The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

The Bonds in Graft Polymers of Cellulose

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June, 1962

THE BONDS IN GRAFT POLYMERS OF CELLULOSE

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from Lawrence College,
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June, 1962

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SUMMARY

Although the field of graft polymers of cellulose has been of particular interest in recent years, little fundamental work has been reported in the literature. Many recent workers have suggested that a primary chemical bond is involved in the formation of the graft polymer, and insolubility or inseparability of the two components of the graft, in contrast to their physical mixture, has been presented as indicative of chemical grafting. However, because of the unusually intimate intermixing of the two components resulting from the reaction procedures, such evidence does not provide conclusive proof of chemical bonding. It was the purpose of this study to obtain additional evidence in support of the formation of a primary graft bond.

Several graft polymers of polyvinyl chloride on cellulose were prepared using a ceric-ion redox reaction to initiate free radical polymerization on the regenerated cellulose substrate. Several of the substrates contained randomly labeled carbon-14 cellulose to aid in the later identification of the carbohydrate materials. The homopolymer was removed from the graft polymer by extraction with tetrahydrofuran on Soxhlet extractors. The cellulose portion of the graft polymer was hydrolyzed in 72% sulfuric acid to produce a product soluble in tetrahydrofuran, a cellulose nonsolvent. The hydrolyzed graft product was regenerated from the optically clear solution and studied for carbohydrate content. The methods employed were specific radioactivity and chlorine analysis, infrared spectrophotometry, and paper partition chromatography in conjunction with additional hydrolyses.

It was found that the solubilized graft product contained as much as 15% carbohydrates, and subsequent formic acid hydrolyses released a material which was identified chromatographically as being predominantly glucose. In the case of the carbon-14 labeled product, the additional hydrolyses tended to reduce

the carbohydrate content to a constant value. The minimum radioactivity was larger than that representative of the expected one glucose unit per polymer molecule; this is believed to be due to a general resistance of the cellulose in the immediate vicinity of the graft. Physical sorption of carbohydrates was shown to be absent in the hydrolyzed graft products. The homopolymer extracted from the labeled graft polymers exhibited a small but significant amount of radioactivity, indicating a carbohydrate content. This unexpected phenomenon is additional evidence of the graft bond, and is believed to be due to the extraction of part of the graft polymer which had been made soluble by carbohydrate hydrolysis under the extreme conditions of the graft reaction.

It is concluded that a primary chemical bond was formed to link together the two components of the graft polymer. However, considerable protection of the cellulose by the polyvinyl chloride was noted, and it is believed that incasement and entanglement may play a significant role in the unusual properties characteristic of graft polymers.

INTRODUCTION

GRAFT POLYMERS

A graft polymer is a polymer in which a polymeric chain of one monomer is chemically bonded to a polymer molecule of another monomer. The two components are known as the substrate, or backbone, polymer, and the side-chain, or rib, polymer. When the addition takes place at the end of the substrate polymer, the product is referred to as a block copolymer; otherwise, the product is a graft polymer. In both cases the product differs from a true copolymer in that there is no random arrangement of monomers, but rather the configuration looks as though two separate polymers had been linked together.

The conditions of the formation of the graft polymer are often such that portions of either or both component polymers remain ungrafted. The ungrafted substrate polymer is normally given no special name, but the ungrafted portion of the polymer intended as the side-chain is known as the homopolymer. In practice this term is applied to that portion of the side-chain polymer which can be extracted from the graft polymer by a suitable solvent.

GRAFT POLYMERS OF CELLULOSE

The use of cellulose as the substrate polymer allows the use of a large number of chemical and physical methods of preparing a graft polymer. Graft polymers of cellulose are of particular interest because new and often more desirable properties have been noted which have been obtainable in no other way (1-4). Much work has been carried out to investigate the various products available and their possible uses, but very little fundamental work has been reported. In particular, only a small amount of evidence is available to prove that a primary chemical bond actually is involved in the products commonly referred to as graft polymers.

Several excellent reviews of the field of graft polymers of cellulose have been published (1-3); only a brief summary will be presented here. The most basic method of preparing a graft involves chain transfer between a growing polymer chain and another material such as the terminated chain, cellulose, or a cellulose derivative added to the reaction mixture (5-7). However, graft polymers are usually prepared through initiation of free radical polymerization under conditions designed to provide the initial free radical on the substrate material itself.

One of the first chemical methods involved the use of ferrous ions and hydrogen peroxide in a redox method of initiating vinyl polymerization in the presence of cellulose (8-13). Similar methods employ manganous ions and potassium persulfate (11, 12), persulfate alone (12), and, more recently, the ceric-ion redox system (see next section). Cellulose derivatives have been employed (14-16), making use of their ability to break down or to be readily oxidized to form a free radical. High and low energy irradiation has been employed; one successful application from a research standpoint is the use of photon-excited quinoid dyes (17, 18).

The earlier workers made no attempt to show that a chemical graft was involved in their work, and they usually employed the word "deposition" rather than "grafting" (8, 9, 11). Most believed, however, that grafting was quite probable, although Cook (9) suggested that the intimate interlocking of the two polymers might be sufficient to provide solubility protection. Later work, principally by Stannett and his co-workers (7, 12, 18), discussed not only the possible mechanisms of several methods of grafting but also possible methods for proving the existence of the graft bond.

Geacintov, et al. (17, 18) suggested that the action of the UV-excited quinone dye was to abstract a hydrogen ion from one of the carbon atoms of the cellulose chain. The resulting free radical was then capable of entering into vinyl polymerization, thus producing a graft polymer. Through a series of solubility studies it was shown that the graft polymer, unlike a mere physical mixture, was essentially inseparable into its two component polymers. For example, a physical mixture of 27% cellophane and 73% polyacrylonitrile was found to be 75% insoluble in cuprammonium hydroxide solution, while a graft polymer of comparable composition was 89% insoluble. A more conclusive study made use of the solubility of both cellulose and polyacrylamide in cuprammonium and the fact that only the cellulose is regenerated upon acidification. A physical mixture of 40% cellulose and 60% polyacrylamide was compared with a comparable graft polymer by dissolving each in cuprammonium solution and then acidifying. About 35% of the physical mixture was recovered, but 75% of the graft polymer was recovered as the precipitate. This difficulty in separating the components was presented as proof of the chemical graft bond.

Chaudhuri, et al. (7), and others to be discussed in the next section, reported similar results. Chaudhuri also pointed out that the intrinsic viscosity

of the graft polymer was much greater than that of the simple physical mixture, an additional indication of grafting.

Schwab, et al., presented a comprehensive review of the various methods of initiation of graft polymerization (12). In particular, the probable mechanism of the ferrous ion-hydrogen peroxide initiating system was discussed, and again it was suggested that a hydrogen ion is abstracted from a carbon atom which is also attached to one or more oxygen atoms.

CERIC-ION REDOX IN GRAFTING

The use of the ceric ion as a chemical means of initiating graft polymerization is a fairly new developement. Duke and Forist (19) reported in 1949 that the ceric ion formed a co-ordinated complex with glycol groups and that nitrate and hydrogen ions somehow affected the complex formation. Mino and co-workers (20-23) extended this work, reporting that certain ceric salts form redox systems in the presence of organic reducing agents such as alcohols, thiols, glycols, aldehydes, and amines. The ceric ion forms a complex with the reducing agent, and the subsequent disproportionation yields a cerous ion, a hydrogen ion, and a transient free radical capable of initiating vinyl polymerization.

In a study of the oxidation of pinacol, Mino found that one acetone molecule was formed for each ceric ion consumed in a scavenger-free solution. The reaction was accordingly presented as,

$$Ce^{+4} + (CH_3)_2\underset{\underset{HO}{|}}{C}\text{-}\underset{\underset{OH}{|}}{C}(CH_3)_2 \longrightarrow (CH_3)_2\overset{\overset{O}{\|}}{C} + (CH_3)_2\underset{\underset{OH}{|}}{C}\cdot + Ce^{+3} + H^+,$$

$$\text{and } Ce^{+4} + (CH_3)_2\underset{\underset{OH}{|}}{C}\cdot \longrightarrow (CH_3)_2\overset{\overset{O}{\|}}{C} + Ce^{+3} + H^+,$$

with the first reaction rate controlling. The stoichiometry of this reaction

excluded disproportionation of the radicals but not coupling. However, in the presence of a monomer, or radical scavenger, two molecules of ceric ion were reduced per molecule of acetone formed. This was interpreted to mean that at the point of initiation one molecule of ceric ion was reduced and one acetone molecule was produced, and the second ceric ion was reduced as it terminated the reaction by radical oxidation. Thus, the second reaction above is replaced by a similar reaction involving the growing polymer chain as the radical to be oxidized. The stoichiometry of Mino's work indicated that at no time does the free radical transfer to a different molecule; the radical is always attached to the pinacol residue and accordingly no homopolymer should result.

Mino also showed that the length of the new polymer side-chain was proportional to the ratio of initial monomer concentration to initial ceric-ion concentration and that increased hydrogen and nitrate-ion concentration favored increased termination. In addition it was suggested that cleavage of the glycol carbon-carbon bond, as shown above, is the predominant reaction, but some complex formation with secondary hydroxyls might also take place under certain conditions.

The extension of this theory to the analogous system of grafting onto cellulose is fairly simple. The graft should be initiated primarily at the numbers two and three carbon atoms in the anhydroglucose unit (see Fig. 1), and the important variables should include monomer, ceric-ion, hydrogen-ion, and nitrate-ion concentrations. Moreover, it is expected that the graft would be accomplished through the formation of a carbon-carbon bond and little or no ungrafted polymer, or homopolymer, would be formed.

Several workers have reported studies on the use of ceric ion in grafting of cellulose. Kamogawa and Sekiya (24) reported that a peak yield in graft product was obtained at a pH of about 1.5 and that dilute nitric acid was the most

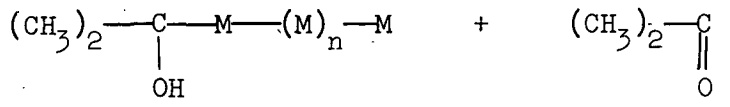
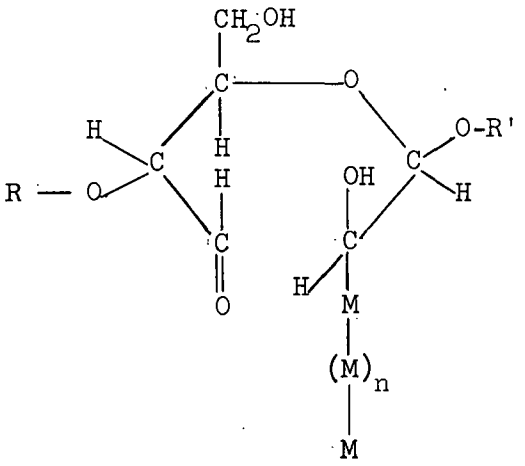


Figure 1a. The Products of the Action of Ceric Ion on Pinacol in the Presence of a Monomer as Suggested by Mino, et al. (20)



(Note: The R groups indicate that the grafted unit may be attached to neighboring glucose units.)

Figure 1b. The Product of the Action of Ceric ion on Cellulose in the Presence of a Monomer, as Deduced from its Action on Pinacol

satisfactory solvent system for the nitratocerate salt employed. Solubility evidence similar to that previously discussed was reported as proof of grafting. Ide and Takayama (25) extended the study of variables using the same system and a variety of vinyl monomers. The yield of graft product was reported to be directly proportional to time, temperature, and nitrate-ion concentration and inversely proportional to monomer concentration. Most of the variables, however, showed a tendency to approach an optimum.

Mino, et al. (26) also reported on the use of the ceric-ion redox system in grafting onto cellulose, but the work was concerned primarily with methods rather than mechanism. Solubility protection was again reported, and in addition a dye study revealed that while most of the polymer remained at the surface of the cellulose some of the polymer almost completely penetrated the fibers. In a similar study, Richards (13) conducted various solubility tests which were interpreted as proof of grafting. He also showed that some ungrafted cellulose and polymer were present in the graft product.

PRESENTATION OF THE PROBLEM

The theory of the chemical reactions involved and the experimental solubility evidence available both suggest that in many cases graft polymers may be obtained through the formation of a primary chemical bond at the point of "grafting." However, there are cases of reasonable doubt in which it is suggested that because of the conditions under which the grafted polymer was formed there may be sufficient tangling and/or physical forces to provide the observed changes in physical and chemical characteristics. More direct evidence on the nature of the graft linkage is required, and it was the purpose of this investigation to provide such evidence.

A specific graft polymer was chosen to represent the typical chemically initiated graft polymer, although results obtained on the nature of the graft bond are not necessarily representative of all graft polymers. The ceric-ion initiator was chosen because it is a relatively specific system and easy to handle; although it is rather new, it seems promising on a commercial scale (26). The monomer chosen was vinyl chloride because its polymer is probably best suited to the reactions to which it was later subjected.

PROCEDURES AND RESULTS

PRELIMINARY STUDIES ON THE PREPARATION OF A GRAFT PRODUCT

A number of preliminary grafting experiments were carried out in an effort to gain experience in the preparation of a graft polymer. At the outset, cellophane was employed as the substrate but was found to be difficult to process; cotton linters were employed thereafter with more satisfactory results.

A general survey of various monomers and chemical means of free-radical initiation was conducted on a limited scale, using the general conditions reported in the initial work with the various systems involved (8, 11). It was found that the sulfatocerate ion was a very poor initiator.

The persulfate and manganous-ion--persulfate systems were also rather poor initiators, but the ferrous-ion--hydrogen peroxide system was normally more satisfactory. In all cases the nitratocerate ion appeared to produce at least some grafting and was clearly the most successful initiator.

Under the conditions employed in these preliminary experiments the monomers styrene and vinyl acetate apparently did not polymerize at all, while acrylonitrile polymerized to such an extent that washing and extracting was essentially impossible. Acrylamide and vinyl chloride were much more controllable monomers, polymerizing to the extent of 10 to 30%, based on the substrate, depending upon the initiator and conditions employed.

PREPARATION OF REACTANTS

The reactants employed in preparation of the desired graft polymer were the monomer, vinyl chloride, the substrate or backbone polymer, cotton linters, and the initiator, the nitratocerate ion. The vinyl chloride was prepared through

the action of sodium hydroxide and methanol on dichloroethane, according to the method of Shalit (27). The details of this procedure are outlined in Appendix I. The substrate was prepared from acetate-grade cotton linters by washing the linters thoroughly in water. The linters were solvent exchanged by redispersing, filtering, and washing the linters first in ethanol and then in benzene. This procedure will later be referred to as "WAN exchanging" (water, alcohol, nonpolar solvent) and the dried product so exchanged as "WAN-dried." The linters were dried from benzene in a 58°C. vacuum oven (ca. 5 mm.), briefly fluffed in a Waring Blendor, and stored in sealed bottles until used. The ceric ion was prepared just prior to each use because of the instability of the nitrate form (28). Sufficient ceric ammonium nitrate (reagent grade, G. F. Smith Chemical Co.) to provide the required volume of 0.5N solution was dissolved in a pH 1.7 nitric acid solution to give a stock solution pH of about 0.6. The final suspension of reactants was accordingly maintained at a pH of approximately 1.5, depending upon the dilution of the stock solution.

REACTION PROCEDURES

Because of the low boiling point of the vinyl chloride monomer (-13.6°C.), it was necessary to employ a tightly sealed reaction vessel in the formation of the graft polymers. Initially, seven stainless steel tubes of about 1/2-liter capacity were employed. These tubes had been previously prepared for use as a "multi-unit" digester by the Engineering and Technology Section, and the details of construction were reported in a recent article (29). However, these reaction vessels were in occasional use in pulping studies, and it soon became apparent that such use led to inhibition or retardation of the graft reaction. Several authors (30-34, 4) have reported the inhibition of free radical polymerization by foreign molecules or radicals, particularly mercaptans, so the apparent retardation in the presence of

minute pulping residues is not very surprising. A new set of reaction vessels was built on the same specifications (29), with the exception that the base was constructed to receive a replaceable rupture disk. The rupture disk employed in this study was designed to rupture at a pressure of 1000 p.s.i. at 400°F. The new tubes were cleaned with a variety of acids and thereafter reserved for use as high-pressure reaction vessels only.

The reaction vessels were charged by adding the cellulose substrate and the amount of water required to bring the final aqueous phase to 300 ml. After some mixing and a soak period of several hours, the vessels were placed in a portable chest-type cooler to which chipped dry-ice was then added. Two hours were allowed for the water to freeze and subcool to -20 to -30°C., and the calculated volume of 0.5N cerate solution was added. Two more hours were allowed for freezing and subcooling, following which the vinyl chloride was added through the use of a previously cooled graduated cylinder. The remaining space in the reaction vessel was flushed with carbon dioxide gas and the lid and screw-cap were tightened with a wrench. The vessels were transferred to a special rack in an oil bath (29) and warmed to 60±2°C. The rack rotated slowly in the oil bath to provide mild agitation of the reactants.

The reaction was allowed to continue for ten hours, a time indicated by previous work (35) to be sufficient for completion of the reaction. The vessels were transferred to a cold-water shower and the excess oil was wiped away. The vessels were then replaced in the dry-ice chest and the contents frozen sufficiently to allow the vessels to be opened without a sudden release of pressure. The vessels were frozen in a horizontal position so that after they were opened and the contents allowed to thaw a channel would be available for the release of pressure at the bottom of the vessel. During the thawing period some evaporation of monomer was

indicated. The thawed contents were filtered on coarse, sintered-glass extraction thimbles, washed with water until the filtrate was no longer cloudy, and then WAN-exchanged and dried in the 58°C. vacuum oven. The weights were recorded as the yield of raw graft polymer.

HOMOPOLYMER EXTRACTION

The practice of the separation of a homopolymer from the graft polymer on the basis of solubility has been discussed by Blanchette and Nielson (36). Probably the best solvent for polyvinyl chloride (PVC) is tetrahydrofuran (THF) (37).

The extraction of the homopolymer was accomplished by placing each product, contained in a sintered-glass extraction thimble, in a Soxhlet extractor on a hot plate. The heat was adjusted to provide a THF reflux rate of less than one drop per second in an effort to avoid overheating of the homopolymer. The extraction was continued for 12 hours, after which time it was considered to be essentially complete (35). The extraction thimbles were allowed to drain and were transferred directly to the vacuum oven. The dried weight was recorded as the extracted yield of graft polymer.

PRODUCT HYDROLYSIS

The product resulting from the foregoing procedures is essentially a graft polymer of polyvinyl chloride on cellulose. The first step in the analysis of this graft polymer in terms of the nature of the graft linkage requires the acid hydrolysis of the cellulose backbone polymer. The recommended procedures for the sulfuric acid hydrolysis of cellulose (38, 39) were followed with only slight modification. To each product was added 160 ml. of cold (10°C.) 72% sulfuric acid, with stirring. The stirring, and maceration if necessary, was continued intermittently for four hours during which time the acid temperature was allowed to rise

to room temperature. The dispersion was then washed into four liters of warm water and the resulting 4 to 5% acid dispersion warmed on a water bath about 12 hours at 60 to 65°C. The diluted acid was allowed to cool to room temperature, and the agglomerated product filtered off on the sintered-glass extraction thimble. This product was water washed and then dried from ethanol in the vacuum oven. The yield was recorded on the hydrolyzed product.

PRODUCT PURIFICATION

In order to establish the purity of the hydrolyzed graft product, it was dissolved in THF following the sulfuric acid hydrolysis. Solubility studies indicated that while glucosides such as lauryl-β-D-glucoside were soluble in THF, glucose and cellobiose were essentially insoluble. On this basis it was expected that dissolution in THF should minimize sorption or physical retention of ungrafted glucose or cellulose fragments. The THF solution of the hydrolyzed graft product was passed through sintered-glass into three volumes of ethanol, which resulted in the regeneration of the graft product. The supernatant liquid was decanted after brief centrifugation. After several washes with ethanol, the product was transferred to a weighing bottle and dried in the vacuum oven. The weight was recorded as the regenerated product yield.

MOLECULAR WEIGHT

The molecular weight of the hydrolyzed graft product was of particular interest as a basis for calculating the expected and, later, actual amount of glucose or cellulose remaining per PVC molecule. This was accomplished through the measurement of the intrinsic viscosity. A 0.4 to 0.5% solution of the product in cyclohexanone was prepared. The intrinsic viscosity was obtained in the usual manner by extrapolation to zero concentration of the plot of concentration versus

specific viscosity per unit concentration (40). Flow times were obtained at 25°C. using an Ubbelohde-type dilution viscometer.

Several workers have reported intrinsic viscosity studies of PVC in cyclohexanone. D'Alelio (41) and Ciampa and Schwindt (42) suggest relationships between intrinsic viscosity and the so-called "viscosity-average" molecular weight but their agreement is not good. The latter workers also reported an intrinsic viscosity--number average molecular weight ($\underline{M}_n$) relationship. Oth (43) reported a similar relationship which also agrees with the results of Breitenbach, et al. (44). Although all three of these intrinsic viscosity versus $\underline{M}_n$ equations differ slightly in their constants, they agree very well in the range of molecular weight employed herein. The relationship recommended by Ciampa and Schwindt (42) was used throughout this study, given for PVC in cyclohexanone at 25°C. as:

$$[\eta] = 2.4 \times 10^{-5} \underline{M}_n^{0.77}$$

OPTIMIZATION OF THE GRAFT REACTION

The variables of the graft reaction include time, temperature, ceric-ion concentration, pH, nitrate-ion concentration, monomer concentration, and cellulose consistency. Time and temperature were held essentially constant at values shown by previous work to be satisfactory (35). The pH and nitrate-ion concentration were employed herein as functions of the ceric-ion concentration because of the use of the standard stock solution. A series of graft reactions were carried out to determine the relative importance of and the relationships between the three remaining major variables, consistency and monomer and ceric-ion concentration.

The reaction conditions and general results of the optimization study are tabulated in Appendix II. The first two groups of experiments were based on a statistical design, but the results were not statistically significant; however,

it is evident that the general trend is as might have been predicted. Thus, increased consistency and ceric-ion concentration and decreased monomer concentration all tend to decrease the molecular weight, and all three variables directly affect the product yield. In both cases, only the ceric-ion concentration seems to have an appreciable effect in the ranges studied.

The third group of experiments reported in Appendix II explored the practical limits of the variables of the graft reaction. Apparently, a monomer charge of about 1% or below does not provide sufficient monomer activity to result in significant polymerization. Similarly, increasing the ceric-ion concentration above about 0.20N leads to increased and eventually dominant degradation of the substrate cellulose rather than initiation of the graft.

The experiments reported in groups four and five of Appendix II indicated that the optimum and limiting reaction conditions are somewhat different for cellulose regenerated from cupriethylenediamine (cuene) than for the original acetate-grade cotton linters. The results suggest that the ceric-ion concentration should be decreased to one-half in order to avoid degradation of the regenerated substrate. On the basis of these experiments, it was decided that the desired combination of high yield and minimum PVC molecular weight would best be provided at the levels, 0.10N ceric ion and 3% vinyl chloride, when the substrate cellulose has been regenerated.

PREPARATION OF A RADIOACTIVE GRAFT PRODUCT

Randomly labeled carbon-14 cellulose prepared from artichoke stem was obtained from Nuclear Research Chemicals, Inc., Orlando, Florida. The material as received had the general appearance of semichemical wood pulp. The raw labeled cellulose was subjected to a chlorine dioxide bleach and caustic extraction. The

carbon-14 cellulose, 8.2 grams, was macerated in a mortar and pestle and then covered with cold 5% chlorine dioxide solution. Sodium bicarbonate was added as a buffer, and additional chlorine dioxide and buffer were added over a period of 24 hours as needed to maintain the faint yellow color of the chlorine dioxide. A total of 250 ml. of chlorine dioxide solution was employed. The liquid was decanted after centrifugation and the cellulose washed with several volumes of water. To the bleached product were added 100 ml. of 10% sodium hydroxide solution. After 40 minutes the extraction liquor was decanted following centrifugation and the cellulose was washed first with water and then with 150 ml. of acetic acid. The resulting bleached and extracted labeled cellulose was washed to neutral pH and WAN-dried. The yield was 1.95 grams, about 24% of the original cellulose charge.

A portion of the purified labeled cellulose was mixed with acetate-grade cotton linters for use as a labeled substrate. The required intimate mixing was obtained by dissolving the two cellulose samples in cuene and regenerating. The detailed procedures employed are given in Appendix III. Exactly 0.950 gram of the labeled cellulose was dispersed in cuene and stored in the refrigerator for several days with occasional agitation. The cotton linters (4.55 g.) were dissolved in a separate cuene solution and the two solutions were mixed by shaking together under nitrogen. The mixed cuene solution was passed through a fritted-glass filter under vacuum to remove that portion of the labeled cellulose which was cuene-insoluble. The filtrate was immediately regenerated by pouring into dilute nitric acid. The regenerated cellulose was filtered and washed until the blue color and faint copperlike taste were no longer detectable. A moisture sample was taken and the substrate cellulose stored at about 90% moisture in a sealed bottle; the substrate was not dried to avoid a loss of accessibility.

A radioactive graft product was prepared by grafting onto the labeled substrate cellulose using the methods previously outlined. At the same time two control products were prepared using regenerated cotton linters. The reaction conditions are given in Table I. Following the hydrolysis step, the hydrolyzed product B was redispersed in the radioactive (C) hydrolyzate and then warmed for several hours, cooled, filtered, and washed in the usual manner. Product B thus prepared was designed to provide a measure of the physical sorption of radioactive glucose by product C. A flow chart is presented in Fig. 2 representing the various stages of work-up and analysis of the radioactive product, C, and in most cases of the control products as well. It should be noted that after sulfuric acid hydrolysis the graft polymer is no longer referred to as such but rather as a hydrolyzed graft product. In subsequent discussion the term product, as in "product A", will refer to the hydrolyzed graft product, and in some cases the term will be modified to indicate the completion of later stages of study.

The group six products reported in Appendix II were prepared as a pilot series for the above products. Although the reaction conditions and specific product properties differ somewhat from those given in Table I, the general results of the analyses of these two groups are in agreement. The results discussed herein are representative of only the one group of products, but their reproducibility should be noted.

Two homopolymers were also prepared by extraction with and regeneration from THF and studied along with products A, B, and C. One homopolymer was obtained upon extraction of the labeled graft polymer and is referred to as the product C homopolymer. The other homopolymer sample was obtained from the combined extracts of several nonlabeled graft polymers and is referred to as a general homopolymer.

TABLE I

REACTION CONDITIONS AND RESULTS FOR THE RADIOACTIVE AND CONTROL GRAFT PRODUCTS

	Nonlabeled Control Graft Products		C-14 Labeled Graft Product
Experiment	A	B	C
Ceric-ion conc., N	0.10	0.10	0.10
Vinyl chloride, %	3.0	3.0	3.0
Cellulose, g.[a]	5.000	5.000	5.000[b]
Raw polymer, g.	10.247	10.127	8.871
Extracted polymer, g.	7.867	8.222	7.137
Hydrolyzed product, g.	1.367	1.430	1.009
Regenerated product, g.	1.056	1.166	0.800
Molecular weight, $\underline{M}_n$	27,600	27,600	35,000

Note: All concentrations are based on 300 ml. total aqueous phase.

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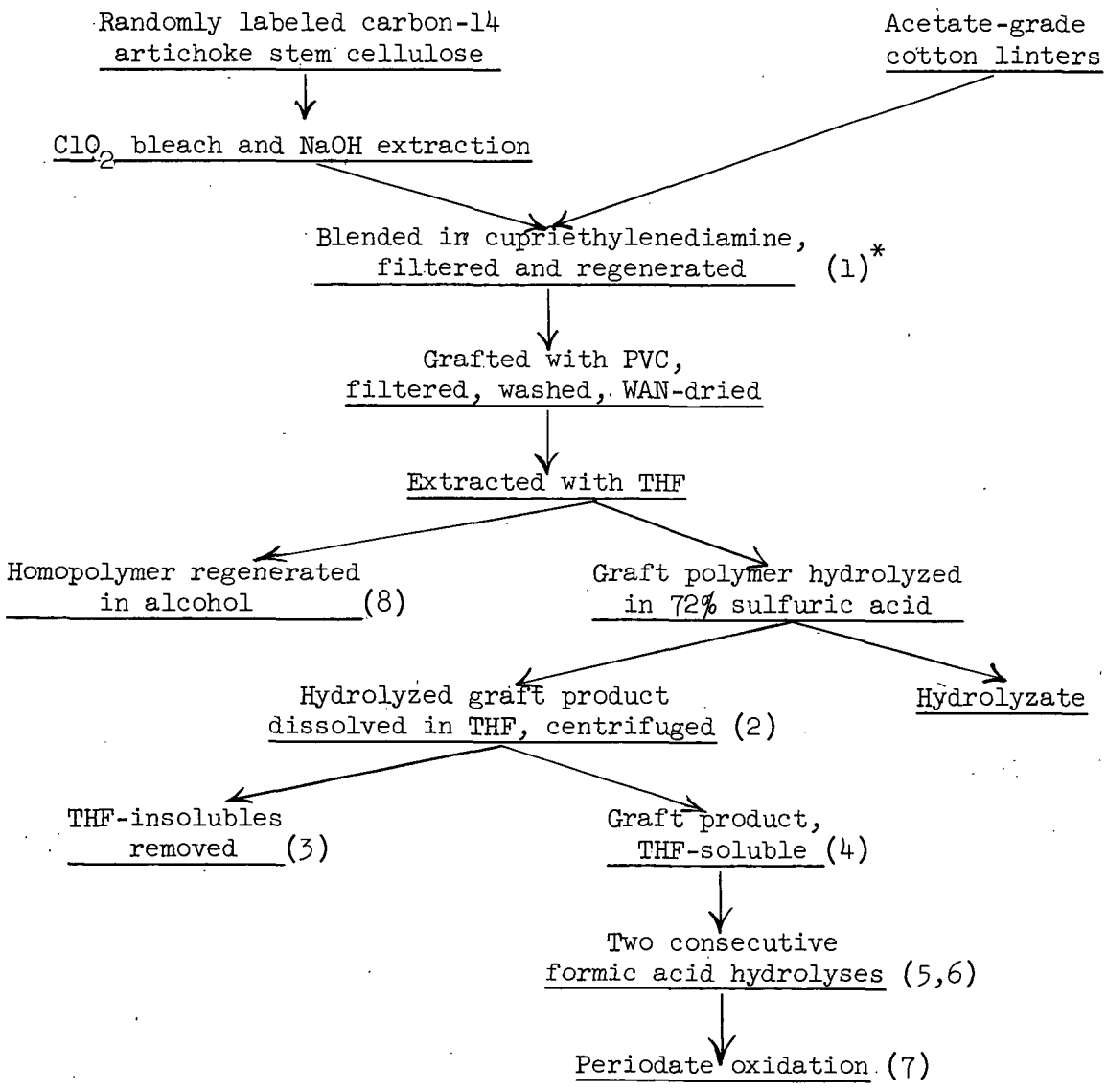
[a] All substrates were regenerated from cupriethylenediamine solution.

[b] Randomly labeled carbon-14 cellulose.



* The numbers in parentheses represent the Table II item number under which the analytical results for the numbered product appear.

Figure 2. Flow Diagram of the Preparation of the Radioactive Graft Product

ANALYSIS OF THE RADIOACTIVE GRAFT PRODUCT

PREPARATIVE PROCEDURES

Upon dissolution of the hydrolyzed and regenerated graft products in cyclohexanone for determination of the molecular weight, it was noted that product C was not completely soluble. The intrinsic viscosity was determined in spite of the cloudiness of the solution, and the corresponding molecular weight ($\underline{M}_n$) is recorded in Table II, item 2. The product was further purified by redissolving it in THF and then centrifuging at about 20,000 times gravity. The THF-soluble portion was shown to be capable of passing a 2500 A, polypore filter without a significant loss of material. The two fractions, THF-soluble and THF-insoluble, were regenerated in ethanol and dried. The insoluble portion represented about 10% of the total product C. The $\underline{M}_n$ of the THF-soluble portion was obtained and is reported in item 4 of Table II.

Because the products apparently contained a relatively large amount of cellulose, a secondary hydrolysis was undertaken. The products were no longer wetted by water, so the hydrolysis was carried out in THF solution. About 200 mg. of each product were dissolved in 100 ml. of THF and 50 ml. of 98% formic acid were added, bringing the polymer just to the point of precipitation. The reactants were refluxed for 18 hours in a 90°C. water bath. The bath was then cooled to 75°C. and the condensers were removed from the flasks containing the reactants. Exactly 50 ml. of 2.0$\underline{N}$ sulfuric acid were pipetted into the reactants, causing precipitation of the polymer. After 8 hours the water bath was cooled to room temperature, following which the hydrolysis products were transferred to centrifuge bottles and separated by centrifugation. The supernatant liquid was set aside for chromatographic analysis. The precipitate was washed to pH 6 with successive volumes of water and dried from ethanol in the vacuum oven. On a portion of this product a second formic

TABLE II

CHARACTERIZATION OF THE HYDROLYZED GRAFT POLYMERS AND SEVERAL HOMOPOLYMERS

Carbon-14 Labeled Materials	$\overline{M}_n$	Yield, %[a]	Activity, c.p.m./mg.	Chlorine Content, %[b]
1. Substrate cellulose	--	--	8900	--
2. C, total	35,000	--	2970(33.3)[c]	--
3. C, THF-insoluble	--	--	10,500	--
4. C, THF-soluble [d]	36,000	--	1320(14.8)	52.3(7.8)
5. C-sol., after first formic acid hydrolysis	34,000	94.0	585(6.6)	54.5(3.9)
6. C-sol., after second formic acid hydrolysis	--	96.1	430(4.8)	55.3(2.5)
7. C-sol., after periodate oxidation	--	--	425	55.3
8. C homopolymer	26,000	--	96(1.1)	55.7(1.8)
9. C homopolymer, after formic acid hydrolysis	--	96.0	40	55.4
Nonlabeled Materials				
10. Cotton linters	--	--	0	--
11. A	27,000	--	1	52.2(7.9)
12. A, after formic acid hydrolysis	--	95.4	1	54.6(3.7)
13. B	27,000	--	2	52.0(8.3)
14. B, after formic acid hydrolysis	--	95.0	< 1	54.4(4.0)
15. General homopolymer	20,000	--	0	55.4(2.3)
16. Gen. homopolymer, after formic acid hydrolysis	--	96.8	0	55.8

[a] These figures represent the yield of product recovered from the formic acid hydrolysis as based on the weight of product charged.

[b] The chlorine content of pure PVC would be 56.7%.

[c] The figures in parentheses represent the percentage cellulose calculated from the adjacent activity or chlorine content value.

[d] The specific rotation of 0.112 g. of this product in 3.0 ml. (25°C.) of THF was zero as measured in the sodium-D light in a 2-dm. tube.

acid hydrolysis was performed in an identical manner. The product yields at the several stages are included in Table II. The yields are not necessarily indicative of the carbohydrate material removed, however, because of varying mechanical losses.

RADIOACTIVITY

The relative carbon-14 content of the various products was determined through wet combustion and proportional counting of the resulting carbon dioxide according to standard methods. This procedure is discussed in more detail in Appendix IV. The specific activity, that is, counts per minute per milligram (c.p.m./mg.), of the cellulose substrate was determined and used as a basis for calculating the cellulose content of the various products. Sample calculations are also presented in Appendix IV. The results of the radioactivity analyses are recorded in Table II. These results are reproducible to ±5% of the gross count. Based on the recorded molecular weights, the C, total (Table II, item 2) count represents a cellulose content of about 72 glucose units per PVC chain. In the next three stages of work-up of product C (items 4, 5, and 6) the counts represent 33, 14, and 10 glucose units per PVC molecule. The intrinsic viscosities from which were calculated the $\underline{M}_n$ values recorded in items 2, 4, and 5 were 0.76, 0.79, and 0.75 dl./g., respectively; these viscosities are very close, in the range of experimental error, even though the apparent carbohydrate content changed considerably. The C homopolymer also exhibited radioactivity, representing 2.9 glucose units per molecule. However, very little if any physical sorption of radioactive glucose was indicated by the activity of product B.

CHLORINE CONTENT

The chlorine content of the various products was determined using a variation of the method of Fertig (45). A 4 to 6-mg. sample was weighed exactly

on a piece of ashless filter paper cut into a one-inch square with a one-inch long "tail" at one corner. The paper was folded over the sample twice in each direction and clamped into a platinum wire grid suspended from a ground-glass stopper. A 500-ml. iodine bottle had been previously prepared by placing in it 10 ml. of a 30% hydrogen peroxide solution and bubbling oxygen through the peroxide for one minute. The tail of the filter paper was ignited and the glass stopper quickly thrust into the iodine bottle. The bottle was inclined somewhat during the combustion to present a dry side wall to any unburned material that might fall through the grid. The bottle was shaken vigorously after the combustion was completed and allowed to stand an additional 3 minutes. The stopper was then removed and rinsed and the bottle placed on a hot plate. In a period of 5 minutes the peroxide solution was brought to a light boil and the vapors were occasionally flushed out with oxygen. The bottle was removed from the heat, and the solution was cooled slightly by the addition of washings. The absorbed hydrogen chloride was titrated with 0.01N sodium hydroxide to a standard methyl red end point. The method was standardized against commercial PVC and 2,4-dichlorophenoxyacetic acid.

Several authors have discussed the effect of heat and light on PVC (46-48). At temperatures near 100°C. and above, hydrochloric acid is stripped from the molecule in a zipperlike manner, producing conjugated double bonds and thus a highly colored product. For this reason the temperatures were held to a minimum during the work-up of the products, as in the lower temperature in the second stage of the sulfuric acid hydrolysis (65°C. rather than 100°C.). Roff (37) reported that PVC is relatively unaffected by most acids but is slowly decomposed by concentrated oxidizing acids. However, Cornell (35) noted that little, if any, loss of chlorine during the hydrolysis step could be detected by a chlorine analysis. The additional precaution of lowering the hydrolysis temperature was made to avoid compounding the effect of the acid and unnecessary heat. Most of the products

exhibited very little color, being a faint tan. The results of the chlorine analysis, as reported in Table II, suggest that a small amount of chlorine may have been lost; these results range from 52.0 to 55.8% chlorine with the theoretical maximum being 56.7%. The accuracy of the procedure is only about ±1.0% however. For convenience of comparison of the chlorine content results with the radioactivity results, the glucose or carbohydrate content represented by the original figure is given in parentheses.

CHROMATOGRAPHY

The products were tested chromatographically for the presence of glucose or similar sugars both before and after the secondary, or formic acid, hydrolysis (cf. Preparative Procedures). Because of the sulfuric acid present in the product hydrolyzates, barium carbonate clarification was required. This was accomplished by adding the stoichiometric amount of barium carbonate required to remove the sulfate ion (49). The resulting barium sulfate was removed by centrifugation and the solution reduced to 50 ml. on a rotating evaporator.

In all cases the product solutions were spotted on Whatman no. 1 chromatographic paper in sufficient volume to represent a minimum of 400 μg. of solid material based on the original weight of product charged to the solution. When the sugar content was expected to be low, 800 μg. were spotted. The control samples employed were glucose and cellobiose, usually spotted in 10 or 20 μg. amounts. The developers were ethyl acetate (8):pyridine (2):water (1) and ethyl acetate (9): acetic acid (2):water (2). The spray reagent employed was p-anisidine hydrochloride prepared by dissolving 1.0 g. of the reagent in 10 ml. of water and adding 20 ml. of 95% ethanol and 170 ml. of n-butanol. The color of the spots was developed by heating the chromatogram for 15 minutes in a 105°C. oven. The chromatograms were inspected under both natural and ultraviolet (UV) light.

None of the graft product or homopolymer solutions in THF exhibited a distinguishable sugar content before hydrolysis; all of the chromatograms were absolutely clean with the exception of the control spots. The chromatograms of the hydrolyzates, in contrast, all exhibited at least a suggestion of glucose and some other mobile material. The general results of the chromatographic analyses are summarized in Table III. In the case of the general homopolymer hydrolyzate, only a faint indication of a sugar content was noted. The relative intensities of the spots from the control product hydrolyzates, A and B, were about equal and the spots were somewhat heavier than for the general homopolymer. The C homopolymer chromatograms indicated an intermediate sugar content, the spots being faint but apparent. The radioactive product (C) hydrolyzate exhibited considerable sugar content; the component identified as glucose suggested a glucose content of about 10% as based on relative spot size and intensity under UV. In contrast, the A and B glucose spots were estimated at 1 to 2% of the total product weight. Using $\underline{R_f}$ values as a guide, the spots in addition to glucose were tentatively identified, in decreasing order of apparent content of material, as pentoses (probably arabinose and xylose) and cellobiose or uronic acids. Some of this material may be representative of degradation products from the formic acid hydrolysis, however. The basic developer usually produced only glucose spots in sufficient resolution and intensity for identification, whereas the acid developer produced the more complete separation described. Qualitative measurements using a thin-window Geiger tube indicated that all of these spots were radioactive, although the glucose spot exhibited the highest activity.

A sample of the purified artichoke cellulose was hydrolyzed in sulfuric acid and the hydrolyzate analyzed chromatographically. Glucose was noted to be the principal constituent, but 5 to 10% xylose and traces of galacturonic acid, galactose, arabinose, mannose, and rhamnose were also suggested. Although the

TABLE III

RESULTS OF THE CHROMATOGRAPHIC ANALYSES
FOLLOWING FORMIC ACID HYDROLYSIS

Hydrolyzate Source	Relative Spot Intensities [a]		
	Glucose	Pentoses [b]	Misc. [c]
General homopolymer	0.5	0.5	0.1
Product A	2	0.8	0.5
Product B	2	0.8	0.5
Homopolymer C	0.8	1	0.5
Product C	10	4	2

[a] The relative intensities were rated from 0 to 10, with the most intense spot being assigned the rating of 10.

[b] The term pentose is used to represent the general R_f range which includes xylose and arabinose.

[c] The miscellaneous grouping includes apparent uronic acids and unidentified spots and streaks.

substrate cellulose contains only about 15% of this material, this analysis indicates that some nonglucose material is to be expected in the product hydrolyzates.

PERIODATE OXIDATION

Periodate oxidation of product C was attempted after the second formic acid hydrolysis. A combination of the methods of several authors (38, 50-52) was employed.

Exactly 88.0 mg. of product C, taken after recovery from the second formic acid hydrolysis, were dissolved in 50 ml. THF. To this solution and a THF blank

were added 5.0 ml. of 0.01M aqueous sodium metaperiodate from a pipet. Samples were taken for analysis of zero-time periodate content and the solutions were stored in the dark at room temperature for 24 hours. At the end of this period samples were again taken for periodate content. This analysis was accomplished by the method outlined by Smith and Montgomery (53). A 5.0-ml. aliquot of the reaction mixture was added to a mixture of 1.0 g. sodium bicarbonate, 1.0 ml. of 20% aqueous potassium iodide, and 5.0 ml. of 0.004N sodium arsenite. The mixture was swirled and allowed to stand 20 minutes, then titrated with 0.002N iodine solution. The natural yellow iodine end point was employed because the starch indicator did not function properly.

The results of the periodate titration were essentially identical for each sample, including the blank. The maximum change, or error, noted in the titer was representative of about 3% of the periodate charged, while the minimum expected use of periodate based on one oxidation site per polymer molecule was more than 5%. The polymer was regenerated by the addition of sulfuric acid as in the formic acid hydrolysis and tested for activity and chlorine content. The results as reported in Table II indicate no loss of cellulose in the product.

INFRARED SPECTRA

The infrared (IR) spectra of products A, B, C (THF-soluble), and C after formic acid hydrolysis, and the general homopolymer and product C homopolymer, were obtained using a Perkin-Elmer model 21 recording spectrophotometer. The samples were powdered and pressed into potassium bromide disks. The spectra are reproduced for comparison in Fig. 3. The homopolymer spectra differ from those reported by Billmeyer (54) and others for PVC only at 2.9 and 5.8 microns. These differences may be interpreted as the addition to the molecule of hydroxyl groups and carbonyl groups, respectively (55). The other spectra show additional absorption

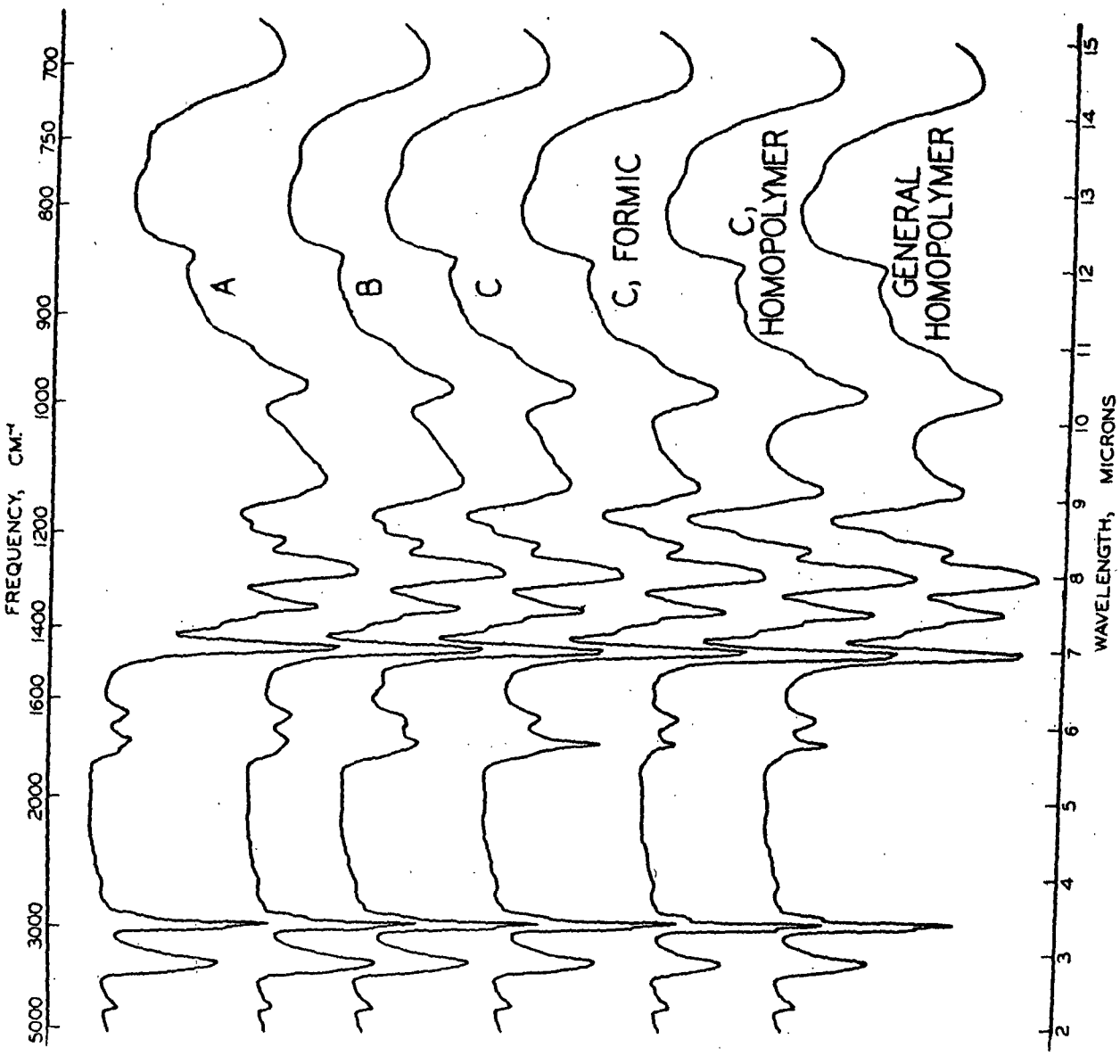


Figure 3. IR Spectra of Several PVC Homopolymers and Hydrolyzed Graft Polymers

between 8.5 and 10 microns, which is quite characteristic of the addition of cellulose to the molecule. In general, the change in the relative absorption in these three regions corresponds to the change in cellulose content indicated by the activity and chlorine content for the various polymers. These comparisons must be made only qualitatively, however, because the concentration of polymer in the KBr pellet was not held exactly constant. Of additional interest is a possible absorption peak at about 6.1 microns on each spectrum which may be indicative of unsaturation. This is somewhat clouded by a possible moisture content in the samples or pellet which would also cause some absorption in this area.

The spectrum of a mixture of 5% regenerated cotton linters and 95% general homopolymer was also obtained. The results were inconclusive in terms of the effect of the cellulose on the IR absorption of PVC. The only change in the spectrum was a slight broadening of the hump at 9 to 10 microns; there was no definite increase in absorption as noted for the control polymers, even though the cellulose content is believed to be comparable. However, this may be due in part to the difficulty in preparing a homogeneous sample from the mixture.

LIGHT SCATTERING

Light-scattering measurements were made on product A using a Brice-Phoenix 1937 series photometer (56). Because the cyclohexanone solvent exhibited some fluorescence in the blue light region (4360 A.),the measurements were made in the green region (5460 A.) The weight average molecular weight ($\underline{M}_w$) so obtained, corrected for dissymmetry, was 3.4 million. The weight average root-mean-square end-to-end separation, calculated from dissymmetry measurements and assuming a poly-disperse coil and that ($\underline{M}_w/\underline{M}_n$) = 2, was 1140 A. These results agree well with those of Doty, et al. (57) who reported agglomeration of PVC to give excessively high light-scattering results. It was suggested that the "cluster" was very nearly the same length as the single molecule and thus must be very closely coiled.

The polymer end-to-end separation was calculated from the intrinsic viscosity, using the universal constant discussed by Flory (58), to be about 250 A. Using a number average molecular weight, the ratio between this length and the theoretical maximum is about 0.15. This ratio does not reflect excessive coiling of the polymer.

DISCUSSION OF RESULTS AND CONCLUSIONS

The radioactivity of the labeled product at the various stages aids considerably in our understanding of the nature of the graft polymer. The most important result of this study is the fact that the activity indicates that a rather large (about 15% of the molecule by weight) portion of the material recovered from an optically clear solution in a cellulose nonsolvent was cellulose or carbohydrate material. This unexpected result requires that the cellulose be bound very strongly to the PVC. The release of carbohydrates from the graft product upon further hydrolysis and the apparent approach to a minimum activity indicates that the cellulose portion is not totally incased but rather must be bound through a primary chemical bond.

Additional information on the nature of the graft polymer is provided by the fact that the apparent minimum activity is at least six to eight times higher than that expected for the single glucose unit predicted. This may have been caused by one or more of several possible interfering phenomena. In any study involving isotopes there is a possibility that the reaction is influenced by the presence of the slightly heavier isotopic species. However, the effect of the isotope is usually to lead to sluggishness in the reaction. Any isotope effect should therefore lead to a lower activity rather than the higher activity experienced.

A higher resistance of the artichoke portion of the substrate could play a role in producing the unexpectedly high minimum activity of the labeled product. That the original artichoke sample contained noncellulosic impurities is apparent from the loss of 75% of its original weight during bleaching and extraction. There is no assurance that all of the impurities were removed in this step. However, the filtration of the cuene solution prior to regeneration should have limited the

substrate impurities to cuene soluble, carbohydrate materials. The activity of the THF-insoluble portion of product C was seen in Table II (item 3) to be about 18% higher than that of the substrate cellulose itself. This suggests a higher resistance to hydrolysis of the labeled material, but probably indicates a further purification of the substrate rather than an over-all higher resistance of the artichoke cellulose.

The repeated hydrolyses required to reduce the activity of the product suggest a third interfering phenomenon which might account for the apparent minimum activity at such a high count level. As suggested by several previous workers (9, 35), there may be sufficient intimate intermingling of the two component polymers or incasement of the cellulose by the PVC to provide chemical protection. It appears that there is a large amount of tangling and that the PVC penetrates and partially incases portions of the cellulose substrate. The incasement of the cellulose in the vicinity of the graft by neighboring PVC molecules would probably be quite sufficient to retard the rate of hydrolysis so that under normal conditions the cellulose appears to be resistant to hydrolysis. This would also lead to increased solubility of a partially hydrolyzed product because the solvent-repelling carbohydrate portions would not be "seen" by the solvent, or at least they would be "seen" in lesser amounts than are actually present.

The chlorine analyses corroborate the general trend of the activity studies. The cellulose or glucose contents calculated by difference from the chlorine contents are in most cases 50 to 60% of those calculated from the product activities. This may be indicative of a higher resistance to hydrolysis of the artichoke material, but it also suggests another interesting phenomenon. Because of the addition of the lower molecular weight artichoke cellulose to the cotton linters and the longer time required in handling the cuene solution, the particle size of this substrate was apparently less than that of the regenerated linters

substrate used for products A and B. The polymerization is believed to take place along the surface of the cellulose molecule, so the smaller particle may have led to a tighter grafted particle and accordingly to increased protection of the cellulose during hydrolysis. However, the chlorine analyses are not accurate enough to confirm or deny this possibility on the basis of the comparison of chlorine contents between the products. The primary value of the chlorine analysis is in corroboration of the trend of the cellulose content during the hydrolysis steps. In addition, the high chlorine contents are gratifying in that they suggest that very little attack on the PVC polymer has occurred. It should be pointed out that these high results possibly suggest a higher cellulose content than is actually the case; it has been noted that the chlorine content of several of these products decreased slightly with time, so it is possible that all of the products lost a small amount of chlorine. The results are seen to be approximately correct, however, when it is considered that one glucose unit would represent about 0.6 or 0.7% carbohydrate material.

The chromatographic analyses serve to clarify several points in question. Of primary interest is proof of the presence of a tightly bound cellulosic material in the portion of the various products which were soluble in the PVC solvent, THF. The content of carbohydrate material in each of the products is further indication of the protection afforded the substrate in the vicinity of the grafted PVC. The fact that this material can be hydrolyzed further indicates that its solubility in the cellulose nonsolvent may be due to the primary chemical linkage rather than total incasement in the polymer. The higher content of hydrolyzable material in the labeled product (see Table III, page 28) provides some evidence for the greater protection by the PVC for the labeled substrate than for the nonlabeled substrate on the basis of particle size alone (p. 34).

The IR spectra provide an interesting qualitative corroboration of the cellulose contents of the several graft products. The presence of absorption attributable to the addition of carbonyl groups also suggests that the proposed mechanism is correct. It will be remembered (cf. Introduction) that the ceric-ion initiator is believed to produce a carbonyl group at the same time as the free radical is produced upon the cleavage of the glycol bond between carbon atoms 2 and 3 of the anhydroglucose unit. This evidence agrees with the picture of the graft product suggested in Fig. 1. It should be noted that the product in Fig. 1 does not indicate unsaturation of the PVC chain. Although the chlorine analyses suggest a loss of chlorine and the present PVC theory suggests that such a loss involves the loss of hydrogen chloride and the introduction of unsaturation, the IR spectra do not indicate significant unsaturation.

The IR spectra of products A, B, and C are of additional interest in their extreme similarity. Since the products A and B were prepared on acetate-grade cotton linters, this comparison suggests that the product C substrate was relatively free of impurities. The IR spectrum of the physical mixture of the two polymers is inconclusive, primarily because it is difficult to know whether the sample is truly representative of such a mixture.

The failure of periodate to produce any significant additional oxidation was not entirely unexpected. A certain amount of protection or hindrance had previously been noted in the case of hydrolysis; if the protection were sufficient to hinder hydrolysis, it should certainly hinder the introduction of the much larger periodate ion. Also, the initiation step produces periodate-type cleavage and thus the more accessible sites may have already been oxidized by the initiator. The agreement between the activity, chlorine content, and periodate consumption in indicating that no reaction took place attests to the stability of the PVC portion of the product as well.

Probably the most surprising result of this study, at least at the outset, was the presence of a significant quantity of homopolymer and its apparent cellulosic content. Much of the homopolymer obtained was probably due to the failure to remove all of the air from the reaction vessels; this is in agreement with the fact that the amount of homopolymer varied from essentially none to roughly 5%, as determined by extraction and regeneration of the homopolymer. The cellulose content of the homopolymer as indicated by the several analyses suggests a second reason for obtaining what has been defined as homopolymer. The low pH, elevated temperature, and relatively long duration of the graft reaction no doubt led to hydrolysis or some other mode of degradation of the cellulose substrate similar to that noted in the optimization studies. Although the reaction conditions ultimately employed were more mild, there was probably a small degree of degradation that still took place. In a small number of cases, this degradation was sufficient to solubilize some of the graft polymer, resulting in the apparent cellulose content of the homopolymer. This removal of cellulose during the extraction step further attests to the presence of the primary chemical bond.

The studies on the shape and size of the PVC molecule are not highly accurate but are extremely interesting. It was pointed out (p. 24) that the apparent molecular weight, or rather the intrinsic viscosity, does not change significantly with decreasing cellulose content. This suggests that the cellulose portion of a product does not contribute much to the product viscosity. The light-scattering study yielded results similar to those of Doty (57) in terms of the agglomeration of a number of molecules to give a high apparent molecular weight. Doty explained this and other data as representative of very tight coiling of the agglomerate or "cluster," and that the cluster just happens to be short enough to give reasonably correct viscosity data. The present data suggest that the coiling of the cluster is not sufficient to provide the low viscosity results; it is rather

believed that the agglomeration is due to the charge of the molecule and that the shear in the viscometer capillary may be sufficient to break up at least part of the agglomeration. The relatively poor reproducibility of the individual viscometer flow times might also suggest such an explanation.

Considerable evidence has been presented that a primary chemical bond links the two component polymers in the particular graft polymer studied. The total solubility in a cellulose nonsolvent of a PVC polymer containing as much as 15% cellulose and the apparent absence of simple physical sorption is strong evidence of the graft bond. The subsequent hydrolysis of the cellulose portion to an apparently limiting minimum shows that the bond is probably primary, ruling out simple incasement as the sole cause.

It is believed that the PVC polymer provides some protection for the cellulose substrate because of intermeshing and incasement, and it is probable that in many cases this physical intimacy contributes to the chemical and physical properties characteristic of graft polymers. In the case of the hydrolyzed graft polymer, however, entanglement cannot play such a significant role; the retardation of hydrolysis is probably due primarily to steric problems in the immediate vicinity of the primary chemical graft bond.

The extension of the theory of Mino, et al., to the cellulose system as presented in the introduction is believed to be essentially correct. Little evidence has been presented on the mechanism involved, but no deviations from the theory have been noted. Thus, in addition to the foregoing conclusions based on the weight of evidence from this study, it is also presumed that the graft polymer involves the formation of a carbon-carbon bond rather than an ether bond. This, however, remains to be proved, as does the belief that the graft takes place on the number 2 or 3 carbon atom of the anhydroglucose unit of the cellulose substrate.

RECOMMENDATIONS FOR FUTURE STUDIES

The major interest at present in graft polymers of cellulose rests with the preparation of a commercial product; a number of laboratories are already concerned with such pursuits. The most pressing need in the research field, however, is not to lengthen the list of apparent graft polymers and their properties but rather to broaden our knowledge of the present products. This investigation is a very small portion of, or perhaps only an introduction to, the vast amount of fundamental work required for a better understanding of the nature of graft polymers.

Probably the greatest need at the present time is an increased knowledge of the initiators being employed and, in this particular case, of the ceric-ion initiator system. The mechanism of the ceric-ion--cellulose reaction remains unproven; even though the general theory (cf. Introduction) appears to be adequate under normal conditions there are several questions yet to be answered. The major problem encountered herein was the degradation of the substrate cellulose at higher initiator concentrations and, particularly, the apparent increase in the severity of degradation with the increase in accessibility of the substrate. Because the optimum ceric-ion concentration and the point of appearance of degradation varied in the same manner, it is apparent that increased initiation is directly related to increased hydrolysis. However, the pH of the reactants changes very little during the reaction, so it may be that the degradation is caused by a secondary reaction which becomes more important with increasing accessibility and ceric-ion concentration. It is clear that the effect of the variables on the initiating reaction must be determined more accurately in terms of yield, side-chain molecular weight, and cellulose degradation, or more broadly, in terms of initiating and terminating efficiency. A study of the mechanism should also include an indication

of the sites of oxidation and grafting on the anhydroglucose unit, and the effect of using substituted or otherwise modified cellulose substrates.

It is recommended that in future work involving the use of labeled cellulose great care be taken to obtain a cellulose type which will introduce as few variables of its own as possible. Perhaps bacterial cellulose would be the most satisfactory, particularly if it could be obtained in the never-dried or at least freeze-dried state.

The next phase of study should be to expand the proof of bonding to indicate whether the bond is a carbon-to-carbon, as the theory predicts in this and many other cases, or an ether linkage. This step is expected to be much more difficult because of the low rates of reaction and hindrance demonstrated in this study. Perhaps such proof could best be obtained through degradation of both polymers to obtain an identifiable compound of very low molecular weight or the degradation of the side-chain rather than the substrate polymer. In both cases the choice of polymers to be degraded will be a very important step.

On a larger scale the major goal is to expand this type of work to other methods of preparation of graft polymers; there is no reason to believe that these results can necessarily be extrapolated to include the products of other systems. In each case, the approach should be first to prove the mechanism of the reaction under study, then to go on to proof of bonding and bond type. In some cases the proof of mechanism may be sufficient to indicate grafting since the existence of grafting has been proven. In many cases, however, the proof of bonding may constitute, or at least corroborate, proof of mechanism.

ACKNOWLEDGMENT

The author wishes to gratefully acknowledge the assistance and suggestions of his thesis advisory committee: J. W. Green, N. S. Thompson, and Kyle Ward, Jr. The author also wishes to express appreciation to J. V. Koleske for his help in the light-scattering studies and Lowell Sell for preparing the IR spectra.

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APPENDIX I

PREPARATION OF THE VINYL CHLORIDE MONOMER

The vinyl chloride monomer was prepared by the method of Shalit (27). The apparatus consisted of a 3-neck, one liter flask fitted with a mercury seal and electric stirrer, a glass-stoppered, 200-ml. dropping funnel with a side-arm for vacuum release, and a condenser system. The condenser system included a reflux condenser, a 90° adapter, a second condenser with a small flask at the bottom for collection of condensate, and a second adapter leading to a flask maintained at -70°C. in a dry-ice--acetone bath. In the reaction flask were placed 80 g. of sodium hydroxide pellets and 150 ml. of methanol. The mixture was warmed in a heating mantle to 60°C. with slow stirring and the heat was adjusted to maintain a good reflux rate without introducing "bumping" of the visible vapors. A total of 250 ml. of dichloroethane was added over a period of several hours from the dropping funnel at a rate of about 100 drops per minute.

When the reaction was essentially complete the reaction flask was replaced by the cold receiver containing the condensed vinyl chloride. As the receiver and its contents slowly warmed to room temperature the monomer was redistilled into a clean receiver. The monomer, in a yield of about 90%, was then transferred to a plastic bottle in a metal can and stored at -40°C. in a dry-ice chest until needed.

APPENDIX II

SUPPLEMENTARY REACTION CONDITIONS AND RESULTS

Exp. No:	Ceric-ion Concn., N	Vinyl Chloride, %	Cellulose Charge, g.[a]	Raw Polymer, g.	Extracted Polymer, g.	Hydrolyzed Product, g.	Regenerated Product, g.	$\overline{M}_n$
1A	0.20	5.0	5.000	6.308	5.713	0.517	0.461	29,100
1B	0.20	5.0	3.000	4.372	3.680	0.440	0.412	34,100
1C	0.20	3.0	5.000	6.058	5.396	0.391	0.343	26,300
1D	0.20	3.0	3.000	4.888	3.757	0.636	0.583	36,100
1E	0.02	5.0	5.000	7.082	5.356	0.366	0.359	68,400
1F	0.02	5.0	3.000	4.976	3.263	0.272	0.262	66,000
1G	0.02	3.0	5.000	6.321	5.292	0.319	0.305	48,700
1H	0.02	3.0	3.000	4.467	3.212	0.225	0.217	57,900
1I	0.11	4.0	4.000	7.996	5.287	1.143	1.079	45,800
1J	0.11	4.0	4.000	8.787	5.126	0.956	0.917	57,900
1K	0.20	4.0	4.000	5.686	4.833	0.556	0.513	34,100
1L	0.02	4.0	4.000	5.793	4.301	0.299	0.298	67,400
2A	0.11	3.0	4.000	7.332	4.981	0.844	0.754	39,400
2B	0.11	3.0	4.000	6.346	5.021	0.899	0.838	31,900
2C	0.11	3.0	4.000	7.811	5.120	0.925	0.900	26,700
2D	0.11	3.0	4.000	7.556	4.985	0.819	0.776	30,400
3A	0.20	5.0	5.000	6.851	6.037	0.653	--	--
3B	0.20	5.0	3.000	4.344	3.648	0.538	--	--
3C	0.20	1.0	5.000	5.155	5.167	0	--	--
3D	0.20	1.0	3.000	2.931	2.939	0	--	--
3E	0.02	5.0	5.000	7.082	5.353	0.282	--	--
3F	0.02	5.0	3.000	4.767	3.373	0.303	--	--
3G	0.02	1.0	5.000	4.992	5.028	0	--	--
3H	0.02	1.0	3.000	3.013	3.024	0	--	--
3I	0.20	1.33	5.000	5.667	5.663	0.080	0.071	8,900
3J	0.20	1.83	5.000	6.809	6.157	0.478	0.419	30,200
3K	0.20	2.33	5.000	7.332	6.342	0.718	0.641	34,900
3L	0.30	3.0	5.000	6.155	5.686	0.340	0.293	51,200
3M	0.50	3.0	5.000	4.734	4.731	0	0	--
3N	1.00	3.0	5.000	4.271	4.240	0	0	--
4A	0.20	2.0	5.000[b]	6.664	5.682	0.634	0.555	51,200
4B	0.20	2.0	5.000[b]	6.747	6.086	0.583	0.420	28,100
5A	0.20	2.0	5.000[b]	--	4.726	--	trace	--
5B	0.20	3.0	5.000[b]	--	4.692	--	trace	--
5C	0.10	2.0	5.000[b]	--	6.907	--	0.340	22,400
5D	0.10	3.0	5.000[b]	--	7.372	--	0.649	26,300
5E	0.30	2.0	5.000[b]	--	4.641	--	0	--
5F	0.30	3.0	5.000[b]	--	4.447	--	0	--
6A	0.20	2.0	5.000	6.865	5.748	0.737	0.639	53,500
6B	0.15	1.67	5.000[c]	6.953	5.946	0.780	0.660	55,000
6C	0.20	2.0	5.000[c]	5.838	5.734	0.196	0.109	37,600

Note: All concentrations are based on 300 ml. total aqueous phase.

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[a] Cotton linters unless otherwise noted.
[b] Regenerated from cuene solution.
[c] Regenerated, carbon-14 labeled cellulose.

APPENDIX III

REGENERATION OF CELLULOSE

Cellulose was dissolved in cuene by essentially the same procedure used in viscosity determinations. For example, 15 g. of cellulose were steeped for two hours in 750 ml. of cold water. Then, 150 ml. of 1.0M cuene (Ecusta Paper Division, Olin Mathieson Chemical Corporation) were added and the container flushed with nitrogen and placed in the refrigerator. The contents of the container were agitated frequently over a period of 12 hours, following which an additional 600 ml. of cuene were added. The final solution, roughly 1% in cellulose and 0.5M in cuene, was agitated by shaking and replaced in the refrigerator.

When solid material was still evident after 24 hours, the solution was filtered under vacuum through a coarse, sintered-glass filter. The solution was regenerated by pouring slowly, with vigorous stirring, into 2N nitric acid. The nodules were broken up with the stirring rod, and the regenerated cellulose was filtered and washed on a sintered-glass funnel. About three volumes of water were required to remove the characteristic color and taste of the copper salts.

APPENDIX IV

RADIOACTIVITY ANALYSES

The activities of the cellulose substrate and the labeled products were determined using the wet combustion and proportional carbon dioxide counting methods outlined by Van Slyke and his co-workers (59-61). The use of the apparatus presently available has been previously discussed in considerable detail by Most (62), Daniel (63), and Russo (64). Reference should be made to these authors for details of the mechanics as well as the theory of the analysis.

The substrate sample sizes were limited to weights providing a total count of less than 100,000 c.p.m. The product samples were limited to 15 or 16 mg. in order to avoid the drop-off in counting efficiency at high partial pressures of carbon dioxide described by Russo (64). Several checks were also made to ensure that the proportional counting tubes exhibited the reported counting rate plateau in the range of 3500 to 3800 volts.

The various samples were "burned" for a total time of 8 minutes, including 2 minutes of "sweep" time, in the prescribed fuming sulfuric-phosphoric acid mixture. The resulting carbon dioxide gases were absorbed in an alkaline hydrazine solution and the other gases were expelled. The absorbed carbon dioxide was released through the addition of lactic acid and collected in the counting tube. The collection was accomplished by evacuating the counting tube and the connecting glassware and then passing the gas through a cold-trap to remove the water vapor and into the counting tube, the tip of which was immersed in liquid nitrogen. The counting tube stopcock was closed, and the tube was warmed to room temperature. The contents of the counting tube were brought to atmospheric pressure by the careful addition of methane. The tube was then connected to a Nuclear-Chicago model 182 scaling unit for counting of the relative radioactivity. The total counting time

in all cases was 10±0.05 minutes. The background count of each proportional counting tube was obtained by carrying through the entire procedure without charging a sample to the combustion tube. Subsequent counts were then corrected for the corresponding background count.

The following sample calculation represents the method of determining the product activity and cellulose content:

Substrate sp. act. = 8,900 c.p.m./mg. cellulose

= 8,900/0.445 = 20,000 c.p.m./mg. carbon

Product 6C, THF-soluble:

$\underline{M}_n$ = 36,000

For one carbon atom/PVC molecule,

$$\frac{12}{36,000} \quad (20,000) = 6.67 \text{ c.p.m./mg. PVC/carbon.}$$

For one glucose unit/PVC molecule,

6(6.67) = 40 c.p.m./mg. PVC/glucose.

Actual count = 1320 c.p.m./mg. PVC

Glucose represented = 1320/40 = 33 units/PVC

Cellulose content: 1320/8900 = 0.148, or 14.8%

Or, 33(162)/36,000 = 0.148