

Separation and Characterization of the Vinyl Side Chains from Grafted Polyacrylonitrile-Cotton Copolymers*

NELLE J. MORRIS, FLORINE A. BLOUIN, and JETT C. ARTHUR, JR., *Southern Regional Research Laboratory, Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture, New Orleans, Louisiana 70119*

Synopsis

A method of separation of polyvinyl side chains from grafted polyacrylonitrile-cotton copolymers was developed in order to study the effect of length of side chain on copolymer properties. The method consists of dispersion of the copolymer (1 g.) containing 20% polyacrylonitrile in 75% aq. $ZnCl_2$ (100 ml.), addition of 6*N* HCl (100 ml.), heating for 1 hr. at 100°C., and precipitation and purification of the resulting vinyl polymer. The effect of hydrolysis on the intrinsic viscosity, the nitrogen content, and the infrared absorption spectra of the polyacrylonitrile polymers was investigated. It was concluded that this method of separation of the grafted polymers permitted a comparison of samples grafted by various techniques. A series of grafted copolymers was hydrolyzed, and the molecular weights of the isolated products were determined by measurements of intrinsic viscosity. Copolymer samples prepared by a post-irradiation grafting technique had the longest polyacrylonitrile side chains (molecular weight, 1×10^6). Samples grafted by a simultaneous irradiation technique varied in side-chain length, depending upon the monomer-solvent system used in the preparation of the copolymer (molecular weight, 3×10^4 - 5×10^5). Chemically initiated grafting to cotton resulted in a copolymer containing relatively short side chains (molecular weight, 9×10^4).

INTRODUCTION

Cotton cellulose is a natural polymer with many good textile properties; however, it lacks some of the desirable properties of synthetic polymers. Within recent years there has been considerable interest in altering the properties of natural polymers, such as cotton, by graft polymerization with vinyl monomers. The copolymers produced could possess new and interesting properties representing a combination of the properties of the two polymers used. Numerous reports are now in the literature on the many vinyl monomers which can be graft-polymerized onto cellulose by radiation and chemical initiation.¹ Even though the conditions of the grafting reactions have been rather extensively studied, the physical and

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mechanical properties of the copolymers produced have not been as thoroughly investigated.² It is found that in some cases the properties of the grafted copolymer are not significantly different from the properties of the ungrafted cellulosic polymer. In other cases new and improved properties resulted from the grafting reaction. Under still other circumstances a loss of some of the useful properties of the cellulosic base polymer due to the grafting is observed. The authors believe that the properties of the copolymers produced by the grafting reaction are dependent on many factors, such as the type of monomer used, the method of initiation, the solvent system employed, the distribution of the vinyl polymer in the cellulosic structure, and the molecular weight of the vinyl polymer. Until such factors are correlated with the properties of the grafted copolymers, predictions cannot be made as to which combinations of vinyl monomers and experimental conditions will result in cotton copolymers with useful properties.

A method was developed for the separation of the polyvinyl side chains from grafted polyacrylonitrile-cotton copolymers. The determination of the molecular weights of the vinyl polymers isolated from copolymers prepared by several different methods of graft polymerization is reported.

EXPERIMENTAL

Materials

Cotton yarns (7/3 s, 253 tex) and fabrics (86 × 80 printcloth, 3.40 oz./yd.²) were purified by extracting with hot ethanol and by boiling in 1% NaOH.³

Polyacrylonitrile of low viscosity was obtained commercially (K & K Labs.). High-viscosity polyacrylonitrile was prepared in the laboratory by extraction of homopolymer from a post-irradiation-grafted cotton fabric. The dry cotton fabric was irradiated in nitrogen to 1×10^6 r. and then treated with 15% acrylonitrile in 75% aq. ZnCl₂ for 3 days. The washed, grafted fabric was extracted overnight at room temperature with *N,N*-dimethylformamide (DMF), and the extracted polyacrylonitrile was precipitated, dissolved in DMF, and reprecipitated.

The acrylonitrile used was alkali-extracted, washed, dried, and distilled. ZnCl₂ of A.C.S. grade was used to prepare saturated aqueous stock solutions (about 81% at 25°C.). Other chemicals used were reagent grade.

Grafted Copolymers. The polyacrylonitrile-cotton copolymers used in this study were prepared as indicated below. More detailed descriptions are given in the literature references.

Post-irradiation Grafting.^{4,5} Purified cotton yarns or fabrics were vacuum-dried over P₂O₅ and sealed in a nitrogen atmosphere. The samples were irradiated with gamma rays in SRRL's cobalt-60 facility⁶ to the desired dosage. Dose rates were 0.21–0.36 × 10⁶ r./hr. Immediately after irradiation the samples were immersed in a solution of the monomer (15% acrylonitrile in 75% aq. ZnCl₂ or 32% AN in 80% aq. ZnCl₂). The system

was evacuated several times, to remove entrapped air, and then flushed with nitrogen. The samples were allowed to react at about 23°C. for the desired times and were then washed with water, to remove unreacted monomer and solvent. The air-dried samples were extracted overnight at room temperature with DMF, to remove ungrafted homopolymer, and again washed and dried.

Simultaneous Irradiation Grafting.⁷ Purified cotton fabrics were soaked overnight in a solution of the monomer. The samples soaked in 32% acrylonitrile (AN) in 80% aq. $ZnCl_2$ were then padded to approximately 230% wet pickup and irradiated in SRRL's cobalt-60 source to the desired dosage. The samples soaked in 30% AN in DMF were irradiated to the desired dosage in the presence of an excess of the monomer solution (1 g. of cotton to 4.6 ml. of monomer solution). After irradiation the samples were water-washed and air-dried. They were then extracted overnight at room temperature with DMF and again water-washed and dried.

Chemical Grafting.^{8,9} Ceric ion-initiated grafting was done according to the procedure of Kaizerman et al.⁸ Purified cotton fabrics were immersed in a 4% AN solution in 0.005*M* ceric ammonium nitrate and 0.05*M* HNO_3 solution for 1 hr. at about 23°C. The grafted samples were then water-washed and air-dried. The ungrafted homopolymer was removed by extraction overnight at room temperature with DMF.

The method of Bridgefurd⁹ was used for preparing grafted samples by initiation with the ferrous ion-peroxide system. Fabrics were soaked in a 0.1% ferrous ammonium sulfate solution for 2 min. and rinsed in distilled water, to remove excess ferrous solution. Samples were then immersed in a boiling 8% solution of acrylonitrile, and hydrogen peroxide (0.03%) was added. The samples were refluxed for 30 min. and then water-washed. The grafted samples were extracted overnight at room temperature with DMF, water-washed, and dried.

Methods

Hydrolysis. Copolymer samples containing about 20% polyacrylonitrile were ground to 20 mesh in a Wiley mill. A mixture of 4 g. of copolymer sample and 400 ml. of 75% aq. $ZnCl_2$ solution was stirred overnight with a magnetic mixer. An equal volume of 6*N* HCl was added, and the mixture was stirred for 1–2 hr. (dispersion of the copolymer samples was complete at this stage). The solution was heated for 1 hr. on a steam bath and then filtered through a fritted-glass funnel of coarse porosity. A flocculent, white precipitate of polyacrylonitrile (PAN) was obtained by pouring the solution with stirring into 2.4 l. of a 3:1 mixture of methanol–water. The precipitate was allowed to settle, and as much liquid as possible was decanted. The precipitate was then collected on a fritted-glass funnel (medium porosity), washed, and air-dried. The dried PAN was then dissolved by shaking overnight in 200 ml. of DMF. The solution was filtered (medium porosity funnel) and the PAN reprecipitated by mixing the filtrate with 1.2 liter of a 3:1 methanol–water solution. The excess liquid was

again decanted, and the precipitate collected and washed on a weighed fritted-glass crucible (medium porosity). The PAN samples were dried over P_2O_5 in vacuum, weighed, and ground to a fine powder.

Intrinsic Viscosity. The powdered PAN samples were dried over P_2O_5 in vacuum, weighed, and dissolved in DMF. The reduced viscosity at several concentrations was determined at 25°C. with Cannon-Fenske viscometers. The intrinsic viscosity $[\eta]$ in deciliters per gram was obtained by extrapolation of a plot of η_{sp}/c versus c to infinite dilution.

Molecular Weight. The viscosity average molecular weights (\bar{M}_v) were calculated by using the relationship for polyacrylonitrile developed by Cleland and Stockmayer:¹⁰ $[\eta] = 2.43 \times 10^{-4} \bar{M}_v^{0.75}$.

Analytical Methods. Nitrogen contents of the samples were determined by the Kjeldahl method.¹¹ Infrared spectra were obtained with the KBr disc technique described by O'Connor et al.¹² Quantitative spectral calculations were done by the base-line method.

RESULTS AND DISCUSSION

To determine the molecular weight of the vinyl side chains in polyacrylonitrile-grafted cotton, a method of separation was needed that would completely hydrolyze or degrade the cellulose polymer and leave the polyacrylonitrile polymer as unaltered as possible. The grafted copolymer was first dispersed in a 75% aq. $ZnCl_2$ solution. This step helps ensure complete hydrolysis of the cellulose and should not alter the polyacrylonitrile. Next, an equal volume of 6*N* HCl was added, and the solution was heated on a steam bath. Under these conditions the following reactions could occur: (1) hydrolysis of the cellulose, (2) partial hydrolysis of the nitrile groups in PAN to amides, (3) complete hydrolysis of the nitrile groups in PAN to carboxylic acids, and (4) crosslinking of the PAN polymer.

Hydrolysis of Controls

When a purified cotton control is hydrolyzed by this method, soluble degradation products are formed (no precipitation on addition to a large volume of 3:1 methanol-water). The presence of the $ZnCl_2$ in the hydrolysis mixture ensures complete hydrolysis of the cellulose.

When a commercial polyacrylonitrile control of low intrinsic viscosity (2.20 dl./g.) was hydrolyzed by this procedure, only a slight decrease in viscosity was observed; see Table I. Nitrogen analysis indicated a 4% loss in nitrogen (hydrolysis of nitrile to carboxyl groups). Infrared spectral analysis indicated a 35% decrease in $C\equiv N$ absorption (partial hydrolysis of nitrile to amide and complete hydrolysis to carboxyl). A strong new absorption band in the 1600–1800 cm^{-1} region (carbonyl absorption) of the infrared spectra was observed. A 90% yield of partially hydrolyzed PAN was obtained (uncorrected for carboxyl and amide content).

TABLE I
 Characterization of Polyacrylonitrile Isolated from Controls and Grafted Samples
 Subjected to Hydrolysis Treatment

Sample	Intrin. visc., dl./g., for hydrolysis time, hr.			Yield of PAN, ^{a,b} %	Hydrolysis of C—N groups ^{b,c}			
	0	0.5	1.0		1.5	Unchanged C≡N, ^d %	Complete hydroly. to COOH, ^e %	Partial hydroly. to CONH ₂ , ^f %
Commercial PAN control	2.20		1.95	1.95	90	65	4	31
Laboratory PAN control	9.10		9.65	9.70	75	67	6	27
Laboratory PAN control, hydrolyzed with cotton	9.10		9.25	9.70	85	36	13	51
Grafted sample, low viscosity	—	0.60	0.60	0.60	102	61 ^g	9	30
Grafted sample, medium viscosity	—	4.90	4.60	4.50	101	90	6	4
Grafted sample, high viscosity	—	8.62 ^g	8.53 ^g	11.45 ^g	91	93	5	2

^a Uncorrected for COOH and CONH₂ content.

^b One hour hydrolysis samples.

^c Before hydrolysis C≡N is 100%.

^d Based on nitrile absorptivity.

^e Based on nitrogen content.

^f Calculated by difference.

^g Average values.

A laboratory-prepared polyacrylonitrile control of high intrinsic viscosity (9.10 dl./g.) was hydrolyzed alone and in the presence of purified cotton; see Table I. Under both conditions there was a slight increase in intrinsic viscosity. Analyses indicated a somewhat greater extent of alteration of the PAN structure when the hydrolysis was in the presence of the cotton (about 13% loss of nitrogen and 64% decrease in nitrile absorption). Yields of PAN were high.

Hydrolysis of Grafted Samples

The intrinsic viscosities of three PAN samples separated from grafted polyacrylonitrile-cotton copolymers by this hydrolysis method are shown in Table I. Samples of low and medium intrinsic viscosity showed essentially no change in viscosity over the hydrolysis times studied. The high-viscosity sample, however, showed a very marked increase in intrinsic viscosity after 1.5 hr. of hydrolysis. This increase probably is due to the occurrence of crosslinking of the polymer chains on extended hydrolysis.¹³ Characterization of these samples by nitrogen analysis and infrared absorption of the C≡N band indicated that two of the grafted samples were much less altered by the hydrolysis than were the control samples. However, a strong absorption was still obtained in the 1600–1800 cm.⁻¹ spectral region. There were no absorption bands that could be attributed to a detectable amount of carbohydrate.

Molecular Size of Grafted Side Chains

On the basis of the results thus far described it was concluded that this hydrolysis method could be used to make a comparison of the length of the vinyl side chains in polyacrylonitrile-cotton copolymers grafted by various techniques. Results of such a comparison are shown in Table II.

The post-irradiation-grafted samples gave the highest molecular weights. The length of the vinyl side chain varied with the radiation dosage used and with the composition of the solution of acrylonitrile and aq. ZnCl₂ used in the grafting treatment. The two copolymers prepared by the simultaneous irradiation-grafting procedure were widely different in molecular weight. The copolymer prepared in the aq. ZnCl₂ medium was almost as high in molecular weight as those prepared by the post-irradiation-grafting treatment. The grafting carried out in DMF solution produced the copolymer sample with the shortest vinyl side chains. Ceric ion-initiated grafting resulted in a polymer of low molecular weight, intermediate between the molecular weights of the two samples prepared by the simultaneous irradiation-grafting method. The grafting initiated by ferrous ion and peroxide and carried out at an elevated temperature resulted in grafted side chains of about the same size as those in the copolymer produced by ceric ion initiation at room temperature.

A very interesting picture of the wide range of molecular sizes of the vinyl side chains, which can be obtained simply by varying the conditions

TABLE II
 Characterization of the Molecular Size of Polyacrylonitrile Grafted to Cotton by Various Techniques

Method of Initiation	Grafting conditions	PAN content on grafted sample, %	PAN yield on hydrolyt., % ^a	Intrin. visc., dl./g.	Mol. wt.	Deg. polymzn.
Post-irradiation grafting	1 × 10 ⁶ r., 15% AN in 75% aq. ZnCl ₂ , 2.5 hr.	21	88	8.60	1,200,000	23,000
	1 × 10 ⁶ r., 32% AN in 80% aq. ZnCl ₂ , 25 hr.	23	122	8.40	1,100,000	21,000
	6 × 10 ⁶ r., 32% AN in 80% aq. ZnCl ₂ , 7.5 hr.	18	100	5.16	590,000	11,000
	0.2 × 10 ⁶ r., 32% AN in 80% aq. ZnCl ₂ , 0.9 hr.	21	87	6.83	850,000	16,000
	1 × 10 ⁶ r., 30% AN in DMF, 4.7 hr. 4% AN in 0.005M Ce ⁴⁺ in 0.05M HNO ₃ , 1 hr.	22	101	4.60	510,000	9,600
	8% AN in aq. Fe ³⁺ /H ₂ O ₂ system, 0.5 hr.	22	91	4.70	520,000	9,800
Simultaneous irradiation grafting	1 × 10 ⁶ r., 30% AN in DMF, 4.7 hr. 4% AN in 0.005M Ce ⁴⁺ in 0.05M HNO ₃ , 1 hr.	20	98	0.60	33,000	620
	8% AN in aq. Fe ³⁺ /H ₂ O ₂ system, 0.5 hr.	22	102	0.60	33,000	620
Chemical	4% AN in 0.005M Ce ⁴⁺ in 0.05M HNO ₃ , 1 hr.	22	110	1.20	84,000	1,600
	8% AN in aq. Fe ³⁺ /H ₂ O ₂ system, 0.5 hr.	24	95	1.33	96,000	1,800
		23	110	1.20	84,000	1,600

^a Uncorrected for COOH and CONH₂ content.

of grafting, is indicated by the data presented in Table II. The degree of polymerization of the PAN varies from 620 to 23,000. Subsequent work will present a comparison of the variations in mechanical properties of these grafted copolymers with the variations of molecular weights of the side chains, in order to evaluate the importance of molecular weights in the production of useful grafted copolymer products.

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