

## Grafting onto Cellulose and Cellulose Derivatives Using Ultraviolet Irradiation\*

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### INTRODUCTION

Graft copolymers are prepared by reacting a monomer with a previously formed polymer. Many different properties of the substances may be combined in the final graft copolymer to give different and useful properties not exhibited by either of the materials alone. Various methods of grafting are reported in the literature and adequate review articles are available.<sup>1-3</sup>

The methods of grafting can be roughly divided into three categories:

(1) Polymerization of a monomer in the presence of a polymer, where growth is initiated by chain transfer; (2) polymerization of a monomer in the presence of a polymeric backbone containing reactive groups (These groups are capable of being activated by heat, light, or other means and thus initiate monomer at these sites.); (3) irradiation methods, which can be further subdivided into (a) high energy irradiation and (b) low energy irradiation. (The latter method usually requires the use of a photosensitizer.)

Relatively few methods for grafting monomers onto cellulosic and other natural high polymers have been described in the literature.

Mino and Kaizerman<sup>4</sup> have found that certain ceric salts form effective redox systems when coupled with certain reducing agents, such as alcohols and amines. The reaction proceeds via a single electron transfer step, resulting in cerous ion and partially oxidized reducing agent in free radical form. Thus, if the reducing agent is a polymer molecule like polyvinyl alcohol or cellulose and the oxidation is carried out in the presence of vinyl monomer, a graft polymer will be produced. Undesirable homopolymerization does not occur, since the initiating free radical is formed exclusively on the polymeric backbone.

Borunsky<sup>5</sup> has reported a method for grafting

\* Presented at the Second Cellulose Conference, Syracuse, N. Y. May 1959. A fuller account of the earlier part of this work may be found in *Makromol. Chem.*, **36**, 52 (1959).

various vinyl monomers onto cellulose, cellulose derivatives, natural rubber, and other polymers. The polymeric backbone is first oxidized in an aqueous solution of ozone and then reacted with a vinyl monomer at 50°C. A graft copolymer of carboxymethyl cellulose containing 30% acrylonitrile by weight has been prepared by this method.

Restaino,<sup>6</sup> as well as Magat and Tanner,<sup>7</sup> have used  $\gamma$ -irradiation to graft various vinyl monomers onto cellulose, cellulose acetate, rayon, filter paper, and wool. Restaino, for example, obtained graft polymers of methyl methacrylate on filter paper and cellophane (86 and 57% graft, respectively).

Oster and Shibata,<sup>8</sup> Cooper and Fielder<sup>9</sup> have employed ultraviolet light with suitable sensitizers to graft vinyl monomers onto natural rubber.

In the present work, several vinyl monomers have been grafted onto cellophane and other materials, using low energy (ultraviolet) irradiation and an anthraquinoid dye sensitizer. Many anthraquinone dyes, when adsorbed on cellulose, will undergo reaction with the cellulose in the presence of light. This process, called "phototendering," is initiated by a photoexcited dye molecule, which abstracts a hydrogen atom from the cellulose.<sup>10</sup> The free radical which is thus produced on the cellulose backbone has been found capable of initiating vinyl polymerization.

### EXPERIMENTAL

The polymeric film is placed in a 20 × 200 mm. test tube which contains about 20 ml. of a monomer, solvent, and dye solution. The tube is placed 3 in. from the light source, and a heat-absorbing filter is interposed. After the irradiation period, the film is removed and washed with the solvent for the homopolymer until a constant weight is obtained. As much as 365% increase in weight of the film due to graft may occur. Homopolymer is also formed during the irradiation process.

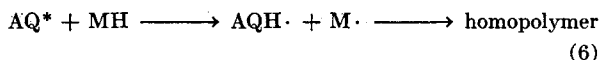
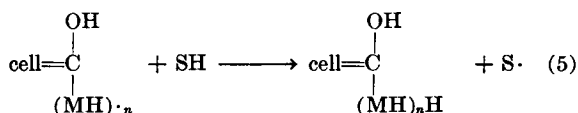
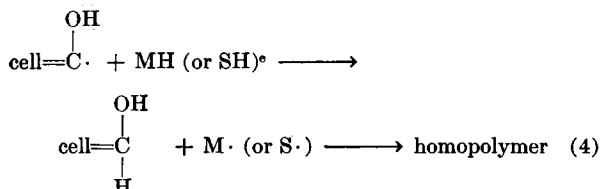
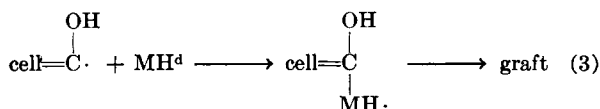
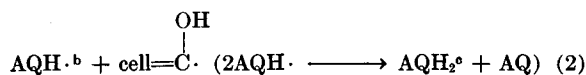
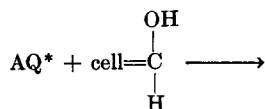
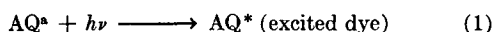
The light source is a General Electric AH<sub>4</sub> 100-w. mercury vapor lamp enclosed in a water cooled housing. The total energy received by the sample was measured with a calibrated thermopile and Leeds & Northrup amplifier and found to be  $3.2 \times 10^4$  ergs/cm.<sup>2</sup>-sec. From the relative energy distribution (fraction of total energy emitted at each wavelength), of a similar lamp<sup>11</sup> and the optical density of the irradiated solution, it is estimated that approximately  $10^{14}$  quanta/cm.<sup>2</sup>-sec. are absorbed. However, this figure is a crude estimate, since the energy distribution depends on many variables and no two lamps have exactly the same energy distribution.

## RESULTS AND DISCUSSION

### Proposed Mechanism

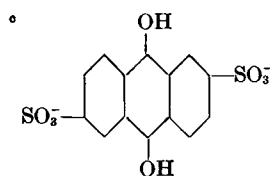
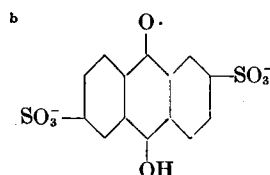
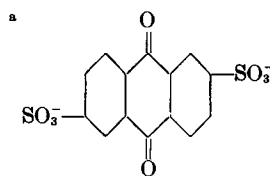
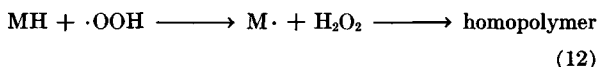
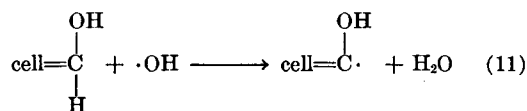
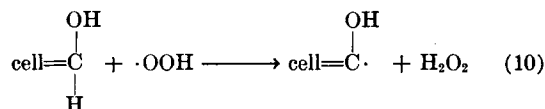
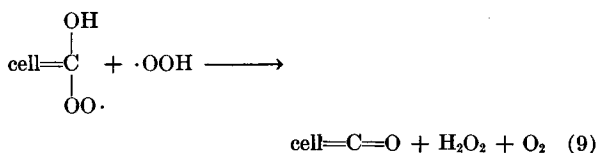
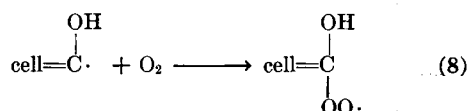
A plausible mechanism for phototendering has been proposed by Bolland and Cooper.<sup>10</sup> It is reasonable to assume that grafting arises through a similar mechanism. The presence of oxygen (if not excessive) has been found to enhance rather than inhibit the extent of grafting. The following mechanisms in the absence of, as well as in the presence of, air are proposed.

#### (A) Absence of Oxygen



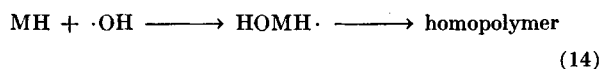
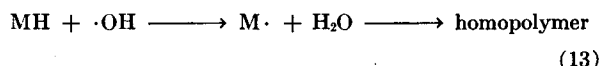
The entire process is initiated by step (1). Grafting is initiated by (2) and (3). Homopolymerization can be initiated by (4), (5), and (6). Under the conditions of our experiments, the reaction (6) appears to be predominant, since the amount of homopolymer produced is large and is not dependent on the presence of cellulose. The dye molecule may be regenerated by the bimolecular combination of two dye semiquinones.

#### (B) Presence of Atmospheric Oxygen



<sup>d</sup> Monomer.

<sup>e</sup> Solvent, possible hydrogen donor.



It is apparent that in the presence of oxygen the mechanism is more complicated since the number of possible reactions increases.

The following differences appear to be important when oxygen is present.

1. The amount of dye AQ capable of further hydrogen abstraction may be increased by step (7).

2. The possibilities for initiation of grafting are increased by steps (10) and (11) but decreased by step (8).

3. The number of ways leading to homopolymerization is increased by reactions (12), (13), and (14).

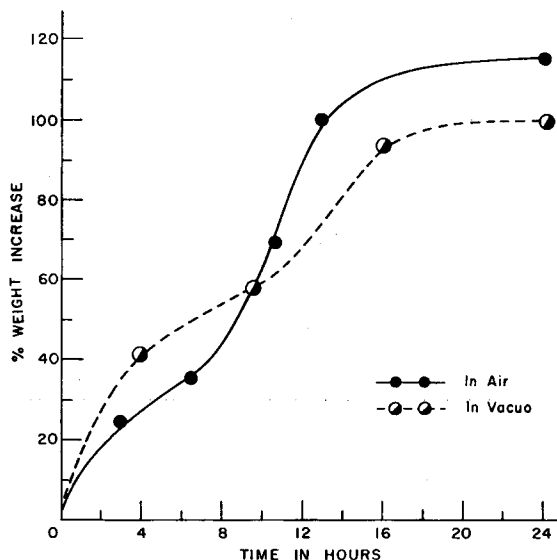


Fig. 1. Effect of irradiation time on amount of grafting.

The extent of monomer conversion is up to three times as great in the presence of air as when carried out *in vacuo*. It has also been found that the amount of grafting in presence of air is twenty per cent higher after a twelve hour irradiation period has been exceeded (Fig. 1). When air is bubbled through the reaction mixture, both grafting and homopolymerization are inhibited. In the mechanism proposed, this would indicate that under these conditions reactions (8) and (9) predominate to inhibit grafting. Homopolymerization is inhibited by a similar mechanism.

## Monomer-Solvent Systems

Certain monomer-solvent systems yield better results with cellophane than others.

A 20% aqueous solution of acrylamide at a 0.01M concentration of dye gives a weight increase of cellophane in the order of 150%, based on its original weight. (Twenty-four hour irradiation period in presence of air.) Films of cellulose derivatives, which are soluble in organic solutions can be grafted easily in this system. For example, acrylamide has been grafted onto cellulose acetate and ethyl cellulose.

A 45% solution of acrylonitrile, 45% of dimethylformamide, 10% water, otherwise same conditions as above, will lead to a 120% weight increase. Replacing the acrylonitrile by other monomers, keeping other conditions the same, leads to lower grafting as is shown in Table I, where the amount of grafting is expressed in mg. per cm.<sup>2</sup> of film. These units were chosen because it was found that a change in the film dimensions leads to an amount of grafting that was not proportional to the total weight of the film but more nearly proportional to its surface area. However, this is only approximately true; the experimental evidence obtained so far does not suffice to conclude that the grafting is exclusively a surface reaction.

TABLE I  
Grafting of Monomer onto Cellophane in Standard Mixture,<sup>a</sup>  
*in vacuo* (Twenty-four Hour Irradiation)

Monomer	Grafting mg./cm. <sup>2</sup>
Acrylonitrile	2.6
Methyl methacrylate	0.8
Styrene	0.3
Vinyl acetate	0.1

<sup>a</sup> Forty-five per cent monomer, 45% dimethylformamide, 10% water, and 0.01M dye concentration.

Replacing about two-thirds of the acrylonitrile by styrene leads to a 365% weight increase irradiating in presence of air, other conditions being equal. The dependence of grafting on the molar ratio of acrylonitrile to styrene is shown in Figure 2. It is interesting to note that when the water content of the reaction mixture is decreased from 10 to 3.8% (replacing by dimethylformamide), the extent of grafting drops considerably. During the reaction at 10% water content, the cellophane film swells to approximately 1.3 times its original dimensions; this is not the case when the water concentration is 3.8%.

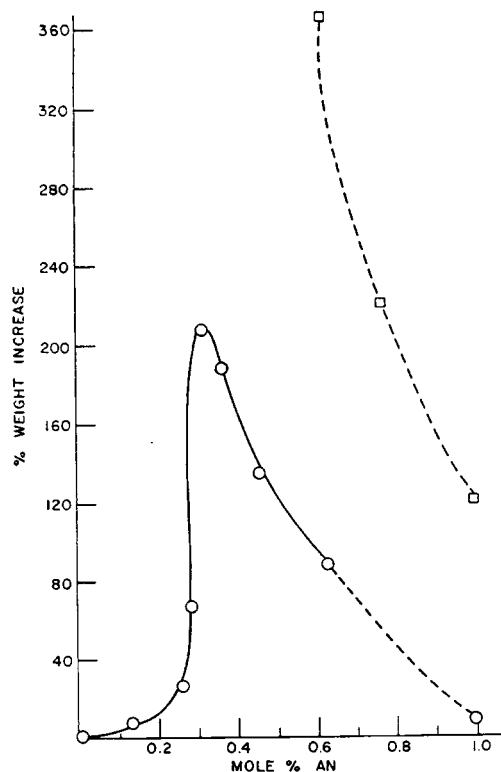
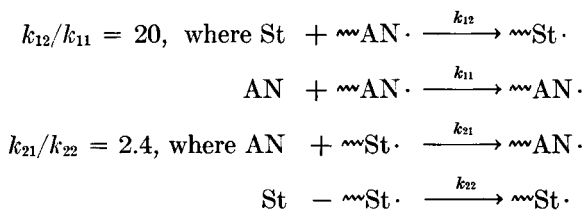


Fig. 2. Effect of acrylonitrile:styrene ratio on grafting: (○) 3.8% water, 57.5% total monomer; (□) 10% water, 54% total monomer.

In the region indicated by the broken lines in Figure 2, the film disintegrates into numerous smaller pieces as a result of the reaction.

The occurrence of a maximum in Figure 2 is qualitatively understandable. It is evident (from Fig. 2 and Table I) that the grafting of pure styrene onto cellophane is low. However, once acrylonitrile has been grafted onto cellulose, the styrene can react with chains having a free-radical-bearing acrylonitrile unit, and the rate of this addition is 20 times that of the addition of acrylonitrile onto its own radical. This, and the following values are taken from Flory.<sup>12</sup>



Furthermore, chains having styrene as their radical bearing unit are relatively stable and will, therefore, be terminated less rapidly by other radicals and by chain transfer. Finally, it must

be remembered that the curve in Figure 2 represents the weight increase and that the monomer weight of styrene is almost twice as large as that of acrylonitrile.

### Grafting onto Polymers Other Than Cellophane

Various polymer films were substituted for cellophane and irradiated in the presence of acrylonitrile in the standard mixture (Table I). Polyvinyl alcohol gave the highest amount of grafting per unit surface area, followed by cellophane, glassine paper, and filter paper (Table II). It is interesting to note the extent of grafting of the three cellulosic substances: cellophane is transparent, filter paper is opaque, and glassine paper is translucent. These results seem to indicate that grafting is somewhat dependent on the transparency of the substrate; compare the effect of the turbidity caused by polyacrylonitrile homopolymer (see below). At this time, no explanation can be offered as to why amylose is such a poor substrate even though it is similar to cellulose in structure.

TABLE II  
Grafting of Acrylonitrile onto Various Polymer Films in Standard Mixture, in Air (Twenty-four Hour Irradiation)

Film material	PAN grafted, mg./cm. <sup>2</sup>
Polyvinyl alcohol	4.9
Cellophane, 0.02 mm.	3.6
Glassine paper, 0.04 mm.	2.6
No. 2 Whatman filter paper	2.0
Amylose	0.9
Amylose, no dye ("blank")	0.2
Nylon	0.45
Rubber hydrochloride	0.1
Polyethylene	0

### Some Variables Affecting Extent of Grafting onto Cellophane

#### (A) Monomer Concentration

The effect of monomer concentration on extent of grafting for the three following systems have been investigated: (1) acrylonitrile, dimethylformamide, 10% water, 0.01M dye concentration, 12 hr. irradiation in presence of air; (2) acrylamide, water, 0.01M dye concentration, 12 hr. irradiation in presence of air. (3) acrylonitrile, styrene, dimethylformamide, 12 and 24 hr. irradiation in presence of air (acrylonitrile:styrene ratio held constant at a volume ratio of 1:1).

The results of monomer concentration plotted against per cent weight increase are shown in

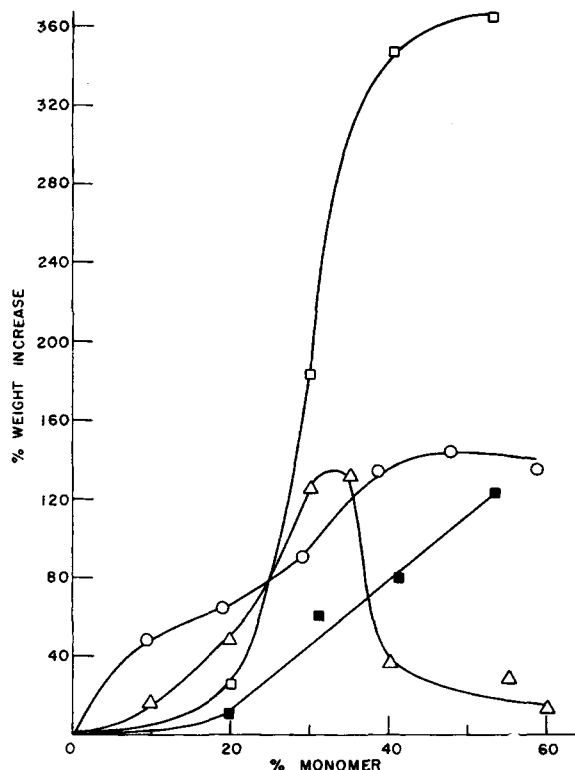


Fig. 3. Grafting as a function of monomer content: (□) acrylonitrile:styrene = 1:1, 24 hr.; (■) acrylonitrile:styrene = 1:1, 12 hr.; (△) acrylonitrile, 12 hr.; (○), acrylamide, 12 hr.

Figure 3. For both systems (2) and (3) the per cent weight increase reaches a constant maximum value. The acrylonitrile system, however, reaches a maximum at a monomer concentration of 35 per cent and then sharply decreases. In system (1), however, the polyacrylonitrile is not very soluble in the reaction mixture, with the result that turbidity develops which prevents light penetration to the film. At the higher acrylonitrile concentrations a layer of solid homopolymer forms on the wall of the tube facing the light; this polyacrylonitrile layer blocks the light to the film, and both grafting and homopolymerization are prevented.

#### (B) Effect of Irradiation Time

The extent of grafting seems to be roughly proportional to irradiation time up to approximately 24 hours, when the grafting levels off and remains constant. This is true for the acrylonitrile system. With an acrylonitrile solution in dimethylformamide, the extent of grafting begins to level off much earlier (after a 12 hour irradiation period); this again is a turbidity effect. Reirradiating a previously grafted acrylonitrile-cellophane graft

polymer in fresh monomer-solvent mixture leads to further weight increase. Subjecting such a sample to three successive irradiation periods, in a fresh mixture every time, leads to a 277% weight increase (compare with Fig. 1). This weight of the graft remains constant upon further irradiation.

#### Effect of Dye Concentration

Very little grafting has been obtained employing  $10^{-4}$  molar dye solutions. The required dye concentration is at least  $10^{-3}$  molar, better results are obtained with  $10^{-2}$  molar solutions. Very much higher dye concentrations are not possible because of the limited solubility of the dye in the monomer-solvent system (in the sodium sulfonate form). Experiments employing tendering dyes soluble in organic solvents will be made in the future.

#### Proof of Grafting

No direct and straightforward proof of a carbon-to-carbon bond between the substrate and grafted polymer has been established as yet. However, the solubility data below indicate strongly that an actual graft has been obtained.

The solubility of several graft polymers in solvents for either substrate or homopolymer was quantitatively investigated. The graft polymers whose solubility was to be determined, were usually ground in the presence of liquid air in a mortar and pestle; on several occasions Dry Ice was used instead of liquid air.

#### Solubility of Grafted Cellulose Derivatives

Acrylamide was grafted onto cellulose acetate and ethyl cellulose; much poorer grafting was obtained with ethyl cellulose; the grafted films were completely insoluble in water. The solubilities in hot acetone and methyl alcohol, respectively, are indicated below; nitrogen determinations were made on the soluble and insoluble fractions to give a measure of acrylamide present.

Cellulose acetate-acrylamide graft (22.3% AA)	hot acetone 24 hr.	21.7% sol.	2.8% AA in soluble fraction
		78.3% insol.	27% AA in residue
Ethyl cellulose-acrylamide graft	hot methanol 24 hr.	88% sol.	0% AA in soluble fraction
		12% insol.	51% AA in residue

TABLE III  
Extractions of Ground Graft Polymers and of Physical Mixtures

Expt.	Material	Composition	Extraction		Material soluble, %	Wt. original material recovered on acidification of solution, %
			Solvent	Conditions		
1a	Physical mixture	Cellophane/PAN, 27/73	DMF	125°C., 4 hr.	73.7 <sup>a</sup>	
1b	Graft	Cellophane/PAN, 27/73	DMF	125°C., 4 hr.	17 <sup>b</sup>	
2a	Physical mixture	Cellulose powder/PAA, 55/45	Water	25°C., 24 hr.	40	
2b	Graft	Cellophane/PAA, 55/45	Water	25°C., 24 hr.	2	
3a	Physical mixture	Cellulose powder/PAN, 27/73	Cuprammonium	72 hr.	80 <sup>c</sup>	
3b	Physical mixture	Cellophane/PAN, 27/73	Cuprammonium	48 hr.	25 <sup>c</sup>	
3c	Graft	Cellophane/PAN, 27/73	Cuprammonium	72 hr.	11 <sup>c</sup>	
4a	Physical mixture	Cellophane/PAA, 40/60	Cuprammonium		100	35 <sup>d</sup>
4b	Graft	Cellophane/PAA, 40/60	Cuprammonium		100	75 <sup>d</sup>

<sup>a</sup> Residue turned light brown.

<sup>b</sup> Residue turned deep brown.

<sup>c</sup> No nitrogen was found in the reprecipitated soluble fraction.

<sup>d</sup> Polyacrylamide and cellophane are soluble in cuprammonium, but upon acidification cellulose becomes insoluble.

Under the same conditions, the unmodified films (not grafted and not ground to a powder) dissolved within a few minutes. In the case of grafted cellulose acetate, some grafted chains have dissolved in hot acetone as indicated by the nitrogen content of the soluble fraction.

#### *Solubility of Grafted Cellophane*

Acrylonitrile and acrylamide were grafted onto cellophane, the graft polymers were ground to a powder in liquid air and extracted with either dimethylformamide, water, or cuprammonium solution. Physical mixtures, identical in composition to the corresponding graft polymers were made; polyacrylonitrile (PAN) and polyacrylamide (PAA) obtained as a by-product in the grafting reaction were dissolved in a small amount of dimethylformamide or water. Cellophane (or cellulose powder) were added to the viscous solution and mixed. The solution of PAN required heating of the dimethylformamide (DMF). The solvents were evaporated and the solids ground in liquid air. This procedure was followed to obtain as intimate a physical mixture as possible, and also because it was possible to grind the cellophane when it was covered with homopolymer, but not in the absence of homopolymer.

#### *Extraction of Graft Polymers and Physical Mixtures*

The ground graft polymers and physical mixtures were then subjected to extraction by various solvents (under constant stirring).

Experiments (4a) and (4b) represent the best proofs of grafting obtained so far. The fact that 75% of the graft was recovered whereas it contained only 40% cellulose is an excellent indication that a chemical bond between acrylamide and cellulose exists. The fact that the graft dissolved completely seems to exclude the possibility that extensive crosslinking took place.

#### References

1. Immergut, E. H., and H. Mark, *Makromol. Chem.*, **18-19**, 322 (1956). Also see Proceedings to First Cellulose Conference, Syracuse, N. Y., 1958.
2. Gaylord, N., *Interchem. Rev.*, **15**, 91 (1956-57).
3. Pinner, S. H., and Wycherly, W., *Plastics (London)*, **22**, 456, 503 (1957); *ibid.*, **23**, 27-30 (1958).
4. Mino, G., and S. Kaizerman, *J. Polymer Sci.*, **31**, 242 (1958).
5. Borunsky, T., Can. Pat. 549,110 (Nov. 19, 1957).
6. Restaino, A. J., in *Effects of Radiation on Materials*, Reinhold, New York, 1958, p. 287.
7. Magat, E. E., and D. Tanner, Belg. Pat. 546,817 (1955).
8. Oster, G., and O. Shibata, *J. Polymer Sci.*, **26**, 233 (1957).

9. Cooper, W., and J. Fielder, *J. Polymer Sci.*, **28**, 442 (1958).

10. Bolland, T. L., and H. R. Cooper, *Proc. Roy. Soc. (London)*, **A225**, 405 (1954).

11. Reeve, L., *J. Phys. Chem.*, **29**, 39 (1925).

12. Flory, P. T., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, p. 188.

### Synopsis

The cellulose-tendering properties of anthraquinone-2,7-disulfonic acid disodium salt have been successfully applied to graft various vinyl monomers onto cellulosic materials. A cellophane (or cellulose derivative) film is suspended in a solution containing monomer, solvent, dye, and water and irradiated with a 100-w. AH-4 mercury-vapor lamp. The photoexcited dye molecule abstracts a hydrogen atom from the substrate. The radical formed on the cellulose backbone initiates vinyl polymerization and a graft polymer is formed. The grafted film may be up to three and one-half times as heavy as the original substrate and has entirely different solubility characteristics. The degree of grafting is dependent on the monomer concentration in the solution and on the irradiation time. Maximum grafting is usually obtained employing a 24 hour irradiation period. The grafting is always accompanied by homopolymerization, which is not inhibited by atmospheric oxygen, but bubbling air through the solution will completely inhibit both the homopolymerization and the grafting. Substantial grafting can be obtained employing the following monomer-solvent systems: acrylonitrile-*N,N*-dimethylformamide; acrylamide-water; styrene-acrylonitrile-*N,N*-dimethylformamide. Good evidence for grafting has been obtained by comparing the solubility characteristics of the graft with those of a physical mixture of the cellulose and the homopolymer.

### Résumé

Les propriétés du sel disodique de l'acide anthraquinone disulfonique dans l'appât de la cellulose ont été employées avec succès à la réalisation du greffage de divers monomères vinyliques sur des matériaux celluloseux. Un film de cellophane (ou d'un dérivé celluloseux) est suspendu dans une solution contenant le monomère, le solvant, le colorant et l'eau, et est irradié à l'aide d'une lampe à vapeur de mercure AH-4 de 100 watts. La molécule de colorant photoexcitée provoque l'arrachement d'un atome d'hydrogène du substrat. Le radical formé sur le squelette celluloseux initie la polymérisation et amorce le greffage. Le film greffé peut avoir un poids 3½ fois supérieur au poids du

substrat initial et possède des caractéristiques de solubilité totalement différentes. Le degré de greffage dépend de la concentration en monomère dans la solution et de la durée d'irradiation. Le greffage maximum est obtenu habituellement à l'issue d'une période d'irradiation de 24 heures. Le greffage est toujours accompagné d'une homopolymérisation non-inhibée par l'oxygène atmosphérique. Cependant le barbotage d'air dans la solution inhibe totalement tant la homopolymérisation que le greffage. Un greffage important peut être réalisé au départ de systèmes solvant-monomère suivants: acrylonitrile-*N,N*-diméthylformamide; acrylamide-eau; styrène-acrylonitrile-*N,N*-diméthylformamide. Une bonne preuve du greffage à été obtenue en comparant les caractéristiques de solubilité du greffé avec celles d'un mélange physique de cellulose et d'homopolymère.

### Zusammenfassung

Die Einwirkung des Dinatriumsalzes der Anthrachinon-2,7-disulfonsäure auf Cellulose wurde mit Erfolg zur Aufpfropfung von verschiedenen Vinylmonomeren auf Cellulosematerialien herangezogen. Ein Cellophanfilm oder ein solcher aus einem Cellulosederivat wird in eine Lösung eingebracht, die Monomeres, Lösungsmittel, Farbstoff und Wasser enthält und mit einer 100 Watt AH-4-Quecksilberlampe bestrahlt. Die photochemisch angeregte Farbstoffmolekel entzieht dem Substrat ein Wasserstoffatom. Das an der Cellulosekette gebildete Radikal startet die Vinylpolymerisation und es entsteht ein Pfropfpolymeres. Der gepfropfte Film kann bis zu dreiundeinhalbmal so schwer sein, wie das ursprüngliche Substrat und besitzt völlig verschiedene Löslichkeitseigenschaften. Der Pfropfungsgrad hängt von der Monomerkonzentration in der Lösung und der Bestrahlungsdauer ab. Eine maximale Aufpfropfung wird normalerweise bei Anwendung einer 24-stündigen Bestrahlungsdauer erreicht. Während der Pfropfung findet immer auch eine Homopolymerisation statt, die durch atmosphärischen Sauerstoff nicht verhindert wird; Durchleiten von Luft durch die Lösung verhindert jedoch sowohl Homopolymerisation als auch Aufpfropfung vollständig. Eine starke Aufpfropfung kann mit folgenden Monomer-Lösungsmittelsystemen erhalten werden: Acrylnitril-*N,N*-Dimethylformamid; Acrylamid-Wasser; Styrol-Acrylnitril-*N,N*-Dimethylformamid. Durch Vergleich der Löslichkeitseigenschaften des Pfropfproduktes mit denen einer physikalischen Mischung von Cellulose und dem Homopolymeren konnte die Aufpfropfung eindeutig nachgewiesen werden.

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