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Structure and Properties of Cellulose Graft Copolymers. II. Cellulose–Styrene Graft Copolymers Synthesized by the Ceric Ion Method*

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Synopsis

Styrene was graft-copolymerized onto wood cellulose by the ceric ion method of Mino and Kaizerman. The grafting reaction was found to depend strongly on the concentration of ceric ion in the grafting system and maximum grafting occurred in a narrow range of concentration of initiator, 1.0×10^{-3}–1.8×10^{-3} mol/l, at 58 ± 1°C. A pretreatment technique, developed to enhance the monomer diffusion into cellulose, was found to increase the grafting considerably. The structures of the cellulose–styrene graft copolymers were studied by hydrolyzing away the cellulose backbone to isolate the grafted polystyrene branches. The molecular weights and the molecular weight distributions of the grafted polystyrene were determined using gel permeation chromatography. The number-average molecular weight ($\bar{M}_n$) ranged from 23,000 to 453,000 and the polydispersity ratios ($\bar{M}_w/\bar{M}_n$) varied from 2.5 to 8.0. The grafting frequencies calculated from the per cent grafting and molecular weight data were of the order of 0.05–0.4 polystyrene branches per cellulose chain.

INTRODUCTION

The purpose of this series of investigations is to compare the structure and properties of cellulose graft copolymers prepared by various methods of graft copolymerization. In the previous paper,[1] the structure of rayon–styrene graft copolymers prepared by the direct γ-ray irradiation method was reported. The present investigation is concerned with the structure of cellulose–styrene graft copolymers synthesized by the ceric ion method.

The ceric ion method for grafting vinyl monomers onto polyhydroxyl substrates was first reported by Mino and Kaizerman.[2] Extensive applications of this technique for grafting onto cellulose have been reported in the literature. However, most of these grafting studies have been carried out with acrylic type monomers or with monomers such as vinyl chloride, which are soluble in water to some extent. Relatively little work has been reported on styrene which is only sparingly soluble in water. Ide[3] studied the graft copolymerization of styrene onto cellulose using ceric ion initiation and reported that grafting occurred only in a narrow range of ceric ion

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concentration. Sumitomo and Hachihama[4] used cellulose pretreated with ceric ion and carried out the grafting reaction in a styrene–methanol mixture.

It is now well established that the molecular weights of the grafted polystyrene branches in cellulose graft copolymers are generally very high.[1,4–6] This results in a low grafting frequency (average number of grafted polymer branches per cellulose chain) for a given per cent grafting. The grafted polymer branches are also presumed to have a broad molecular weight distribution, although experimental results have not yet been reported for cellulose graft copolymers. In this study, gel permeation chromatography (GPC) has been used to obtain information on the molecular weights and molecular weight distributions of the grafted polystyrene branches in cellulose–styrene graft copolymers synthesized by the ceric ion method.

EXPERIMENTAL

Materials

Cellulose. Novocell K wood pulp obtained from International Cellulose Research Limited, Hawkesbury, Ontario, was used in all the graft copolymerization runs.

Monomers. Acrylonitrile, acrylamide, methyl methacrylate, and *n*-butyl acrylate were obtained from Monomer-Polymer Laboratories, Philadelphia, Pa. Styrene monomer (highest purity) was obtained from Eastman Organic Chemicals Limited. Monodisperse standard polystyrene samples were obtained from Pressure Chemicals Limited, Pittsburgh, Pa.

Chemicals. Cerium ammonium nitrate (reagent grade) was obtained from J. T. Baker Chemicals Ltd. Methanol, acetone, tetrahydrofuran, methylene chloride, benzene, *N*,*N*-dimethylformamide, acetic acid, acetic anhydride, sulfuric acid, and nitric acid (all of reagent grade) were obtained from Fisher Scientific Co. Ltd.

Purification of Monomers

Methyl methacrylate, *n*-butyl acrylate, and styrene were purified by washing with a 6–8% sodium hydroxide solution to remove the inhibitor. After this treatment, the monomers were washed with distilled water and dried overnight over anhydrous calcium chloride. The monomers were then distilled under vacuum in a distillation apparatus and stored in a refrigerator.

Preparation of Initiator Stock Solution

A 0.1*M* stock solution of the initiator was prepared by dissolving the required amount of cerium ammonium nitrate, $Ce(NH_4)_2(NO_3)_6$, in a 1*M* nitric acid solution. During the course of the experiments it was observed that the activity of the initiator appeared to decrease with time. There-

fore, stock solutions which were stored for more than 4 days were discarded and fresh solutions were prepared.

Grafting Procedure

The graft copolymerization reactions were carried out in standard three-necked taper-joint flasks of 500 ml capacity. The samples of cellulose (1–2 g) were first swollen in water for 30 min and then dispersed in a Waring Blendor. The dispersed cellulose was transferred to the reaction flask and maintained at the reaction temperature in a constant temperature bath. Nitrogen was continuously bubbled through the system. After adequate purging, the required amount of monomer was added, followed by the initiator. The reaction was then allowed to proceed for the required amount of time. After the completion of the reaction, the grafted cellulose was taken out and washed with distilled water and acetone to remove excess monomer and initiator. It was then oven-dried at 60°C under vacuum to constant weight. The per cent grafting and the grafting frequency were calculated according to eqs. (1) and (2).

$$\text{Per cent grafting} = \frac{(\text{weight of grafted sample} - \text{weight of cellulose}) \times 100}{\text{weight of cellulose}} \quad (1)$$

$$\text{Grafting frequency} = \frac{\text{average number of polystyrene chains in graft copolymer}}{\text{average number of cellulose chains in graft copolymer}}$$

$$= \frac{\text{Per cent polystyrene in graft copolymer}}{\text{Per cent cellulose in graft copolymer}} \times \frac{\bar{M}_n \text{ of cellulose}}{\bar{M}_n \text{ of polystyrene}} \quad (2)$$

All calculations are based on a moisture-free cellulose weight basis.

Pretreatment Technique. A pretreatment technique was developed to aid the diffusion of styrene into cellulose, in order to improve styrene grafting onto cellulose. In this method, after the initial swelling and dispersion in water, the cellulose was transferred to a glass beaker and styrene monomer was added to the cellulose. The contents of the beaker were stirred vigorously for 15 min to facilitate styrene diffusion into cellulose. The contents were then transferred to the reaction vessel and the grafting reaction carried out according to the method described earlier, except that no additional monomer was added to the reaction flask.

Styrene Graft Copolymerization in Presence of Methanol. The effect of methanol, a solvent for styrene, on the grafting was investigated. In this method, after the initial swelling and dispersion in water, the cellulose was transferred to a glass beaker and a measured amount of methanol was added to the cellulose. The contents of the beaker were stirred

vigorously for 15 min. Styrene monomer was then added and the stirring continued for another 15 min. The remainder of the grafting procedure was identical to the pretreatment technique described above.

Hydrolysis of Cellulose–Styrene Graft Copolymers

In order to study the molecular weight distributions of the polystyrene grafted branches, the cellulose–styrene graft copolymers were acetolyzed to hydrolyze away the cellulose backbone. The hydrolysis was carried out in 300-ml Erlenmeyer flasks with ground joint stoppers. Approximately 2 g of graft copolymer sample was first swollen in *N,N*-dimethylformamide and then transferred to the flask containing the hydrolysis mixture. This mixture consists of 70 ml acetic anhydride, 70 ml benzene, and 12 ml sulfuric acid (72%). The flask was clamped to a Burrel wrist action shaker to ensure continuous stirring. The reaction was carried out at 60°C for 72 hr.

After the completion of the reaction the sample was precipitated in methanol, filtered, and dissolved in methylene chloride. This was repeated three or four times and the isolated polystyrene was reprecipitated in methanol after flash evaporating the excess methylene chloride. The precipitated polystyrene was then oven-dried at 60°C under vacuum.

Molecular Weight Determinations

Viscometry. The molecular weights of the cellulose wood pulp samples were obtained by measuring the intrinsic viscosities in 0.5*M* cupriethylenediamine in a Cannon-Ubbelohde dilution viscometer, size 100. The relationship of Immergut et al.[7] was used to calculate the number-average molecular weight $\bar{M}_n$ of the cellulose:

$$[\eta] = 1.33 \times 10^{-4} \bar{M}_n^{0.905}$$

The intrinsic viscosities of polystyrene were measured in benzene in a Cannon-Ubbelohde dilution viscometer at 30°C. The average molecular weights were calculated by using Mayo's equation[8] for polydisperse polystyrene:

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

Molecular Weight Distributions of Isolated Polystyrene Branches by Gel Permeation Chromatography. A Model 200 Water Associates gel permeation chromatography unit was used to obtain the molecular weight distributions of the isolated polystyrene branches. The weight-average $\bar{M}_w$ and number-average $\bar{M}_n$ molecular weights were calculated from the molecular weight chromatograms by using a calibration chart. Tetrahydrofuran was the eluting solvent, and the flow rate was maintained at 1 ml/min. The oven temperature was maintained at 25 ± 0.5°C. Eleven monodisperse ($\bar{M}_w/\bar{M}_n$ = 1.06–1.20) standard polystyrene samples in the range 900 to 1.8 × 10^6 were used to calibrate the gel permeation chromatograph. The calibration was carried out by injecting 2 ml of each of the standards at 0.5%, 0.25%, 0.125%, and 0.0625% concentrations

by weight in tetrahydrofuran. The elution count corresponding to the peak of the chromatogram was plotted against the concentration for each of the standards. The plots were extrapolated to zero concentration to minimize concentration effects, and the concentration-corrected peak elution count of each standard was plotted against the logarithem of molecular weight. The calibration chart is shown in Figure 8.

The gel permeation chromatograms for the grafted polystyrene samples were obtained by injecting 2 ml of a 0.25% solution in tetrahydrofuran. The solutions were filtered in a pressure filter under nitrogen atmosphere to remove any impurities that might clog the pores of the crosslinked polystyrene gel packing in the columns. Four columns, of pore sizes 3×10^6, 10^5, 10^4, and 10^3 Å, were used. The weight-average and number-average molecular weights and the polydispersity ratios $\bar{M}_w/\bar{M}_n$, were calculated from the GPC chromatograms and the calibration plot of molecular weight versus elution volume. The method of Tung[9] was used to correct for imperfect resolution resulting from axial dispersion in the GPC columns. For these calculations, computer programs were written in Fortran IV and all computations were carried out on the IBM 350/75 computer at the University of Waterloo Computing Center.

RESULTS AND DISCUSSION

Graft Copolymerization of Acrylic Monomers onto Cellulose

The dependence of ceric ion-initiated vinyl graft copolymerization on such factors as the concentration of initiator and monomer, grafting time, temperature, etc., has been widely reported. As can be seen from Figure 1, the per cent grafting increases to a maximum and then decreases with further increase in the concentration of the initiator. The decrease in grafting beyond a certain concentration can be explained by the fact that the oxidative termination rates begin to increase with increasing initiator concentration. The optimum range of initiator concentration found in the present work was $3.0–6.0 \times 10^{-3}$ mol/l. This is in good agreement with the published results of Schwab et al.,[10] Reyes et al.,[11] and Richards and White.[12]

Graft Copolymerization of Styrene onto Cellulose

Figure 1 clearly shows that no appreciable grafting of styrene onto cellulose can be observed under the grafting conditions employed for the acrylic monomers.

The effect of the concentration of initiator on per cent grafting is shown in Figure 2. It is interesting to note that, unlike acrylic grafting, styrene grafting occurred only in a narrow range of concentration of initiator. The pretreatment technique which was developed to enhance the diffusion of monomer into the cellulose increased the per cent grafting considerably. The maximum in the per cent grafting was obtained in a narrow concentration range of initiator between 1.0 and 1.8×10^{-3} mol/l for both the

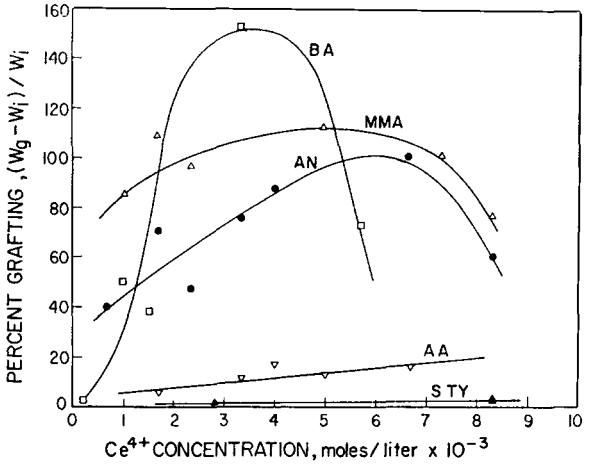

Fig. 1. Effect of initiator concentration on the grafting of vinyl monomers onto cellulose: (▽) acrylamide; (●) acrylonitrile; (□) *n*-butyl acrylate; (△) methyl methacrylate; (▲) styrene. Grafting time, 90 min (45 min for methyl methacrylate); grafting temperature, 35°C; total polymerization mixture volume, 300 ml.

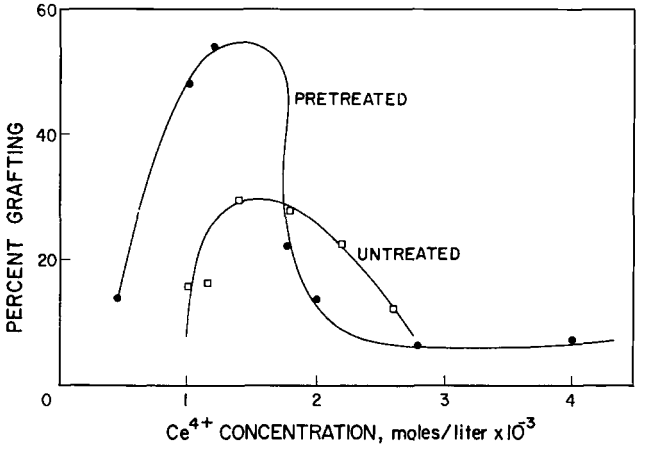

Fig. 2. Effect of initiator concentration on the graft copolymerization of styrene onto cellulose: (●) pretreated styrene grafting; (□) untreated styrene grafting. Grafting time, 60 min (pretreated), 240 min (untreated); temperature, 60°C; amount of styrene, 10 ml (pretreated), 25 ml (untreated); total polymerization mixture volume, 250 ml.

pretreated and untreated cases. The molar ratio of cellulose (moles of anhydroglucose units) to ceric ion in the reaction mixture is shown in Figure 3. The optimum ratio is 36 and 27, respectively, for the pretreated and untreated cases. Careful control of the cellulose/ceric ion ratio in the reaction mixture was found to be important in order to achieve good grafting with styrene. The dependence of the per cent grafting on a narrow concentration range of initiator supports the earlier findings of Ide.[3] Figure 4 shows that while per cent grafting increased gradually with graft-

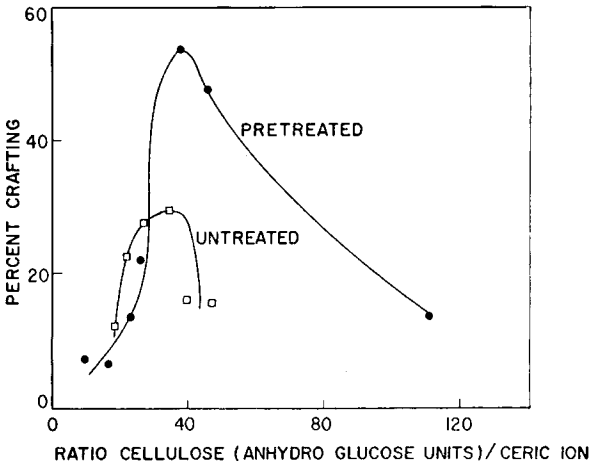

Fig. 3. Effect of cellulose/ceric ion molar ratio on the grafting of styrene onto cellulose.

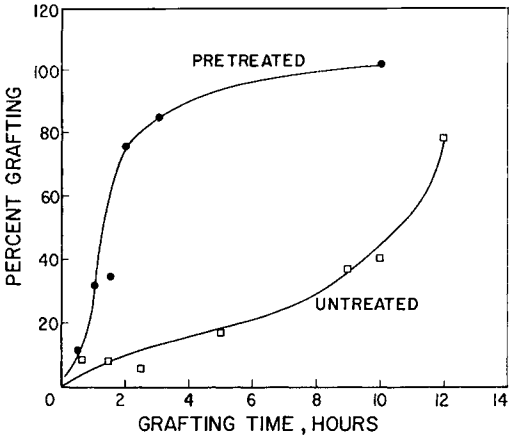

Fig. 4. Effect of grafting time on the graft copolymerization of styrene onto cellulose: (●) pretreated grafting; (□) untreated grafting. Grafting temperature, 58 ± 1°C; initiator concentration, 1.2×10^{-3} mol/l (pretreated), 1.6×10^{-3} mol/l (untreated); total polymerization mixture volume, 250 ml; amount of monomer, 10 ml (pretreated), 25 ml (untreated).

ing time for untreated styrene grafting, a rapid initial increase in the per cent grafting can be noted in the case of pretreated styrene grafting. This can be explained by the fact that the pretreatment technique facilitates the initial diffusion of styrene into cellulose resulting in the availability of a larger amount of monomer for grafting.

One of the reasons for the poor grafting yields with styrene is believed to be the limited solubility of the monomer in water. As shown in Table I, the solubility of styrene in water rises from 0.027 to 0.038 g/100 ml as the temperature increases from 20 to 50°C. Reactions carried out at three different temperatures showed an increase in per cent grafting with temper-

TABLE I
Monomer Solubility Data (in Water)

Temperature, °C	Solubility, g/100 ml water			
	Acrylonitrile[a]	Methyl methacrylate[b]	Styrene[c]	Acrylamide
20	7.93	1.62	0.027	—
30	8.17	1.50	—	21.55
40	8.58	1.43	0.032	—
50	—	1.38	0.038	—
60	10.00	—	—	—

[a] Data of American Cyanamid Co.[17]
[b] Data of Kanamaru et al.[18]
[c] Data of Bovey et al.[19]

ature. This is shown in Figure 5 and substantiates the earlier results of Ide.[3] The per cent grafting–temperature studies were restricted to temperatures <60°C due to the reported instability of the ceric ion initiator above 70°C.[10] All the pretreated styrene graft copolymerization runs were carried out with 10 ml of styrene in a total reaction mixture volume of 250 ml.

A brief study of the effect of methanol on the graft copolymerization of styrene onto cellulose showed that it had little effect on the grafting of styrene by the pretreatment technique. The results are shown in Figures 6 and 7. There is a reduction in the per cent grafting at the optimum initiator concentration ranges described earlier (1.0–1.8 $\times$ 10^{-3} mol/l). However, there is an increase in the per cent grafting at higher concentrations of initiator compared to grafting in the absence of methanol. This can be attributed to the fact that methanol can also react with ceric ions, thereby reducing the effective concentration of ceric ion.

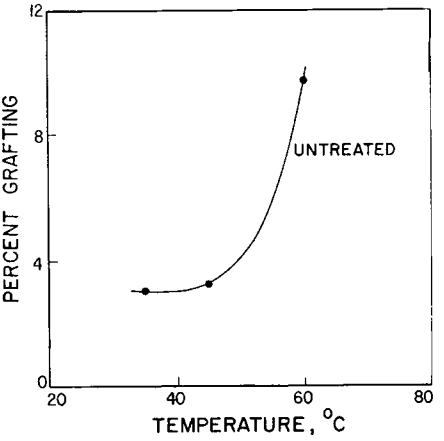

Fig. 5. Effect of temperature on the graft copolymerization of styrene onto cellulose. Grafting time, 60 min; initiator concentration, 1.6 $\times$ 10^{-3} mol/l; amount of styrene, 10 ml; total volume of reaction mixture, 250 ml.

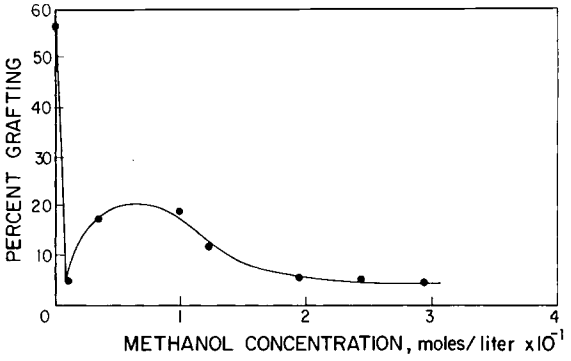

Fig. 6. Effect of methanol on the pretreated graft copolymerization of styrene onto cellulose. Grafting time, 60 min; grafting temperature, 60 ± 1°C; initiator concentration, 1.2×10^{-3} mol/l; total polymerization mixture volume, 250 ml.

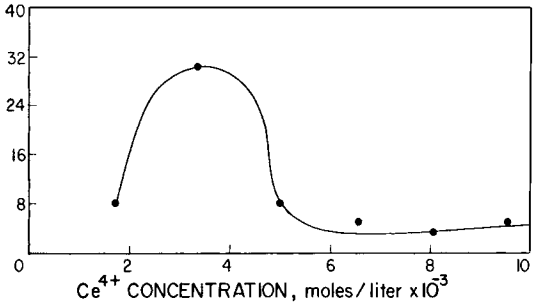

Fig. 7. Effect of initiator concentration on pretreated styrene grafting onto cellulose in the presence of methanol. Grafting time, 90 min; grafting temperature, 60 ± 1°C; amount of styrene, 15 ml; total polymerization mixture volume, 300 ml.

Characterization of Cellulose–Styrene Graft Copolymers

The polystyrene branches were isolated from the cellulose backbone through hydrolysis. Gel permeation chromatography was used to determine the molecular weight distributions of these polystyrene branches. The weight-average and the number-average molecular weights and the polydispersity ratios $\bar{M}_w/\bar{M}_n$ were calculated from the chromatograms by using the calibration chart shown in Figure 8. A typical GPC chromatogram and the calculated integral distribution curve are shown in Figures 9 and 10, respectively.

The effect of the concentration of initiator on the number-average molecular weights $\bar{M}_n$ of the polystyrene branches, the polydispersion ratios, and the grafting frequencies is shown in Figure 11 and in Table II. For the pretreated case, the change in $\bar{M}_n$ of the grafted polystyrene branches with the initiator concentration follows the per cent grafting curve. However, for ordinary grafting, $\bar{M}_n$ decreased initially with the concentration of initiator, increased near the optimum concentration range and finally decreased. The change of $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and grafting frequencies with

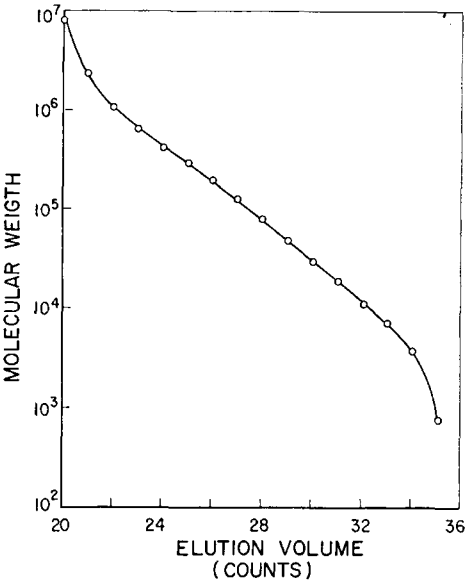

Fig. 8. Gel permeation chromatography calibration curve. Solvent flow rate, 1 ml/min; sample concentrations, 0.5, 0.25, 0.125, and 0.0625% by weight of each standard sample in tetrahydrofuran; sample injection time, 60 sec; molecular weight range, 900–1,800,000; column pore size, 3×10^6, 10^5, 10^4, and 10^3 Å.

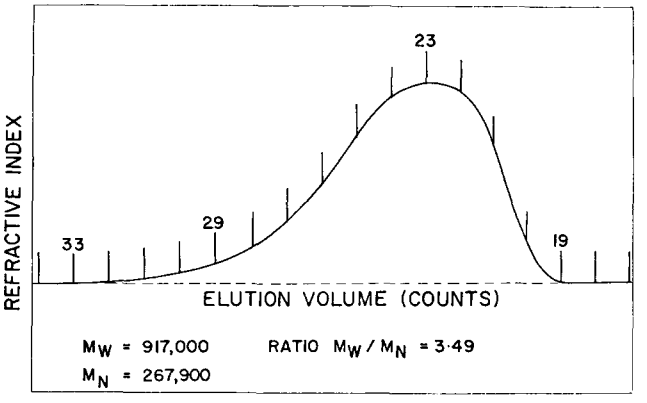

Fig. 9. Typical GPC chromatogram of isolated polystyrene branches. Sample concentration, 0.25%; injection time, 1 min; oven temperature, 25°C; sensitivity; 8×.

grafting time is shown in Table III. For the pretreated case, $\bar{M}_n$ rapidly dropped to a minimum and then increased gradually, while in the untreated case $\bar{M}_n$ increased gradually. These different trends reveal the complex nature of the ceric ion initiated graft copolymerization reactions which cannot be explained by the kinetic schemes of Mino et al.,[13] Marchessault et al.,[14] and Wallace and Young.[15] It is quite probable that more than one termination mechanism is taking part in the graft copolymerization reac-

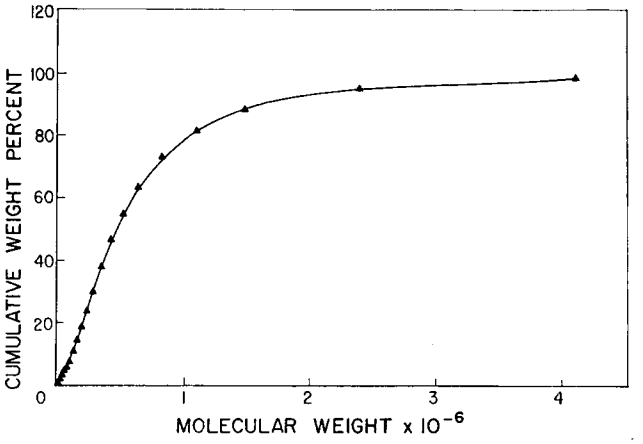

Fig. 10. Integral distribution curve of isolated polystyrene branches (calculated from data of Fig. 9).

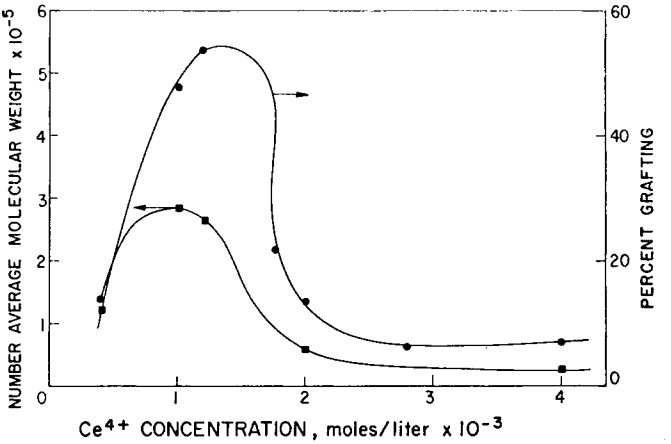

Fig. 11. Effect of initiator concentration on the number-average molecular weights of polystyrene branches in cellulose–styrene graft copolymers (pretreated grafting): (●) pretreated grafting curve; (■) number-average molecular weight curve.

tion. However, a detailed investigation of the kinetics will be required in order to understand this heterogeneous mechanism more fully.

The $\bar{M}_n$ of the isolated polystyrene branches varied from 23,000 to 453,000. The molecular weight distributions of the polystyrene chains are shown in Tables II and III. The polydispersity ratios ranged from 2.5 to 8.0, indicating a broad molecular weight distribution. The grafting frequencies, which are a measure of the number of polystyrene chains per cellulose molecule were generally very low. On the average, only 0.05–0.4 polystyrene chains were grafted per cellulose chain. The calculated grafting frequencies are only average values and are based on the assumption that all the cellulose chains are available for the graft copolymerization reaction. The number-average molecular weights $\bar{M}_n$ of polystyrene

TABLE II
Effect of Initiator Concentration on the Molecular Weights and Molecular Weight Distributions of Grafted Polystyrene Branches[a]

Run[b]	Grafting, %	(Ce^{IV}) $\times 10^3$, mol/l	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	Grafting frequency
Pr-23	7.30	4.0	1.18	0.23	5.26	0.241
Pr-24	13.55	2.0	3.82	0.62	6.12	0.378
Pr-25	13.83	0.8	4.31	1.19	3.61	0.109
Pr-26	47.69	1.0	8.92	3.13	2.85	0.144
Pr-27	53.76	1.2	8.22	2.84	2.90	0.179
Un-59	15.60	1.0	7.64	2.65	2.88	0.056
Un-58	16.00	1.2	7.22	1.72	4.20	0.088
Un-55	29.29	1.4	4.26	0.51	8.32	0.511
Un-56	27.63	1.8	6.30	1.61	3.91	0.162
Un-57	22.35	2.2	4.80	0.92	5.24	0.231
Un-60	12.07	2.8	4.04	0.35	11.68	0.328

[a] Cellulose molecular weight $\bar{M}_n$ = 94,600.
[b] Pr = pretreated grafting; Un = no pretreatment.

TABLE III
Effect of Grafting Time on the Molecular Weights and Molecular Weight Distributions of Grafted Polystyrene Branches[a]

Run[b]	Grafting, %	Time, min	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	Grafting frequency
Pr-37	11.20	30	10.17	4.36	2.34	0.020
Pr-31	31.31	60	7.08	3.90	1.82	0.079
Pr-63	34.33	90	25.87	4.53	5.71	0.075
Pr-61	75.82	120	3.72	0.95	3.90	0.784
Pr-62	85.21	180	6.31	1.93	3.26	0.435
Pr-6	102.30	600	11.51	4.29	2.69	0.235
Un-79	8.25	45	4.57	0.89	5.11	0.087
Un-80	7.90	90	5.55	1.09	5.07	0.068
Un-81	5.43	150	5.50	1.14	4.81	0.045
Un-82	17.10	300	5.41	0.86	6.28	0.188
Un-65	37.10	540	3.27	1.41	2.32	0.249
Un-64	40.75	600	4.76	1.29	3.68	0.298
Un-66	79.68	720	3.54	0.86	4.10	0.873

[a] Cellulose molecular weight: $\bar{M}_n$ = 94,600.
[b] Pr = pretreated grafting; Un = no pretreatment.

branches obtained in the present study are comparable with those reported by Iwakura et al.,[16] but they are much lower than the values reported by Sumitomo and Hachihama.[4] These discrepancies probably arise from the use of intrinsic viscosity molecular weight relationships to determine molecular weights. At higher molecular weight ranges and for polydisperse polystyrene, the so-called $\bar{M}_n$ values calculated from empirical viscometric equations tend to be closer to the $\bar{M}_w$ values, as shown in Table IV. The use of Mayo's equation, for example, yields $\bar{M}_n$ values which are too high. It is of interest to note that the $\bar{M}_n$ of the polystyrene branches obtained in

TABLE IV
Comparison of Polystyrene Molecular Weights Obtained from Viscometry and Gel Permeation Chromatography (GPC) Data

Run	Intrinsic viscosity, $[\eta]$	Molecular weights of polystyrene branches			
		Calcd.[a]	From GPC data		
		$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
Pr-6	3.3	8.60	11.50	4.28	2.69
Pr-23	0.92	1.49	1.18	0.23	5.26
Pr-24	1.36	2.54	3.82	0.62	6.12
Pr-25	3.10	7.85	4.31	1.19	3.61
Pr-26	2.50	5.85	8.92	3.13	2.85
Pr-27	2.25	5.08	8.22	2.84	2.90

[a] By Mayo's equation.

TABLE V
Effect of Methanol on the Molecular Weights and Molecular Weight Distributions of Grafted Polystyrene Branches

Run	Grafting, %	Methanol concentration, mol/l	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	Grafting frequency
76	4.67	0.0098	8.89	2.56	3.47	0.017
77	17.81	0.029	9.20	2.10	4.38	0.081
78	11.72	0.122	8.70	1.57	5.54	0.068
74	5.12	0.244	12.68	3.52	3.60	0.019

the present study are generally lower than the values reported for the polystyrene branches in radiation grafting.[1,5,6] The effect of methanol on the molecular weights and molecular weight distributions of the grafted polystyrene branches is shown in Table V. A definite lowering in the molecular weights $\bar{M}_n$ for radiation grafting of styrene in presence of solvents was observed by Stannett et al.[5,6] and Huang.[1] However, in the present work, no noticeable differences can be found in the $\bar{M}_n$ values obtained in the presence and absence of methanol.

The graft copolymerization reaction is thought to proceed according to the following mechanism. Ceric ions complex with cellulose hydroxyl groups and the decomposition of the complex results in the formation of free radicals on the backbone. The success of the initiation of graft copolymer chains depends primarily on the diffusion rate of the monomer onto cellulose. The initiation step is favored only when the diffusion rate is at least comparable to the rate of oxidative termination. In the case of the pretreated styrene graft copolymerization, the increased availability of styrene monomer at the free-radical sites on the cellulose backbone accounts for the improved grafting results.

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