at about 7μ decreased and that at about 11.15μ increased with decrease of the degree of crystallinity. They adopted the ratio of these two absorptions as the index indicating degree of crystallinity and referred to that this value was found by Conrad¹¹⁾ to be in proportion to the value of crystallinity obtained by X-ray method.

It is shown in Fig. 4 that the absorptions at 7μ decrease and those at about 11.2μ increase in order of untreated, mercerized and decrystallized cottons. The absorption at 4.4μ , found only in decrystallized cotton, is assigned to CN unit¹⁰⁾,

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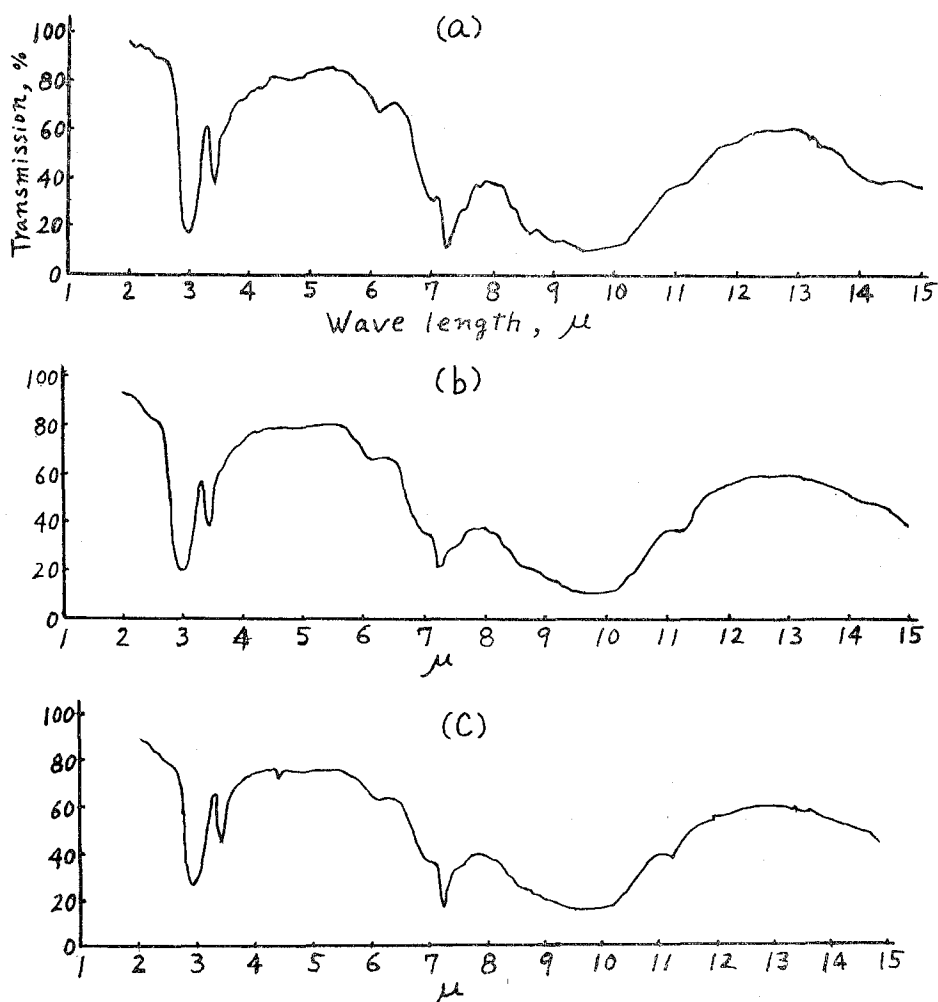


Fig. 4. Infrared absorption spectra.
(a) Untreated cotton, (b) Mercerized cotton, (c) Decrystallized cotton.

which shows that nitrogen is introduced in the form of cyanoethyl unit. Though the formation of carbamoylethyl ($-\text{CH}_2-\text{CH}_2-\text{CONH}_2$) or carboxyl units by alkali saponification of cyanoethyl unit is presumed, the absorptions assigned to those units ($-\text{CONH}_2$ $6.00\sim 6.06\mu$, $-\text{COOH}$ 5.85μ)¹⁰ are not observed.

g) Electron Microscopic Observation of Acid Hydrolysis Residue

On the electron microscopic observation of the dilute water dispersion of acid hydrolysis residues of untreated, mercerized and decrystallized (degree of crystallinity estimated by acid hydrolysis method was 30.5%), it was found that the residue from decrystallized cotton was much more finely dispersed in water and slowly precipitated than those from two others.

h) Graft Copolymerization onto Decrystallized Cotton Fabric

It is expected that the cotton fabrics thus decrystallized has high chemical reactivity. Though the detailed investigation on this problem depends a great deal upon future works, some experimental results are shown here on graft

copolymerization onto decrystallized cotton.

The results of grafting of acrylonitrile with ceric ion method are shown in Table 7. The polymerization medium was aqueous solution of 4% acrylonitrile, 0.002 mole ceric ammonium nitrate and 0.01 mole nitric acid. The polymerization temperature was 30°C. It was found that the grafting rate was much higher for the decrystallized cotton than for others.

Table 7. Graft copolymerization of acrylonitrile by ceric ion method onto chemically treated cotton fabrics.

Sample	Degree of crystallinity (Acid hydrolysis) (%)	Degree of cyanoethylation (mole %)	Grafting % ^{a)}		
			Polymerization time (hr)		
			0.5	1.0	2.0
Untreated	92.6	—	24.3	30.2	32.7
Mercerized	88.3	—	45.1	48.6	54.6
Decrystallized	52.8	10	71.0	76.3	76.5
Cyanoethylated ^{b)}	—	11	42.1	45.8	52.5

^{a)} Homopolymer was extracted with dimethyl formamide at 80°C, for 4 hrs.

^{b)} Ordinary cyanoethylation using 3~4% caustic soda aqueous solution and acrylonitrile.

Further, grafting of styrene was carried out using high energy irradiation method. In the pre-irradiation method using Van de Graaff accelerator, the order of grafting rate of styrene was found to be untreated > mercerized > carboxymethylated > decrystallized cotton (Table 8), contrary to that in the catalyzer method

Table 8. Graft copolymerization of styrene by high energy radiation*.

Sample	Grafting %				
	Pre-irradiation in air by Van de Graaf accelerator, total dose 3.6 Mrad		Mutual irradiation by Co ⁶⁰ γ -ray (30°C)		
	Polymerization at 50°C		Dose rate (r/hr)	4.8x10 ³	6.7x10 ³
	4 hrs.	24 hrs.	Total dose (r)	2.0x10 ⁵	3.0x10 ⁵
Untreated	117	470		104	177
Mercerized	107	274		132	138
Carboxymethylated	66	152		108	119
Decrystallized	25	75		111	167

* Composition of polymerization liquor, styrene 20 : methanol 80 (vol.%)

shown in Table 7. It was supposed that in the catalyzer method the increase of grafting rate was caused by the higher accessibility of the decrystallized cotton for polymerizing medium, but in the pre-irradiation method the decrease of grafting rate in the decrystallized cotton might be attributed to faster deactivation of trapped radicals in the amorphous region of cotton cellulose. From this point of view it is presumed that in mutual irradiation method the effect of decrystallization on grafting rate will be lesser than that in pre-irradiation method.

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This guess appears to be nearly right as shown in Table 8.

Summing up above experimental results, it may be concluded that cotton cellulose is certainly decrystallized by this alkali-acrylonitrile treatment.

ACKNOWLEDGEMENT

The authors wish to express their thanks to Professor I. Sakurada for his suggestion and discussion; to Dr. K. Hirabayashi and Mr. S. Tamanura for taking X-ray and electron microscopic photographs; to Dr. Y. Ito for X-ray diffractometry; to Dr. T. Okada for infrared spectroscopy; and to Miss Y. Kadono and Miss M. Kawaguchi for their cooperations in the present work.

This work is a part of the research carried out by the request of Japan Cotton Technical Institute and under the aid of Toyo Spinning Company. The authors wish also to thank them.

REFERENCES

- (1) K. Hess, H. Kiessig and J. Gunderman, *Z. Physik. Chem.*, **B49**, 64 (1941).
- (2) P. H. Hermans and A. Weidinger, *J. Am. Chem. Soc.*, **68**, 2547 (1946).
- (3) R. St. J. Manley, *J. Polymer Sci.*, **A1**, 1893 (1963).
- (4) L. Segal *et al.*, *J. Phys. Colloid Chem.*, **55**, 325 (1951); *Text. Res. J.*, **23**, 428 (1953); *J. Polymer Sci.*, **13**, 193 (1954); *Text. Res. J.*, **25**, 516 (1955).
- (5) G. Susich, *Amer. Dyest. Repr.*, **42**, 713 (1953); R. S. Orrs, *Text. Res. J.*, **25**, 592 (1955); J. N. Grant, *Text. Res. J.*, **26**, 74 (1956); H. M. Ziifle *et al.*, *Text. Res. J.*, **29**, 13 (1959); R. S. Orrs, *Text. Res. J.*, **29**, 349 (1959).
- (6) H. T. Janssen, *Text. Res. J.*, **27**, 622 (1957).
- (7) H. Maeda, *J. Soc. Text. Cell. Ind., Japan*, **11**, 721 (1955).
- (8) N. B. Patil, N. E. Dweltz and T. Radhakrishnan, *Text. Res. J.*, **35**, 517 (1965).
- (9) I. L. Wadehra, R. St. J. Manley *et al.*, *J. Appl. Polymer Sci.*, **9**, 2627, 2634 (1965).
- (10) O'Conner *et al.*, *Text. Res. J.*, **23**, 382 542, (1958).
- (11) C. M. Conrad, Private communication to O'Conner.