

Radiochemical Yields of Graft Polymerization Reactions of Cellulose*

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Synopsis

The preparation of radiation-induced graft polymers of cotton cellulose, while retaining the fibrous nature and high molecular weight of the cellulose, depended primarily on the radiochemical yields of cellulose reactions and of graft polymerization reactions. Yields of the initial major molecular changes in cellulosic polymer indicated that, in the case of scission of the molecule and carboxyl group formation, chain reactions were not initiated by radiation; however, in the case of carbonyl group formation chain reactions were initiated but quickly terminated. Generally, experimental procedures, used in graft polymerization reactions, were: (1) simultaneous irradiation reactions, that is, application of monomers or solutions of monomers to cellulose or chemically modified celluloses, then irradiation; and (2) post-irradiation reactions, that is, irradiation of cellulose or chemically modified celluloses, then after removal from the field of radiation, contacting the irradiated cellulose with monomer. Some of the most important factors influencing the radiochemical yields of graft polymerization reactions of styrene and acrylonitrile onto cellulose were: concentration of monomer in treating solution; solvent; ratio of monomer solution to cellulose; prior chemical modification of cellulose; and absence of oxygen, particularly in post-irradiation reactions. Experimental data were presented, and the direct and indirect effects of Co^{60} γ -radiation on these reactions were discussed.

INTRODUCTION

The effects of ionizing radiation on the properties and reactions of polymers have been actively investigated by many workers during recent years.¹ Synthetic or man-made polymers have been emphasized as compared with naturally occurring high polymers, such as cellulose, starch, wool, silk, and proteins. There has been some work on changing the properties of naturally occurring high polymers by radiation-induced graft polymerization of selected monomers or man-made polymers onto these natural polymers.¹

Work at the Southern Regional Research Laboratory has been concerned with the preparation of radiation-induced graft polymers of cotton cellulose, while retaining the fibrous nature and high molecular weight of the

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cellulose.²⁻¹⁰ Several important factors are: (1) radiochemical yields of cellulose reactions; (2) radiochemical yields of the graft polymerization reactions; and (3) experimental conditions which will increase the accessibility of activated sites in the cellulose molecule to monomers.

Graft Polymerization Reactions

For the purposes of this discussion, the graft polymerization reactions are those in which radiation-induced grafting of a vinyl monomer onto high molecular weight cotton cellulose occurs. During the process, the molecular weight of the cellulose probably decreases, and the molecular weight of the grafted polyvinyl polymer increases. The grafting of the polymer may be initiated at more than one activated site on the cellulose molecule. As the percentage of the grafted polyvinyl polymer and its molecular weight increase, the resulting graft copolymer has some of the characteristic properties of both polymers. In this way the fibrous and textile properties of the naturally occurring cotton cellulose can be generally retained in the graft copolymer while other desirable properties, such as thermoplasticity, elasticity, and abrasion resistance, are being acquired.

Two procedures, commonly used in these reactions are: (1) simultaneous irradiation reactions, that is, application of monomers in the gaseous phase or solutions of monomers to cellulose or chemically modified celluloses, then irradiation; and (2) post-irradiation reactions, that is, irradiation of cellulose or chemically modified celluloses, then after removal from the field of radiation, contacting the irradiated cellulose with monomer. In the simultaneous procedure, the radiolyses of all of the components of the solution are factors in initiating graft polymerization reactions. In both procedures, the initiation of grafting by activated sites trapped in the cellulose molecule is a major factor. Consequently, in both procedures the accessibility of these trapped activated sites to the vinyl monomer can determine the radiochemical yields of given reactions. The use of selected solvents, which open the more ordered regions of cotton cellulose and in which the monomers also dissolve, would be obviously advantageous in increasing radiochemical yields.

Elementary steps for the radiation-induced graft polymerization reactions of cotton cellulose (C) and vinyl monomer (V) may be written as shown in eqs. (1)-(9).

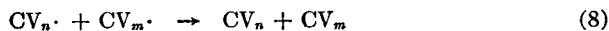
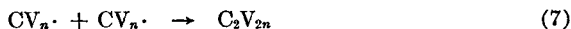
Initiation:



Propagation:



Termination:



In the simultaneous irradiation procedure, each of the elementary reactions is possible. In addition the indirect effects of the radiolysis of the solvent on the production of activated sites on the cellulose molecule and on the vinyl monomer are also possible. However, in the post-irradiation procedure, reactions (2), (4), (6), and (9) are less likely to occur than with the simultaneous procedure, since the vinyl monomer and also the solvent are not irradiated.

On initiation, reaction (1) is more likely to occur than reaction (2), since the cellulose molecule interacts more readily with high energy radiation, particularly through dehydrogenation,^{11,12} than the vinyl monomer. Also, the activated sites on the cellulose molecule will probably tend to be longer lived, particularly in the crystalline region, than activated sites on the vinyl monomer. On propagation, reactions (3), (4), and (5) will be largely controlled by the rate of the diffusion of the vinyl monomer in the system. The effects of experimental conditions, particularly those increasing the accessibility of the activated sites in the cellulose, will be important factors. On termination, reactions (7) and (8) will be the least likely to occur, since the high molecular weight graft copolymers will have low mobility in the system. Reaction (8) would proceed by disproportionation. The product of reaction (9) will, of course, be homopolymer and not graft copolymer. Reaction (9) will be least likely to occur when the post-irradiation procedure is used. Chain transfer reactions, involving cellulose, monomer, and/or solvent, could also occur; however, no activated species would develop that are not indicated in the elementary steps.

EXPERIMENTAL

Cobalt-60 Radiation Source

The SRRL Co⁶⁰ radiation source, previously described by Arthur et al.¹³ and similar to that described by Ghormley and Hochanadel,¹⁴ was used. The dose rate, determined by ferrous-feric dosimetry,¹⁵ was about 1.5×10^{19} e.v./g./hr. over the experimental volume irradiated.

Preparation of Samples

Cotton cellulose of the Deltapine variety was purified by extraction with hot ethanol followed by boiling in dilute sodium hydroxide solution, precautions being taken to minimize air oxidation. The sodium hydroxide was removed by washing the cellulose with distilled water, then followed by souring with dilute acetic acid, neutralizing with dilute ammonium

hydroxide, and again washing with distilled water.¹⁶ The purified cellulose was allowed to condition at 21°C. and 65% R.H., resulting in a product with a moisture content of about 7%. The viscosity-average molecular weight of the purified cellulose was about 700,000. (Generally for convenience in handling and in evaluating the physical properties of the cellulose, the cotton was spun into 7s/3 yarn and wound into 18-yd. skeins prior to purification.)

In the preparation of graft copolymers of fibrous cotton cellulose and vinyl monomers, two procedures were followed. In the simultaneous irradiation procedure, the cotton cellulose was irradiated in a solution of the vinyl monomer. After the desired dosage was reached, the copolymer was removed from the solution, washed with monomer solvent, and then exhaustively extracted at room temperature with solvent normally used for the polyvinyl polymer. When styrene was the monomer, benzene was used as the solvent; when acrylonitrile was the monomer, *N,N*-dimethylformamide was used as the solvent. The extracted copolymer was washed with distilled water, and then allowed to dry at room temperature. The vinyl polymer weight gain on the cellulose was determined and evaluated as the extent of graft copolymerization.^{4-6,9,10}

In the post-irradiation procedure, the cotton cellulose was irradiated in a solid state. After the desired dosage was reached, the irradiated cellulose was placed in solutions of monomer under varying experimental conditions for selected periods of time.⁸ The resulting copolymer was removed from the solution and treated as described above.

Purified cotton cellulose irradiated, but not reacted with vinyl monomer, was analyzed to determine the radiochemical yields for major molecular changes. Analytical methods used have been previously described.¹⁷

RESULTS

Purified Cotton

At irradiation dosages where the fibrous nature of cotton cellulose was retained, the major macromolecular changes in the nonvolatile products were scission of the molecule and carboxyl and carbonyl group formations.¹⁷ When purified cotton cellulose was irradiated in an atmosphere of oxygen to a dosage of 5.2×10^{19} e.v./g., the radiochemical yields (molecular actions per 100 e.v.) for scission, carboxyl group, and carbonyl group formations were, respectively, about 7.3, 5.8, and 70. When the atmosphere was nitrogen, the yields were about 6.5, 3.5, and 58. These values would indicate that chain reactions were not initiated in the case of scission and carboxyl group formation and that in the case of carbonyl group formation chain reactions were probably initiated but quickly terminated. At a dosage of 5.2×10^{19} e.v./g., the viscosity-average molecular weight of the cellulose was reduced from about 700,000 to about 130,000; however, the tensile strength of the cellulosic fiber was reduced only about 10%.¹⁷

Simultaneous Reaction

Influence of Dose. In the simultaneous procedure the radiochemical yield and the extent of graft copolymer formation are determined by the total dosage, as shown in Figure 1. As the total dosage increased, the efficiency of the initiation of graft copolymerization decreased, as shown by the decreasing radiochemical yields. However, with the increase in dosage and consequently the increase in number of activated sites on the cellulose where initiation of copolymerization could occur, the extent of graft copolymerization increased, as shown by the increase in the polystyrene to cellulose ratio.

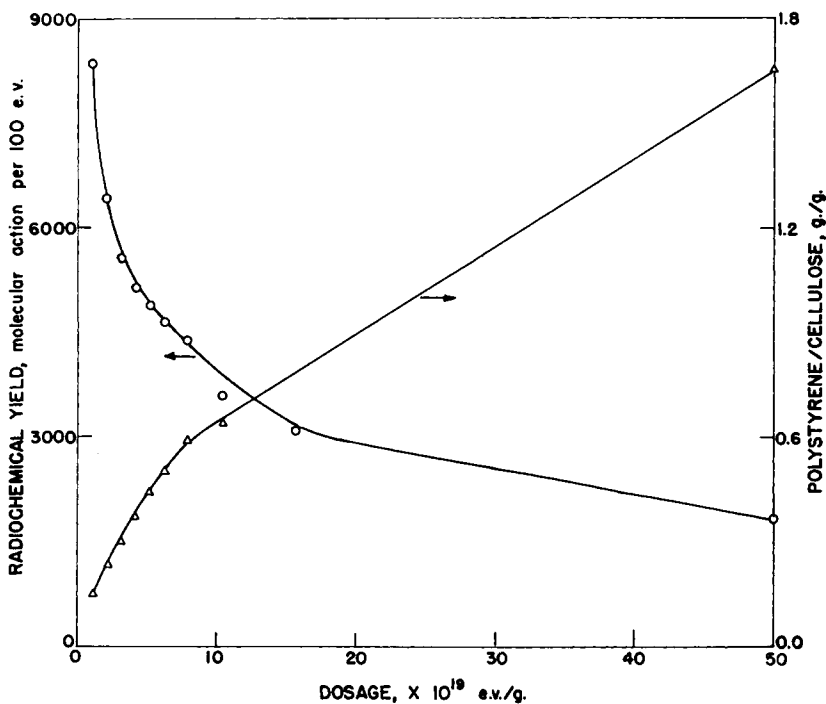


Fig. 1. Effect of dosage on the radiochemical yield and formation of styrene-cellulose copolymer (simultaneous procedure; about 25°C.; 70/30 styrene-methanol/cellulose = 10/1).

Solvent-Monomer Mixture. The effects of the composition of the solvent-monomer mixture, in which the cellulosic polymer is immersed during irradiation, on the radiochemical yields of graft copolymers are shown in Tables I and II. On dilution of styrene with methanol or *N,N*-dimethylformamide the yield of copolymer increased to a maximum and then decreased. Methanol was more effective in increasing the efficiency of the copolymerization at a lower concentration and also over a wider range of concentration than *N,N*-dimethylformamide. With aqueous $ZnCl_2$ as the solvent for acrylonitrile, the effects of solvent concentration,

TABLE I
Effect of Concentration of Solvent-Monomer Mixture on the Radiochemical Yields of Graft Copolymers of Cellulose and Styrene^a

Composition		Radiochemical yield, molecular actions/100 e.v.	
Styrene, %	Solvent, %	Methanol	<i>N,N</i> - Dimethylformamide
100	0	0	0
99	1	440	220
98	2	5100	1000
97	3	5000	3300
96	4	4600	3400
95	5	—	3600
94	6	—	4000
92	8	4000	—
90	10	—	4200
85	15	4300	4700
80	20	—	4800
75	25	4800	5000
70	30	4300	5000
67	33	4800	4300
60	40	4600	4200
50	50	4500	3300
40	60	4500	2200
33	67	4000	1400
30	70	—	1200
25	75	3300	—
20	80	2200	440
15	85	1800	220
0	100	0	0

^a Simultaneous procedure; radiation dosage: 5.2×10^{19} e.v./g. cellulose; monomer-solvent/cellulose = 10/1; temperature, about 25°C.⁹

TABLE II
Effect of Concentration of Solvent-Monomer Mixture on the Radiochemical Yields of Graft Copolymers of Cellulose and Acrylonitrile^a

Solvent (aqueous ZnCl ₂), %	Monomer concentration, %	Radiochemical yield, molecular actions/100 e.v.
65	32	80
75	20	1100
75	32	1400
75	40	1800
80	32	8100

^a Simultaneous procedure; radiation dosage: 4.2×10^{19} e.v./g. cellulose; solution/cellulose = 25/1 overnight at about 25°C., then padded to 2-4/1 prior to irradiation at about 25°C.⁴

as well as monomer concentration, on the yields of copolymer are shown in Table II.

In the simultaneous procedure, the ratio of the solvent-monomer mixture to cotton cellulose was also an important factor in determining the efficiency of copolymerization, as shown in Table III.

TABLE III
Effect of Solvent-Monomer Mixture to Cellulose on the Radiochemical Yields of Graft Copolymers of Cellulose and Styrene^a

Monomer-solvent/cellulose, g./g.	Radiochemical yield, molecular actions/100 e.v.
1	0
2	430
3	1200
5	4100
10	4300
20	4500
50	4600
100	4600

^a Simultaneous procedure; radiation dosage: 5.2×10^{19} e.v./g. cellulose; monomer-solvent = 70% styrene-30% methanol; temperature about 25°C.⁹

Chemical Modification. The effects of cyanoethylation of cotton cellulose on the radiochemical yields of acrylonitrile copolymer are shown in Table IV. As the degree of substitution increased, the yields increased, indicating greater efficiency in the use of the activated sites in the cellulose to initiate graft copolymerization.

TABLE IV
Effect of Cyanoethylation of Cellulose on the Radiochemical Yields of Graft Copolymers of Cellulose and Acrylonitrile^a

Degree of substitution	Radiochemical yield, molecular actions/100 e.v.
0.00	8,100
0.34	11,900
0.57	12,200
0.72	14,500
0.99	17,700
1.29	29,800

^a Simultaneous procedure; radiation dosage: 5.2×10^{19} e.v./g. cellulose; 32% acrylonitrile in 80% ZnCl₂ solution/cyanoethylated cellulose = 25/1 overnight at about 25°C., then padded to 2-4/1 prior to irradiation at about 25°C.¹⁰

Post-Irradiation Reaction

Influence of Dose and Time. In the post-irradiation procedure the radiochemical yield is also determined by the total dosage, as shown in Figure 2. The time of post-irradiation reaction is a factor due to dif-

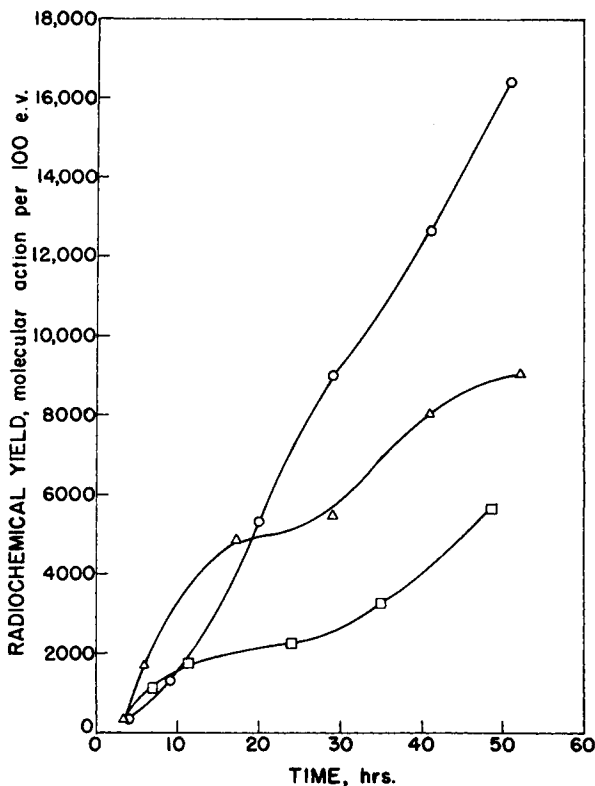


Fig. 2. Effect of dosage on the radiochemical yield of acrylonitrile-cellulose copolymer (post-irradiation procedure; about 25°C.; 32% acrylonitrile in 80% ZnCl_2): (O) 5.2×10^{19} e.v./g. cellulose; (Δ) 12×10^{19} e.v./g.; (\square) 32×10^{19} e.v./g.

fusion effects in contacting the monomer with the activated sites, particularly those in the highly ordered or crystalline regions. At the longer reaction times, the yields decreased with increasing dosage. However, it has been shown that the extent of graft copolymerization increased with increasing dosage.⁸

Solvent-Monomer Mixture. The composition of the solvent-monomer mixture was an important factor in determining the radiochemical yield and extent of copolymer formation in post-irradiation reactions. With acrylonitrile, when the solvents used were water and *N,N*-dimethylformamide, low yields were obtained. As shown in Figure 3, when aqueous ZnCl_2 was used as the solvent, high radiochemical yields of graft copolymers were obtained.

When the radiochemical yields were low, less than 1000, increasing the temperature of the post-irradiation reaction over the range of 23–100°C. generally increased the yields and also the extent of graft copolymer formation.⁸ The irradiation of cotton cellulose (containing regain moisture) in air generally resulted in lower post-irradiation radiochemical yields than when the cellulose, containing a very low content of moisture, was irradiated

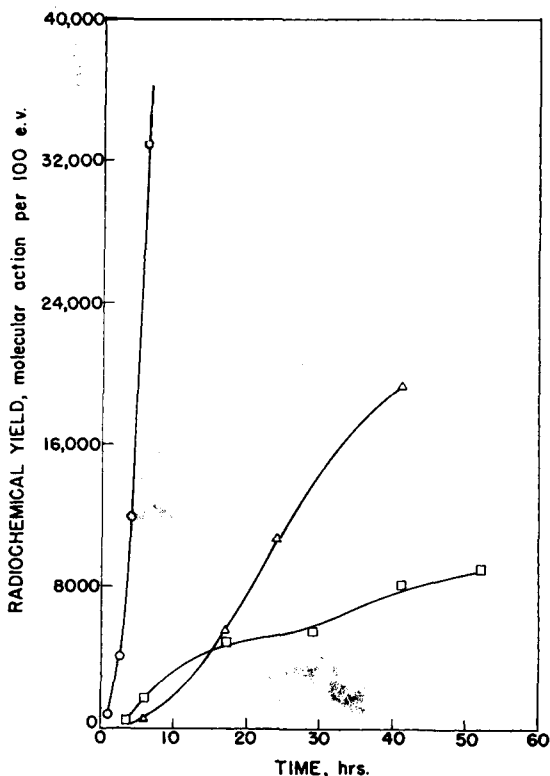


Fig. 3. Effect of composition of solvent-monomer mixture on radiochemical yield of acrylonitrile-cellulose copolymer (post-irradiation procedure; about 25°C.; cellulose irradiated dry in nitrogen to 12×10^{19} e.v./g.): (O) 16% acrylonitrile in 75% $ZnCl_2$; (Δ) 16% acrylonitrile in 80% $ZnCl_2$; (\square) 32% acrylonitrile in 80% $ZnCl_2$).

in nitrogen. The extent of graft copolymer formation under these conditions has been reported elsewhere.⁸

Diffusion Effects

During the formation of a graft copolymer of a vinyl monomer with cotton cellulose, the location of the grafted polymer within the macrostructure of the cellulosic fiber can be partially determined. In the simultaneous procedure, the structure of the fiber can be altered by swelling with selected solvents which also dissolve the monomer. On irradiation the monomer is polymerized and forms a graft copolymer with the cellulose. A cross section of a fibrous graft copolymer of cotton cellulose and polyacrylonitrile is shown in Figure 4a. The solvent used was 80% aqueous $ZnCl_2$ containing 32% acrylonitrile. A cross section of a fibrous graft copolymer of cotton cellulose and polystyrene is shown in Figure 4b. The solvent used was methanol containing 70% styrene.

In the post-irradiation procedure, the cellulosic fiber is irradiated, and then contacted with the solution of the monomer. The effect of the

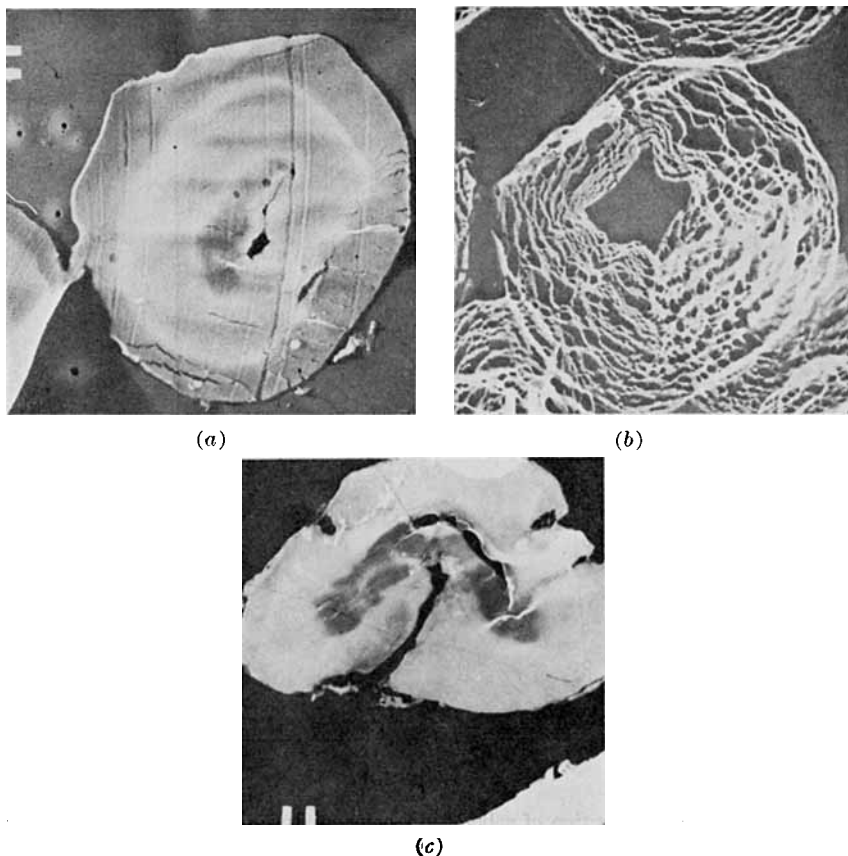


Fig. 4. Location of grafted polymer in cellulose structure as shown by electron micrographs of ultrathin sections (photos by Anna T. Moore): (a) acrylonitrile-cellulose copolymer (simultaneous procedure, about 25°C., 4.2×10^{19} e.v./g., 32% acrylonitrile in 80% ZnCl_2 ; graft polymer between lumen and outer cellulose wall 5000 \times); (b) styrene-cellulose copolymer (simultaneous procedure, about 25°C., 5.2×10^{19} e.v./g., 70% styrene and 30% methanol; graft polymer within growth layers 4500 \times); (c) acrylonitrile-cellulose copolymer (post-irradiation procedure, about 25°C., 32×10^{19} e.v./g., 32% acrylonitrile in 80% ZnCl_2 ; graft polymer from outer wall inward 6000 \times).

solvent on swelling of the macrostructure of the irradiated cellulosic fiber determines the rate of diffusion of the monomer to the activated sites and the depth of penetration of the graft polymer in the structure. A cross section of a fibrous graft copolymer of cotton cellulose and polyacrylonitrile is shown in Figure 4c. The solvent used was 80% aqueous ZnCl_2 containing 32% acrylonitrile.

DISCUSSION

Graft copolymers of cotton cellulose and vinyl monomer can be initiated by direct irradiation of the vinyl monomer and the cellulosic polymer (simultaneous procedure). The direct grafting is probably initiated, in part, by radiation activated sites on the surface of the cellulosic polymer;

however, the importance of the accessibility of the activated sites to the initiation of graft polymerization is shown by the effects of the solvent, the concentration of the solvent-monomer mixture, and the relative amount of cellulose to the solvent-monomer mixture on the radiochemical yields. The location of the deposition of the graft polymer within the macrostructure of the cellulosic polymer is determined by the solvent-monomer mixture used, by only wetting the cellulosic polymer with the solvent-monomer mixture prior to irradiation, or by suspending the cellulosic polymer in the solvent-monomer mixture during irradiation.

The importance of trapped activated sites in the cellulosic polymer for initiating graft polymerization of vinyl monomer onto cellulose was further demonstrated in the post-irradiation procedure. The radiochemical yields were principally dependent on the composition of the solvent-monomer mixture with less dependence on temperature or presence of oxygen. The location of the deposition of the graft polymer within the macrostructure of the cellulosic polymer, from the surface of the polymer to within the polymer with increasing time of reaction, also demonstrated the importance of solvent and diffusion effects of the monomer.

The properties of the graft copolymer are dependent on its composition, in that the characteristic properties of both the cellulosic polymer and the graft polymer determine the resultant properties.⁷ In order to increase the percentage of the graft polymer in the copolymer, it is generally necessary to accept a lower radiochemical yield. This is observed in both simultaneous and post-irradiation procedures.

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Résumé

La préparation de polymères greffés par radiation induite de la cellulose du coton tout en conservant la nature fibreuse et poids moléculaire élevé de la cellulose, dépend principalement des rendements radiochimiques des réactions de la cellulose des réactions de greffage de polymérisation. Les rendements des changements moléculaires initiaux importants du polymère cellulosique indiquent que, dans le cas de la scission de la molécule et de la formation d'un groupe carboxylique, des réactions en chaîne sont pas initiées par radiation; cependant dans le cas de la formation du groupe carbonyle, des réactions en chaîne sont initiées mais rapidement terminées. Généralement les procédés expérimentaux employés dans les réactions de greffage sont: (1) des réactions avec irradiation simultanée, c.à.d. addition de monomères ou de solution de monomères à la cellulose ou à des celluloses modifiées chimiquement, et ensuite irradiation et (2) des réactions avec post-irradiation, c.à.d. irradiation de la cellulose ou de la cellulose chimiquement modifiée, ensuite, après éloignement de la source de radiation, mise en contact de la cellulose avec le monomère. Les facteurs les plus importants influençant les rendements radiochimiques de réaction de greffage du styrène et de l'acrylonitrile dans la cellulose sont: la concentration du monomère dans la solution traitée, le solvant, le rapport de la solution du monomère à la cellulose, la modification chimique initiale de la cellulose, et l'absence d'oxygène, particulièrement dans la réaction de post-irradiation. Les données expérimentales sont exposées, et les effets directs et indirects de la radiation du cobalt-60 gamma sur les réactions sont discutés.

Zusammenfassung

Die Darstellung von strahlungsinduzierten Pfropfpolymeren auf Baumwollcellulose unter Beibehaltung der Fasernatur und des hohen Molekulargewichts der Cellulose, hing primär von der radiochemischen Ausbeute der Cellulosereaktionen und Pfropfpolymerisationsreaktionen ab. Die Ausbeute an den hauptsächlich primären Molekülveränderungen bei Cellulosepolymeren zeigte, dass im Falle der Molekülsplaltung und Carboxylgruppenbildung durch die Strahlung keine Kettenreaktionen gestartet wurden; im Falle der Carbonylgruppenbildung wurden zwar Kettenreaktionen gestartet jedoch auch rasch abgebrochen. Im allgemeinen wurden bei der Pfropfpolymerisationsreaktion folgende Versuchsmethoden verwendet: (1) Reaktionen bei Simultanbestrahlung, d.h. Einwirkung von Monomeren oder Monomerlösungen auf Cellulose oder chemisch modifizierte Cellulose und Bestrahlung und (2) Reaktionen bei Strahlungsnacheffekten, d.h. Bestrahlung von Cellulose oder chemisch modifizierter Cellulose und Einwirkung des Monomeren auf die bestrahlte Cellulose nach ihrer Entfernung aus dem Strahlungsfeld. Die wichtigsten Faktoren für die radiochemische Ausbeute der Pfropfpolymerisationsreaktion von Styrol und Acrylnitril auf Cellulose waren: die Monomerkonzentration in der verwendeten Lösung; das Lösungsmittel; das Verhältnis von Monomerlösung zu Cellulose; die vorhergehende chemische Modifizierung der Cellulose sowie die Abwesenheit von Sauerstoff, besonders bei Strahlungsnacheffekts-Reaktionen. Versuchsergebnisse werden vorgelegt und die direkten und indirekten Einflüsse der Cobalt-60- γ Strahlung auf die Reaktionen diskutiert.

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