

Structure and Properties of Cellulose Graft Copolymers. I. Radiation-Induced Rayon-Styrene Graft Copolymers*

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Synopsis

Rayon-styrene graft copolymers were prepared by the direct radiation method, with the use of the preswelling technique, by irradiation with γ -rays from ^{60}Co . The grafting was carried out in bulk styrene and in styrene-solvent mixtures, such as styrene-methanol and styrene-acetone, to study their effect on the graft copolymerization reaction and the structure of the resulting graft copolymer. The effects of carbon tetrachloride, a chain-transfer agent, was also investigated. Three different types of rayon yarn were used; Fortisan, a modifier-type high wet-modulus rayon, and a high-tenacity tire yarn, in order to study the effect of rayon microstructure on the grafting reaction. The molecular structure of the rayon-styrene graft copolymers was studied by hydrolyzing away the cellulose backbone and measuring the molecular weights of the grafted polystyrene branches. For grafting in bulk styrene, the molecular weights of the grafted polystyrene ranged from 400,000 to 1,000,000, while those of the polystyrene homopolymer formed in the outside solution were of the order of 30,000-50,000. The molecular weights of the grafted polystyrene branches tended to increase with per cent grafting in the graft copolymer. For grafting in styrene-methanol and styrene-acetone mixtures, the molecular weights of the polystyrene branches decreased with increasing solvent content. The addition of carbon tetrachloride to bulk styrene resulted in a sharp decrease in the molecular weights of the grafted branches. The grafting frequency or number of polystyrene branches per cellulose chain was calculated from the per cent grafting and the molecular weights of the polystyrene branches. The morphology of the rayon-styrene graft copolymers and some of their physical properties are discussed.

INTRODUCTION

Graft copolymerization onto cellulose has been the subject of numerous investigations in recent years, and adequate reviews of progress in this field are available in the literature.¹⁻⁵ While a considerable amount of research has been concentrated on the methods of preparing cellulose graft copolymers, relatively little effort has been directed toward a systematic investigation of their structure and properties. It is essential to obtain a better understanding of the structure of cellulose grafts, in

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order to properly evaluate their physical properties, and to establish an accurate physical picture of the mechanism of the grafting reaction.

All of the existing methods of grafting onto cellulose involve heterogeneous reaction systems, consisting of the cellulose and the monomer solution phases. Since grafting occurs onto a pre-existing solid-state substrate, cellulose morphology and microstructure are important factors which affect the course of the reaction and the nature of the graft product. In investigating the structure of cellulose graft copolymers, it is helpful to consider two structural levels, (a) the molecular level and (b) the macroscopic fiber level. At the molecular level, information is required concerning the molecular weights of the grafted branches, and their frequency and distribution on the cellulose chains. It is also desirable to determine the actual proportion of chemically grafted polystyrene and cellulose in the product. On the other hand, the macroscopic physical properties of polymer films and fibers depend not only on their molecular structure but also on their morphology and microstructure. With respect to the macroscopic fiber structure, it is thus important to have a knowledge of the distribution of grafted polymer through the fiber cross-section and to determine whether the cellulose graft copolymers are surface or volumetric grafts.

Previous investigations on the molecular structure of cellulose-styrene grafts have been reported by Huang et al.,⁶ Kobayashi,⁷ Kesting and Stannett,⁸ and by Sumitomo and Hachihama.⁹ Shirakashi and co-workers¹⁰ recently investigated the effect of cellulose fine structure on the graft copolymerization of methyl methacrylate onto cellulose. An electron microscopic study of the structure of rayon-styrene graft copolymers has recently been completed by Kaepfner and Huang.¹¹

The purpose of the present investigation is to study in greater detail the structure and properties of cellulose grafts, both molecular and macroscopic. Another aspect of these studies is to compare and evaluate cellulose grafts prepared by various known methods of grafting and under different conditions, and to investigate the effects of cellulose morphology and microstructure. The present paper deals with cellulose-styrene grafts prepared by grafting by the direct radiation method of styrene onto three different types of rayon: Fortisan, a modifier-type high wet-modulus rayon and a high-tenacity tire yarn.

EXPERIMENTAL

Materials

Rayon. Three different types of rayon yarn, Fortisan, modifier-type high wet-modulus (HWM) rayon, and high-tenacity tire yarn were used. The properties of these rayons are listed in Table I.

(It should be mentioned that the HWM rayon and high-tenacity tire yarn used are not necessarily representative of modern fibers of these classes.

TABLE I

	Fortisan	High wet-modulus rayon	Tire yarn
Denier	1.0	1.0	1.92
Tensile strength, g./den.			
Conditioned	8.77	5.31	4.92
Wet	6.55	3.72	3.31
Crystallinity index ^a	0.85	0.75	0.72
Orientation index ^a	0.712	0.448	0.515

^aFrom Krässig and Kitchen.¹²

They were used because of available data in earlier studies^{11,12} concerning their physical characteristics and microstructure.)

Styrene. Styrene monomer (Eastman Kodak Organic Chemicals) was purified by washing with 10% sodium hydroxide solution to remove the inhibitor, washed with distilled water, and then dried overnight over anhydrous calcium chloride. It was then distilled under reduced pressure and stored in a refrigerator.

Methanol acetone, carbon tetrachloride, and pyridine were all reagent grade (Fisher ACS Certified).

Preparation of Rayon-Styrene Graft Copolymers

Radiation Grafting. The rayon-styrene grafts were prepared by the direct radiation method with the use of the preswelling technique described by Huang and Rapson.¹³ Rayon samples (0.5 g.) were placed in 25 ml. glass screw-cap sample bottles; 0.4 ml. of water, corresponding to approximately 80% of the weight of rayon, was carefully added to the rayon to preswell it. The bottles were tightly capped and allowed to stand overnight. For grafting in bulk styrene, 10 ml. of styrene monomer was added to the bottle. For grafting in styrene-solvent mixtures, 20 ml. of solution containing various compositions of styrene-methanol and styrene-acetone were added. For some experiments small amounts of carbon tetrachloride were added to the bulk styrene to investigate the effect of a chain transfer agent. The sample bottles were irradiated with γ -rays from a ⁶⁰Co source at doses ranging from 0.5–2.0 Mrad. Irradiations were carried out in a Gamma-Cell 220 γ -ray irradiator¹⁴ at the laboratories of the Commercial Products Division, Atomic Energy of Canada Ltd., Ottawa, Ontario. The radiation intensity of the ⁶⁰Co-source was 0.85 Mrad/hr., and the irradiation temperature was 30–35°C. All irradiations were performed in the presence of air.

Extraction. After irradiation the grafted rayon was soaked overnight in 200 ml. of benzene to remove styrene monomer and any loosely held polystyrene homopolymer. The samples were then extracted continuously with benzene in a Soxhlet apparatus for 72 hr. After the extraction, the samples were washed in acetone, dried, and weighed. The weight increase

or add-on was considered to be grafted polystyrene. The per cent grafting was calculated in the following way:

$$\text{Per cent grafting} = \frac{\text{Grafted weight} - \text{Original weight rayon} \times 100}{\text{Original weight rayon}}$$

Hydrolysis

Hydrolysis of the rayon-styrene grafts was carried out in a mixture of acetic acid-benzene-72% sulfuric acid. A 0.5-1.0 g. sample of the grafted rayon was placed in a flask containing 100 ml. of acetic acid, 100 ml. of benzene and 25 ml. of 72% sulfuric acid and hydrolyzed at 10°C. for 48-72 hr. The flask was shaken vigorously on a mechanical shaker at 4 hr. intervals during the hydrolysis. The benzene phase was separated in a funnel, concentrated under vacuum, and added to methanol to precipitate the polystyrene branches.

Molecular Weight Determinations

The intrinsic viscosity of polystyrene was measured in benzene at 30°C., in a Cannon-Ubbelohde type viscometer and converted to number-average molecular weights by using the relationship

$$\bar{M}_n = 167,000[\eta]^{1.37}$$

of Mayo et al.¹⁵:

The molecular weight of the cellulose was determined by measuring the intrinsic viscosity of the nitrated cellulose in acetone at 28°C. The relationship $[\eta] = 1.1 \times 10^{-4} \bar{M}_n^{0.9}$ recommended by Immergut et al.,¹⁶ was used to convert intrinsic viscosities to number-average molecular weights.

Acetylation

The acetylation of rayon-styrene graft copolymers was carried out under nondegradative conditions in acetic anhydride-pyridine mixtures.^{17,18} Rayon-styrene grafts (0.5-1.0 g.) were first soaked in *N,N*-dimethylformamide for 30 min. and then placed in a 200 ml. flask containing 100 ml. of a 1:2 acetic anhydride-pyridine mixture. The acetylation reaction was carried out for 24-48 hr. at 10°C. During the reaction, the flask was shaken vigorously on a mechanical shaker at 4 hr. intervals. Additional pyridine was sometimes added to prevent the reaction mixture from becoming too viscous. After the acetylation was completed, the reaction mixture was precipitated into an excess of methanol. It was then filtered and dried under vacuum. Extraction of the acetylation graft to remove polystyrene homopolymer was carried out in paper thimbles in a Soxhlet apparatus with benzene for 72 hr. The benzene extract was concentrated and added to methanol to precipitate the polystyrene homopolymer.

RESULTS AND DISCUSSION

Effects of Rayon Microstructure

The effect of rayon microstructure on the radiation grafting of styrene onto rayon is shown in Figure 1. The grafting was carried out in bulk

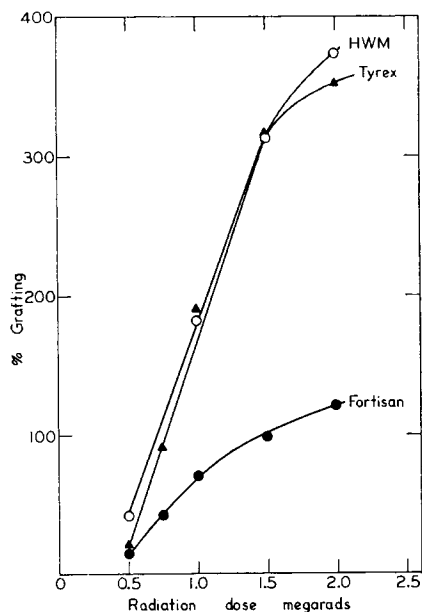


Fig. 1. Radiation grafting of bulk styrene onto rayon. Effect of rayon microstructure and radiation dose.

styrene without any additives or diluents. After an initial induction period lasting up to a radiation dose of 0.5 Mrad, graft copolymerization occurs rapidly, with per cent grafting increasing linearly with radiation dose up to 1.5 Mrad. Beyond this radiation dose, the grafting curves tend to level off slightly. For Fortisan, there is a slight break in the grafting curve at 1.0 Mrad, after which grafting proceeds at a somewhat reduced rate. When comparing the grafting behavior of the different rayons, it is clear that Fortisan has a considerably lower rate of grafting than was observed for both HWM and tire yarn rayon. There is no significant difference in the grafting behavior of HWM and tire yarn rayon. It is now generally agreed^{10,13,21,24} that in grafting onto a solid state polymer backbone, only those areas which are accessible to the diffusing monomer are available for graft copolymerization. In terms of rayon microstructure, the accessible areas correspond to the amorphous regions and the surface of the crystallites.²⁶ The crystalline regions are tightly hydrogen-bonded in a regular manner and are consequently inaccessible to the diffusing monomer. No grafting can take place, therefore, in the crystalline regions. The differences observed in the grafting behavior of the rayons can be explained by considering two important physical factors which influence the course of the grafting reaction: (a) the microstructure of the rayon and (b) the diffusion rate of styrene onto the rayon. In Fortisan, the cellulose microstructure is highly crystalline with a high degree of orientation. Consequently it contains less amorphous material than either HWM or tire rayon. Because of the highly ordered microstructure of Fortisan, the

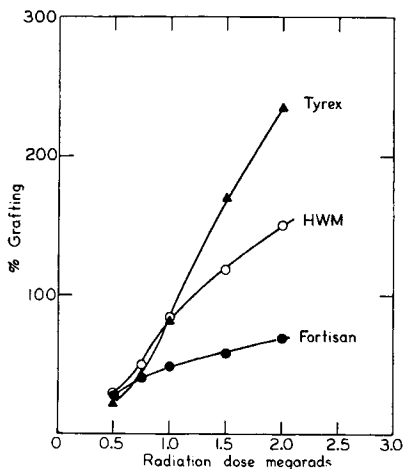


Fig. 2. Radiation grafting in 1:1 styrene-methanol solution. Effect of rayon microstructure and radiation dose.

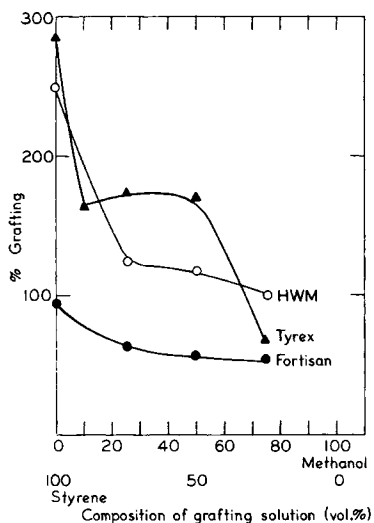


Fig. 3. Radiation grafting of styrene onto different rayons. Effect of methanol and rayon microstructure, radiation dose 1.5 Mrad.

diffusion rate of styrene onto it can also be considered to be lower than for HWM and tire yarn rayon. On the other hand, the effect of γ -rays is a random process which initiates cellulose free radicals throughout the cellulose, regardless of amorphous and crystalline regions. Since the free-radical sites in the crystalline region are inaccessible, Fortisan has considerably fewer accessible initiation sites for graft copolymerization. Coupled with a slower rate of diffusion, these factors result in an overall lower rate of grafting for Fortisan, than for HWM and tire yarn rayon. In a previous investigation of radiation grafting of styrene onto cellulose,

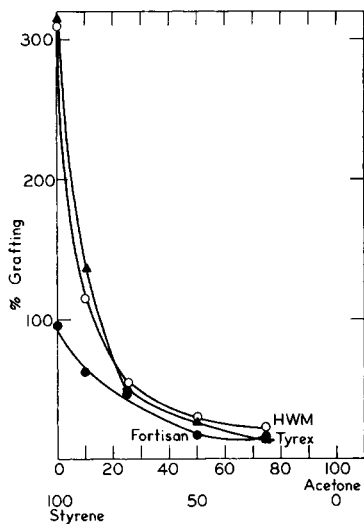


Fig. 4. Effect of acetone on the radiation grafting of styrene onto rayon, radiation dose, 1.5 Mrad.

Huang and Rapson¹³ have shown significant differences in the grafting behavior of cotton cellulose and rayon. Sakurada and co-workers²⁵ recently investigated the radiation grafting of styrene-butadiene onto rayon and reported differences in grafting behavior in rayons of different microstructure.

The effect of methanol on the radiation grafting of styrene onto rayon is shown in Figures 2 and 3. As can be seen, the addition of methanol to the styrene in the grafting solution results in a general decrease in the per cent grafting. This is similar to results reported previously for radiation grafting onto cotton cellulose.¹³ The decrease in grafting is probably caused by a reduction of swelling of the rayon due to methanol dilution. It is interesting to note that the effect of methanol on grafting is less pronounced for Fortisan, throughout the entire range of methanol dilution. Figure 3 shows the grafting behavior of Fortisan, HWM, and tire yarn rayon in 1:1 methanol-styrene. As in the case of bulk styrene, Fortisan has the lowest rate of grafting, but differences can now be observed for HWM and tire yarn rayon. The effect of acetone on grafting is shown in Figure 4. A preliminary study of the effect of a chain transfer agent on the radiation grafting was carried out to explore the possibilities of producing cellulose-styrene grafts with shorter polystyrene branches. The addition of small amounts of carbon tetrachloride to styrene results in a drastic decrease in the per cent grafting, as shown in Figure 8.

Structure of Rayon-Styrene Graft Copolymers

The molecular structure of the rayon-styrene graft copolymers was investigated by removing the cellulose backbone by hydrolysis and measur-

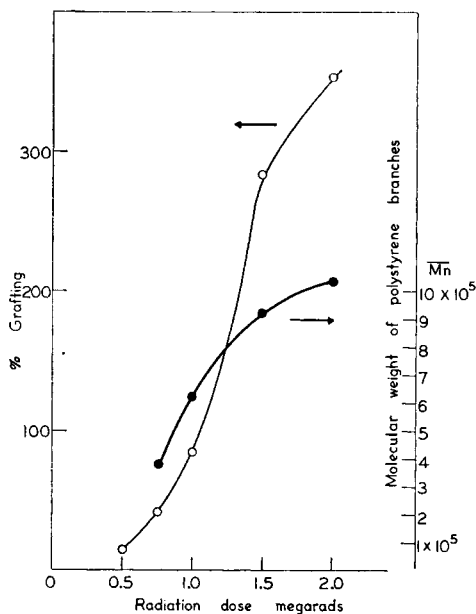


Fig. 5. Molecular weights of polystyrene branches in rayon-styrene grafts. Radiation grafting in bulk.

ing the molecular weights of the isolated polystyrene branches. The results are shown in Figure 5, where \bar{M}_n (the number-average molecular weight of the polystyrene branches) is plotted against the per cent grafting. It is of considerable interest to note that the molecular weights increase with per cent grafting, rising from 380,000 to 1,000,000 as the per cent grafting increases from 42.7 to 353%. High molecular weights of polystyrene branches in cellulose-styrene grafts have been reported by previous workers^{6,7,9,19} and this finding has been attributed to the gel or Trommsdorf effect. The present results confirm these observations and provide further evidence of the strong gel effect. The highly viscous condition existing within the cellulose fiber during the grafting reaction is the primary cause of the gel effect. As the grafting proceeds, more styrene monomer is converted to polystyrene, thus causing an increase in the viscosity of the solution within the fiber and further enhancing the gel effect. The propagating polystyrene chains can thus grow to increasingly high molecular weights before chain termination can occur. The molecular weights of the polystyrene homopolymer formed in the reaction solution did not change very much and were considerably lower, in the range of 30,000–50,000. Based on these molecular weight data, the grafting frequency (i.e., the average number of grafted polystyrene branches per cellulose chain) was calculated. The results are given in Table II. It can be seen that, because of the high molecular weight of the grafted polystyrene, on the average only a small proportion of the cellulose chains carry grafted polystyrene branches. The present calculations represent, of course, only an approximate statis-

TABLE II
Structure of Rayon (Tire Yarn)-Styrene Graft Copolymers
from Radiation Grafting in Bulk Styrene

Radiation dose, Mrad	Grafting, %	Composition of graft		\overline{M}_n of polystyrene branches	\overline{M}_n of rayon	Grafting frequency, PS branches/cellulose chain
		Poly-styrene, %	Cellulose, %			
0.75	42.7	30.0	70.0	378,000	60,000	0.068
1.00	85.8	46.3	53.7	627,000	60,000	0.083
1.50	284.1	74.0	26.0	910,000	60,000	0.188
2.00	353.0	77.9	22.1	1,040,000	60,000	0.207

tical average and are based on the assumptions that (a) the cellulose chains are all accessible and (b) all of the polystyrene is grafted to the cellulose. It should be also emphasized that since the molecular weight distribution of the grafted side chains is very broad, the calculated number averages for polystyrene are of a highly approximate nature. Figure 6 shows the molecular weights of polystyrene branches of rayon-styrene grafts which were prepared in methanol-styrene. It demonstrates the effect of methanol addition on the grafting reaction, in terms of the molecular weights of the grafted polystyrene and per cent grafting. It can be noted that the molecular weight curve of the polystyrene branches closely follows the pattern of the grafting curve. There is an initial drop in the molecular weight of polystyrene which is probably caused by a decrease in viscosity resulting from the addition of methanol. As the amount of methanol

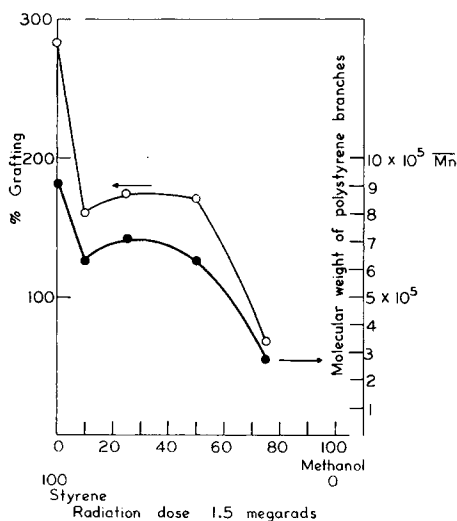


Fig. 6. Molecular weights of polystyrene branches in rayon-styrene grafts. Effect of methanol.

TABLE III
Effect of Methanol Dilution on Composition and Structure of
Rayon-Styrene Graft Copolymers^a

Composition grafting solution, vol.-% methanol in styrene	Grafting, %	Composition of graft		\overline{M}_n of poly- styrene branches	\overline{M}_n of rayon	Grafting frequency, PS branches/ cellulose chain
		Poly- styrene, %	Cellu- lose, %			
0	284.1	74.0	26.0	910,000	60,000	0.188
10	161.2	61.6	38.4	630,000	60,000	0.152
25	174.5	62.7	37.3	710,000	60,000	0.144
50	171.0	63.1	36.9	630,000	60,000	0.163
75	68.2	40.5	59.5	270,000	60,000	0.151

^a Radiation dose 1.5 Mrad, radiation grafting in methanol-styrene solution.

increases, the molecular weight remains fairly constant up to 50% methanol content and then decreases again at higher dilutions. The leveling off in molecular weights is probably caused by the fact that the lowering of viscosity due to the addition of methanol is counteracted by the Trommsdorf effect of the growing polystyrene chains in methanol which is a precipitating medium for polystyrene. The results of the calculations for grafting frequency are shown in Table III. It can be seen that the calculated values for grafting frequency remain surprisingly constant for the entire range of methanol addition. This indicates that the actual number of polystyrene branches per cellulose chain remains unchanged. The decrease in per cent grafting results from the fact that the polystyrene grows to shorter chain lengths due to changes in the composition of the grafting solution.

The accelerating effect of methanol on the radiation grafting of styrene onto cellulose was first reported by Okamura and co-workers.²⁷ Huang and Rapson¹³ have also shown that when cellulose is preswollen with water or other swelling agents, addition of methanol has no accelerative effect. Odian and co-workers²⁰⁻²³ made a detailed study of the accelerative effect of methanol on the radiation grafting of styrene onto synthetic polymers, such as polystyrene, nylon etc. They concluded that the acceleration is caused by either a Trommsdorf effect or a swelling effect and sometimes by a combination of both factors. The present results show that in the absence of a preswelling treatment the effect of methanol on grafting onto cellulose is primarily a swelling effect, which aids in the diffusion of styrene into the fiber. However, in certain regions of methanol-styrene composition there is a Trommsdorf effect which prevents the molecular weights of the polystyrene branches from decreasing steadily with dilution.

Figure 7 shows the effect of acetone on the molecular weight of the polystyrene branches of rayon-styrene grafts prepared in acetone-styrene mixtures. The molecular weights of the polystyrene branches decrease with increasing acetone content. No leveling-off region is observed as in

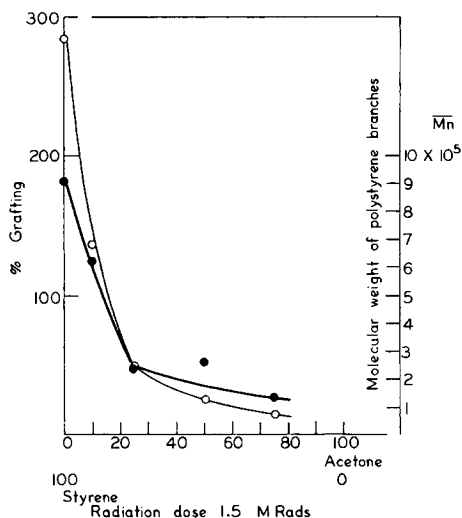


Fig. 7. Molecular weights of polystyrene branches in rayon-styrene graft copolymers. Effect of acetone dilution.

the case of methanol. The rapid decrease in molecular weight is caused by the lowering of viscosity due to dilution with acetone and also by the higher chain transfer constant of acetone. Calculations for the grafting frequency are shown in Table IV. Grafting frequency decreases with increasing acetone content, unlike the case for methanol. The decrease in per cent grafting with acetone dilution is therefore the result of both a lowering in molecular weight and a decrease in the number of polystyrene branches.

The effect of adding a small quantity of a chain transfer agent, such as carbon tetrachloride, on the molecular weights of the grafted polystyrene branches is shown in Figure 8. As can be seen, the molecular weights

TABLE IV
Effect of Acetone Dilution on Composition and Structure of
Rayon-Styrene Graft Copolymers^a

Composition of grafting solution, vol.-% acetone in styrene	Grafting, %	Composition of graft		\bar{M}_n of polystyrene branches	\bar{M}_n of rayon	Grafting frequency, PS branches/cellulose chain
		Poly-styrene, %	Cellulose, %			
0	204.1	74.0	26.0	910,000	60,000	0.188
10	137.6	57.9	42.1	621,000	60,000	0.133
25	49.2	33.0	67.0	239,000	60,000	0.124
50	26.1	20.7	79.3	264,000	60,000	0.059
75	15.1	13.1	86.9	133,000	60,000	0.068

^a Radiation dose 1.5 Mrad; grafting in acetone-styrene mixtures.

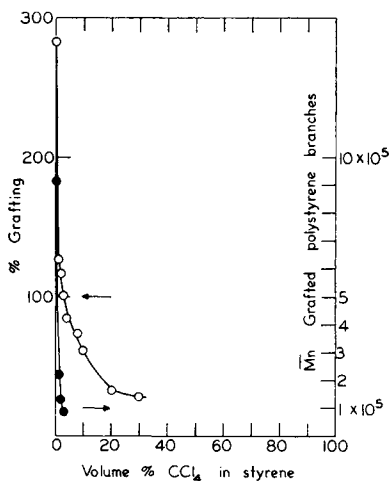


Fig. 8. Effect of carbon tetrachloride on the radiation grafting of styrene onto rayon, radiation dose 1.5 Mrad.

decrease sharply with addition of carbon tetrachloride in the bulk styrene used for grafting. This is due to the high chain transfer action of carbon tetrachloride, which causes the polystyrene branches to terminate at shorter chain lengths. Calculations for the grafting frequency are shown in Table V. The grafting frequency increases with addition of carbon tetrachloride, indicating an increase in the number of grafted polystyrene branches per cellulose chains. The reason for this increase is not clearly understood at the present, but a possible cause may be an increase in the G value of cellulose free-radical formation in the system, resulting from the secondary radiation action of radiolyzed carbon tetrachloride. Such an effect would result in more free-radical sites on the cellulose, leading in turn to an increase in the number of grafted polystyrene chains. On the other

TABLE V
Effect of Carbon Tetrachloride Additive of Composition and Structure of Rayon-Styrene Graft Copolymers*

Composition of grafting solution % carbon tetrachloride in styrene	Grafting, %	Composition of graft			Grafting frequency, PS branches/cellulose chain
		Poly-styrene, %	Cellulose, %	\bar{M}_n of polystyrene branches	
0	284.1	74.0	36.0	910,000	0.188
1	127.1	56.0	44.0	296,000	0.264
2	117.9	54.1	45.9	220,000	0.321
3	100.9	50.2	49.8	133,000	0.450
4	92.8	48.1	51.9	89,000	0.625

* Radiation dose 1.5 Mrad.

hand, it is also possible that there is more homopolymer polystyrene formed within the fiber which cannot be removed. It was also observed that with increased addition of carbon tetrachloride in the grafting solution, the rayon became badly degraded. This degradation effect appeared to be caused by the secondary action of radiolyzed fragments of carbon tetrachloride on the cellulose and supports in part the earlier speculation concerning the increase in G value of cellulose free-radical formation.

On the basis of these preliminary experiments, it would appear that suitable chain-transfer agents can be used to some advantage in radiation grafting to produce cellulose graft copolymers with higher grafting frequency and shorter grafted chains.

Acetylation of Rayon-Styrene Graft Copolymers

There has been considerable controversy concerning the problem of how much of the grafted polystyrene (as defined by weight increase) is chemically bound to the cellulose. In a recent electron microscopic investigation of rayon-styrene graft copolymers,¹¹ it has been shown that a certain amount of polystyrene could be removed by benzene extraction of ultra-thin cross sections (ca. 500 Å. thick) of the grafted rayon filament. This polystyrene was considered to be entrapped homopolymer which could not be removed by extracting the intact grafted filament, because of morphological restrictions in the diffusion of the large polystyrene molecules out of the rayon. It was also observed that the polystyrene homopolymer appeared to be located mainly in the voids of the filament structure. In

TABLE VI
Acetylation and Extraction of Rayon-Styrene Graft Copolymers
Obtained by Radiation Grafting in Bulk

Copolymer	Grafting, %	Grafted Polystyrene removed by benzene extraction following acetylation, %	Poly- styrene [η]	\overline{M}_n
Tire yarn-styrene	20.8	10.4	—	
	55.8	27.5	1.70	374,000
	107.4	24.1	2.65	635,000
	281.6	29.3	3.24	836,000
HWM-styrene	42.8	18.0	—	
	233.5	29.9	2.72	656,000
	285.5	33.2	3.23	737,000
	420.6	29.4	3.64	986,000
Fortisan-styrene	41.2	20.0	—	
	70.9	20.2	2.10	432,000
	98.4	19.4	1.45	276,000
	121.7	22.1	1.55	302,000

order to obtain a quantitative estimate of the polystyrene homopolymer present in the graft, the rayon-styrene grafts were acetylated under non-degradative conditions in acetic anhydride-pyridine mixtures, and the acetylated graft was extracted with benzene. Since the entrapped polystyrene homopolymer was located mainly in the voids, it was reasoned that acetylation would completely change the morphological structure of the original rayon and render the homopolymer extractable. The results are shown in Table VI. It can be seen that approximately 20-30% of the grafted polystyrene can be extracted following acetylation. The polystyrene removed in this manner is considered to be homopolymer and corresponds to the polystyrene occupying the voids, as previously observed in the electron microscopic investigation.¹¹ The molecular weights of the extracted polystyrene homopolymer are also shown in Table VI and are comparable to those of the polystyrene branches isolated by hydrolysis of the rayon-styrene graft copolymers. It can also be noted that the percentage of polystyrene removed from Fortisan-styrene grafts is somewhat lower than for grafts on HWM and tire yarn rayons. This is probably related to the morphology and microstructure of the original rayon.

Solubility of Rayon-Styrene Grafts in CED

The solubility of rayon-styrene graft copolymers in 0.5*M* cupriethylenediamine (CED) is shown in Figure 9. It can be seen that the percentage of graft copolymer which dissolves in CED decreases with per cent grafting. The portion which dissolves in CED is considered to be ungrafted cellulose. Earlier in this paper, it was shown that only a small proportion of cellulose chains in the rayon carry grafted polystyrene branches. The present results indicate, however, that the amount of cellulose removed by CED is considerably less than that based on previous calculations. This discrepancy can probably be ascribed to the fact that not all the chains are accessible. In terms of rayon microstructure, grafting of polystyrene which takes place on the surfaces of the microfibrils and in the amorphous regions renders the inner cellulose chains inaccessible to the dissolving action of CED. Electron microscopic observation¹¹ on ultra-thin cross sections

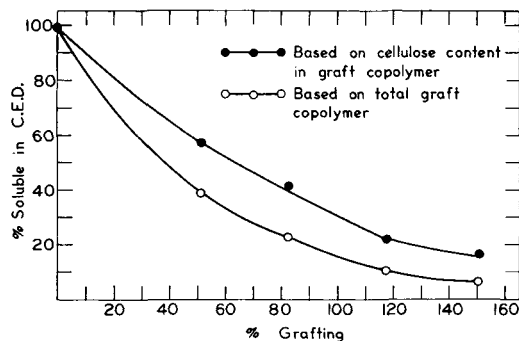


Fig. 9. Solubility of rayon-styrene graft in 0.5*M* cupriethylenediamine.

(ca. 500 A. thick) of rayon-styrene grafts containing 112% polystyrene graft also indicate that only a small portion of the grafted rayon can be removed by treatment with CED.

Hygroscopicity of Styrene Grafted Rayons

The equilibrium moistures content of three rayon-styrene graft copolymers and of the corresponding ungrafted rayon are shown in Figure 10. There is a decrease in equilibrium moisture content of the grafted rayons with increase in per cent grafting. However, if the equilibrium moisture contents are based on the weight of cellulose in the graft copolymer rather than on the total weight of the graft copolymer, all the data fall on the isotherm for the ungrafted control rayon. In other words, the hygroscopic nature of the cellulose portion of the grafted rayon has not changed. In cellulose, the hydroxyl groups in the amorphous regions are mainly responsible for the absorption of water, since the crystalline regions are inaccessible.²⁶ It is also in these amorphous regions and on the surfaces of the crystallites that graft copolymerization of styrene takes place. Since the grafting frequency is quite low, the actual number of hydroxyl groups which participate in the graft copolymerization is negligible and should not affect the hygroscopicity of the cellulose. One would expect, however, that the large amounts of hydrophobic polystyrene would render certain parts of the amorphous regions inaccessible to the diffusion of water vapor. The present results suggest, therefore, that the amorphous regions of the rayon remain relatively loose and permit the water molecules to diffuse despite the presence of polystyrene.

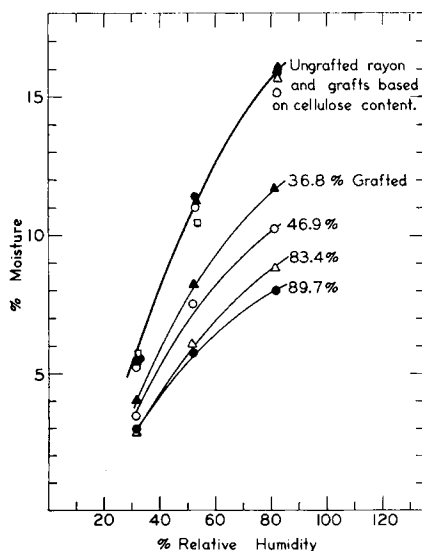


Fig. 10. Moisture absorption of rayon-styrene graft copolymers.

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Résumé

Des copolymères greffés de rayonne-styrène ont été préparés par la méthode d'irradiation directe en utilisant la technique de prégonflement par irradiation aux rayons- γ du cobalt-60. Des greffages ont été effectués sur du styrène en bloc et en des mélanges styrène-solvant, tels styrène-méthanol et styrène-acétone, afin d'en étudier l'effet sur la copolymérisation greffée et la structure du copolymère greffé qui en résulte. L'effet

du tétrachlorure de carbone, comme agent de transfert a également été étudié. Trois types différents de fils de rayonne ont été utilisés; le fortisan, un type modifié de rayonne à module humide élevé, et un fil à pneu de haute tenacité en vue d'étudier l'effet de la microstructure de la rayonne sur le greffage. La structure moléculaire des copolymères greffés rayonne-styrène a été étudiée en hydrolysant la squelette cellulosique et en mesurant le poids moléculaire des branches de polystyrène greffé. Pour les greffages dans le styrène en bloc, le poids moléculaire des greffons de polystyrène s'élevait de 400.000 à 1.000.000 tandis que ceux du polystyrène homopolymère formé dans la solution s'élevait de 30.000 à 50.000. Les poids moléculaires des branches de polystyrène greffés tendent à croître avec le pourcent de greffage au sein du copolymère greffé. Dans le cas de greffage dans le mélange styrène-méthanol et styrène-acétone, le poids moléculaires des branches de polystyrène décroissait avec une teneur croissante en solvant. L'addition de tétrachlorure de carbone au styrène en bloc avait comme conséquence une forte diminution de poids moléculaire des branches greffées. La fréquence de greffage, c.à.d. le nombre de branches de polystyrène par chaîne cellulosique a été calculée au départ du pourcent de greffage et des poids moléculaires des branches de polystyrène. La morphologie des copolymères greffés de rayonne-styrène et certaines de leurs propriétés physiques ont été soumises à discussion.

Zusammenfassung

Rayon-Styrolpfropfcopolymere wurden durch direkte Bestrahlung nach dem Vorquellungsverfahren mit γ -Strahlen von ^{60}Co dargestellt. Die Aufpfropfung wurde in reinem Styrol und in Styrol-Lösungsmittelgemischen, wie Styrol/Methanol und Styrol/Aceton, zur Untersuchung ihres Einflusses auf die Pfropfcopolymerisationsreaktion und auf die Struktur der gebildeten Pfropfcopolymeren ausgeführt. Der Einfluss von Tetrachlorkohlenstoff, einem Kettenüberträger, wurde ebenfalls untersucht. Drei verschiedene Rayongarntypen wurden zur Untersuchung des Einflusses der Rayonmikrostruktur auf die Pfropfreaktion verwendet: Fortisan, ein Rayon von modifiziertem Typ mit hohem Nassmodul und ein Reifengarn hoher Festigkeit. Die Molekülstruktur der Rayon-Styrolpfropfcopolymeren wurde durch Hydrolyse der Zellulosehauptkette und Messung des Molekulargewichts der gepfropften Polystyrolzweige untersucht. Bei der Pfropfung in reinem Styrol lag das Molekulargewicht des aufgepfropften Polystyrols zwischen 400.000 und 1.000.000, während dasjenige des in der Aussenlösung gebildeten Homopolymers in der Größenordnung von 30.000–50.000 lag. Das Molekulargewicht der aufgepfropften Polystyrolzweige nahm mit prozentueller Aufpfropfung im Pfropfcopolymeren zu. Bei der Aufpfropfung in Styrol/Methanol- und Styrol/Aceton-Mischungen nahm das Molekulargewicht der Polystyrolzweige mit steigendem Lösungsmittelgehalt ab. Der Zusatz von Tetrachlorkohlenstoff zum Styrol führte zu einer scharfen Abnahme des Molekulargewichts der aufgepfropften Zweige. Die Pfropffrequenz, oder die Anzahl der Polystyrolzweige pro Zellulosekette wurde aus der prozentuellen Aufpfropfung und dem Molekulargewicht der Polystyrolzweige berechnet. Die Morphologie der Rayon-Styrolpfropfcopolymeren und einige ihrer physikalischen Eigenschaften werden diskutiert.

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