# Location of Some Typical Vinyl Polymers Within Radiation-Grafted Cotton Fibers: An Electron Microscopical Survey

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## Synopsis

Electron microscopical observations of radiation-induced rayon–styrene graft co-polymers were published by Kaeppner and Huang in 1965. The present paper reports electron microscopical investigations on the relationship of the structure of vinyl–cotton graft polymers to the original morphology of the cotton fiber and into the distribution of the grafted vinyl polymer in the cotton fiber structure. The grafted vinyl monomers investigated in this study were acrylonitrile, styrene, methyl methacrylate, and vinyl acetate. Two radiation-induced procedures were used: simultaneous irradiation grafting and post-irradiation grafting. Ceric ion grafting of acrylonitrile to cotton was included for purposes of comparison. Distribution of the vinyl polymer within the cotton fiber is illustrated by a series of electron micrographs, selected as typical of the particular grafted species under consideration. Results indicate that the diffusion rate of monomer into the cellulose fiber plays an important role in the final distribution of polyacrylonitrile grafts within the fiber. Uniform distribution of polyacrylonitrile in the fiber was achieved by simultaneous irradiation grafting of acrylonitrile on a highly substituted cyanoethylated cotton. In samples of low degree of cyanoethylation the distribution of graft polymer was non-uniform. In grafting initiated by ceric ion the acrylonitrile graft polymer was evenly distributed. Polystyrene–cotton copolymers from grafts, made by simultaneous irradiation of cotton in methanol solutions of the styrene monomer, were uniform throughout the fiber but showed opening of structure associated with the amount of graft formed. Grafting of methyl methacrylate occurred only in the peripheral regions of the fiber; by contrast, grafting of vinyl acetate was uniform throughout the fiber wall. Important factors governing the successful irradiation grafting in cotton fibers are choice of solvent, ratio of monomer to cellulose, nature of prior chemical modification of the cellulose, and total irradiation dosage.

## INTRODUCTION

The interaction of high-energy radiation with polymers and the production of graft copolymers by radiation-induced reactions of polymers and vinyl monomers have been actively investigated by many workers during recent years.[1] A large number of reports on the radiation-induced inter-

action of styrene, acrylonitrile, methyl methacrylate, and other vinyl monomers with cellulosic films, filter paper, cellulose esters, cotton, and regenerated cellulosic fibers have been published.[2-4]

Work in this area by Arthur and his co-workers at the Southern Utilization Research and Development Division has been concerned with preparing radiation-induced graft copolymers of cotton and various vinyl monomers while retaining the fibrous nature and high molecular weight of the cotton cellulose.[5-13]  The copolymer technique results in enhancement of the best properties of cotton and acquisition of the properties of the grafted vinyl polymer and therefore more useful, new cotton products for specific end uses.  These workers have found that the radiation-induced grafting of vinyl monomers to cotton leads to increased elongation, toughness, abrasion resistance, thermoplasticity, and rot resistance, and decreased stiffness and permanent set.[10,14]  However, these property changes are dependent not only on the nature and amount of graft polymer formed but on its location within the cotton fiber structure.

Electron microscopical observations of radiation-induced rayon–styrene graft copolymers were published by Kaeppner and Huang in 1965.[4]  The present paper reports electron microscopical investigations into both the relationship of the structure of the vinyl–cotton graft polymer to the original morphology of the cotton fiber and the distribution of the grafted vinyl polymer in the cotton fiber structure.  The grafted vinyl monomers investigated in this study were acrylonitrile styrene, methyl methacrylate, and vinyl acetate.  Two radiation-induced grafting procedures were used: simultaneous irradiation grafting and post-irradiation grafting.  Ceric ion grafting of acrylonitrile to cotton was included for purposes of comparison.  Distribution of the vinyl polymer within the cotton fiber is illustrated by a series of electron micrographs, selected as typical of the particular grafted species under consideration.

## MATERIALS

### I. Cotton

Deltapine cotton fibers and yarns (7/3, 84 × 3 tex) were purified by extraction with hot ethanol and by boiling in 1% NaOH.[15]  The fabric used was derived from a commercial 68 × 72 grey print cloth subjected to enzyme desizing, alkali scouring, and peroxide bleaching on a pilot-plant scale before laboratory purification.

### II. Cyanoethylated Cotton

Cyanoethylation was accomplished by padding onto the yarn a 2% NaOH solution to approximately 85% wet pickup, immersing it in a water-saturated acrylonitrile solution, and agitating at 55°C.  The cotton was removed at predetermined times of reaction to give the desired degree of substitution, washed in dilute acetic acid, thoroughly rinsed in distilled water, and dried under ambient conditions.[6]

## III. Monomers and Solvents

The monomers of acrylonitrile, styrene, methyl methacrylate, and vinyl acetate were commercial products. For post-irradiation grafting treatments the monomers were distilled prior to use, with the exception of acrylonitrile, which was alkali-extracted, washed, and dried before distillation. Saturated aqueous stock solutions of zinc chloride (about 81% at 25°C.) were made from ACS-grade reagent. Other chemicals used were commercial grade.

## IV. Cupriethylenediamine Hydroxide Solution (CED)

Cupriethylenediamine hydroxide solution (CED), used as a cellulose solvent in microscopical observations, was made according to ASTM Designation D-539-53 to a concentration of approximately $0.5M$ in copper.[16] It was kept refrigerated until used in microscopical observations.

## METHODS

## I. Irradiation

Irradiations were carried out with the SURDD cobalt-60 source.[17] Dose rates ranged from $0.25$–$0.60 \times 10^6$ r./hr. (roentgens per hour). Calibrations were based on ferrous–ferric dosimetry in $0.5M$ $H_2SO_4$.

## II. Sample Preparation

### A. Polyacrylonitrile–Cotton Graft Polymers

**1. Simultaneous Irradiation Grafting in Aqueous $ZnCl_2$ Solution.**[5] After immersion in an 80% aqueous $ZnCl_2$ solution containing 32% acrylonitrile (25 g. of solution per gram of cotton) the purified cotton yarns were padded to approximately 200% wet pickup. They were irradiated in air to the desired dosage ($0.2$–$1.0 \times 10^6$ r.), water-washed, to remove monomer and $ZnCl_2$, and then air-dried. The grafted samples were refluxed overnight with $N,N$-dimethylformamide (DMF) to remove homopolymer and again water-washed and air-dried. In this paper the per cent grafted polymer is the per cent increase in weight after extraction, based on the original weight of the ungrafted sample.

**2. Simultaneous Irradiation Grafting in DMF Solution.**[4] Purified cotton yarns were pretreated by overnight immersion in a solution of 30% acrylonitrile in DMF (19 ml. of solution per gram of cotton). The cottons and solutions were irradiated in air to $1.0 \times 10^6$ r. After irradiation the samples were water-washed, to remove monomer and solvent, and extracted overnight with DMF, to remove homopolymer.

**3. Simultaneous Irradiation Grafting to Cyanoethylated Cotton in Aqueous $ZnCl_2$ Solution.**[6] Cyanoethylated yarns of varying degrees of substitution (D.S. = 0.3–1.3) were immersed overnight in 80% aqueous $ZnCl_2$

solution containing 32% acrylonitrile (25 g. of solution per gram of cotton). After padding, to give 200–400% wet pickup, the substituted yarns were irradiated in air to the desired dosage of $0.2–1.5 \times 10^6$ r. They were then water-washed, to remove monomer and $ZnCl_2$, and extracted overnight with DMF, to remove homopolymer.

**4. Post-irradiation Grafting in Aqueous $ZnCl_2$ Solutions.**[9,13] Purified cotton fibers, yarns, and fabrics were placed in glass cylinders and dried over $P_2O_5$ in high vacuum for 16 hr. The atmosphere in the cylinders was exchanged with nitrogen, and the samples were irradiated to the desired dosage $(1.0–6.1 \times 10^6$ r.). Within $1/2$ hr. after irradiation the samples were placed in either 15 or 32% acrylonitrile in 70, 75, or 80% aqueous $ZnCl_2$ solutions (30 ml. of solution per gram of cotton). Entrapped air was removed from the samples by repeated short evacuations of the system. The top of the treating vessel was flushed with nitrogen and closed at atmospheric pressure. The samples reacted at about 23°C. for the desired times. The grafted samples were then water-washed, to remove monomer and $ZnCl_2$, and extracted overnight with DMF, to remove homopolymer.

**5. Post-irradiation Grafting in DMF Solution.**[9] Purified cotton fibers were treated as described in the preceding paragraph, except that the irradiation dosage ranged from $2.3 \times 10^6$ to $6.1 \times 10^6$ r. Within $1/2$ hr. after irradiation the samples were immersed in a solution of 32% acrylonitrile in DMF (20 ml. of solution per gram of cotton) and sealed in glass tubes under high vacuum. The samples then reacted for various times at either 23 or 80°C. The samples were allowed to come to atmospheric pressure, washed with water, to remove monomer and solvent, and extracted overnight with DMF, to remove homopolymer.

**6. Ceric Ion Grafting in Acidic Aqueous Solution.** Grafting of polyacrylonitrile to cotton by means of ceric ion initiation was accomplished by the method of Kaizerman et al.[18] Purified fabrics were immersed in a solution of $0.005M$ ceric ammonium nitrate, $0.05M$ $HNO_3$, and 4% acrylonitrile. The samples were allowed to stand at 23°C. for the desired times, removed from the solution, water-washed, and refluxed overnight with DMF.

*B. Polystyrene–Cotton Copolymer; Simultaneous Irradiation Grafting in Methanol Solution*[8]

Purified cotton yarns were immersed in solutions containing various proportions of styrene and methanol (10 g. of solution per gram of cotton) and irradiated in air to the desired dosage $(0.2–10.0 \times 10^6$ r.). After irradiation the samples were rinsed with methanol, to remove monomer, and then water-washed. The yarns were extracted overnight with benzene, to remove homopolymer.

### C. Poly(methyl Methacrylate)–Cotton Copolymer: Post-irradiation Grafting in Aqueous ZnCl₂ Solution[13]

Purified cotton fibers, yarns, and fabrics were placed in glass cylinders and dried over $P_2O_5$ in high vacuum for 16 hr. The atmosphere in the cylinders was exchanged with nitrogen, and the samples were irradiated to $1.0 \times 10^6$ r. Within $1/_2$ hr. after irradiation the samples were placed in an 80% aqueous $ZnCl_2$ solution containing 15% methyl methacrylate (30 ml. of solution per gram of cotton). Entrapped air was removed from the samples by repeated short evacuations of the system. The top of the treating vessel was flushed with nitrogen and closed at atmospheric pressure. The samples were reacted at about 23°C. for the desired times. After being rinsed with methanol to remove the monomer, and water-washed, the grafted samples were then refluxed overnight with methyl ethyl ketone, to remove homopolymer.

### D. Poly(vinyl Acetate)–Cotton Copolymer: Post-irradiation Grafting in Aqueous ZnCl₂ Solution[13]

The procedure described in the preceding paragraph was used in preparation of the poly(vinyl acetate)–cotton copolymer, except that the treating solution was 15% vinyl acetate in 70% aqueous $ZnCl_2$ solution and acetone was the solvent for the extraction of homopolymer.

## III. Microscopical Analysis

The distribution of graft polymer within the cotton fiber wall was evaluated by electron microscope observations of ultrathin sections 600–1000 A. thick, cut with a diamond knife from small bundles of grafted cotton. The fiber bundles were embedded for sectioning in either (1) a mixture of polymethacrylates [methyl and butyl 4:1, catalyzed by 1.0% Luperco CDB (50% of 2,4-dichlorobenzoyl peroxide with dibutyl phthalate)] or (2) an aqueous solution of poly(vinyl alcohol). Embedding polymer was removed from the sections by extraction with either an equivolume mixture of chloroform and methyl ethyl ketone or distilled water.

To detect regions of grafting, sections were exposed, prior to shadowing, to solvents for the vinyl polymers or for unreacted cellulose or both. Immersion of the thin section freed from embedding medium in CED, followed by thorough washing with water prior to shadowing,[19] identified the areas of unreacting cellulose and indicated the relative distribution of the grafted material within the fiber. Conversely, immersion of the sections in a solvent for the vinyl polymer rather than CED showed the location of the polymer and the extent of its association with the cellulose.[20] The samples were shadowed by evaporation of platinum at a suitable angle and photographed with the electron microscope.[19–21]

## RESULTS

The responses of ultrathin sections of the polymer-grafted cotton fibers studied to solvents for cellulose and for the respective polymers are summarized in Table I and illustrated by the electron micrographs in this report; the latter were selected as typical of the characteristics observed in this survey. In Figure 1 are shown fiber sections of control samples of unreacting cotton before and after immersion in CED.

### I. Acrylonitrile

(1) Simultaneous irradiation grafting of acrylonitrile to cotton with a 32% monomer solution in 80% aq. ZnCl₂ (padded) resulted in a copolymer with a dense band of grafted polyacrylonitrile located about half-way between the less-reacting outer and inner surfaces of the cotton fiber. This



(a)                                        (b)
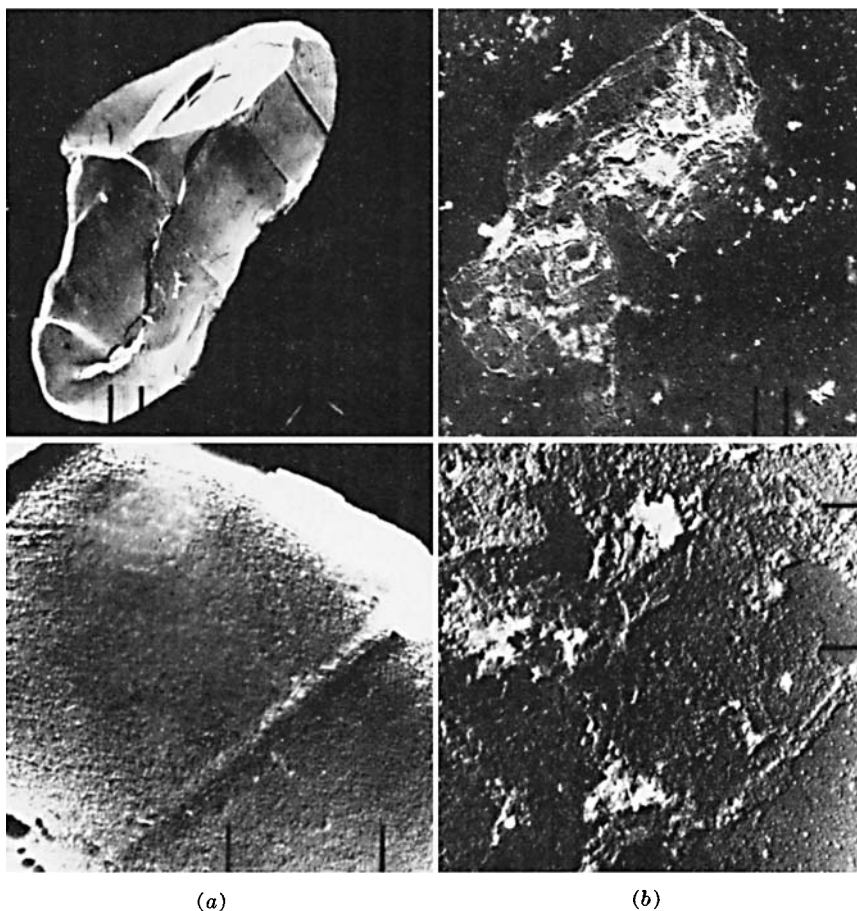
Fig. 1. Scoured cotton. (a) Shadowed section after removal of polymethacrylate embedding medium; (b) section of (a) after CED immersion. Distance between marks is 1 μ.
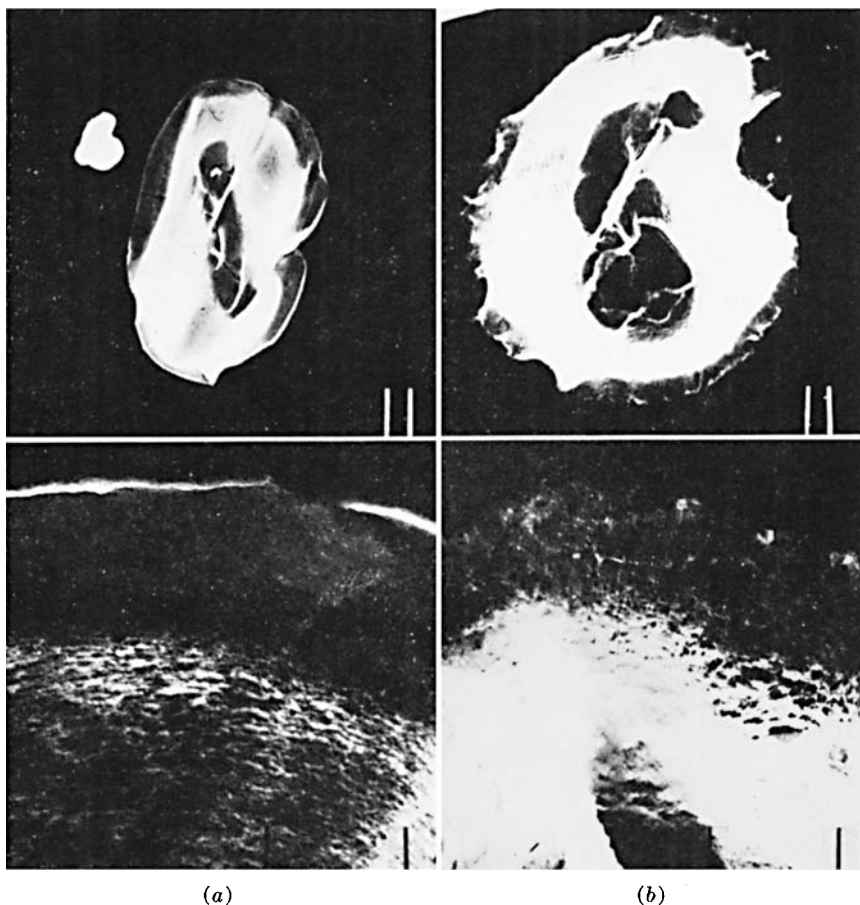
(a)                 (b)

Fig. 2. Polyacrylonitrile–cotton copolymer. Simultaneous irradiation grafting, 32% acrylonitrile in 80% aq. $ZnCl_2$, $1.0 \times 10^6$ r., 31% grafted polymer. (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion.

is illustrated by the fiber cross-section in Figure 2a. The polyacrylonitrile–cotton copolymer had a more rounded cross-section than is normal, and the texture, as shown in the high magnification micrograph, is not as smooth as that of native cotton fibers. Immersion of the grafted cross-section in CED, a solvent for unmodified cellulose, resulted in some dissolution of cellulose from the outer edge and inner portion of the fiber cross-section; however, most of the fiber section is composed of the dense band of grafted polyacrylonitrile that remained and became spongy in appearance (Fig. 2b). The outer edge, which has a less dense appearance, has become porous (observed in the high-magnification micrograph of Fig. 2b) and remains after immersion in CED, indicating that some reaction had occurred throughout the greater portion of the fiber.

TABLE I

Microscopical Observations of Grafted Polymers in Cotton Fibers

| Sample[a] | Monom. soln.[b] | Grafting treatment | Graft. poly. add-on, % [c] | Embed. medium[c] | Microscopical appearance | Behavior in solvents[d] |
|---|---|---|---|---|---|---|
| SC | — | — | — | MA | Solid | Dissolved in CED |
| SC | Ac 32% in 80% aq. ZnCl$_2$ | Simult. irrad., 1.0 × 10$^6$ r. | 31 | MA | Dense band intermediate between outer and inner regions | Outer and inner areas dissolved in CED, intermediate band remained but became spongy in appearance |
| SC | Ac, 30% in DMF | Simult. irrad., 1.0 × 10$^6$ r. | 37 | MA | Uniform deposition throughout fiber section | Section became thinner and rougher in texture but did not dissolve in CED |
| CC, D.S. 1.01 | — | — | — | MA | Section separated into layers by swelling of cyanoethyl cellulose in methacrylate | Fibrillar structure altered by solution of cellulose by CED; after repeated treatment with CED and DMF the insoluble residue had a gel pattern |
| CC, D.S. 1.01 | Ac, 32% in 80% aq. ZnCl$_2$ | Simult. irrad., 1.0 × 10$^6$ r. | 42 | MA | Cross-section rounded and much larger. No layering, uniform deposition throughout fiber section | CED had little effect; after repeated treatment with CED and DMF the insoluble residue had a gel pattern |
| CC, D.S. 0.34 | — | — | — | MA | Section separated into layers by swelling effect of methacrylate on cyanoethyl cellulose | Fibrillar structure altered by solution of cellulose in CED; after repeated treatment with CED and DMF the insoluble residue had a gel structure |

| | | | | | | |
|---|---|---|---|---|---|---|
| CC, D.S. 0.34 | Ac, 32% in 80% aq. ZnCl$_2$ | Simult. irrad., 1.0 × 10$^6$ r. | 43 | MA | No layering but section appeared more dense than unreacted control | Non-uniformity of deposit revealed by solution of unreacted cellulose in CED; after successive immersions in CED and DMF sections became thinner. |
| SC | Ac, 32% in 80% aq. ZnCl$_2$ | Dry irrad., 1.0 × 10$^6$ r.; post-irrad. treat. 48 hr. at 23°C. | 78 | MA | Deposit made heavy band in peripheral region of fiber | In CED most of the fiber center dissolved, indicating little or no reaction in fiber interior; peripheral band remained |
| SC | Ac, 32% in 80% aq. ZnCl$_2$ | Dry irrad., 6.0 × 10$^6$ r.; post-irrad. treat. 35 hr. at 23°C. | 89 | MA | Fiber appeared to be reacted throughout but with heavier deposit at periphery | CED little effective, indicating little unreacted cellulose |
| SC | Ac, 15% in 70% ZnCl$_2$ | Dry irrad. 1 × 10$^6$ r.; post-irrad. treat. 0.9 hr. at 23°C. | 44 | MA | Section slightly swollen, with dense band at periphery | CED dissolved some unreacted cellulose, leaving porous structure, but grafting reaction continuous throughout section |
| SC | Ac, 15% in 75% aq. ZnCl$_2$ | Dry irrad., 1 × 10$^6$ r.; post-irrad. treat. 2 hr. at 23°C. | 57 | MA | Section rounded with dense peripheral band | CED dissolved center of fiber, indicating no reaction beyond peripheral region |

TABLE I (continued)

| Sample[a] | Monom. soln.[b] | Grafting treatment | Graft. poly. add-on, % | Embed. medium[c] | Microscopical appearance | Behavior in solvents[d] |
|---|---|---|---|---|---|---|
| SC | Ac, 15% in 80% aq. $ZnCl_2$ | Dry irrad., $1 \times 10^6$ r.; post-irrad. treat. 10.6 hr. at 23°C. | 50 | MA | Section not rounded; peripheral band prominent | In CED fiber center dissolved; peripheral band became spongy in texture |
| SC | Ac, 32% in DMF | Dry irrad., $6 \times 10^6$ r.; post-irrad. treat. 22 hr. at 80°C. | 22 | MA | Section uniform | In CED some cellulose dissolved but section remained intact with rougher texture |
| SC | Ac, 4% in $0.005M$ ceric ammonium nitrate + $0.05M$ $HNO_3$ | 10 min. at 23°C. | 10 | MA | Section uniform | In CED cellulose dissolved; section became much thinner but retained its shape |
| SC | Ac, 4% in $0.005M$ ceric ammonium nitrate + $0.05M$ $HNO_3$ | 1 hr. at 23°C. | 31 | MA | Section somewhat swollen | In CED some cellulose dissolved, but section retained its shape and much of its thickness; texture of residue became spongy |
| SC | St., 70% in methanol | Simult. irrad. $1.5 \times 10^6$ r. | 59 | MA | Sections much swollen and rounded; layering pronounced owing to swelling in methacrylate | In CED some cellulose dissolved, but little change in appearance of section; after repeated treatments in CED and DMF section became thinner with gel-like texture |

| SC | St, 70% in methanol | Simult. irrad. 1.5 × 10⁶ r. | 59 | PVA | Fiber section rounded; slight opening of structure in incipient layers | Some cellulose dissolved; section remained intact with very open texture |
|---|---|---|---|---|---|---|
| SC | — | — | — | PVA | Fiber sections normal | Fiber section dissolved |
| SC | MMA, 15% in 80% aq. ZnCl₂ | Dry irrad., 1 × 10⁶ r.; post-irrad. treat. 6.5 hr. at 23°C. | 59 | MA | Fiber section solid at center but much expanded in peripheral regions by swelling in methacrylate | In CED center portion dissolved completely, leaving very thin residue of peripheral band |
| SC | MMA, 15% in 80% aq. ZnCl₂ | Dry irrad., 1 × 10⁶ r.; post-irrad. treat. 6.5 hr. at 23°C. | 59 | PVA | Fiber section round with small solid center and large peripheral band of less density | In CED center portion dissolved completely, and outer band became spongy |
| SC | PVAc, 15% in 70% aq. ZnCl₂ | Dry irrad., 1 × 10⁶ r.; post-irrad. treat. 4 hr. at 23°C. | 50 | MA | Section very round with pronounced layering | In CED some cellulose dissolved, section became thinner, with blurred appearance; after repeated CED and DMF treatment section became very thin, but layered fibrous texture remained |
| SC | PVAc, 15% in 70% aq. ZnCl₂ | Dry irrad., 1 × 10⁶ r.; post-irrad. treat. 4 hr. at 23°C. | 50 | PVA | Section very round; slight layering in opening of structure | In CED some cellulose dissolved, leaving uniformly distributed solid polymer |

[a] SC, scoured cotton; CC, cyanoethylated cotton.

[b] Ac, acrylonitrile; St, styrene; MMA, methyl methacrylate; PVAc, poly(vinyl acetate).

[c] MA, methacrylate; PVA, poly(vinyl alcohol).

[d] CED, cupriethylenediamine hydroxide solution; DMF, dimethylformamide.

(2) Simultaneous irradiation of acrylonitrile and cotton in a DMF solution at low dosage, $1.0 \times 10^6$ r., resulted in a uniform distribution of the grafted vinyl polymer throughout the cotton fiber cross-section. The cross-section of the copolymer (Fig. 3a) still closely resembles a native fiber but has a somewhat denser appearance. After immersion in CED
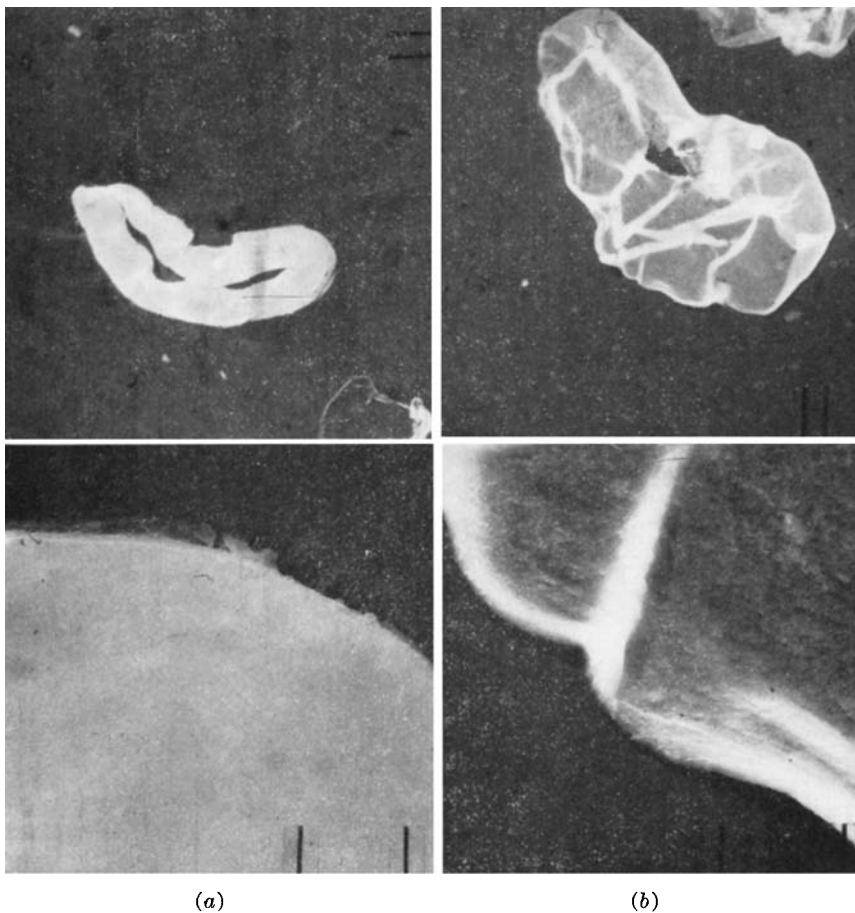


(a)                                    (b)

Fig. 3. Polyacrylonitrile–cotton copolymer. Simultaneous irradiation grafting, 30% acrylonitrile in DMF, $1.0 \times 10^6$ r., 37% grafted polymer. (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion.

the cross-section was somewhat swollen but still retained the normal fiber structure (Fig. 3b). Loss of cellulose was indicated by the thinner appearance of the swollen cross-section and, at high magnification, a rougher texture.

(3) Simultaneous irradiation grafting of cyanoethylated cotton was studied over a range of degrees of substitution. Figure 4a shows a cross-
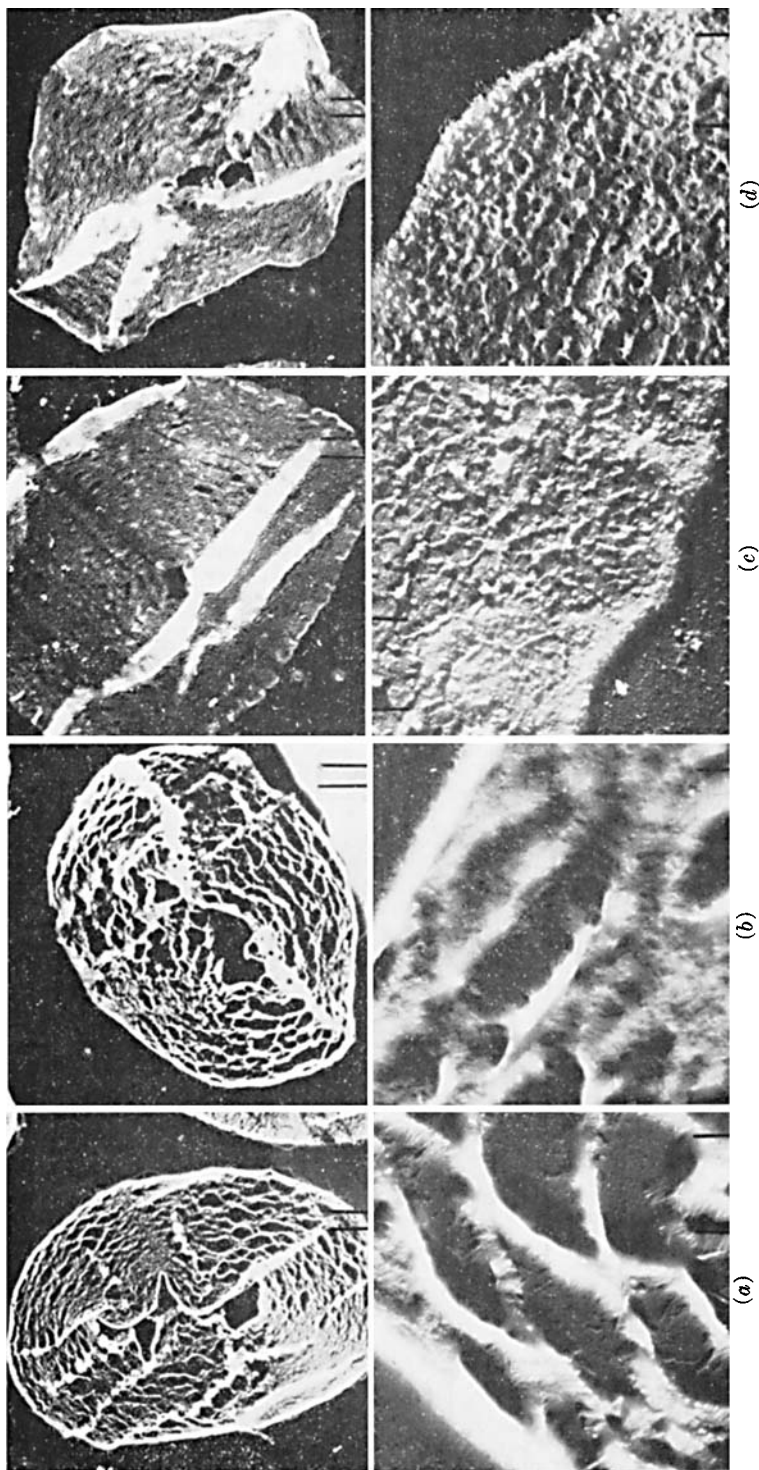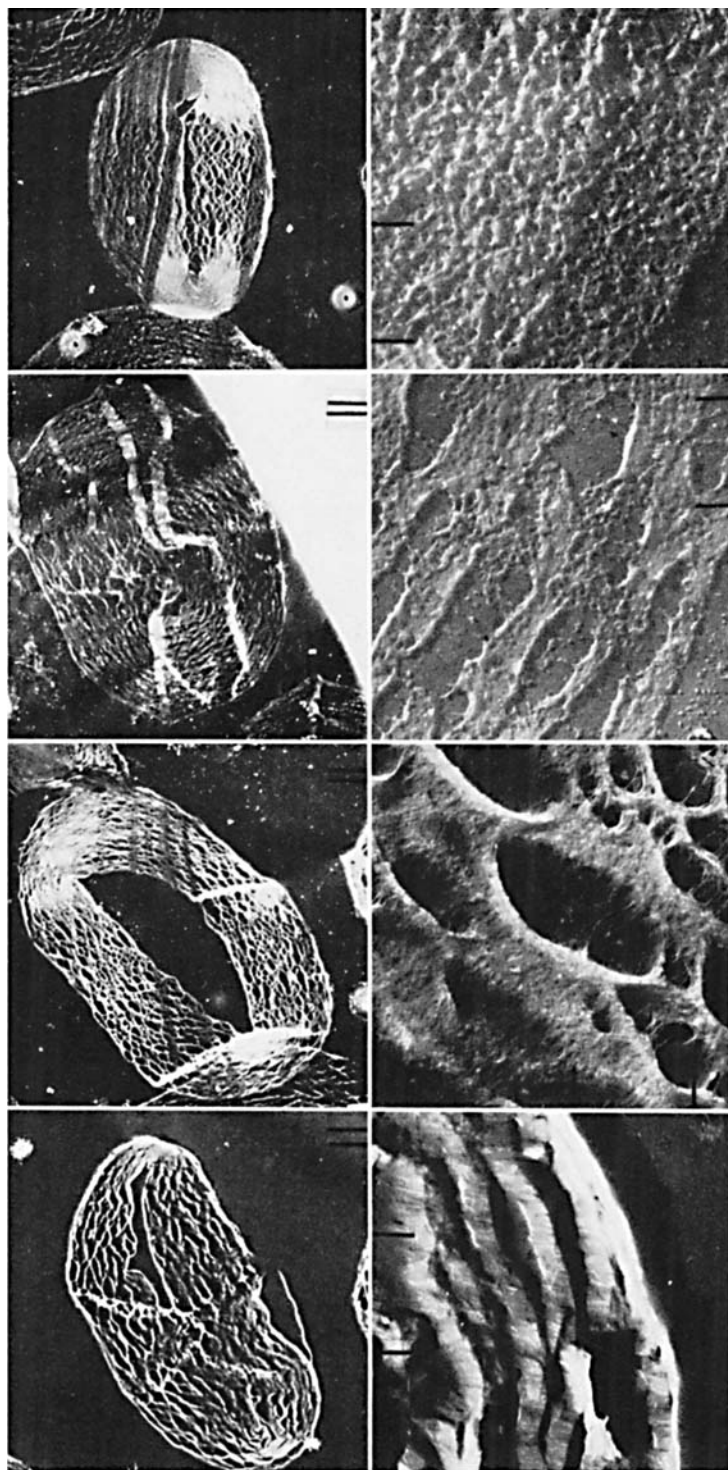
Fig. 4. Cyanoethylated cotton, D.S. 1.01, control sample for Fig. 5. (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion. (c) Section of (a) after CED, DMF, CED, and DMF immersion. (d) Section of (a) after DMF, CED, DMF and CED immersion.
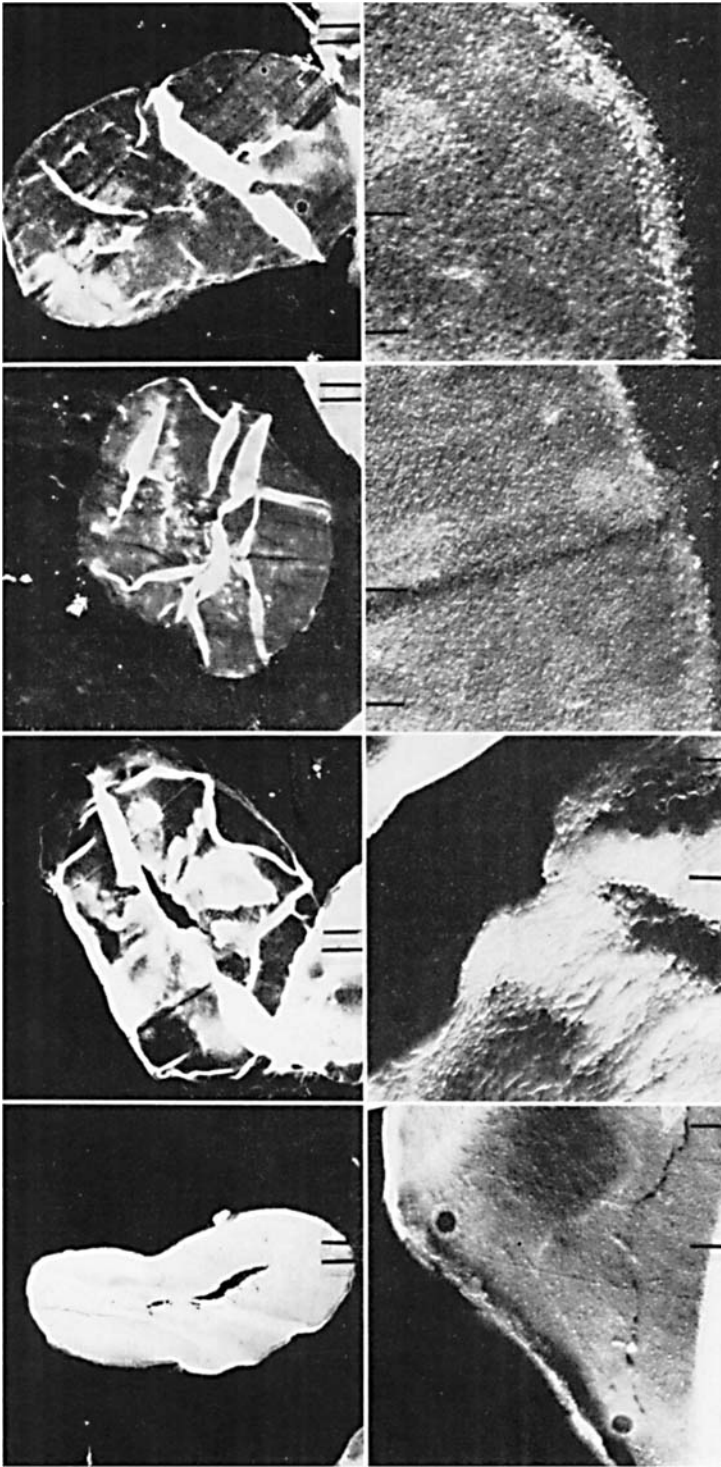
(a)          (b)          (c)          (d)
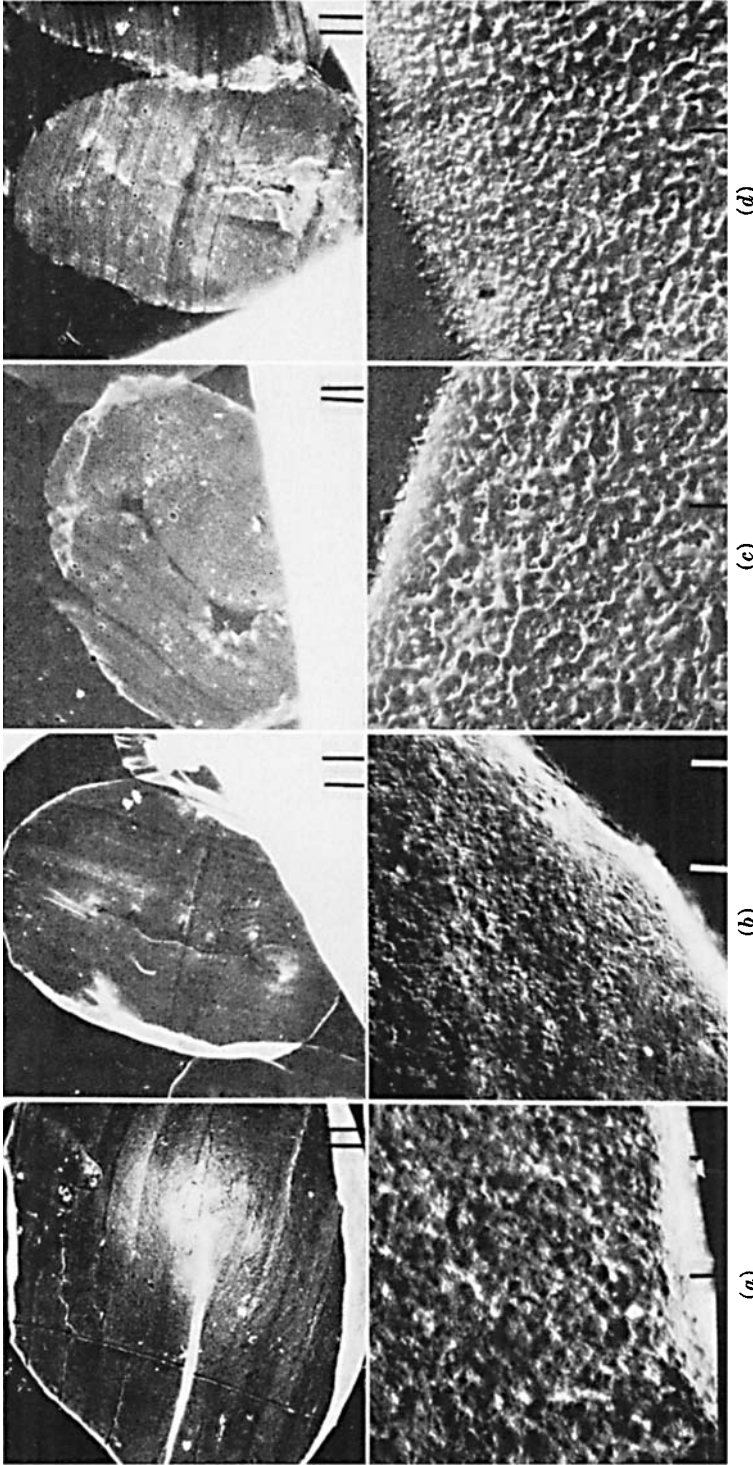
Fig. 5. Polyacrylonitrile–cyanoethylated cotton copolymer, D.S. 1.01. Simultaneous irradiation grafting, 32% acrylonitrile in 80% aq. ZnCl$_2$, 1.0 × 10$^6$ r., 42% grafted polymer. (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion. (c) Section of (a) after CED, DMF, CED, and DMF immersion. (d) Section of (a) after DMF, CED, DMF, CED, and CED immersion.

Fig. 6. Cyanoethylated cotton, D.S. 0.34, control sample for Fig. 7. (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion. (c) Section of (a) after CED, DMF, CED, and DMF immersion. (d) Section of (a) after DMF, CED, DMF, and CED immersion.

Fig. 7. Polyacrylonitrile–cyanoethylated cotton copolymer, D.S. 0.34.   Simultaneous irradiation grafting, 32% acrylonitrile in 80% aq. ZnCl₂, 1.0 × 10⁶ r., 43% grafted polymer.   (a) Shadowed section after removal of polymethacrylate embedding medium.   (b) Section of (a) after CED immersion.   (c) Section of (a) after CED, DMF, CED, and DMF immersion.   (d) Section of (a) after DMF, CED, DMF and CED immersion.

section of cotton cyanoethylated to a D.S. of 1.01. Swelling of this cellulose derivative in the methacrylate embedding medium used in the microscopical sectioning technique resulted in pronounced layering of the fiber wall (Fig. 4a). The cross-section appeared slightly altered by the CED; loss of fibrillar structure was observed (Fig. 4b). Repeated treatment with CED and DMF, solvents for cellulose and polyacrylonitrile,



(a)                                    (b)
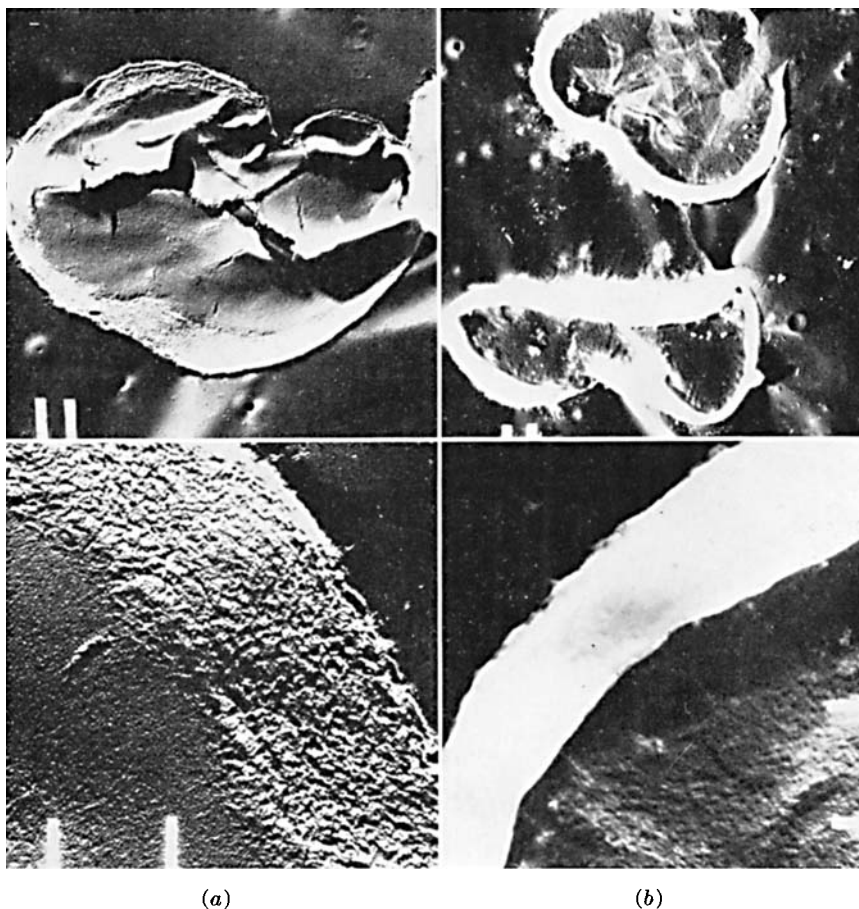
Fig. 8. Polyacrylonitrile–cotton copolymer. Post-irradiation grafting 32% acrylonitrile in 80% aq. ZnCl₂, 1.0 × 10⁶ r., 48 hr. at about 23°C., 78% grafted polymer. (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion.

respectively, caused a fusion of the cross-sections (Figs. 4c and 4d). In the final high-magnification micrograph (Figs. 4c and 4d) the cross-sections resemble a typical gel pattern.

With these pictures, which are representative of the behavior of a substituted cotton of relatively high degree of substitution, one may now evaluate the effect of graft polymerization on a cyanoethylated cotton of

the same degree of substitution. After simultaneous irradiation grafting of acrylonitrile to cyanoethylated cotton from a 32% monomer solution in 80% aq. $ZnCl_2$ (padded) the cross-section of the copolymer was very rounded, and the vinyl polymer appeared to be uniformly distributed throughout the cross-section (Fig. 5a). The grafted material did not layer in the embedding medium used in the sectioning technique. Immersion
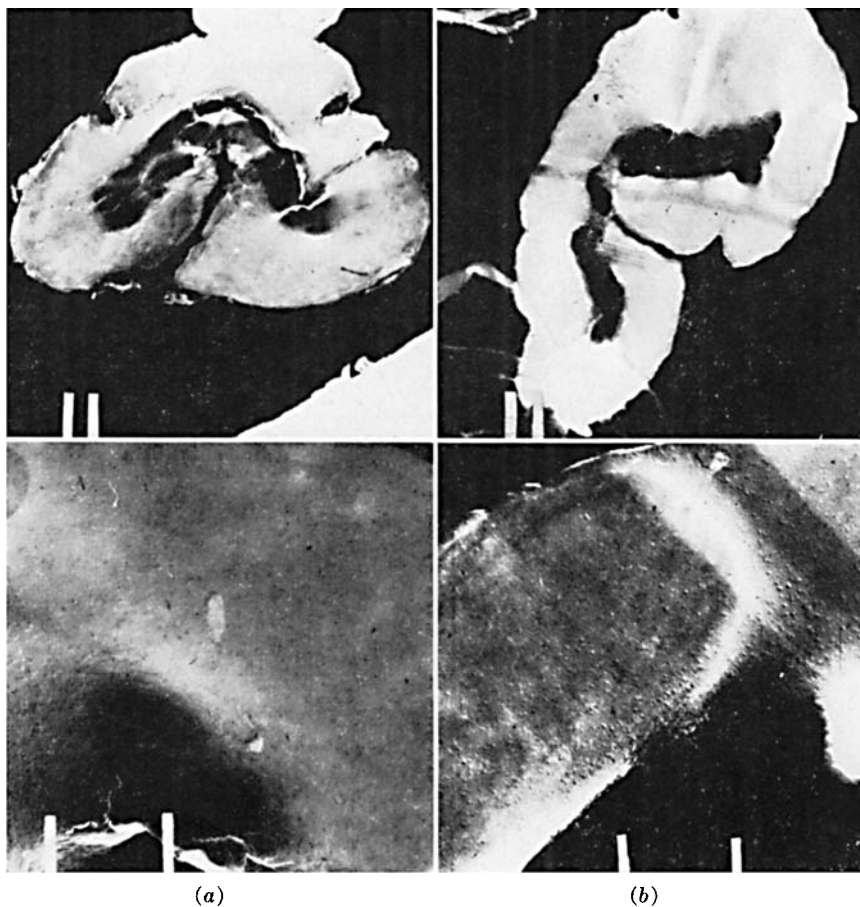


(a)                                    (b)

Fig. 9. Polyacrylonitrile–cotton copolymer. Post-irradiation grafting, 32% acrylonitrile in 80% aq. $ZnCl_2$, $6.1 \times 10^6$ r., 35 hr. at about 23°C., 89% grafted polymer. (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion.

of the fiber section in CED appeared to have little effect (Fig. 5b). Repeated treatments of the grafted cross-section with CED and DMF, however, resulted in a thinner but still intact section with a gel-like texture (Figs. 5c and 5d). The amount of grafting cannot be ascertained, since the original cyanoethylated sample had quite a bit of the gel-like structure remaining.

In contrast to Figures 4 and 5 the effect of radiation grafting to a cyano-
ethylated cotton of lower D.S. is illustrated in Figures 6 and 7.    Figure 6a
represents a cross-section of the control sample of cyanoethylated cotton
with a D.S. of 0.34.    Layering of the cross-section due to swelling in the
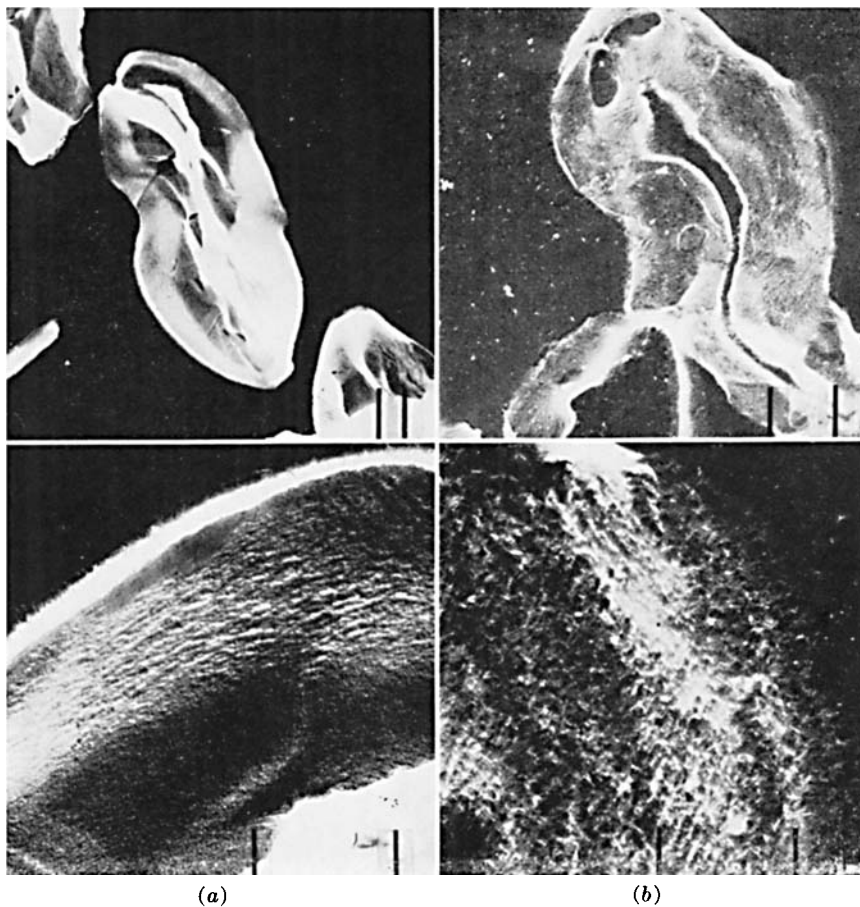embedding methacrylate was again pronounced.    The effect of successive



(a)                                                                     (b)

Fig. 10. Polyacrylonitrile–cotton copolymer.   Post-irradiation grafting, 15% acryloni-
trile in 70% aq. $ZnCl_2$, $1.0 \times 10^6$ r., 0.9 hr. at about 23°C., 44% grafted polymer.   (a)
Shadowed section after removal of polymethacrylate embedding medium.   (b) Section
of (a) after CED immersion.

immersions in CED and DMF (Figs. 6b, 6c, and 6d) was similar to the
effects observed with the highly substituted cotton of D.S. 1.01 in Figure 4.
    When cyanoethylated cotton of D.S. 0.34 was grafted with acrylonitrile
by the simultaneous-irradiation technique, the cross-section of the copolymer
(Fig. 7a) did not layer during the methacrylate embedding for sectioning;
it has a more dense appearance than the native fiber.    After treatment
with CED the appearance of the swollen section indicated that the vinyl

polymer was distributed non-uniformly in the fiber and appeared to be concentrated in a random fashion within the cell wall of the fiber (Fig. 7b). After successive immersions in CED and DMF the sections became thin (Figs. 7c and 7d).    A considerably less spongy texture was observed in the high-magnification micrographs of this grafted sample of low D.S. (Figs.
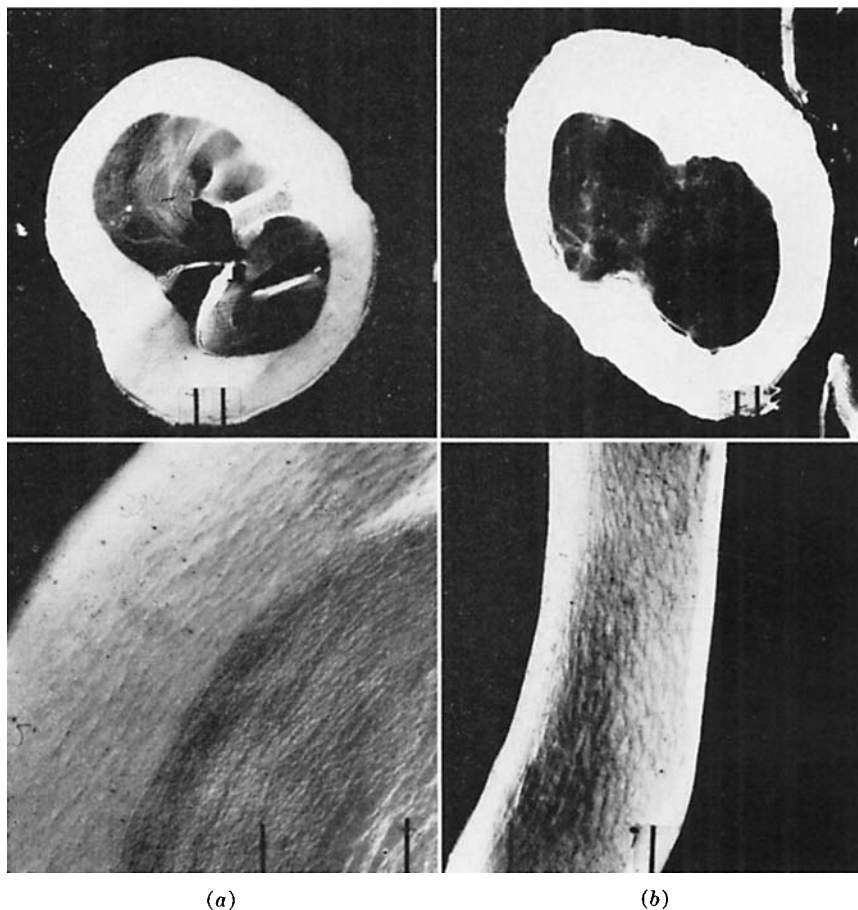


(a)                                                      (b)

Fig. 11. Polyacrylonitrile–cotton copolymer. Post-irradiation grafting, 15% acrylonitrile in 75% aq. $ZnCl_2$, $1.0 \times 10^6$ r., 2 hr. at about 23°C., 57% grafted polymer.  (a) Shadowed section after removal of polymethacrylate embedding medium.  (b) Section of (a) after CED immersion.

7c and 7d) than in those of the grafted sample of high D.S. (Figs. 5c and 5d).

(4) Post-irradiation grafting of acrylonitrile to cotton in concentrated aqueous $ZnCl_2$ solutions was investigated under a number of different solution conditions and radiation dosages.

Most of the earliest work[8] was done at low, intermediate, and high doses

(1.0, 2.3, and 6.1 $\times$ 10⁶ r.) and with 32% acrylonitrile in 80% aq. ZnCl₂ solution as grafting medium. Electron microscopical observations indicated that under these conditions the reaction started at the outer edge of the fiber section and extended into the fiber structure in a random exterior-to-interior direction. Figure 8a illustrates a fiber given a dosage of 1.0 $\times$ 10⁶ r. and treated in 32% acrylonitrile in 80% aq. ZnCl₂ for 48 hr.
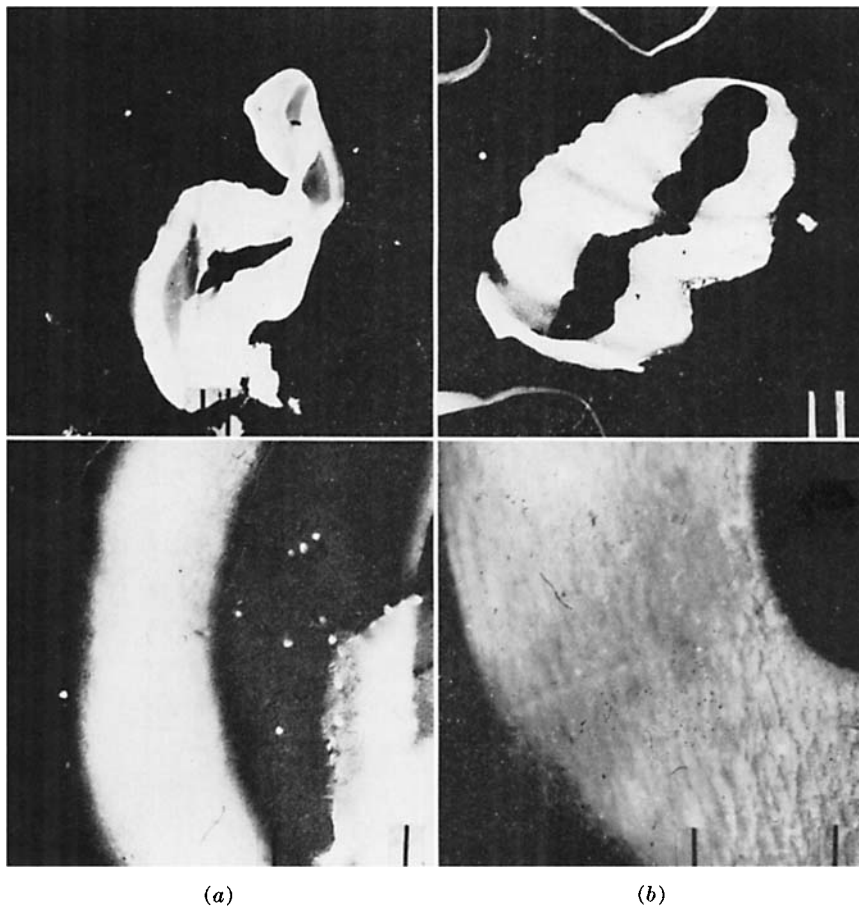


(a)                         (b)

Fig. 12. Polyacrylonitrile–cotton copolymer. Post-irradiation grafting, 15% acrylonitrile in 80% aq. ZnCl₂, 1.0 $\times$ 10⁶ r., 10.6 hr. at 23°C., 50% grafted polymer. (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion.

In this sample the grafted vinyl polymer is observed as a heavy band in the outer layers of the swollen fiber structure. After CED treatment either the centers of the cross-sections were completely dissolved or a very slight amount of the center material remained, as in Figure 8b. These results indicated that the center of the cross-section was predominantly unreacted cellulose.

At very high radiation doses, $6.1 \times 10^6$ r., and with the 32% monomer solution in 80% aq. $ZnCl_2$ it was found that in many of the fibers, but not all, the reaction had penetrated into the lumen area, as illustrated in Figure 9a. Although reacting throughout, the fiber still retained the kidney shape of the native fiber. Treatment with CED appeared to have very little effect on the grafted cross-section (Fig. 9b).
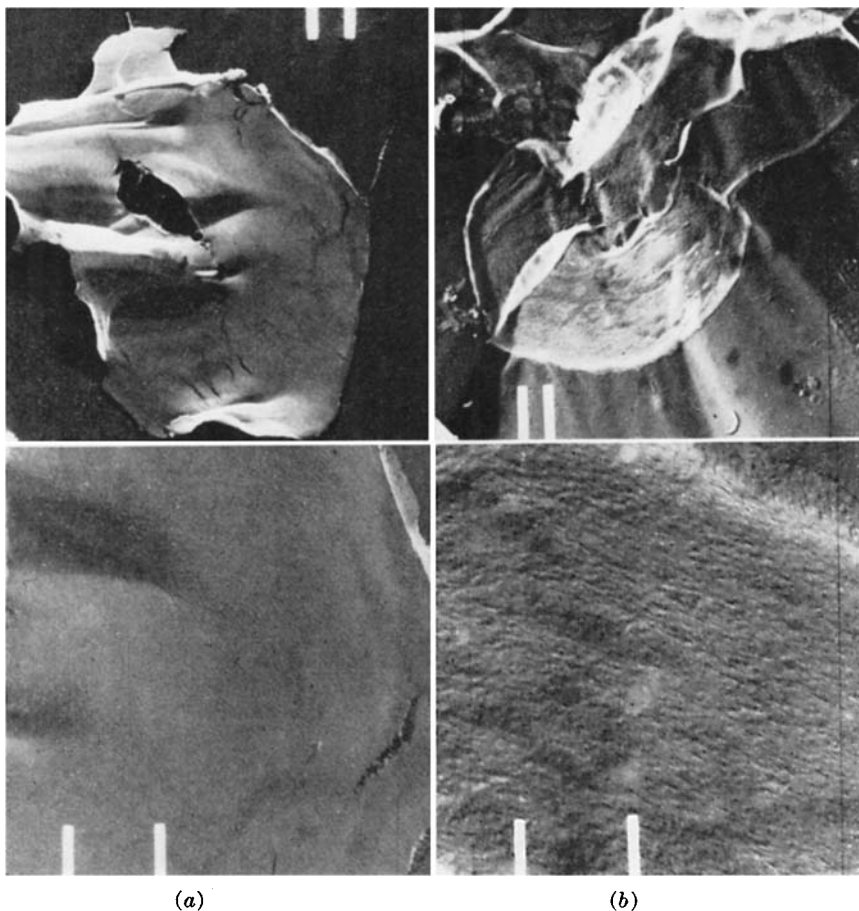


(a)                              (b)

Fig. 13. Polyacrylonitrile–cotton copolymer. Post-irradiation grafting, 32% acrylonitrile in DMF, $6.1 \times 10^6$ r., 22.0 hr. at 80°C., 22% grafted polymer. (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion.

Later work[12] on the post-irradiation grafting of acrylonitrile to cotton was carried out with a low dosage, $1.0 \times 10^6$ r., and 15% acrylonitrile in 70, 75, and 80% aq. $ZnCl_2$ solutions as grafting media. Electron microscopical examinations of cross-sections of these fibers indicated that, as was observed in the earlier work, the grafting reaction started in the outer layers of the cellulose fiber and penetrated inward (Figs. 10, 11, and 12). Some distinct

differences were observed, however, among the copolymers produced under the three grafting conditions.

Grafting in a medium composed of 15% acrylonitrile in 70% aq. $ZnCl_2$ resulted in a slightly swollen cross-section with a relatively dense band of grafted polyacrylonitrile in the outer layers of the fiber structure (Fig. 10a).
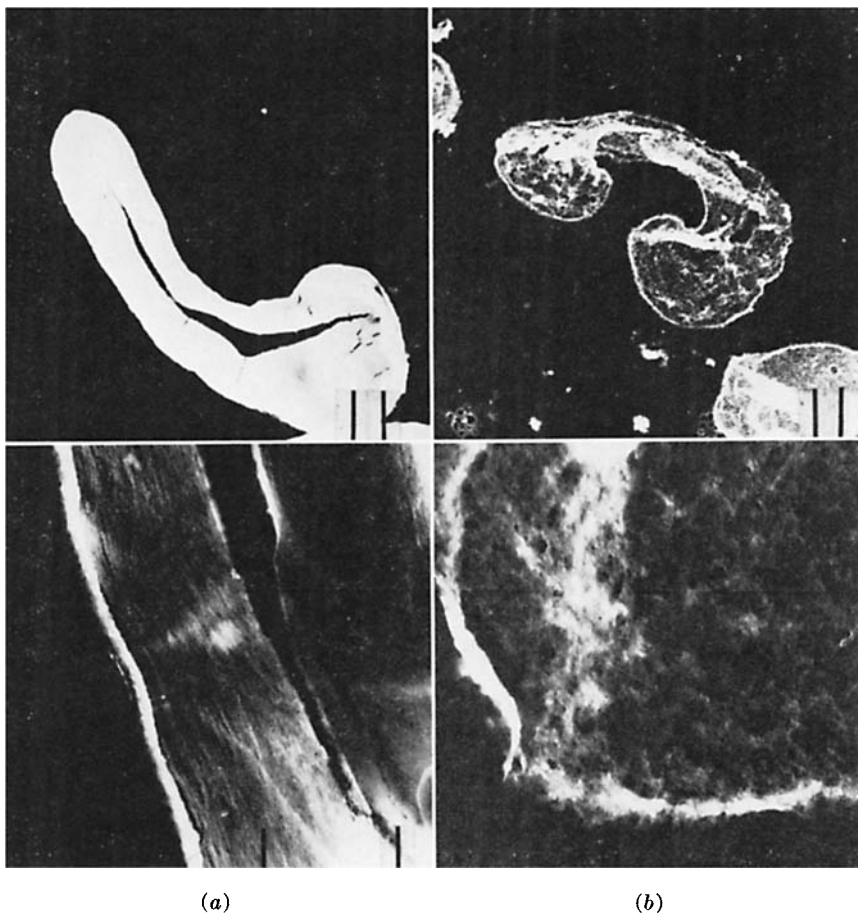


(a)                                                      (b)

Fig. 14. Polyacrylonitrile–cotton copolymer.   Ceric ion grafting, 4% acrylonitrile in 0.005$M$ ceric ammonium nitrate and 0.05$M$ HNO$_3$, 10 min. at about 23°C., 10% grafted polymer.   (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion.

Treatment of the cross-section with CED, however, showed that in most cases the grafting reaction had occurred not only in the dense area but in the inner layers all the way to the lumen of the fibers (Fig. 10b).   A considerable amount of ungrafted cellulose was removed by the CED, and the grafted polyacrylonitrile remaining had a porous structure, as illustrated in the high-magnification micrograph (Fig. 10b).

Cross-sections of fibers, treated in a grafting medium of 15% acrylonitrile in 75% aq. $ZnCl_2$, were more rounded than native fibers and showed a dense polymer band in the peripheral layers of the fiber (Fig. 11a).   At least 50% of the section is made up of the dense grafted material. After CED immersion the center portion of the fiber dissolved (Fig. 11b), leaving the dense band of grafted polyacrylonitrile, illustrated in the high-magnification
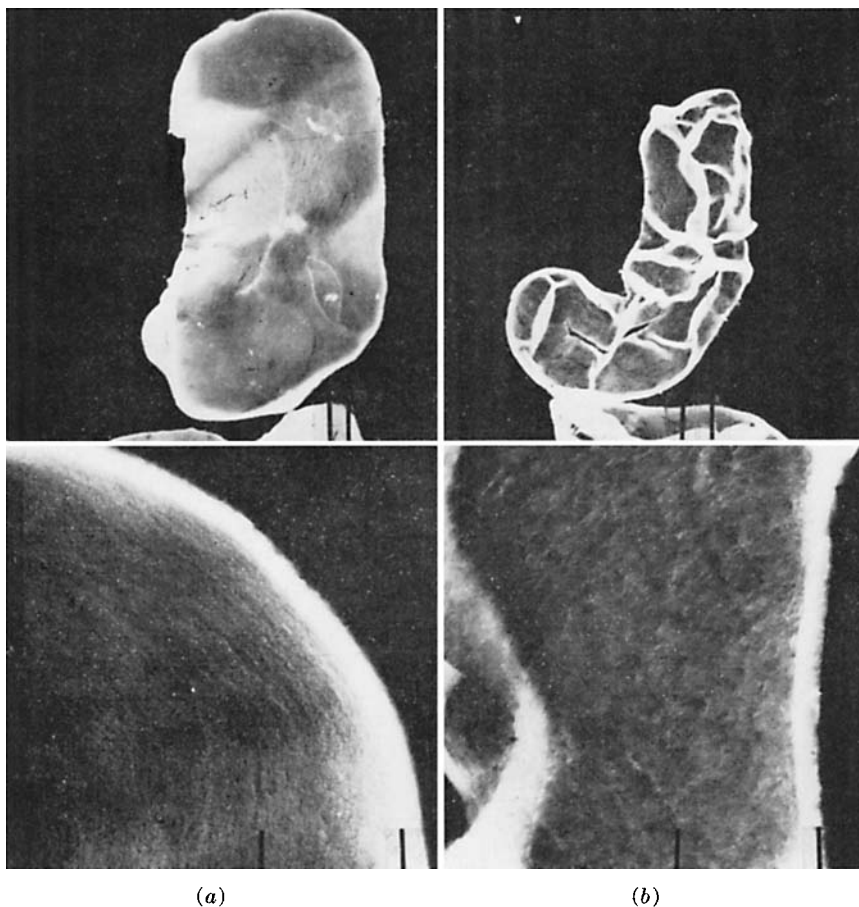


(a)                                    (b)

Fig. 15. Polyacrylonitrile–cotton copolymer.   Ceric ion grafting, 4% acrylonitrile in 0.005$M$ ceric ammonium nitrate and 0.05$M$ $HNO_3$, 1 hr., at about 23°C., 31% grafted polymer.   (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion.

micrograph (Fig. 11b), in contrast to the porous structure of the sample in Figure 10b.

In Figure 12a the cross-section of a fiber that reacted in a medium composed of 15% acrylonitrile in 80% aq. $ZnCl_2$ showed the same heavy banding in the outer fiber layers without much rounding of the fiber structure. In fibers grafted under these conditions there appeared some swelling in the

fiber region containing grafted polyacrylonitrile after treatment with CED (Fig. 12b). The high-magnification micrograph (Fig. 12b) showed that after CED extraction the band grafted polyacrylonitrile was still very dense in appearance, even though it was expanded.

(5) Post-irradiation grafting of acrylonitrile to cotton in DMF solution at high dosage, $6.1 \times 10^6$ r., resulted in a uniform distribution of the vinyl polymer throughout the fiber cross-section (Fig. 13a). After immersion in CED the cross-section showed a loss of cellulose (Fig. 13b) similar to that observed in simultaneous irradiation grafting in DMF. Both samples showed some swelling and dissolution in CED and the material remaining had a rough texture when viewed at high magnification: compare cross-sections from post-irradiation treatment with DMF (Fig. 13b) with those from simultaneous irradiation with DMF (Fig. 3b).

(6) Ceric ion grafting in 4% aqueous acrylonitrile solution also resulted in a uniform distribution of polyacrylonitrile throughout the fiber cross-section. Figures 14 and 15 illustrate the copolymer cross-sections obtained at two different levels of grafting. The cross-section containing the higher vinyl polymer add-ons, 31% (Figs. 15a and 15b) was somewhat more swollen, and less cellulose was lost after CED treatment than was observed in the sample containing 10% grafted polymer (Figs. 14a and 14b).
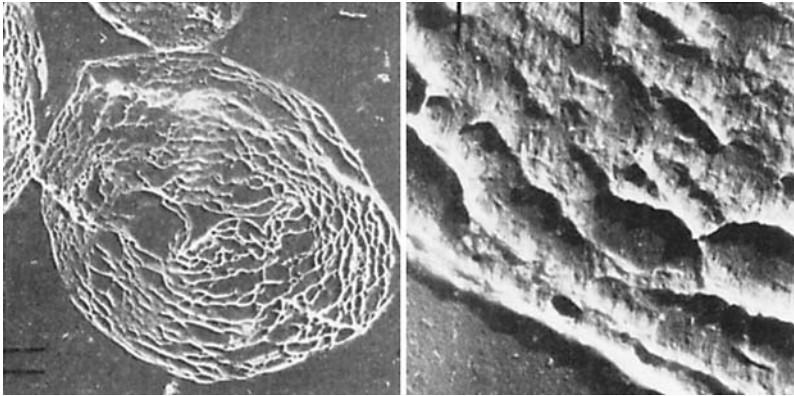
## II. Styrene

Copolymers of polystyrene and cotton prepared by simultaneous irradiation grafting in a styrene–methanol solution resulted in fibers whose cross-sections exhibited pronounced layering when sectioned in methacrylate embedding medium (Fig. 16a). The cross-sections were very swollen and rounded. After immersion in CED very little change in appearance was observed (Fig. 16b). Successive immersions in CED and DMF resulted in a much thinner cross-section with a gel-like texture but with retention of the layering effect (Figs. 16c and 16d).

The layering observed with the polystyrene–cotton copolymer was similar to that observed with some cellulose derivatives, i.e., cyanoethylated cotton (see Figs. 4 and 6), acetylated cotton,[21] and others. According to Tripp et al.,[22] this layering is due to the formation of osmotic cells within the fiber. It is assumed that substituted regions of the fiber permit increased diffusion of the methacrylate; then polymerization of the monomer[23] would set up osmotic forces across a barrier of unreacted cellulose. Separation of the cell wall into concentric layers is undoubtedly a reflection of the natural structure of the fiber. Since such a phenomenon does not occur in unreacted cotton under normal conditions of embedding (Fig. 1) the pattern of swelling in this sample is judged to be related to the location of reacted regions in the fiber.
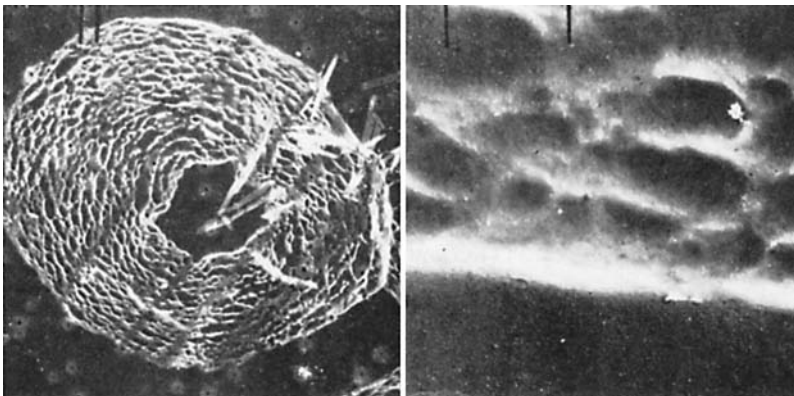
Polystyrene is affected by the methacrylate, and perhaps the same phenomenon that occurs with acetylated cotton serves to explain why the grafted polystyrene–cotton copolymer forms layers. This effect is related
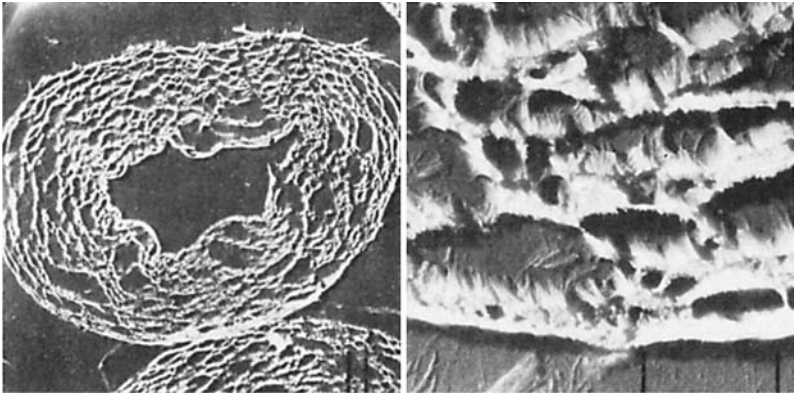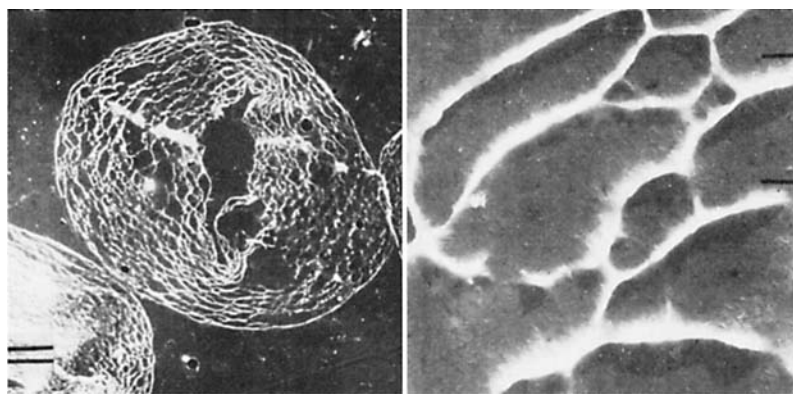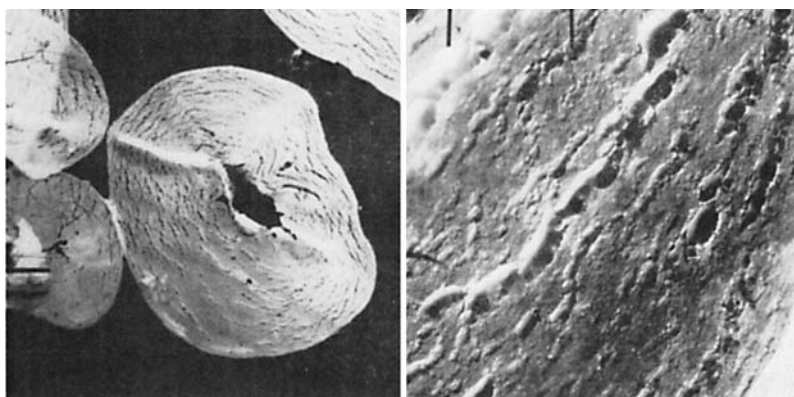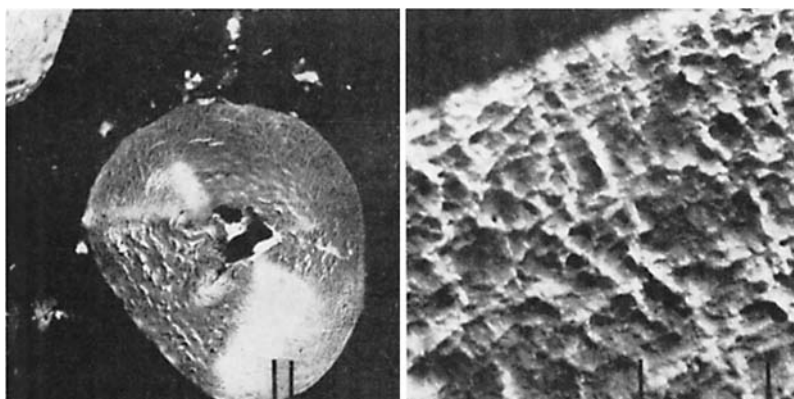
(a)



(b)



(c)

Fig. 16.   See caption, p. 97.

(d)



(e)



(f)

Fig. 16. Polystyrene–cotton copolymer. Simultaneous irradiation grafting, 70% styrene in methanol, $1.5 \times 10^6$ r., 59% grafted polymer.   (a) Shadowed section after removal of polymethacrylate embedding medium.   (b) Section of (a) after CED immersion (c) Section of (a) after CED, DMF, CED, and DMF immersion.   (d) Section of (a) after DMF, CED, DMF, and CED immersion.   (e) Shadowed section after removal of poly-(vinyl alcohol) embedding medium.   (f) Section of (e) after CED immersion.

to the manner of distribution of the grafted vinyl polymer in the fiber structure.

To determine what contribution both these factors had on the observed phenomena, a newly developed technique[21] of embedding in aqueous poly-(vinyl alcohol) was employed for sectioning the polystyrene–cotton copolymer, to obviate any effect of methacrylate embedding medium on the polystyrene. The cross-sections obtained with this technique are shown in
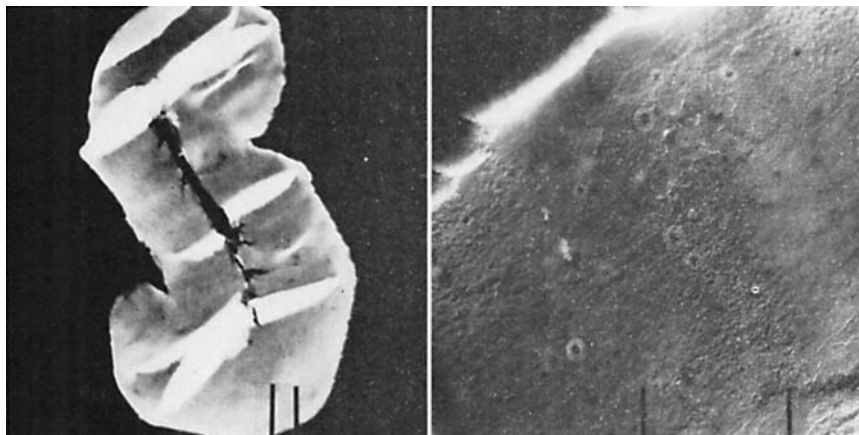


Fig. 17. Scoured cotton: shadowed section after removal of poly(vinyl alcohol) embedding medium.

Figures 16e and 16f. The copolymer fiber is very much rounded, and the vinyl polymer is distributed throughout the section. However, there is a very slight opening of the structure at the cellulose layers, due to the grafted polystyrene.

For comparison with graft polymers sectioned by the PVA embedding technique a section of unreacted cotton prepared by this method is shown in Figure 17. When immersed in CED this section left no residue.

### III. Methyl Methacrylate

Post-irradiation grafting of methyl methacrylate to cotton with a reaction medium containing 15% monomer in 80% aq. $ZnCl_2$ resulted in a copolymer whose cross-section showed a band of methyl methacrylate in the outer area of the fiber, which separated into layers owing to the effect of the methacrylate embedding medium (Fig. 18a). The outer band of grafted methyl methacrylate was very swollen, distended, and thin in appearance. The inner core was compact and had the typical structure of the native fiber, as illustrated in the high-magnification micrograph (Fig. 18a). Treatment with CED resulted in the complete removal of unreacted cellulose from the center portions of the cross-sections and a residual band of copolymer very thin in appearance (Fig. 18b). Since poly(methyl methacrylate) is affected
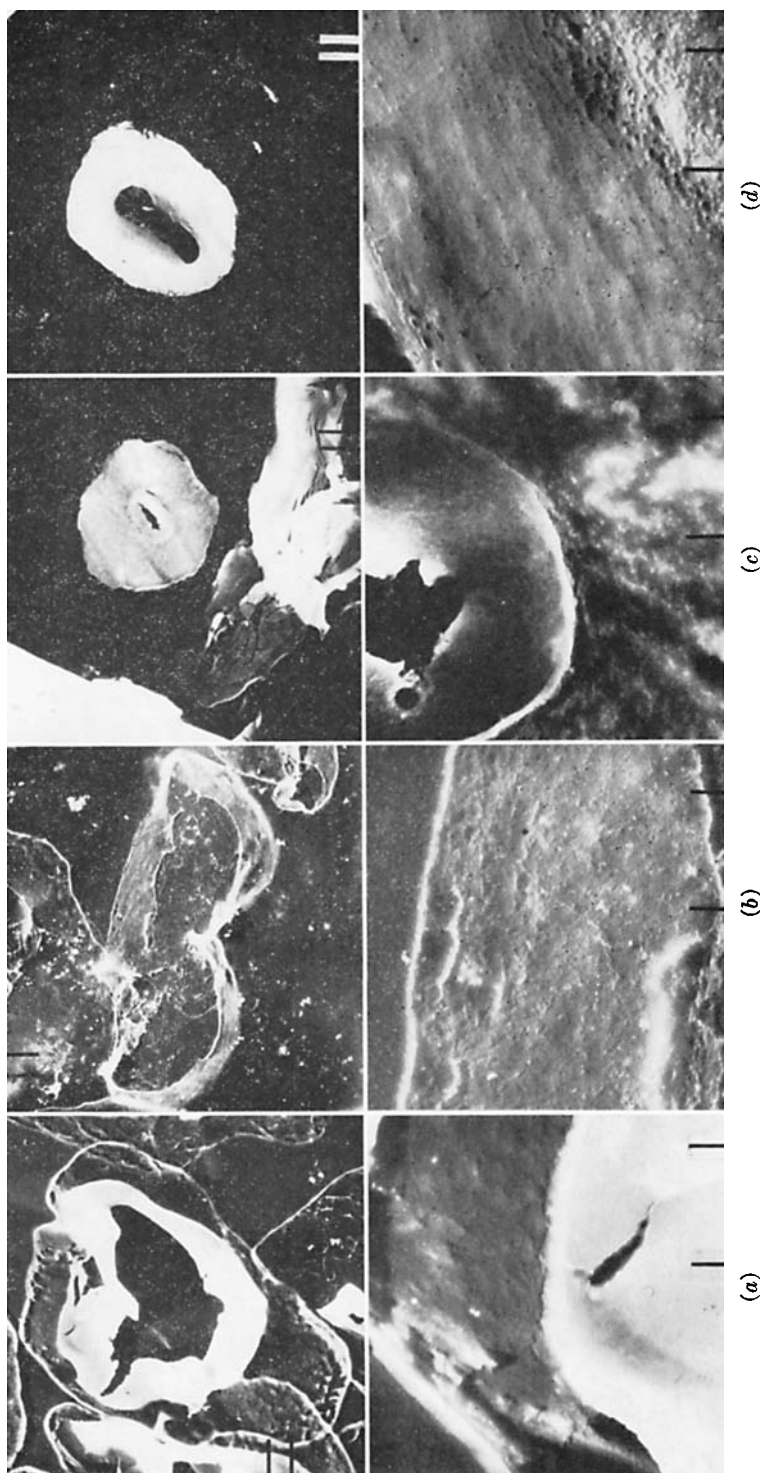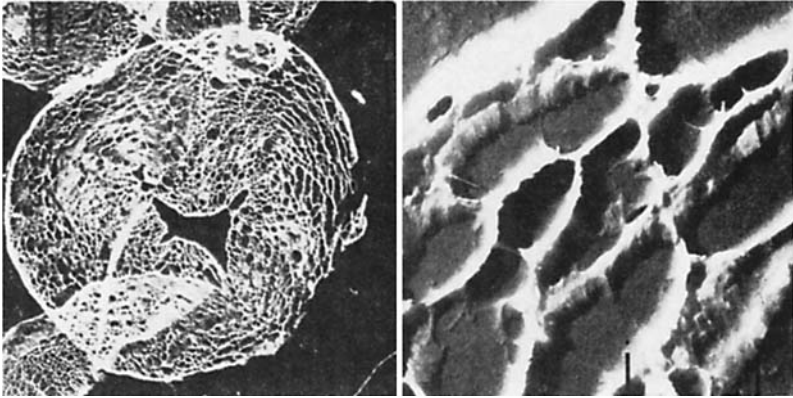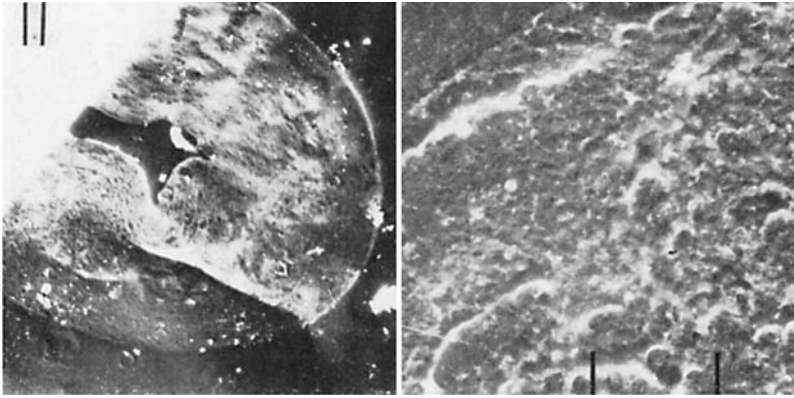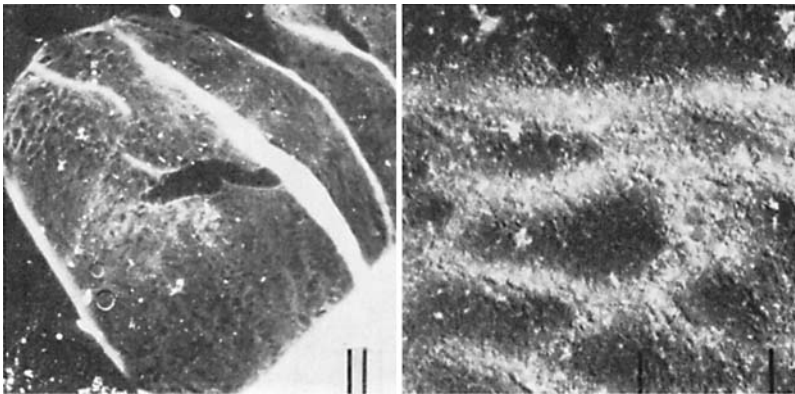
Fig. 18. Poly(methyl methacrylate)–cotton copolymer. Post-irradiation grafting. 15% methyl methacrylate in 80% aq. ZnCl₂, 1.0 × 10⁶ r., 6.5 hr. at about 23°C., 59% grafted polymer. (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion. (c) Shadowed section after removal of poly(vinyl alcohol) embedding medium. (d) Section of (c) after CED immersion.
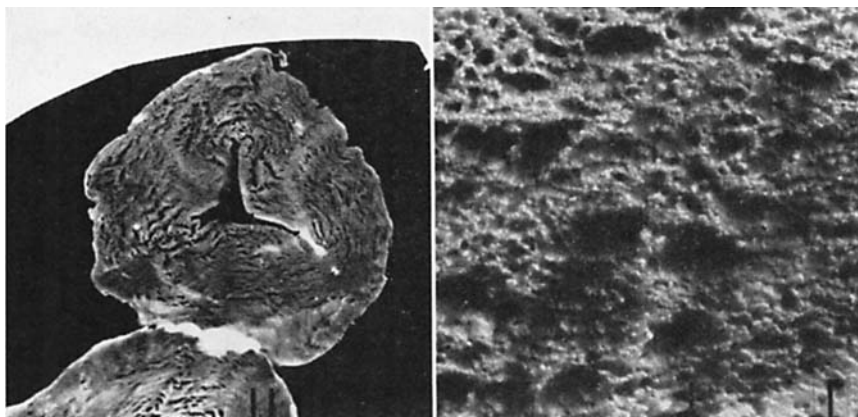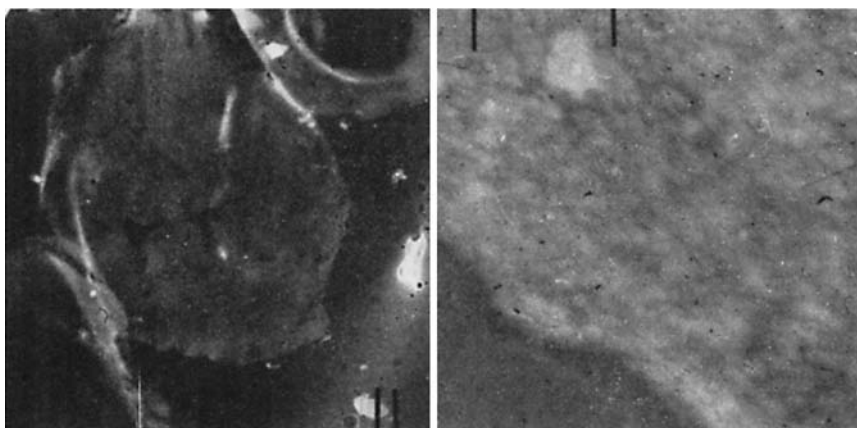
(a)

(b)

(c)

Fig. 19.   See caption p. 101.

(d)



(e)

Fig. 19. Poly(vinyl acetate)–cotton copolymer. Post-irradiation grafting, 15% vinyl acetate in 70% aq. ZnCl$_2$, 1.0 × 10$^6$ r., 4 hr. at about 23°C., 50% grafted polymer. (a) Shadowed section after removal of polymethacrylate embedding medium. (b) Section of (a) after CED immersion. (c) Section of (a) after CED and DMF immersion. (d) Shadowed section after removal of poly(vinyl alcohol) embedding medium. (e) Section of (d) after CED immersion.

by the methacrylate embedding medium, these grafted samples were also sectioned with the poly(vinyl alcohol) embedding technique; the results obtained are illustrated in Figures 18c and 18d. These cross-sections also indicated that the grafted polymer was located in the outer layers of the fiber structure, but with this embedding medium the band of copolymer was dense and compact (Fig. 18c). After CED treatment the unreacted cellulose was removed from the center portions of the cross-section, and a dense outer band of copolymer remained (Fig. 18d).

## IV. Vinyl Acetate

Post-irradiation grafting of vinyl acetate to cotton cellulose with a 15% monomer solution in 70% aq. $ZnCl_2$ as reaction medium resulted in a uniform distribution of the vinyl acetate throughout the fiber cross-section (Fig. 19a). This cross-section, cut after methacrylate embedding, was very rounded and had an open netlike structure somewhat resembling the layering effect. Immersion in CED (Fig. 19b) resulted in a blurring of the texture of the cross-section. Further treatment of the extracted section with DMF resulted in additional loss of material, but the fibrous structure remained (Fig. 19c). Examination of this graft copolymer by the poly-(vinyl alcohol) embedding technique gave the results shown in Figures 19d and 19e. This cross-section shows a uniform distribution of the vinyl polymer, but it is not as swollen or as open in appearance as the sections obtained with the methacrylate embedding medium. CED treatment again resulted in blurring of the cross-sectional structure, with some dissolution, indicating that some unreacted cellulose was present.

## SUMMARY AND CONCLUSIONS

It has been shown that the microscopical structure of the cotton fiber is altered by grafting units of polyacrylonitrile, polystyrene, poly(methyl methacrylate), and poly(vinyl acetate) onto cotton cellulose.

Microscopical studies indicate that the diffusion rate of the monomer into the cell wall plays an important role in the final distribution of polyacrylonitrile grafts within the cellulose of cotton. Simultaneous irradiation grafting of 32% acrylonitrile in 80% aq. $ZnCl_2$ at a low dosage of $1.0 \times 10^6$ r. resulted in a concentration of the graft midway between a less-reacted area in the outer and inner layers of the fiber. Post-irradiation treatments of cotton (dosage varied: 1.0, 2.3, and $6.1 \times 10^6$ r.) in 32% acrylonitrile in 80% aq. $ZnCl_2$ solution and of samples with a low dosage ($1.0 \times 10^6$ r. in a grafting medium of 15% acrylonitrile in 70, 75, and 80% aq. $ZnCl_2$ solution) demonstrated dense areas of grafting, starting at the fiber periphery and penetrating into the inner regions. The depth and homogeneity of penetration into the inner areas is dependent upon the conditions under which the monomer is applied. Distinct differences were observed in the fine structure of material grafted from a low per cent acrylonitrile (15%) and lower concentrations of aq. $ZnCl_2$ (70–75%) solutions.

Uniform distribution of polyacrylonitrile in the cotton fiber was achieved with dimethylformamide as solvent in the simultaneous irradiation technique with low dosage, $1.0 \times 10^6$ r., and also in post-irradiation grafting but with high dosage, $6.1 \times 10^6$ r. Dense areas of grafted polyacrylonitrile did not appear when DMF was used as solvent in the grafting medium; the distribution was uniform.

Uniformity was also achieved when the acrylonitrile graft was made on

highly substituted cyanoethylated cotton. The distribution of graft polymer was non-uniform in the cyanoethylated sample of low D.S.

In chemically initiated grafting of acrylonitrile, as by ceric ion initiation, the polymer was evenly distributed throughout the cell wall of fibers in samples of both high and low add-on of polymer. The sections were of uniform density, in contrast to the results obtained in the grafting of acrylonitrile to cotton by irradiation techniques in which aq. $ZnCl_2$ solutions are used in the grafting medium.

Sections of polystyrene–cotton fibers grafted by simultaneous irradiation of cotton in solutions of the styrene monomer in methanol had a somewhat open structure, believed to be the result of the grafting process. The distribution of graft was uniform throughout the fiber.

Grafting of methyl methacrylate by the post-irradiation technique resulted in distribution of grafted polymer in only the very outer layers of the fibers, although the polymer weight gain was approximately 50%.

In contrast to the peripheral deposition of grafted methyl methacrylate units the grafting of poly(vinyl acetate) units to the cellulose was uniform throughout the fiber wall. The grafting process or the swelling of the graft polymer in reagents used in sectioning techniques resulted in a complete opening up of the fine structure of the fiber.

Important factors governing the success of irradiation grafting are choice of solvent, ratio of monomer to cellulose, nature of prior chemical modification of the cellulose, and total irradiation dosage.

Although more precise methodology exists for the chemical analysis of reacted cellulose, electron microscopy offers the best approach for locating structural alterations within the fiber that may bear on the physical behavior of yarns and fabrics. It is to be expected that the location of graft polymers within the fiber, visually, by means of appropriate solvents on ultrathin sections, may assist further chemical exploration of the possibilities of grafting for useful cotton modification.

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## Résumé

Des observations microscopiques électroniques sur des copolymères greffés par radiation à base de rayonne et de styrène ont été publiées par Kaeppner et Huang en 1965. Le manuscrit présent rapporte des études microscopiques électroniques sur le rapport entre la structure des copolymères greffés vinyliques–coton et la morphologie de départ de la fibre de coton et sur la distribution du polymère vinylique greffé sur la structure fibreuse de coton. Les monomères vinyliques greffés étudiés dans cet travail était l'acrylonitrile, le styrène, le méthacrylate de méthyle et l'acétate de vinyle. Deux procédés de greffage induits par radiation ont été utilisés: le greffage par irradiation simultanée et le greffage après irradiation. Le greffage à l'ion cérique de l'acrylonitrile sur le coton a également été inclus dans cette étude à titre de comparaison. La distribution du polymère vinylique au sein de la fibre de coton est illustrée par une série de micrographies électroniques choisie comme exemple typique d'espèces greffées particulières considérées. Les résultats indiquent que la vitesse de diffusion du monomère dans la fibre de cellulose joue une rôle important dans la distribution finale des greffes de polyacrylonitrile dans la fibre. La distribution uniforme du polyacrylonitrile dans la fibre était achevée par greffage par irradiation simultanée de l'acrylonitrile sur du coton cyanoéthylé fortement substitué. Dans des échantillons de faibles degrés de cyanoéthylation, la distribution du polymère greffé n'était pas uniforme. Dans le greffage initié par ions cériques par contre, l'acrylonitrile était distribué de façon homogène. Le copolymère de coton–polystyrène obtenu par irradiation simultanée du coton en solution dans le méthanol avec du styrène monomère était uniforme à travers la fibre mais montrait des élargissements de structure associés avec la quantité de greffons formés. Le greffage du méthacrylate de méthyle se passait uniquement dans la région périphérique de la fibre; par contre, le greffage de l'acétate de vinyle était uniforme à travers toute la fibre. Des facteurs importants régissant le greffage par irradiation sur les fibres de coton sont le choix du solvant, le rapport monomère–cellulose, la nature de la modification chimique antérieure de la cellulose et la dose d'irradiation totale.

## Zusammenfassung

Elektronenmikroskopische Beobachtungen an durch Strahlung hergestellten Rayon–Styrol-Pfropfcopolymeren wurden von Kaeppner und Huang 1965 veröffentlicht. Die vorliegende Arbeit bringt elektronenmikroskopische Untersuchungen über die Beziehungen der Struktur von Vinyl–Baumwoll-Pfropfpolymeren zur ursprünglichen Morphologie der Baumwollfaser und über die Verteilung des aufgepfropften Vinylpolymeren in der Struktur der Baumwollfaser. Die hier untersuchten aufgepfropften Vinylmonomeren waren Acrylnitril, Styrol, Methylmethacrylat und Vinylacetat. Zwei strahlungsinduzierte Verfahren wurden verwendet: Die Pfropfung während der Bestrahlung und die Pfropfung nach der Bestrahlung. Zu Vergleichszwecken wurde mittels Cer-IV-Ionen Acrylnitril auf Baumwolle aufgepfropft. Die Verteilung des Vinylpolymeren innerhalb der Baumwollfaser wird durch eine Reihe von elektronenmikroskopischen Aufnahmen veranschaulicht, die als typisch für die jeweilig betrachtete aufgepfropfte Spezies ausgewählt wurde. Die Ergebnisse zeigen, dass die Diffusionsgeschwindigkeit des Monomeren in die Cellulosefaser eine wichtige Rolle in der endgültigen Verteilung von Acrylnitril-Zweigen in der endgültigen Faser spielt. Eine einheitliche Verteilung von Polyacrylnitril in der Faser wure durch Aufpropfung von Acrylnitril unter Bestrahlung auf eine hoch substituierte cyanäthylierte Baumwolle erreicht. Bei Proben, die nur in geringem Ausmass cyanäthyliert waren, war die Verteilung der Pfropfpolymeren uneinheitlich. Bei der durch Cer-IV-Ionen gestarteten Pfropfung war das Acrylnitril-Pfropfpolymere gleichmässig verteilt. Polystyrol–Baumwoll-Pfropfcopolymere, die durch gleichzeitige Bestrahlung der Baumwolle in methanolischen Lösungen des monomeren Styrols hergestellt worden waren, waren einheitlich durch die ganze Faser, zeigten aber eine Strukturöffnung, die von der Menge an aufgepfropften Zweigen herrührt. Ein Aufpropfen von Methylmethacrylat erfolgte nur in den peripheren Regionen der Faser. Im Gegensatz dazu war die Aufpropfung von Vinylacetat einheitlich durch die Faserwand hindurch. Wichtige Faktoren, die das erfolgreiche strahlungsbedingte Aufpropfen auf Baumwollfasern beeinflussen, sind die Wahl des Lösungsmittels, das Verhältnis von Monomerem zu Cellulose, die Art der vorangegangenen chemischen Modifizierung der Cellulose und die gesamte Strahlungsdosis.