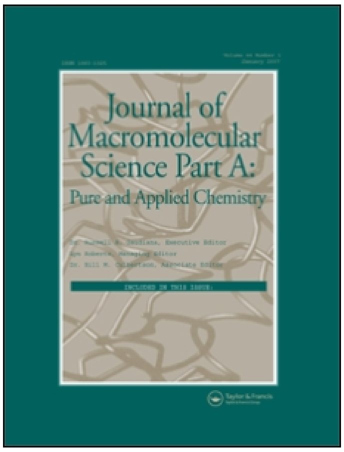

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Grafting Studies on Cotton Cellulose

Jett C. Arthur Jr.[a]
[a] Agricultural Research Service United States Department of Agriculture, Southern Regional Research Center Southern Region, New Orleans, Louisiana

To cite this Article Arthur Jr., Jett C.(1976) 'Grafting Studies on Cotton Cellulose', Journal of Macromolecular Science, Part A, 10: 4, 653 — 670
To link to this Article: DOI: 10.1080/00222337608061208
URL: http://dx.doi.org/10.1080/00222337608061208

J. MACROMOL. SCI.-CHEM., A10(4), pp. 653-670 (1976)

Grafting Studies on Cotton Cellulose

JETT C. ARTHUR, JR.

Southern Regional Research Center
Southern Region, Agricultural Research Service
United States Department of Agriculture
New Orleans, Louisiana 70179

ABSTRACT

Graft copolymerization reactions of vinyl monomers with fibrous cotton cellulose that were initiated at free-radical sites formed on the cellulose molecule are discussed. The effects of experimental conditions on the methods of initiating these free-radical reactions and on the location of these sites on the cellulose molecule are outlined. Some of the properties of the fibrous cellulose graft copolymers are discussed.

INTRODUCTION

Cotton was used by man residing in the valley of the Indus River as early as 3000 B.C., according to archeological findings. As early as 1500 B.C., Hindu laws and religions mention the cultivation of cotton. About 500 B.C., Greek writers reported that wild trees bearing "fleeces" grew in India. Marco Polo recorded that textiles were made from these "fleeces." When annual varieties of cotton were developed and cultivated, the uses of cotton by man increased. Probably as early as the tenth century, annual varieties were grown in the Middle East. The European explorers found cotton growing in the

Americas in the sixteenth century and noted evidence that cotton was used as textiles as early as the Inca period in Peru. In the late eighteenth century, inventions of the flying shuttle, spinning jenny, spinning frame, and cotton gin greatly facilitated the manufacture of cotton textiles. Cultivation of cotton increased, particularly in North America. Cotton became one of the most important raw materials of the industrial revolution. Today cotton comprises the major fraction of the world's textile fibers which include apparel, household, and industrial products. Cotton is cultivated in about 50 countries and on every continent [1].

About 50 years ago, regenerated cellulosic fibers began to compete with cotton for the textile market. More recently, synthetic or chemical fibers (usually made by polymerizing monomers and then forming the polymers into filaments) began to compete with both cotton and regenerated cellulosic fibers. During the 1960s in the United States the total quantity of cotton used in textiles was relatively constant, but the total quantity of synthetic fibers used increased fivefold. Thus cotton's share of the textile market in the United States declined. To meet this competition, cotton has been modified and given new textile properties while still retaining its desirable natural properties [1].

In this report, macromolecular modification of cotton cellulose by graft polymerization with vinyl monomers, and the resultant modification of the textile properties of cotton, are discussed. Some of the concomitant effects of graft copolymerization on the morphology of cotton and the relationships of these changes in morphology to the textile properties of cotton are considered.

COTTON

Since 1950 [2-12], macromolecular engineering of the properties of cellulose in the form of cotton has been the subject of many reports. The methods of these modifications have included free-radical initiated and nonradical processes [4]. Some of the important factors in macromolecular modification of cotton cellulose are reviewed here.

Cotton fiber is a seed hair and originates in the seed coat, growing as a single cell out of the epidermis of the seed coat. A thin tubular structure, the living cell, develops. Glucose is formed by photosynthesis in the leaves of the plant and then transported to within this tubule. Here the glucose is polymerized to form cellulose on the inner wall of the tube. Formation of cellulose continues for 4 to 6 weeks. Due to daily temperature cycles, cellulose is formed in layers. The tubular structure never completely fills, and the open space in its center is called the "lumen" [1]. In any chemical and/or macromolecular modification of cotton fibers the effects of these modifications on the morphology of the fiber as related to useful textile properties must be considered [7]. When the living cells of the seed hairs die, the hairs lose water, collapse, and assume a flattened, twisted, ribbon-like form. The seeds and cotton fibers are harvested and the fibers are mechanically separated from the seed. The fibers, which can be spun into yarns and woven into fabrics, are usually less than 1 to a maximum of about 1-1/4 in. long [1].

Cotton cellulose is composed of repeating units of cellobiose (two anhydroglucose units) with the empirical formula $(C_{12}H_{20}O_{10})_n$, where n ranges from 2000 to 2500. Natural cotton cellulose is about 80% crystalline and has crystal lattice type I. Two cellobiose units comprise the basic monoclinic unit cell which belongs to space group P2 with typical values of $a = 8.35$ Å, $b = 10.3$ Å (fiber axis), $c = 7.9$ Å, and $\beta = 84°$. The other important form of cotton cellulose has crystal lattice type II and is formed by treating cotton cellulose with solutions of sodium hydroxide (mercerizing). For the unit cell of cellulose II, typical values are $a = 8.14$ Å, $b = 10.3$ Å, $c = 9.14$ Å, and $\beta = 62°$. The chemical reactivity of the cellulose molecule depends on the accessibility to chemical reagents and relative reactivities of the hydroxyl groups at carbon positions C_2, C_3, and C_6 [1].

Since retention of cotton in its natural fibrous form after modification is desired, heterogeneous graft copolymerization of vinyl monomers from solution or vapor phase with cotton is usual. Consequently, (1) the crystal lattice structure, crystallinity, and morphology of cotton fibers; (2) the interaction of cotton with solutions of monomers and monomer vapors; and (3) mechanical organization of the fibers at the time of reaction, that is, fibers, yarns, or fabrics, are important factors to consider in preparing fibrous polyvinyl graft copolymers of cotton [1-3, 13, 14].

COPOLYMERIZATION REACTION MECHANISMS

Polyvinyl graft copolymers of cotton have been formed primarily by free-radical-initiated processes [3, 4, 13-15], but can also be formed by ionic-initiated processes [4, 16, 17]. Free radical sites may be formed on the cellulose molecule by dehydrogenation, depolymerization, oxidation, or formation of unstable metal complexes which may lead to one-electron transfer to the metal and cleavage of the glucopyranoside ring. Ionic processes usually involve the formation of an alkoxide of cotton cellulose with which copolymerization of vinyl monomers is initiated.

The most commonly used methods of free-radical initiation on cotton are: high-energy ionizing radiation, ceric ion, redox systems, and oxidative reagents [8]. In each method the free-radical site which initiates graft copolymerization is formed on the cellulose molecule. Important factors in initiating graft copolymerization reactions of vinyl monomers with activated cellulose are: the accessibility of the free-radical sites to the monomers; the lifetime of the free-radical sites; the interaction of the monomer solutions or vapors with activated cellulose to increase the accessibility of the free-radical sites to monomer; and the scavenging of the free radicals by solvents [3-5, 15].

Dehydrogenation

When ionizing radiation, particularly γ-radiation from ^{60}Co and ^{137}Cs, x-rays, or high-energy electrons, is used to activate cotton, both short- and long-lived (trapped) free radicals are formed [18, 19]. In this case the activation of cotton and the copolymerization reaction can take place either simultaneously or consecutively. That is, cotton may first be treated with monomer solution and then irradiated, or be irradiated and then treated with monomer [20-63].

Generalized steps for formation of free-radical sites on cotton cellulose on interaction of high energy ionizing radiation are: (1) depolymerization with radicals formed at carbon C_1 or C_4, and (2) dehydrogenation with radicals formed at carbon C_2, C_3, C_5, or C_6 [8, 9]. Electron spin resonance data indicated that the free radicals that generate singlet spectra are readily accessible to and scavenged by water vapor. Free radicals that generate triplet spectra are less accessible to water vapor. At 25°C about 30% of the free radicals formed in irradiated cellulose I are inaccessible to water; in irradiated cellulose II only about 10% of the free radicals are inaccessible to water [19].

Steps for free-radical-initiated graft copolymerization of vinyl monomer (M) from solvent (S) with cotton cellulose (C) which is irradiated may be represented, as follows:

Initiation (Irradiation)

$$C \rightarrow C^* \rightarrow C^\cdot \tag{1}$$

$$M \rightarrow M^* \rightarrow M^\cdot \tag{2}$$

$$S \rightarrow S^* \rightarrow S^\cdot \tag{3}$$

Propagation

$$C^\cdot + M \rightarrow CM^\cdot \tag{4}$$

$$C + M^\cdot \rightarrow CM^\cdot \ \underline{\text{or}}\ C^\cdot + M \tag{5}$$

$$CM^\cdot + nM \rightarrow CM^\cdot_{n+1} \tag{6}$$

$$M^\cdot + nM \rightarrow M^\cdot_{n+1} \tag{7}$$

Termination

$$C\cdot + M\cdot \rightarrow CM \tag{8}$$

$$CM_n\cdot + CM_m\cdot \rightarrow C_2M_{m+n} \tag{9}$$

$$CM_n\cdot + CM_m\cdot \rightarrow CM_n + CM_m \tag{10}$$

$$M_n\cdot + M\cdot \rightarrow M_{n+1} \tag{11}$$

Chain Transfer

$$C\cdot + S \rightarrow C + S\cdot \tag{12}$$

$$S\cdot + M \rightleftharpoons S + M\cdot \tag{13}$$

When cotton cellulose is irradiated in the presence of monomer and solvent, all of the reactions are likely. If cotton cellulose is irradiated and then contacted with monomer and solvent, Reactions (2) and (3) do not occur. However, depending on the types of monomers and solvents used, chain transfer, as shown in Reactions (12) and (13), can occur, and homopolymer can then be formed as shown in Reactions (7) and (11) [3, 4, 8].

Typical order of molecular reactivity of vinyl monomers for trapped cellulosic radicals, as compared with reactivity of acrylonitrile under similar reaction conditions, to yield graft copolymers is: methyl methacrylate > glycidyl methacrylate > butyl methacrylate > styrene, acrylonitrile > vinylidene chloride > lauryl methacrylate, 1,3-butylene dimethacrylate, vinylpyrrolidone > allyl methacrylate [44]. The concept of monomer reactivity ratio was applied to yield grafted block copolymers of irradiated cotton by reacting the activated cellulose with binary and ternary mixtures of vinyl monomers. In this way the properties of a monomer, which had low reactivity for cellulosic radicals but higher reactivity for polymer radicals, could be more efficiently incorporated into the fibrous copolymer.

One-Electron Transfer

Ceric ion initiation of graft copolymerization of vinyl monomers with cotton has been reported by several investigators [32-35, 64-72]. Oxidative degradation of cellulose is also initiated. It has been suggested that ceric ions in acidic solution form chelates with cellulose, probably through the hydroxyl groups on carbons C_2 and C_3 [19]. After a transfer of one electron from the cellulose molecule to Ce(IV), Ce(III) is formed, the bond between carbons C_2 and C_3 is cleaved, and a short-lived free radical is formed on carbon C_2 or C_3. If vinyl monomer is present, graft polymerization with cellulose is initiated. Chain transfer usually occurs, so that homopolymer is also formed. By quenching the reactions with liquid nitrogen, an electron spin resonance spectrum of the short-lived cellulosic free radical was recorded. Spectra, recorded under flow conditions in the spectrometer at 25°C, showed that excess Ce(IV), which had not been chelated, competed with vinyl monomer and solvent for the free radicals formed on cotton cellulose [19].

Hydrogen Abstraction

Redox systems are similar to the dehydrogenation reactions initiated by ionizing radiation, except that in hydrogen abstraction the free radicals are very short-lived [31]. Cotton is padded with a solution of ferrous ammonium sulfate and dried; then the treated cotton is immersed in a solution containing hydrogen peroxide and vinyl monomer, usually at a temperature higher than ambient temperature. Graft copolymerization of the vinyl monomer with cotton and also homopolymerization are initiated [31-34, 72-76]. By using a flow technique, and indicator ions, electron spin resonance spectra of highly reactive free radicals, ·OH and HO_2, were recorded. By using a liquid nitrogen quenching technique, an electron spin resonance spectrum [31] of the short-lived cellulosic free radical was recorded, probably formed as follows:

$$\text{(cellulose)–H} + {}^{\cdot}\text{OH} \rightarrow \text{(cellulose)}^{\cdot} + H_2O \qquad (14)$$

Oxidation

Thermally initiated decomposition of peroxy compounds in contact with cotton initiates oxidative depolymerization of cellulose [72, 73, 77-91]. Some of the chemical oxidants used are: benzoyl peroxide [73, 75], N,N-azobisisobutyronitrile [80], potassium thiosulfate [81], ammonium thiosulfate [75, 87], sodium thiosulfate [82], copper sulfate + potassium sulfate + sulfuric acid [82], manganic phosphate + pyrophosphate [90], sulfurous acid [85], hydriodic acid [86], activated manganese dioxide [77], and ferric sulfate + sulfurous acid [75]. If vinyl monomers are present, graft copolymerization reactions with cotton are initiated. Instrumental experimental evidence for the presence of free radicals, as determined by electron spin resonance spectroscopy, has not been reported.

Ultraviolet Radiation

When cotton was irradiated with UV light, oxidative reactions were initiated, and cellulosic free radicals were formed [3, 4, 92-98]. Free radicals were formed in dried, purified cotton irradiated with near-UV light that had wavelengths of about 3250 to 4000 Å. Concentration of free radicals was maximum when cotton was irradiated with near-UV light of wavelength about 3600 Å. The electron spin resonance spectrum of the cellulosic radical formed had a line width of 8 to 10 gauss and a g-value of 2.0045 [95, 96, 99]. Two explanations for the process that led to formation of free radicals in irradiated cotton were: (1) absorption of light by a specific chromophore; if there is homolytic bond scission, there should be a direct correlation between formation of radicals and oxidative degradation of the cellulosic molecule; and (2) absorption of light by an electron band structure; an intermediate state should be produced in which the electrons are excited and extremely mobile in this semiconductor-type model [95].

Electron spin resonance spectra of free radical intermediates formed during photoinitiated graft polymerization reactions of vinyl monomers onto purified cotton cellulose were recorded. Photolyzed solutions of vinyl monomers, in the absence of cellulose, did not generate electron spin resonance-detectable radicals. Evidently the cellulose radical formed on photolysis added to the double bond of the vinyl monomer to yield propagating radicals, as follows:

$$\text{(cellulose)–H} \xrightarrow{h\nu} \text{(cellulose)}^{\cdot} + {\cdot}\text{H} \tag{15}$$

$$\text{(cellulose)}^{\cdot} + n\text{M} \rightarrow \text{(cellulose)–(M)}_{n-1}\text{M}^{\cdot} \tag{16}$$

where (cellulose)–H represents the cellulose molecule; (cellulose)$^{\cdot}$, the cellulose radical; M, monomer; and M$^{\cdot}$, monomer radical.

The rates of photopolymerization of selected vinyl monomers, from water solutions, with cotton were: diacetone acrylamide > acrylamide, methacrylamide > N,N-methylenebisacrylamide. Infrared spectra of the copolymer products showed increased carbonyl group absorption. The cotton-poly(acrylamide) and cotton-poly(diacetone acrylamide) copolymer products were stable to solvent extraction and to acid hydrolysis, but only the latter was stable to base hydrolysis. Differential dyeing indicated that the deposition of the polymers within the fabric structure varied. Large increases were observed in the moisture regains of cotton-poly(N,N-methylenebisacrylamide) and cotton-poly(methacrylamide) fabric copolymers, as compared with fabric controls. The fabric copolymers had elongations-at-break slightly greater than that of untreated cotton and retained about 90% of the breaking strength and 70% of the tearing strength of untreated cotton [99-101].

Acrylated and methacrylated cotton fabrics that had been irradiated by near-UV light in nitrogen had increased wrinkle recovery angles, as compared with those of control fabrics. The wrinkle recovery angles of the photolyzed fabrics were dependent on degree of substitution of the chemically modified fabrics [102].

Anionic Initiation

Anionic initiated graft copolymerization of cotton cellulose with vinyl monomers in aqueous systems has been reported [16, 17]. Typical reactions with cotton cellulose are, as follows:

$$\text{(cellulose)–OH} + \text{MOH} \xrightarrow{H_2O} \text{(cellulose)–OM} + H_2O \qquad (17)$$

$$\text{(cellulose)–OM} + nCH_2{=}CHR \rightarrow \text{(cellulose)–O–}(CH_2CHR)_{n-1}CH_2CHR\text{–M} \qquad (18)$$

where M is usually sodium and CH_2CHR is vinyl monomer.

COPOLYMERIZATION METHODS

Solution Phase

The most commonly used copolymerization method is the application of vinyl monomer, dissolved in solution, to cotton before, during, or after the formation of free radicals on cotton cellulose. Important factors, which determine the selection of the solvent for the monomer, are: (1) the monomer must be sufficiently soluble in the solvent, so that its concentration is high enough to maintain a chain reaction; (2) the solvent should have a low degree of reactivity for cellulosic radicals to minimize chain transfer and homopolymerization; (3) the solvent should cause a slight swelling of the crystalline structure of cotton to increase the accessibility of trapped cellulosic radicals to monomer; and (4) the solvent should cause desirable dimensional changes in the fibrous structures of cotton, so that the morphology of the fibrous copolymer can be controlled. Typical solvents are: water; salt solutions, such as aqueous solutions of zinc chloride; organic solvents, such as methanol, acetone, dimethylsulfoxide, and N,N-dimethylformamide; and combinations of these organic solvents with water [3-6].

Solid Phase

Applications of vinyl monomers from solutions to cotton, evaporation of the solvent, and then initiation of polymerization and/or graft copolymerization reactions by high-energy ionizing radiation have been reported. A vinyl monomer, such as methylol acrylamide, which has a functional group that is reacted chemically with cotton, usually in fabric form, during the monomer deposition step is used. Then the treated cotton fabric is irradiated with ionizing radiation, such as high-energy electrons; the reaction of the vinyl group with cotton may be initiated, thereby introducing a cross-link in the cellulose molecule. The surface properties of cotton and textile properties of the fabric are changed. Also, durable polymeric coatings on cotton are formed by irradiation of cottons similarly treated with vinyl monomers [2, 4].

Emulsions

Emulsions of vinyl monomers, organic solvents, and water have been applied to radiation-activated cottons to initiate graft copolymerization reactions. The effects of the composition of the emulsion on the rate of the reaction are critical and must be determined in each case. Generally, the rate of the graft copolymerization reaction was maximum at a composition that produced a homogeneous emulsion, but, if changed slightly, separated in two or more layers of solvent and monomer. This method was investigated for binary and ternary systems of monomers [44].

Vapor Phase

Vinyl monomer in vapor phase has been applied to activated cotton at low pressures [4, 75, 87]. Consequently, the concentration of monomer was relatively low, and chain termination reactions predominated. The amount of monomer in contact with activated cotton was increased by padding the cotton with some solvent which would dissolve the monomer from the vapor state. The usefulness of this method to prepare polyvinyl graft copolymers of cotton has not been demonstrated. Vapor phase application would help to remove inhibitors of polymerization from the monomer and could save monomer and still produce the desired degree of graft copolymerization. This method did not increase uniformity of deposition of grafted copolymer within the fibrous macrostructure of cotton over deposition by other methods.

CHEMICAL CHARACTERIZATION

Polyvinyl graft copolymers of cotton have greatly decreased solubility in solvents for cellulose, such as cupriethylene diamine and cuprammonium hydroxide, and in solvents for the grafted polymer. Decreased solubility is considered evidence for covalent linkage, that is, polymer grafted to cellulose. The molecular degree of substitution of grafted polymer on cellulose ranges from more than one molecule of polymer per molecule of cellulose when copolymerization is initiated by ceric ion of ferrous ion/hydrogen peroxide to less than one molecule of polymer per 20 to 30 molecules of cellulose when it is initiated by radiation [4, 103].

Free radical initiation of the copolymerization reactions of cellulose involves oxidative depolymerization of the cellulose molecule. Consequently, IR absorption increases when concentration of carbonyl groups increases [11]. Copolymerization reactions have also been evaluated by determining increases in IR absorption of characteristic groups of the copolymer [6, 10-12]. Electron spin resonance spectroscopy has been used to determine the free radical reactions of cellulosic radicals, the residual radicals in the copolymer product, and the nature of the living copolymer radical [3, 4, 9].

The densities of cellulose copolymers agree closely with those calculated from the known densities of cellulose and amorphous polymer and the grafted polymer content of the copolymer product [6].

MORPHOLOGY OF FIBROUS COPOLYMERS

The morphologies of fibrous graft copolymers of cotton are related to their useful applications in textiles. The morphology of the fibrous copolymers can be selectively determined if radiation-initiated free-radical copolymerization reactions are used [3, 4, 7]. For example, the fibrous copolymers may generally retain the natural shape of cotton fibers with copolymer in the outer layers. For these copolymers the pre-irradiation method and solvents for acrylonitrile, which had a weak swelling effect on cotton, were used.

The fibrous copolymers may be rounded with the copolymer distributed uniformly throughout the fibrous structure. For these cotton was cyanoethylated, soaked in solvent which contained acrylonitrile and had a swelling effect on cotton, and then was irradiated. When the copolymer was concentrated in the central areas of the fibrous structure, cotton was soaked in solvent which contained acrylonitrile and had a swelling effect and then was irradiated. When copolymer was concentrated in the outer layers of the fibers, the pre-irradiation method and solvents for acrylonitrile, which had a strong swelling effect on cotton, were used.

Graft copolymerizing styrene from methanol with cotton by a simultaneous irradiation process has an opening and layering effect on the fibrous structure. The effects of graft copolymerizing alkyl methacrylates with cotton, by a similar process, on the fibrous structure are dependent on the type of alkyl methacrylate. For example, poly(methyl methacrylate) was uniformly distributed in a collapsed fibrous structure. Poly(ethyl methacrylate) caused a slight opening of the fibrous structure. Poly(butyl methacrylate) and higher alkyl methacrylates caused an opening and layering effect. Graft copolymerization of vinyl acetate with cotton, by a similar process, gave an opening and cellular effect on fibrous structure.

PROPERTIES OF FIBROUS COPOLYMERS

The preparation and properties of polyvinyl graft copolymers of cotton fibers, yarns, and fabrics, as functions of the method of initiation of the copolymerization reaction and of the type of monomer used, are summarized in Table 1.

PROPERTIES OF COPOLYMER COTTON FABRICS

Some of the most important properties of durable-press cottons are: abrasion resistance, soil-release, wrinkle recovery, and wash-wear rating. Copolymer cotton fabrics have improved abrasion resistance, as compared with untreated cotton, particularly as shown by scanning photomicrographs of cotton and copolymer fabrics before and after abrasion tests [6]. The extent of removal of oily soil is several times as great from cross-linked poly(methacrylic acid) copolymer print cloth as from conventionally cross-linked print cloth. Similarly, the removal of aqueous soil is greater from cross-linked copolymer fabric than from cross-linked fabric. Also, the extent of aqueous soiling was less for cross-linked copolymer than for cross-linked fabric [6, 37].

The wrinkle recovery angles are greater for cross-linked copolymer fabrics than for cross-linked fabrics. The wash-wear ratings also are greater for cross-linked copolymer twill than for cross-linked twill fabrics. Blended grafted and untreated cotton fibers

TABLE 1

Grafted vinyl monomer	Property of fibrous copolymer	References
	Radiation Initiated–Dehydrogenation	
Styrene	Thermoplastic	20
Acrylonitrile	Thermoplastic	21-25
Acrylonitrile	Elastic	26
Acrylonitrile	Durable press	27
Styrene	Thermoplastic	28
Methyl, ethyl, butyl, lauryl methacrylates	Morphological effects	29
Acrylonitrile	Abrasion resistance, morphological effects	32-34
Methyl methacrylate	Shrink resistance	35
Methacrylic acid, 2-hydroxyethyl, and hydroxypropyl methacrylate	Soil release	36, 37
Styrene, methyl methacrylate, acrylonitrile + methyl methacrylate, styrene + methyl methacrylate	Spray resistance dimensional stability bacterial resistance	39
Acrylonitrile	Decreased stiffness	42
Acrylonitrile, methyl, ethyl, butyl, hexyl, and lauryl methacrylates	Durable press	43
Styrene	Water repellency	50
1,3-Butadiene	Durable press	51
Methacrylonitrile	Increased strength	52
Acrylonitrile	Mildew resistance	62
Acrylonitrile, methyl methacrylate	Durable press	89, 90

	Ceric Ion Initiated–One Electron Transfer	
Acrylonitrile	Abrasion resistance, morphological effects	32-34
Methyl methacrylate	Shrink resistance	35
Acrylonitrile	Decreased water of imbibtion, stretch yarns	66, 67
Chloroethyl acrylate, chloroethyl methacrylate	Tensile strength increase, thermal stability, light and rot resistance	68
Acrylonitrile	Density decreased	72
	Redox System Initiated–Hydrogen Abstraction	
Acrylonitrile	Abrasion resistance, morphological effects	32-34
Acrylonitrile	Density decreased	72
Acrylic acid, methacrylic acid	Increased hygroscopicity	74
Methylvinylpyridine + H_3PO_4	Flame resistance	76
	Anionic Initiated	
Preformed polystyrene	Wrinkle recovery	16
Latex	Rubberized	17
	Oxidation	
Acrylonitrile	Bacterial resistance	82
Acrylonitrile	Decreased lateral odering	83
Methyl polysiloxane	Waterproof	88
Phosphate salt of diethylaminoethyl methacrylate	Fire retardancy	89

were woven to form twill fabrics which, after cross-linking, gave products with almost the maximum possible wash-wear rating [6, 27, 104-107].

REFERENCES

[1] J. C. Arthur, Jr., "Cotton," in Encyclopedia of Polymer Science and Technology, Vol. 4 (H. F. Mark, N. G. Gaylord, N. M. Bikales, eds.), Wiley-Interscience, New York, 1966, p. 244.

[2] J. C. Arthur, Jr., Cotton Trade J., Int. Ed., 1964-1965, 41.

[3] J. C. Arthur, Jr., Adv. Chem. Ser., 91, 574 (1969).

[4] J. C. Arthur, Jr., Adv. Macromol. Chem., 2, 1 (1970).

[5] J. C. Arthur, Jr., J. Macromol. Sci.—Chem., A4, 1057 (1970).

[6] J. C. Arthur, Jr., Adv. Chem. Ser., 99, 321 (1971).

[7] M. L. Rollins, A. M. Cannizzaro, F. A. Blouin, and J. C. Arthur, Jr., J. Appl. Polym. Sci., 12, 71 (1968).

[8] J. C. Arthur, Jr., Sen'i To Kogyo, 4, 212 (1971).

[9] J. C. Arthur, Jr., "Electron Spin Resonance Studies," in Cellulose and Cellulose Derivatives, High Polymers, 2nd ed., Vol. V, Part V (N. M. Bikales and L. Segal, eds.), Wiley-Interscience, New York, 1971, p. 977.

[10] J. C. Arthur, Jr., "Reactions Induced by High-Energy Radiation," in Cellulose and Cellulose Derivatives, High Polymers, 2nd ed., Vol. V, Part V (N. M. Bikales and L. Segal, eds.), Wiley-Interscience, New York, 1971, p. 937.

[11] J. C. Arthur, Jr., "Radiation Effects on Cellulose," in Energetics and Mechanisms in Radiation Biology (G. O. Phillips, ed.), Academic, London, 1968, p. 153.

[12] J. C. Arthur, Jr., "Intramolecular Energy Transfer in Cellulose and Related Model Compounds," in Energy Transfer in Radiation Processes (G. O. Phillips, ed.), Elsevier, Amsterdam, 1966, p. 29.

[13] J. C. Arthur, Jr., and F. A. Blouin, Am. Dyest. Rep., 51, 1024 (1962).

[14] J. C. Arthur, Jr. and F. A. Blouin, U.S. Atomic Energy Commission Document TID-7643, 319 (1962).

[15] J. C. Arthur and F. A. Blouin, J. Appl. Polym. Sci., 8, 2813 (1964).

[16] Y. Avny and R. F. Schwenker, Jr., Text. Res. J., 37, 817 (1967).

[17] J. J. Schilthius and D. F. Wilhelmi, British Patent 228, 893 (1924).

[18] P. J. Baugh, O. Hinojosa, and J. C. Arthur, Jr., J. Appl. Polym. Sci., 11, 1139 (1967).

[19] J. C. Arthur, Jr., P. J. Baugh, and O. Hinojosa, Ibid., 10, 1591 (1966).

[20] J. C. Arthur, Jr. and D. J. Daigle, Text. Res. J., 34, 653 (1964).
[21] J. C. Arthur, Jr. and R. J. Demint, Ibid., 30, 505 (1960).
[22] J. C. Arthur, Jr. and R. J. Demint, Ibid., 31, 988 (1961).
[23] J. C. Arthur, Jr. and R. J. Demint, U.S. Patent 3,109,798 (1963).
[24] J. C. Arthur, Jr. and R. J. Demint, U.S. Patent 3,157,460 (1964).
[25] J. C. Arthur, Jr., R. J. Demint, W. F. McSherry, and J. F. Jurgens, Text. Res. J., 29, 759 (1959).
[26] J. C. Arthur, Jr. and J. N. Grant, Ibid., 36, 934 (1966).
[27] J. C. Arthur, Jr., J. A. Harris, and T. Mares, Text. Ind., 132, 77 (1968).
[28] J. C. Arthur, Jr., A. R. Markezich, and W. F. McSherry, Text. Res. J., 33, 896 (1963).
[29] F. A. Blouin, A. M. Cannizzaro, J. C. Arthur, Jr., and M. L. Rollins, Ibid., 38, 811 (1968).
[30] F. A. Blouin, N. J. Morris, and J. C. Arthur, Jr., Ibid., 36, 309 (1966).
[31] J. C. Arthur, Jr., O. Hinojosa, and M. S. Bains, J. Appl. Polym. Sci., 12, 1411 (1968).
[32] F. A. Blouin and J. C. Arthur, Jr., Text. Res. J., 33, 727 (1963).
[33] F. A. Blouin and J. C. Arthur, Jr., Polym. Prepr., 6, 359 (1965).
[34] F. A. Blouin, N. J. Morris, and J. C. Arthur, Jr., Text. Res. J., 38, 710 (1968).
[35] E. D. Bolinger and G. Machell, Belgian Patent 640,920 (1964).
[36] G. A. Byrne and J. C. Arthur, Jr., J. Appl. Polym. Sci., 14, 3093 (1970).
[37] G. A. Byrne and J. C. Arthur, Jr., Text. Res. J., 41, 271 (1971).
[38] S. DasGupta, Can. Text. J., 81, 57 (1964).
[39] S. DasGupta, French Patent 1,473,659 (1967).
[40] R. J. Demint and J. C. Arthur, Jr., Text. Res. J., 29, 276 (1959).
[41] R. J. Demint, J. C. Arthur, Jr., A. R. Markezich, and W. F. McSherry, Ibid., 32, 918 (1962).
[42] R. J. Demint, J. C. Arthur, Jr., and W. F. McSherry, Ibid., 31, 821 (1961).
[43] J. A. Harris, T. Mares, J. C. Arthur, Jr., and M. J. Hoffman, Text. Ind., 133, 117 (1969).
[44] J. A. Harris and J. C. Arthur, Jr., J. Appl. Polym. Sci., 14, 3113 (1970).
[45] T. Hoshino, K. Araki, and M. Ichino, Japanese Patent 7878 (1962).
[46] T. Hoshino, K. Araki, and M. Ichino, Japanese Patent 1993 (1963).
[47] R. Y.-M. Huang, B. Immergut, E. H. Immergut, and W. H. Rapson, J. Polym. Sci., A1, 1257 (1963).
[48] R. Y.-M. Huang and W. H. Rapson, J. Polym. Sci., C, 169 (1963).
[49] F. Ibragimov, P. P. Larin, E. P. Sidel'kovskaya, M. A. Askarov, and Yu. T. Tashpulatov, Uzb. Khim. Zh., 11, 61 (1967).

[50] F. Kimura, T. Okada, and I. Sakurada, Nippon Hoshasen Kobunshi Kyokai Nempo, 8, 19 (1967).

[51] J. W. Lynn and W. J. Skraba, U.S. Patent 3,326,788 (1967).

[52] T. Mares, O. Hinojosa, Y. Nakamura, and J. C. Arthur, Jr., J. Appl. Polym. Sci., 15, 2349 (1971).

[53] Y. Nakamura, O. Hinojosa, and J. C. Arthur, Jr., Ibid., 13, 2633 (1969).

[54] Y. Nakamura, O. Hinojosa, and J. C. Arthur, Jr., Ibid., 14, 789 (1970).

[55] Y. Nakamura, O. Hinojosa, and J. C. Arthur, Jr., Polym. Prepr., 10, 788 (1969).

[56] Y. Nakamura, O. Hinojosa, and J. C. Arthur, Jr., J. Appl. Polym. Sci., 15, 391 (1971).

[57] I. Sakurada, T. Okada, S. Hatakeyama, and F. Kimura, J. Polym. Sci., C, 4, 1233 (1964).

[58] I. Sakurada, T. Okada, F. Kimura, and S. Hatakeyama, Nippon Hoshasen Kobunshi Kenkyu Kyokai Nempo, 4, 37 (1962).

[59] K. Shinohara, T. Hoshino, K. Araki, and M. Ichino, Japanese Patent 14,632 (1962).

[60] R. C. Sovish and F. S. Saunders, U.S. Patent 2,998,329 (1961).

[61] W. Tsuji, M. Imai, and Y. Kadono, Bull. Inst. Chem. Res., Kyoto Univ., 42, 68 (1964).

[62] U.S. Atomic Energy Commission, British Patent 960,192 (1964).

[63] C. P. Priesing, H. Volk, and C. E. Gabriel, U.S. Patent 3,281,263 (1966).

[64] K. Dimov and R. Lazarova, Faserforsch. Textiltech., 19, 68 (1968).

[65] J. L. Gardon, J. Polym. Sci., A2, 2657 (1964).

[66] C. Hamalainen, H. H. St. Mard, and A. S. Cooper, Jr., U.S. Patent 3,377,163 (1968).

[67] C. Hamalainen, H. H. St. Mard, and A. S. Cooper, Jr., Am. Dyest. Rep., 57, 219 (1968).

[68] T. G. Kulagina, M. A. Askarov, and S. D. Savranskaya, Uzb. Khim. Zh., 10, 34 (1966).

[69] G. Machell and M. A. Thomas, Belgian Patent 640,919 (1964).

[70] G. Mino and S. Kaizermann, U.S. Patent 2,922,768 (1960).

[71] Y. Ogiwara, Y. Ogiwara, and H. Kubota, J. Polym. Sci., A, 6, 1489 (1968).

[72] T. S. Sydykov, R. M. Livshits, Z. A. Rogovin, E. A. Vershinina, E. Z. Fainberg, and N. V. Mikhailov, Khim. Volokna, 1968, 25.

[73] K. Dimov and R. Lazarova, Khim. Ind., 39, 396 (1967).

[74] Yu. S. Kozlova, A. A. Pogadaeva, and Z. A. Rogovin, Vysokomol. Soedin., Tsellyuloza iee Proizvodnye, Sb. Statei, 3 (1963).

[75] R. M. Livshits, B. P. Morin, and Z. A. Rogovin, Cellul. Chem. Technol., 1, 153 (1967).

[76] Z. A. Rogovin, A. M. Tyuganova, Yu. G. Kryazhev, and T. Y. Zharova, British Patent 1,022,083 (1966).

[77] R. Teichmann and E. Uhlig, British Patent 1,128,316 (1968).

[78] M. Imoto, M. Kondo, and K. Takemoto, J. Chem. Ind., Tokyo, 68, 1302 (1965).

[79] M. Imoto, K. Takemoto, and M. Kondo, Makromol. Chem., 98, 74 (1966).

[80] H. W. Jacobson, U.S. Patent 2,764,503 (1956).

[81] W. Kern, R. C. Schulz, and I. Loflund, German Patent 1,083,051 (1960).

[82] V. Matejka and Z. Rada, Czechoslovakian Patent 118,985 (1966).

[83] C. Mircea, Ind. Text. (Bucharest), 18, 290 (1967).

[84] S. Morimoto, T. Okada, T. Toda, and H. Nakagawa, Japanese Patent 13,881 (1962).

[85] R. C. Schulz and I. Loflund, Angew. Chem., 72, 771 (1960).

[86] F. Stuerzenhofecker, German Patent 1,132,724 (1962).

[87] B. P. Morin, R. M. Livshits, and Z. A. Rogovin, Vysokomol. Soedin., Ser. A, 9, 857 (1967).

[88] J. M. Nielsen, French Patent 1,453,331 (1966).

[89] D. A. Predvoditelev, M. A. Tyuganova, M. A. Korshunov, and Z. A. Rogovin, Zh. Prikl. Khim., 39, 1610 (1966).

[90] Rayonier, Inc., British Patent 962,028 (1964).

[91] N. S. Razumikhina and E. M. Aleksandrova, Nauchn. Dokl. Vyssh. Shk., Khim. Khim. Tekhnol., 3, 460 (1958).

[92] J. C. Arthur, Jr., J. Polym. Sci., C, 36, 53 (1971).

[93] G. O. Phillips and J. C. Arthur, Jr., Text. Res. J., 34, 497 (1964).

[94] G. O. Phillips and J. C. Arthur, Jr., Ibid., 34, 572 (1964).

[95] G. O. Phillips, O. Hinojosa, J. C. Arthur, Jr., and T. Mares, Ibid., 36, 822 (1966).

[96] P. J. Baugh, O. Hinojosa, T. Mares, M. J. Hoffman, and J. C. Arthur, Jr., Ibid., 37, 942 (1967).

[97] A. H. Reine and J. C. Arthur, Jr., Ibid., 40, 90 (1970).

[98] E. H. Daruwalla, S. M. Moonim, and J. C. Arthur, Jr., Ibid., 42, 592 (1972).

[99] A. H. Reine, O. Hinojosa, and J. C. Arthur, J. Appl. Polym. Sci., 17, 3337 (1973).

[100] A. H. Reine and J. C. Arthur, Jr., Text. Res. J., 42, 155 (1972).

[101] A. H. Reine, N. A. Portnoy, and J. C. Arthur, Jr., Ibid., 43, 638 (1973).

[102] N. A. Portnoy, M. C. Nelson, M. F. Margavio, and J. C. Arthur, Jr., Ibid., 44, 449 (1974).

[103] N. J. Morris, F. A. Blouin, and J. C. Arthur, Jr., J. Appl. Polym. Sci., 12, 373 (1968).

[104] J. C. Arthur, Jr. and J. A. Harris, U.S. Patent 3,634,018 (1972).

[105] J. C. Arthur, Jr., J. A. Harris, and T. Mares, U.S. Patent 3,606,993 (1971).
[106] G. A. Byrne and J. C. Arthur, Jr., Text. Res. J., 41, 788 (1971).
[107] J. A. Harris and J. C. Arthur, Jr., Text. Ind., 135, 183 (1971).