

Diazonium Derivatives of Cellulose as Initiators of Graft Polymerization

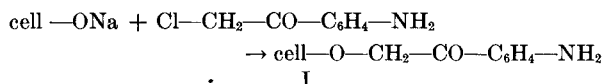
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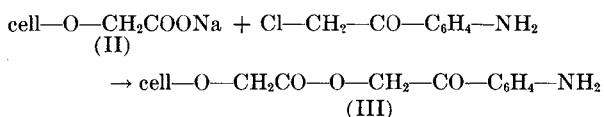
INTRODUCTION

Organic compounds which will degrade to produce free radicals are commonly used to initiate vinyl polymerization. Peroxides, azo- and diazonium derivatives are typical examples. Now if a cellulose derivative of this type can be made to break down to leave a free radical at a point on the cellulose molecule, then any resultant polymerization initiated by such a radical should produce a graft copolymer. This paper describes the use of diazonium derivatives of cellulose in this way to produce graft copolymers.

The production of a diazonium derivative of cellulose requires the preparation of an arylamino derivative. This has been effected in two ways as follows. The *p*-aminophenacyl ether of cotton (I) was prepared by reaction of mercerized cotton with *p*-aminophenacyl chloride according to the method of McLaughlin and Mutton.¹



Next, the partial *p*-aminophenacyl ester of carboxymethyl cellulose (III) was prepared by heating an aqueous solution of sodium carboxymethyl cellulose (II) with a solution of *p*-aminophenacyl chloride in dimethylformamide. Aqueous solutions of (III) when diazotized and coupled with α -naphthol gave a red-brown azo dye.



Both types of cellulose diazonium derivative [derived from (I) and (II)] have now been shown to initiate the graft polymerization of acrylonitrile. Attempts were also made to prepare a third arylamino derivative, cellulose *p*-aminobenzoate, by

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reaction of cellulose derivatives with *p*-aminobenzoyl chloride. The latter reagent, however, readily formed a graft or homopolymer and these reactions are discussed in detail below.

EXPERIMENTAL RESULTS

Vinyl monomers were freed from inhibitor where necessary and fractionally distilled just before use. Unless otherwise stated, all cellulose derivatives were dried at 40°C. and 20 mm. Hg over calcium chloride and then phosphoric oxide.

Carboxymethyl Cellulose *p*-Aminophenacyl Ester (III)

A solution of 25.0 g. of air-dry sodium carboxymethyl cellulose (Courlose P750, DS 0.6) in 1 liter of water was mixed with a solution of 10.0 g. of *p*-aminophenacyl chloride² in 1 liter of dimethylformamide and stirred at 100° for 2 hr. The solution was cooled and added to 2 liters of 1-butanol with vigorous stirring. The resultant precipitate was washed with methanol, dissolved in 750 ml. of water, and reprecipitated with 2.5 liters of ethanol. The final product, when washed with methanol and dried, was a pale yellow powder, 22.1 g., N, 0.44%. The nitrogen content corresponds to DS (ester) ca. 0.07.

The use of an increased proportion of the phenacyl chloride yielded a product of higher nitrogen content (DS 0.6) which was not soluble in water.

Graft Polymerization on the *p*-Aminophenacyl Ether of Cotton

1. Cellulose *p*-aminophenacyl ether (N, 0.64%, DS 0.08) was prepared from scoured cotton sliver,¹ washed with methanol, and dried. A 3.83 g. sample of the fibrous product was covered with 350 ml. of *N*-hydrochloric acid at 0° and 20 ml. of a 10% aqueous solution of sodium nitrite added with stirring. After 5 min. the cotton derivative was

washed twice with ice water and introduced into a solution of 16.5 ml. of acrylonitrile and 0.7 g. of ferrous sulfate heptahydrate in 250 ml. of water, which had been saturated with nitrogen. The mixture was kept under nitrogen at 40° for 18 hr. At this stage a trace of white powdery precipitate was observed and the solution had developed a faintly milky appearance. The fibrous product was washed successively with methanol, hot dimethylformamide (5 × 50 ml., 100°) and methanol, for 15 min. each time, and finally dried. The yield, 8.20 g., corresponded to 114% grafting. The dimethylformamide washings gave no precipitate when diluted with 3 vol. of water. The product was insoluble in cuprammonium hydroxide and dibenzyl dimethyl ammonium hydroxide solutions; the fibers were pale yellow, not brittle, and not readily wetted by water.

2. In a similar experiment, when the ferrous salt was omitted, large amounts of a white powder precipitated from solution. The powder was soluble in dimethylformamide and was presumed to be polyacrylonitrile.

3. An experiment similar to (1), in which the acrylonitrile was replaced by 15 ml. of vinyl acetate, yielded no homopolymer and no increase in weight in the cellulose derivative, but the product was insoluble in cuprammonium hydroxide solution.

TABLE I

Graft Polymerization on the Diazonium Derivatives from the *p*-Aminophenacyl Ether of Cotton

Monomer	Solvent	Temp., °C.	Time, hr.	ΔW , ^a %
Acrylonitrile	Water	40	16	+114
Vinyl acetate	Water	40	20	-2
Styrene	—	80	2	0
Styrene	—	100	2	-19

^a Here ΔW is increase in weight.

4. A 10.16 g. sample of the dry *p*-aminophenacyl ether (I) was diazotized as in (1), washed successively with ice water and methanol (2 × 100 ml., 0°), then pressed dry and added to 80 ml. of styrene. The mixture was degassed, then sealed and heated at 80° for 2 hr. The cotton derivative was washed with boiling benzene, then methanol, and dried. The product (10.14 g.) was straw-colored, still fibrous although obviously tendered, and only partly soluble in cuprammonium hydroxide solution.

5. Experiment (4) was repeated at 100° for 2 hr. to produce a straw-colored powder; yield: 4.03

g. from 5.00 g., which was insoluble in cuprammonium solution.

The results of the above experiments are summarized in Table I.

Graft Polymerization on the *p*-Aminophenacyl Ester of Carboxymethyl Cellulose

1. The ester was ground to pass a 60-mesh sieve and dried. A 1.00 g. sample was stirred with a mixture of 20 ml. of methanol and 5 ml. of 5*N* hydrochloric acid at 0° for 15 min.; then 0.20 g. of sodium nitrite was added. After stirring for a further 5 min. the mixture was centrifuged at 0°, the powder washed with 80% methanol at 0° and then stirred under nitrogen with a solution of 12.5 ml. of acrylonitrile and 0.06 g. of ferrous sulfate heptahydrate in 20 ml. of 80% methanol, which had been saturated with nitrogen. The temperature of the mixture was slowly raised from 0 to 40° over 3 hr. The mixture was kept at 40° for a further 20 hr., then centrifuged and the solids washed successively with 80% methanol, dimethylformamide (at 40° for 3 hr.), and methanol, and dried. The dimethylformamide washings gave no precipitate when diluted with 3 vol. of water. The product, 1.56 g. (found, N 10.0%; 56 parts polyacrylonitrile in 100 parts carboxymethyl cellulose requires N 9.8%), was a buff-colored powder, completely insoluble both in water and in dimethylformamide. It was partly soluble in boiling *N*-potassium hydroxide solution (30 min.) and the residue from this treatment was almost entirely soluble in dimethylformamide.

2. Experiment (1) was repeated with a 50 hr. polymerization at 40°. Yield: 3.466 g. from 1.00 g.

3. A 1.00 g. portion of the cellulose ester was diazotized as in (1) and then treated with 12.5 ml. of acrylonitrile alone, under nitrogen for 20 hr. at 40°. Yield: 1.20 g.; found, N 5.1% (20 parts polyacrylonitrile in 100 parts carboxymethyl cellulose requires N 5.0%).

4. Experiment (2) was repeated, replacing acrylonitrile with 10 ml. of vinyl acetate and washing the product with hot acetone. The product (0.99 g. from 1.00 g.) was insoluble in water.

5. A 1.00 g. sample of the cellulose ester was dissolved in 100 ml. of water, and 50 ml. of *N*-hydrochloric acid was added with stirring, to produce a gelatinous precipitate. The suspension was cooled to 0° and 0.3 ml. of 10% sodium nitrite solution was added. After stirring for 5 min., 48 ml. of *N*-potassium hydroxide solution was added

slowly with stirring at 0° to produce a clear solution. Next, 0.56 g. of ferrous sulfate heptahydrate and 9.4 ml. of acrylonitrile were added; the solution was saturated with nitrogen and then warmed slowly to 40° with stirring under nitrogen. A brown gelatinous precipitate began to separate within 1 hr. at 40°; after keeping at 40° for 20 hr. the precipitate was filtered off, washed with ethanol, and dried. Yield: 1.05 g. (N 0.8%), insoluble in dimethylformamide. No polymer was detected in the filtrate or washings.

The results of the above experiments are summarized in Table II.

TABLE II

Graft Polymerization on the Diazonium Derivatives from Carboxymethyl Cellulose *p*-Aminophenacyl Ester at 40°

Monomer	Solvent	Time, hr.	$\Delta W,^a$ %
Acrylonitrile	Water ^b	20	+5
Acrylonitrile	Aqueous MeOH	20	+56
Acrylonitrile	Aqueous MeOH	50	+247
Acrylonitrile	None	20	+20
Styrene	Aqueous MeOH	50	-8
Vinyl acetate	Aqueous MeOH	50	-1

^a Weight increase.

^b All reactants in solution at beginning of experiment.

Reaction of Cellulose Acetate with *p*-Aminobenzoyl Chloride

Secondary cellulose acetate (DS 2.32) was dried and a 19.7 g. sample dissolved in a mixture of 100 ml. of dry chloroform and 500 ml. of dry pyridine. The solution was stirred at room temperature (20°) while a solution of 20 g. of *p*-aminobenzoyl chloride³ in 150 ml. of dry chloroform was slowly added during 30 min. The temperature of the solution rose to 30° and after standing at room temperature for 18 hr. it had set to a pale yellow gel. The gel was then added, with vigorous stirring, to 1 liter of 95% ethanol and the resultant white flocculent precipitate was washed with ethanol. The product, which was insoluble in chloroform, acetone, benzene, dioxan, and acetic acid, was stirred with 1,1-dimethylformamide at 60° for 15 min. and then kept at 20° for 20 hr. to yield a viscoelastic solution. Nitrobenzene (1 liter) was added slowly with stirring, and the viscous solution filtered through a No. 1 sinter. Ethanol was slowly added to the filtrate with stirring at 20°, to precipitate two fractions as follows (no precipitate was observed until more than 1250 ml. of ethanol had been added).

(a) 1750 ml. of ethanol, 16.7 g. of precipitate, N 1.45%, capacity 31 meq./kg.

(b) 3250 ml. of ethanol (total), 3.2 g. of precipitate, N 1.25%, capacity 28 meq./kg.

Each fraction was washed with a solvent mixture corresponding to the supernatant liquid, then with methanol, and finally dried. The ion exchange capacity was determined by the method of Hoff-pair and Guthrie.⁴

Both fractions (a) and (b) have a considerably lower ion exchange capacity than would be expected for a simple cellulose acetate *p*-aminobenzoate with the observed nitrogen content. The products therefore probably contain poly-*p*-benzamide, probably as a graft copolymer but, possibly, to some extent also as a coprecipitated homopolymer. On the assumption that the fractions are pure graft copolymers and that each sidechain ends in a free amino group, the average DP and DS of the poly-*p*-benzamide sidechains may be calculated as follows. If $C_6H_7O_5R_1R_2R_3$ is the repeating unit of the cellulosic backbone polymer, where $R_1 = H$, $R_2 = (CO \cdot CH_3)_{2-3}$, and $R_3 = [(CO - C_6H_4 - NH)_n]_b$, then

$$n = \frac{10^4 N}{14C} \text{ and } b = \frac{258N}{n(1400 - 119N)}$$

where N is the percentage nitrogen content and C is the ion exchange capacity in meq./kg. On this basis, for fraction (a) $n = 33$, $b = 9 \times 10^{-3}$ and for fraction (b) $n = 32$, $b = 8 \times 10^{-3}$.

Reaction of Soda-Cellulose with *p*-Aminobenzoyl Chloride

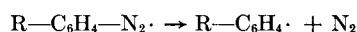
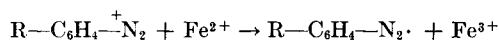
A 2.0 g. sample of air-dried scoured cotton sliver was covered with 5*N* sodium hydroxide for 10 min. at 20°, then pressed and washed twice with ethanol and twice with dry dioxan, the sample being left under solvent 10 min. for each washing. The cotton was finally pressed and then shaken for 2 hr. at 20° with a solution of 2.0 g. of *p*-aminobenzoyl chloride in 100 ml. of dry dioxan. At this stage a trace of a powdery precipitate had formed and the cotton had become yellow. The product was next washed successively with water, methanol, and hot chloroform (in which the precipitated powder was soluble), and then dried. Yield, 2.0 g. The product was a very pale yellow, soluble in cuprammonium hydroxide solution, and not obviously tendered, and gave an intense red color when diazotized and coupled with α -naphthol. The ion exchange capacity was determined⁴ on

samples which had been kept 1 hr. under N-ammonium hydroxide solution and then washed repeatedly with water. Found: N 0.87%, capacity 11.4 meq./kg. This ion exchange capacity would correspond to DS 1.8×10^{-3} for a simple cellulose aminobenzoate, whereas the nitrogen content would correspond to DS 0.11 for the same material. The product therefore probably contains poly-*p*-benzamide either as a grafted copolymer or as occluded homopolymer.

DISCUSSION

Function of Ferrous Ion in Diazo-Initiated Grafting

In the experiment with the *p*-aminophenacyl ether of cotton and acrylonitrile, when ferrous sulfate was omitted considerable amounts of polyacrylonitrile homopolymer formed from solution, whereas in all other experiments in which ferrous sulfate was present homopolymer was never detected in more than trace amount. This suggests that in the absence of ferrous ion, the diazonium cellulose derivative liberates a soluble free radical on thermal degradation whereas, when ferrous ion is present, no soluble free radical is produced. This effect probably is due to the supposed activation of diazonium salts by ferrous ion, which has been interpreted by Cooper⁵ as follows:



In the absence of ferrous ion the diazonium salt may liberate soluble free radicals such as N_2^+ .

Effect of Monomer in Grafting

With both types of cellulose diazonium derivative, grafting occurred readily with acrylonitrile but not with styrene or with vinyl acetate. Difficulties in grafting the latter two monomers, in comparison with acrylonitrile on cellulose, have been reported previously.⁶ Since both acrylonitrile and styrene polymerizations are readily induced by normal diazonium initiators, the absence of grafting with styrene suggests that the hydrated cellulosic radical may be inaccessible to the hydrophobic styrene molecule. This type of explanation, however, is not applicable in the case of vinyl acetate.

Crosslinking of Cellulose Diazonium Derivatives

All cellulose diazonium derivatives were insoluble in all common solvent systems after the grafting process. In some cases this could have been because no common solvent exists for the two parts of the graft copolymer (e.g., cellulose-polyacrylonitrile). In other cases, however, the insolubilization is almost certainly due to crosslinking. This is most obvious in the attempts at grafting styrene or vinyl acetate on cotton *p*-aminophenacyl ether, the product of which showed no increase in weight, but became insoluble in cuprammonium hydroxide solution.

The most probable cause of crosslinking is the combination of the free radicals derived from diazonium groups on neighboring cellulose molecules. This type of reaction would occur more readily in solution than in the solid state and hence, when an attempt was made to graft acrylonitrile on the carboxymethyl cellulose diazonium derivative [from (III)] in aqueous solution, crosslinking predominated, the product became insoluble, and very little grafting occurred. This interpretation is supported by the fact that a similar reaction in a nonsolvent system (80% methanol) produced very extensive grafting.

Proof of Grafting

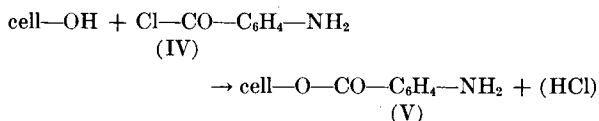
There is no absolute proof that the recorded increases in weight represent true grafting as opposed to occluded homopolymer. However, no more than traces of homopolymer were detected in any reactions in the presence of ferrous ion. Furthermore, it is considered probable that in most cases the extraction procedures used would leave very little occluded homopolymer in the products. Attempts to prepare soluble derivatives for fractionation, by acetylation of the cellulose-polyacrylonitrile products, failed to yield any soluble products, presumably because of crosslinking.

Degradation of Cellulose Diazonium Derivatives

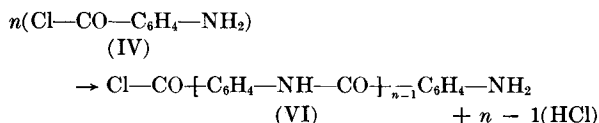
In experiments in which the diazonium chloride derivative of cotton was heated with styrene only at 80 and 100°, extensive tendering occurred; in the latter case the product was no longer fibrous and showed a 19% loss in weight. The degradation which is responsible for these effects probably is due to local concentration of hydrochloric acid in the fibers, resulting from thermal degradation of the diazonium salt. In other experiments, when no obvious tendering occurred, the hydrochloric acid would be largely removed by the aqueous solvent.

Reactions of Cellulose with *p*-Aminobenzoyl Chloride

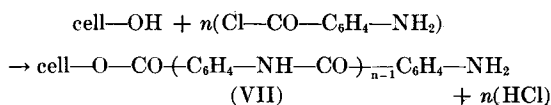
In attempts to produce cellulose *p*-aminobenzoate (V) by reaction of cellulosic hydroxyl groups with *p*-aminobenzoyl chloride (IV) a basic catalyst is



necessary. Unfortunately, the same basic catalysts also induce the polymerization of (IV) to poly-*p*-benzamide (VI).



It is also most probable that some cellulose graft copolymer (VII) is produced.



Because of these competing reactions, this approach proved quite unsuitable for the preparation of (V), but the reaction with partially acetylated cellulose gave a product which is thought to consist, at least in part, of the acetate of the copolymer (VII). The product was subjected to a crude fractional precipitation and showed solution properties to be expected of such a copolymer. The relationship of basic endgroup analysis to nitrogen content suggested an average sidechain length of ca. 30 units and a DS (graft) of ca. 10^{-2} , but the homogeneity of the fractions was not investigated and these figures would not be valid if any homopolymer (VI) were present.

The acyl chloride (IV) also reacted with mercerized cotton to give a product which was either a graft copolymer (VII) or a mixture of cellulose with occluded and nonextractable homopolymer (VI).

References

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Synopsis

Cellulose *p*-aminophenacyl ether (I) has been prepared from cotton and the partial *p*-aminophenacyl ester of carboxymethyl cellulose (III) has also been prepared. Derivatives (I) and (III) have been diazotized and then used to initiate polymerization of acrylonitrile. In the presence of ferrous sulfate the polymerization proceeds to formation of a graft copolymer and no polyacrylonitrile homopolymer was detected. Attempts to graft styrene and vinyl acetate on the same derivatives were not successful. Thermal degradation of the diazonium derivatives leads to insolubilization, probably due to crosslinking by combination of free radicals. Attempts to prepare cellulose *p*-aminobenzoate by reaction of cellulose derivatives with *p*-aminobenzoyl chloride (IV) in the presence of a basic catalyst led to polymerization of (IV) and to the formation of a supposed cellulose-poly-*p*-benzamide graft copolymer.

Résumé

On a préparé l'éther *p*-aminophénacylé de la cellulose (I) à partir de coton et également l'ester *p*-aminophénacylé partiel de la cellulose carboxyméthylée (III). Les dérivés (I) et (III) ont été diazotés et employés ensuite pour initier la polymérisation de l'acrylonitrile. En présence de sulfate ferreux la polymérisation conduit à la formation d'un copolymère greffé; on n'a pas retrouvé d'homopolymère. Des essais de greffage de styrène et d'acétate de vinyle sur les mêmes dérivés n'ont pas donné de résultats. La dégradation thermique des dérivés diazoïques mène à l'insolubilité, due probablement au pontage par combinaison de radicaux libres. Des essais pour obtenir le *p*-aminobenzoate de cellulose par réaction de dérivés de la cellulose avec le chlorure de *p*-aminobenzoyl (IV) en présence d'un catalyseur basique menaient à la polymérisation de (IV) et à la formation probable d'un copolymère greffé de poly-*p*-benzamide cellulose.

Zusammenfassung

Es wurde der Cellulose-*p*-aminophenacyläther (I) aus Baumwolle und auch der partielle *p*-Aminophenacylester der Carboxymethylcellulose (III) dargestellt. Die Derivate (I) und (III) wurden diazotiert und dann zum Start der Acrylnitrilpolymerisation verwendet. In Gegenwart von Eisensulfat bildet sich bei der Polymerisation ein Pfropfcopolymeres und es wurde kein Polyacrylnitrilhomopolymeres gefunden. Versuche, Styrol und Vinylacetat auf die gleichen Derivate aufzupfropfen, waren nicht erfolgreich. Der thermische Abbau der Diazoniumderivate führt zu unlöslichen Produkten, was wahrscheinlich auf Vernetzung durch Kombination freier Radikale zurückzuführen ist. Versuche, Cellulose-*p*-aminobenzoat durch Reaktion von Cellulosederivaten mit *p*-Aminobenzoylchlorid (IV) in Gegenwart eines basischen Katalysators darzustellen, führen zu einer Polymerisation von (IV) und zur masslichen Bildung eines Cellulosepoly-*p*-benzamid-Pfropfcopolymeren.

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