Initiation of Graft Polymerization on Cellulose by Hydroxyl Radicals and by Ceric Salts

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INTRODUCTION

Several oxidant systems have been used, or proposed, to generate free radicals on the cellulose molecule in order to initiate graft polymerization. Examples of such systems are photoactivated quinones,[1] ozone,[2] oxygen (with cellulose ethers),[3] hydroxyl radicals,[4] and ceric salts.[5] Further examination of the latter two examples, described in this paper, forms part of a wide program of investigation of methods of graft polymerization on cellulose. Landells and Whewell[4] claimed only that hydroxyl radicals initiate polymerization "within viscose filaments" and so we have attempted to prove the occurrence of true graft copolymers in this system. Mino and Kaizerman[5] described graft polymerization on polyvinyl alcohol by use of a ceric salt and claimed that the method was also applicable to cellulose. We have verified the applicability of the method to cellulose and have also attempted to isolate a pure copolymer.

EXPERIMENTAL RESULTS

All polymers were dried at 40°C./20 mm. Hg over calcium chloride and then phosphoric oxide, except where otherwise stated. Monomers were purified as described earlier.[6] Acetyl contents were determined by the Eberstadt method.[7]

Graft Polymerization on Cellulose, with Hydroxyl Radicals

The procedure was essentially that described by Landells and Whewell.[4] About 5.5 g. of scoured 2.5 in., 8 denier viscose staple was dried and weighed, covered with a 0.1% solution of ferrous ammonium sulfate in 0.1N acetic acid at 20° for 15 min., then pressed and dried. The weight

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increase at this stage was 0.2–0.4%. The impregnated viscose was added to a solution of 40 ml. of acrylonitrile in 1 liter of 0.03% hydrogen peroxide which had been saturated with nitrogen. The mixture was boiled with stirring under reflux in an atmosphere of nitrogen for 2 hr. Considerable amounts of acrylonitrile homopolymer formed as a white powder. The viscose was washed successively with acetone, hot dimethylformamide (3 × 200 ml. at 80°), and methanol, and dried. Yield: 11.29 g. from 5.98 g.

The procedure was repeated with styrene, the monomer being mostly undissolved in the aqueous peroxide solution and the polystyrene being removed after the polymerization by washing with hot toluene in place of the dimethylformamide. An experiment was also carried out in which the aqueous hydrogen peroxide was replaced by the same volume of a 0.005% aqueous solution of azobisisobutyronitrile; very extensive formation of homopolymer was again observed. The results of these and similar experiments with scoured cotton are summarized in Table I. The products

TABLE I
Graft Polymerization on Viscose and Cotton Using Hydroxyl Radicals

Substrate	Monomer	Time, hr.	ΔW, %	Solubility in cuprammonium
Cotton	Styrene	1	5	Mostly soluble
Cotton	Styrene	1	8.5	Mostly soluble
Cotton	Acrylonitrile	2	13	Partially soluble
Viscose	Acrylonitrile	2	89	Insoluble
Viscose[a]	Acrylonitrile	2	65	Insoluble
Viscose[b]	Acrylonitrile	2	8	Soluble
Viscose	Styrene	2	234	Insoluble
Viscose	Styrene	2	190	Insoluble

[a] The viscose was not impregnated with the ferrous salt, but 1 g. of ferrous ammonium sulfate was added to the hydrogen peroxide solution.

[b] Polymerization initiated by azobisisobutyronitrile; 10 g. sample of viscose.

described below will be named, e.g., "viscose–polymer (OH)," in order to distinguish them from the products of ceric salt initiation, which are designated, e.g., "cotton–polymer (Ce)."

Acetylation and Fractionation of Viscose–Polystyrene (OH)

A 17.46 g. sample of grafted viscose (ΔW 234% polystyrene, Table I) was steeped at 20° for 15 min. each time in 80% aqueous pyridine and in three 250 ml. portions of pyridine successively. The swollen fibers were pressed, added to a mixture of 375 ml. of dry pyridine and 250 ml. of acetic anhydride, and heated under reflux with stirring on an oil bath at 120° for 4 hr. The resultant dark red solution was cooled and poured slowly into 1.5 liter of ice water with vigorous stirring. The product (17.42 g.) was washed with methanol and dried. The infrared spectrum of a film prepared from this product showed absorption at 3500 cm.$^{-1}$ due to hydroxyl groups. A second acetylation was therefore carried out by boiling a solution of 8.04 g. in 185 ml. of pyridine and 125 ml. of acetic anhydride for 6 hr., followed by isolation as before. The product (8.00 g.) showed only very faint infrared absorption at 3500 cm.$^{-1}$.
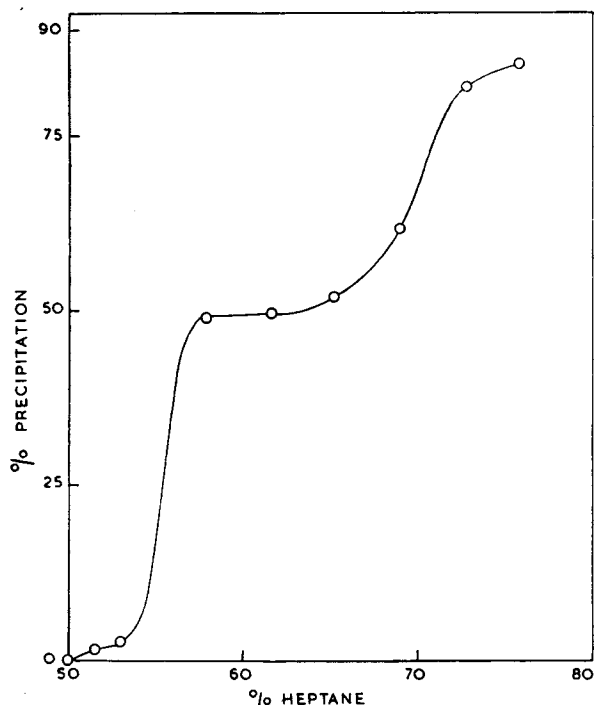

Fig. 1. Fractional precipitation of cellulose triacetate–polystyrene graft copolymer from chloroform solution at 25°.

TABLE II
Fractional Precipitation of Cellulose Triacetate–Polystyrene Graft Copolymer from Chloroform Solution at 25°

Fraction no.	Heptane, %	Precipitate, g.	$-CO \cdot CH_3$ content, %	$[\alpha]_D^{18}$ ($\pm \frac{1}{4}°$)
0	50	0		
1	51.5	0.12		
2	53.0	0.08		
3	57.9	3.40	22 4	−11
4	61.6	0.06		
5	65.2	0.16	20.2	
6	69.0	0.74	19.9	
7	72.8	1.47	16.0	−7.5
8	75.8	0.25	1.1	0
9	a	0.12	0.8	0
10	a	0.63	0.7	0

a See text.

A 7.35 g. sample of the acetylated product was dissolved in 400 ml. of chloroform and precipitated at 25 ± 0.1° with n-heptane (b.p. 95–97°). Fractions were centrifuged, precipitates washed with solvent mixtures corresponding to the supernatant solution, and the washings combined with the bulk solution. Precipitates were finally washed with methanol and dried. After addition of 75.8% heptane and removal of the precipitate, the solution was evaporated to dryness and the residue extracted with two 100 ml. portions of boiling heptane. Fraction 9 represents the soluble, and fraction 10 the insoluble, portion. Optical rotations were observed in 2% solution in chloroform. The results are shown in Table II and Figure 1.

Acetylation and Attempted Fractionation of Viscose–Polyacrylonitrile (OH)

An 11.45 g. sample of grafted viscose (ΔW 89% polyacrylonitrile, Table I) was acetylated for 6 hr. as described above. The filaments, which appeared swollen but otherwise unchanged, were filtered off and washed with acetone. The combined filtrate and washings were added to ice water to give a brown precipitate (1.87 g.) which was reprecipitated from chloroform solution with ethanol and dried (found: N, 0.3%).

The undissolved fibrous acetylation product (13.85 g.) was extracted by shaking 18 hr. with 300 ml. of dimethylformamide in which it was very highly swollen. The extract gave a brown precipitate with water (yield: 0.76 g.; N, 11.4%). A further extraction at 100° for 2 hr. with a mixture of 350 ml. of dimethylformamide and 200 ml. of dioxane, in which the filaments were very highly swollen and completely transparent, gave a further

0.25 g. of soluble material. The insoluble fibrous residue was washed with water, then with methanol, and dried (yield: 10.71 g.; N, 8.6; CO·CH₃, 30.1%.

Graft Polymerization on Cotton with Ceric Salts

Scoured cotton sliver was dried and weighed (12.02 g.) and then added to a solution of 20 ml. of acrylonitrile in 400 ml. of water which had been saturated with nitrogen. Two 10 ml. portions of a 0.1M ceric sulfate solution in 1.0N nitric acid were added at 2 hr. intervals with shaking under nitrogen at 20°. After a total of 4 hr. the solution was opaque, but no solid homopolymer was visible. The cotton was pressed and washed successively with acetone, hot dimethylformamide (2 × 200 ml. at 100°, 10 min.), methanol, and then was dried. No polyacrylonitrile was detected in the washings. The cotton–polyacrylonitrile (Ce) (23.12 g.) was still fibrous but obviously tendered and not readily wetted by water.

Similar experiments were carried out in which acrylonitrile was replaced with styrene or with vinyl acetate. In the latter case the experiment was performed at 50°, but negligible grafting occurred. Attempts were made also to graft styrene both from (a) emulsion and (b) solution, as follows.

(a) A 11.68 g. sample of dry scoured cotton sliver was added to an emulsion of 25 ml. of styrene in a solution of 5 g. of cetyl pyridinium bromide in 600 ml. of water, which had been saturated with nitrogen. The mixture was stirred at 20° under nitrogen while 25 ml. of a 0.1M ceric sulfate solution in 1.0N nitric acid was added dropwise during 2 hr. After a further 1 hr. the cotton was pressed, washed successively with acetone, hot benzene, and methanol, and then dried (yield: 12.09 g.). The recovered emulsion was precipi-

tated with 1 liter of methanol to give 12.32 g. of polystyrene.

(b) A solution of 10 ml. of styrene in a mixture of 150 ml. of tert-butanol and 100 ml. of water was used in place of the emulsion of the preceding experiment (yield: 5.62 g. from 5.52 g. of cotton). A considerable amount of homopolymer formed from solution. The same experiment carried out at 60° instead of 20° yielded 8.25 g. from 8.19 g. of cotton. The results are summarized in Table III.

Acetylation and Attempted Fractionation of Cotton–Polyacrylonitrile (Ce)

A 23.0 g. sample of grafted cotton (ΔW 92.5% polyacrylonitrile, Table III) was steeped successively for 1 hr. each at 20° with water and three separate portions of acetic acid. The product was then pressed, covered with a mixture of 150 ml. of dichloromethane and 150 ml. of acetic anhydride, and cooled to 0°. After 1 hr., a mixture of 0.5 ml. of 60% perchloric acid and 25 ml. of acetic anhydride was added and the mixture stirred and allowed to warm slowly to 20°. After ca. 0.5 hr. at 20° the temperature rose suddenly to ca. 35° and a mobile white slurry formed. Stirring was continued at 20° for a further 2 hr. and then a solution of 0.5 g. of sodium acetate in 25 ml. of 50% aqueous acetone (v/v) was added and the mixture kept at 20° for 18 hr. More dichloromethane (250 ml.) was added and the mixture centrifuged. The fractionation of the solution (A) is described below. The solid residue (B) (13.5 g.) was washed successively with dichloromethane and methanol and dried.

Fraction (B) was dispersed in 800 ml. of dimethylformamide at 80° for 10 min. and then at 20° for 18 hr., to produce a viscoelastic solution which was stirred at 20° while 250 ml. of chloroform was added slowly. The resultant highly swollen precipitate, which did not begin to separate until more than 150 ml. of chloroform had been added, was centrifuged, washed successively with chloroform and ethanol, and dried (yield: 12.8 g.; found: N, 11.1; COCH₃, 26.3%).

The soluble fraction (A) from the acetylation reaction was precipitated with light petroleum (b.p. 60–80°), washed with ether, and dried (yield: 13.0 g). A 5.00 g. sample was dissolved in a mixture of 250 ml. of chloroform and 100 ml. of acetone and a small amount of insoluble material (0.25 g.) removed. The soluble portion was fractionally precipitated by gradual addition of ethanol with

TABLE III
Graft Polymerization on Cotton Using Ceric Salt

Monomer	Reaction conditions	ΔW, %	Cuprammonium solubility
Acrylonitrile	Water, 20°	+92.5	Insoluble
Styrene	Water, 20°	+6	Mostly soluble
Styrene	Aqueous emulsion, 20°	+3.5	Soluble
Styrene	Aqueous tert-butanol, 20°	+2	Soluble
Styrene	Aqueous tert-butanol, 60°	+1	Soluble
Vinyl acetate	Water, 50°	+1	Soluble

TABLE IV
Fractional Precipitation of Cellulose Triacetate–Polyacrylonitrile Graft Copolymer

Fraction no.	Solvent composition, %			Precipitate, g.	Nitrogen content, %	—CO·CH₃ content, %
	Chloroform	Acetone	Ethanol			
1	73	27	0	0.25		
2	58	21	21	0.06		
3	47	18	35	2.50	2.8	40.6
4	38	14	48	2.12	0.12	44.7
5	31	11.5	57.5	0		
6[a]	—	—	—	0.06		

[a] Residue after evaporation to dryness.

stirring at room temperature (20 ± 2°). The precipitates were removed by centrifugation and washed with solvent mixtures corresponding to the mother liquors. The results are shown in Table IV.

DISCUSSION

Initiation of Graft Polymerization by Hydroxyl Radicals

Landells and Whewell,[4] in the original paper describing the polymerization of vinyl monomers in viscose with hydrogen peroxide and ferrous salts as initiator, claimed only that polymerization occurred within viscose filaments and that the polymer so produced was not extractable. We have been chiefly concerned, therefore, with proving the presence of a true graft copolymer. The evidence is most nearly conclusive in the case of the polystyrene graft on viscose. Nondegradative acetylation[8] of the modified viscose yielded a product which was completely soluble in chloroform. Subsequent fractional precipitation by n-heptane yielded a fractionation curve with two distinct steps (Fig. 1). Since cellulose triacetate ($\bar{P}_w$ 300) precipitates from 2% (w/v) chloroform solution on addition of <20% heptane and Figure 1 shows no precipitation with less than 50% heptane, it is concluded that the product contains no cellulose triacetate and hence that the modified viscose was grafted on every cellulose molecule. This result is not in agreement with Landell and Whewell's observation[4] that the modified viscose filaments contain polystyrene only near the surface. It is probable, however, with the much higher extents of grafting used in the present work, that more extensive penetration occurs, and results in substitution of the cellulose throughout the filament. The possibility that a small amount of cellulose triacetate was present but was solubilized by the

graft copolymer[9] cannot be entirely excluded, but this type of effect would be expected to cause an opaque sol and, in the precipitation described in Table II, the solution remained perfectly clear with as much as 50% heptane content.

The first step in the precipitation curve (Fig. 1) is attributed to a copolymer of cellulose triacetate grafted with polystyrene, since polystyrene homopolymer ($\bar{P}_w$ 3000) does not precipitate from 2% (w/v) chloroform solution at less than 65% heptane. The optical rotation of the copolymer represents a 51% polystyrene content, while the acetyl content represents 50% polystyrene. The latter figure, which is the more accurate, corresponds to a cellulose–polystyrene copolymer containing 64% polystyrene, and since the original viscose had shown a weight increase of 234% (i.e., contained 70% polystyrene) it seemed probable that the modified viscose also contained either a graft copolymer with more than 64% polystyrene or that some unextracted polystyrene homopolymer was present. Both of these possibilities are necessary to explain the second step in the fractionation curve (Fig. 1). This step occurs in a region where polystyrene begins to precipitate and is due, at least in part, to precipitation of polystyrene homopolymer. Fractions 5–8 (Table II), however, show a decreasing acetyl content and it seems most probable that all of the fractions in this range (65–75% heptane) contain mixtures of polystyrene with a cellulose triacetate–polystyrene graft copolymer having >64% polystyrene. Some almost pure polystyrene (fractions 9 and 10) remained in solution and its presence demonstrates that the extraction procedure designed to remove homopolymer after the grafting treatment was not completely effective.

When a similar acetylation procedure was applied to the acrylonitrile-treated viscose, only a small fraction (12%) of the acetylated material was

soluble. The soluble portion was almost pure cellulose triacetate and its isolation indicates that part of the original cellulose was not substituted with polyacrylonitrile. The remaining material could not be dissolved, but exhaustive extraction with solvents in which it was very highly swollen removed only small amounts of material, and it seems improbable that the product could retain any large quantity of polyacrylonitrile homopolymer. The material remaining after extraction, therefore, probably represents a copolymer of cellulose triacetate grafted with polyacrylonitrile. The nitrogen analysis corresponds to 32% and the acetyl analysis to 33% polyacrylonitrile content, while the mean value of these figures corresponds to 46% polyacrylonitrile in the copolymer before acetylation.

The impregnation of the cellulose sample with ferrous salt before grafting, as described by Landells and Whewell,[4] is not essential since, in an experiment in which this was omitted and the ferrous salt was added instead to the polymerization solution (Table I), the grafting was only slightly less effective. However, the nature of the cellulosic sample is apparently of great importance. In no experiment with cotton did the grafting exceed $\Delta W + 13\%$, and the differences in this respect between cotton and viscose are much greater than would be expected in a consideration of accessibility differences alone. An additional factor, however, which might be expected to favor grafting in viscose more than cotton, is the increased proportion of acidic groups in the former, which would be expected to fix ferrous ions within the filaments and so favor grafting over homopolymerization.

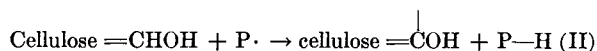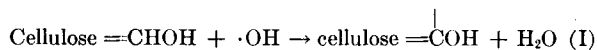## Mechanism of Graft Polymerization Using Hydroxyl Radicals

Hydroxyl radicals are generated by interaction of ferrous ions with hydrogen peroxide as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH$$

$$(\text{or } Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + \cdot OH).[10]$$
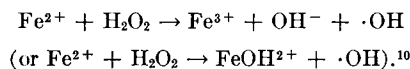
The predominant mode of initiation of homopolymerization of vinyl monomers has been elucidated by Baxendale, Evans, and Park[10] as follows:

$$\cdot OH + CH_2 = CHR \rightarrow HOCH_2 - \overset{|}{C}HR$$
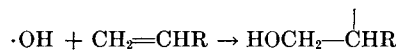
The most probable mechanism of initiation of graft polymerization is the abstraction of hydrogen from cellulose either by hydroxyl radical (I)[12] or by a polyvinyl radical (P·) (II):

$$\text{Cellulose} = CHOH + \cdot OH \rightarrow \text{cellulose} = \overset{|}{C}OH + H_2O \quad (I)$$

$$\text{Cellulose} = CHOH + P \cdot \rightarrow \text{cellulose} = \overset{|}{C}OH + P - H \quad (II)$$

The latter process (the transfer reaction), however, seems much the less likely, for two reasons: first, because our experiments with model compounds[6] have indicated that cellulose itself should be a very poor transfer agent and, second, because when azobisisobutyronitrile was used as initiator (Table I) homopolymer was formed but very little grafting occurred. If graft initiation of the transfer reaction (II) were an important effect, then the grafting process would not be dependent on the nature of the initiator. Furthermore, the azo derivative is known to be a very inefficient oxidant (hydrogen abstractor)[13] and has previously been shown to be ineffective in initiation of graft polymerization in rubber systems.[9] All these arguments suggest that reaction (II) does not play an important part in the grafting process.

The most likely mechanism of graft polymerization is, therefore, reaction (I) followed by

$$\text{Cellulose} = \overset{|}{C}OH + CH_2 = CHR \rightarrow \text{cellulose}$$

$$= C(OH)CH_2 - \overset{|}{C}HR$$
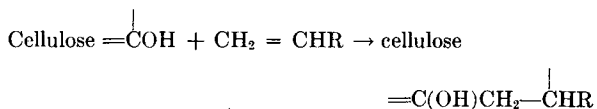
Simultaneous oxidative degradation of the cellulose radical also will occur[11,12] and would be expected to result in tendering of the filaments, either by direct oxidative chain scission or by introduction of alkali-sensitive carbonyl groups.

Initiation of Graft Polymerization by Ceric Salts

The initiation of polymerization of acrylonitrile on cotton by ceric salts in aqueous solution proceeded very efficiently with negligible formation of homopolymer. The experiments described by Mino and Kaizerman[5] referred to water-soluble backbone polymers, or to emulsions of polymers; the present experiments demonstrate that in certain cases this method of graft polymerization can also be applied to insoluble, unemulsified polymers. Attempts to use an insoluble monomer (styrene), however, were unsuccessful (Table III). When a styrene emulsion was used only homopolymer was obtained, presumably because of oxidation of the emulsifier by ceric ion. Similarly, when tert-butanol was added, to bring the styrene into solution, homopolymerization occurred, and it must be presumed that this was due to hydrogen abstraction from the alcohol, although tert-butanol would be expected to lose hydrogen less readily than any

other alcohol.[14] Aqueous solutions of vinyl acetate failed to graft polymerize under conditions that were effective with acrylonitrile.

Acetylation of the cotton grafted with acrylonitrile yielded some cellulose triacetate, indicating that some cellulose molecules were completely unsubstituted (>13.5% of the modified cotton). There was also some indication (Table IV) of a chloroform-soluble graft copolymer containing small amounts of polyacrylonitrile. The greater proportion of the nitrogen-containing material, however, was insoluble in all common solvents with the exception of dimethylformamide in which it formed a viscoelastic solution. The crude fractional precipitation from dimethylformamide solution with chloroform does not exclude the possible presence of a small amount of polyacrylonitrile, but no evidence was found at any stage of the formation of homopolymer. The product is therefore regarded as consisting essentially of a copolymer of polyacrylonitrile grafted on cellulose triacetate. The nitrogen analysis corresponds to 41% and the acetyl analysis to 41.5% polyacrylonitrile content, while the mean of these values corresponds to a cellulose–polyacrylonitrile copolymer with 55.5% polyacrylonitrile.

The viscoelastic nature of the solution of the acetylated copolymer in dimethylformamide is due presumably to intermolecular association of cellulose triacetate chains. Extensive sequences of unsubstituted cellulose triacetate units, which would favor such association, would be expected to result from the absence of graft polymerization in the crystallites of the original cotton. The extensive tendering of the cotton which accompanied the grafting process, would be expected to result from chain scission due to more extensive oxidation of the cellulose by ceric ion.[15]

All microanalyses were performed by Mr. A. T. Masters.

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Synopsis

Landells and Whewell have previously reported that vinyl monomers are polymerized "within viscose filaments" by hydrogen peroxide in the presence of ferrous salts and the polymers are not extractable. Such products, obtained by polymerization of acrylonitrile and styrene in viscose, have now been acetylated. Fractionation of the acetylated products has yielded graft copolymers of polyacrylonitrile and polystyrene, respectively, on cellulose triacetate. It is concluded that hydroxyl radicals initiate graft polymerization of acrylonitrile and styrene on cellulose. A similar approach, utilizing acetylation and fractionation, has been used to demonstrate that Mino and Kaizerman's method of initiation of graft polymerization with ceric salts is applicable to cellulose and results in true graft polymerization.

Résumé

Landells et Whewell ont signalé précédemment que des monomères vinyliques peuvent être polymérisés au sein de filaments de viscose sous l'action d'eau oxygénée en présence de sels ferreux et que les polymères ne peuvent être extraits. De tels produits, obtenus par polymérisation de l'acrylonitrile et du styrène dans la viscose, ont été acétylés. Le fractionnement des produits acétylés donnait des copolymères greffés de polyacrylonitrile et de polystyrène sur le triacétate de cellulose. On peut en conclure que des radicaux hydroxyles peuvent initier la polymérisation de greffage de l'acrylonitrile et du styrène sur la cellulose. La même méthode d'acétylation et de fractionnement a été employée pour prouver que la méthode de Mino et Kaizerman d'initiation de la polymérisation de greffage par des sels cériques est applicable pour le cellulose et forme réellement des polymères greffés.

Zusammenfassung

Landells und Whewell haben vor kurzem berichtet, dass Vinylmonomere mit Wasserstoffperoxyd in Gegenwart von Eisensalzen "innerhalb der Viskosefäden" polymerisiert werden und diese Polymeren nicht extrahierbar sind. Solche durch Polymerisation von Acrylnitril und Styrol in Viskose erhaltenen Produkte wurden nun acetyliert. Fraktionierung der acetylierten Produkte ergab Pfropfcopolymere von Polyacrylnitril bzw. Polystyrol auf Cellulosetriacetat. Es wurde angenommen, dass Hydroxylradikale die Pfropfpolymerisation von Acrylnitril und Styrol auf Cellulose starten. Ein ähnlicher Versuch mit Acetylierung und Fraktionierung wurde durchgeführt, um zu zeigen, dass die Methode von Mino und Kaizerman, die Pfropfpolymerisation mit Cersalzen zu starten, auch auf Cellulose anwendbar ist und eine echte Pfropfpolymerisation ergibt.