Radiation-Induced Reactions with Cellulose. III. Kinetics of Styrene Copolymerization in Methanol

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Synopsis

The kinetics of the radiation-induced grafting of styrene to cellulose in methanol have been studied in air at dose rates of 0.007, 0.014, and 0.078 Mrad/hr. in ^{60}Co and spent fuel element facilities. The variables affecting rate of grafting include monomer concentration, radiation dose rate, and total dose. Grafting reaches a maximum at 60-70% by volume methanol in styrene. The results have been interpreted in terms of possible grafting mechanisms, including charge-transfer intermediates; however, a complete mathematical treatment of the data is not possible at present because of the absence of appropriate swelling data for cellulose in mixtures of styrene and methanol. Poor grafting observed in solutions of up to 10% monomer is attributed to radical scavenging (predominantly from the solvent) by the monomer leading to the formation of scavenged products including homopolymer. Rate of grafting falls off for solutions above 80-90% monomer concentration and radical scavenging by monomer radicals is again postulated to account for the observed behavior.

INTRODUCTION

In the second paper of this series,[1] variables governing the radiation-induced grafting of styrene to cellulose with the use of methanol as the solvent were discussed. The purpose of the present work was to study the kinetics of grafting in the styrene–methanol–cellulose system for air irradiations at dose rates of 0.007, 0.014, and 0.078 Mrad/hr. for monomer concentrations of 10–90 vol.-%. Experiments were confined to irradiations in air because previous results[1] had shown that (1) little difference existed in grafting efficiencies between vacuum and air irradiations in the present system, and (2) the experimental procedure for air irradiations is considerably simpler than for irradiations in vacuum. The kinetic data for the styrene–methanol–cellulose system are unavailable in the literature; however, the kinetics of grafting in styrene–methanol mixtures for the hydrophobic polymers polyethylene[2,3] and nylon[4] have been reported in detail by Odian et al. In the absence of data for the absorption of styrene and methanol by cellulose, a detailed mathematical treatment of the results is not possible at this stage.

EXPERIMENTAL

The experimental procedures were essentially those outlined in the earlier paper.[1]

Irradiations

The irradiations were carried out in the presence of air at 25°C. by using a [60]Co (dose rate 0.078 Mrad/hr.) or spent element fuel source (dose rates of 0.007 and 0.014 Mrad/hr.).

Monomer Solutions

Freshly distilled monomer was diluted with dry methanol to provide monomer concentrations in the range 10–90% by volume. The charges (6 ml.) were added to the cellulose strips (2 × 1 in.) in dry glass tubes (15 × 1.2 cm. diameter, 0.1 cm. wall thickness). Since the tubes were stored at −2°C., ample time was allowed for the tubes and contents to attain pond temperature before commencing the irradiations.

Extractions

Following the irradiation, any homopolymer was removed from the strips by continuous extraction with hot benzene (60–65°C.) for 100 hr. in a large Soxhlet extractor, dried in a low-temperature air oven (65°C.), and equilibrated at 65% R.H. prior to weighing. The grafting yield, expressed as the percentage increase in the original weight of the strip, was assumed to be due to grafted polystyrene. All results are mean values of not less than four determinations.

RESULTS AND DISCUSSION

Reference has already been made to the improved radiation-induced grafting yields obtained on cellulose with methanol as solvent for monomer.[1] In the present work, the results of kinetic grafting experiments for the cellulose–styrene–methanol system are summarized in Figures 1–8. Significant features of the data indicate that the grafting rate depends upon monomer concentration, dose rate, and total dose, passing through a maximum at 60–70% methanol by volume. An accelerative grafting effect is also observed and is shown by the data in Figures 1 and 2. The complete results of the kinetic study at dose rates of 0.078, 0.014, and 0.007 Mrad/hr. for styrene–methanol mixtures are given in Table I.

Of significance are the results in Figures 1 and 2, where initial and final grafting rates are plotted against methanol concentration. The initial and final grafting rates were computed from the linear segments of the data plotted in Figures 3–7. In Figure 1, the accelerative effect attains a maximum at approximately 30% methanol by volume for the highest dose rate employed. At the lower dose rates the plots do not pass through maximum values but remain essentially constant over a wide range of alcohol concentrations, due presumably to the deposition of a relatively

small radiation dose and, consequently, the smaller conversion of monomer to polymer. By contrast, Figure 2 shows considerable change for the final grafting rates and the maximum occurs at 60–70% methanol at each dose rate. Furthermore, this result corresponds to the 30–40% monomer concentration previously reported[1] for the onset of the maximum grafting rate and has been attributed to the Trommsdorff effect.[2-4]
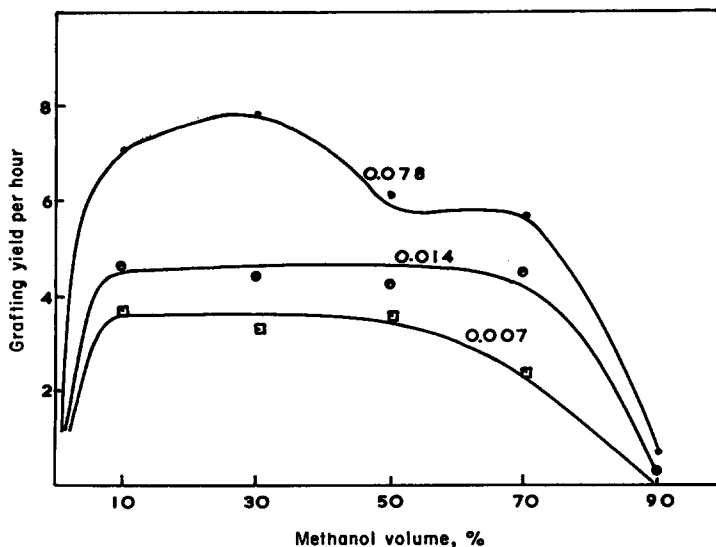

Fig. 1. Grafting rates (initial) in styrene–methanol mixtures at dose rates shown: (●) 0.078 Mrad/hr.; (◉) 0.014 Mrad/hr.; (▣) 0.007 Mrad/hr.
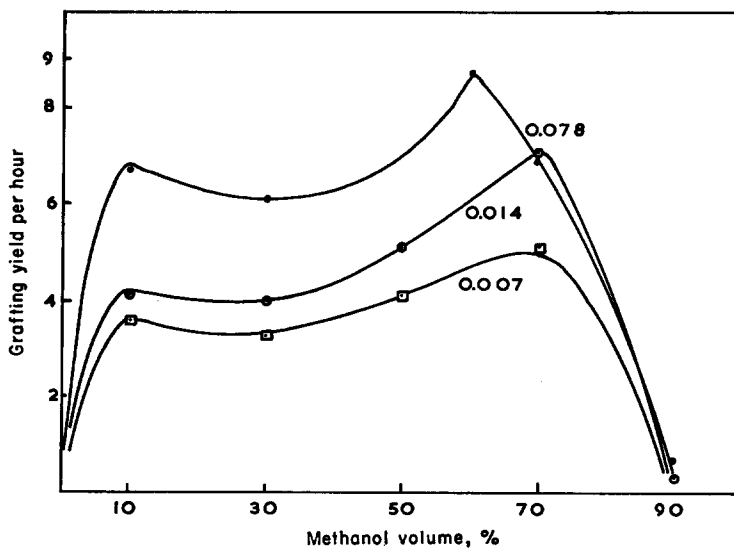

Fig. 2. Grafting rates (final) in styrene–methanol mixtures at dose rates shown:(●) 0.078 Mrad/hr.; (◉) 0.014 Mrad/hr.; (▣) 0.007 Mrad/hr.

TABLE I
Effect of Dose Rate on the Kinetics of Graft Copolymerization

Dose rate, Mrad/hr.	Exposure time, hr.	Grafting yields at various concentrations of styrene in methanol, %[a]					
		10 vol.-%	30 vol.-%	40 vol.-%	50 vol.-%	70 vol.-%	90 vol.-%
0.007[b]	1	0	0		1	0	1
	2	0	0		3	2	4
	4	0	4		13	12	13
	8	0	17		27	26	29
	12	0	33		42	42	46
	20	3	105		74	70	71
	25	2	140		102	88	86
0.014[b]	1	0	0		1	2	2
	2	0	2		6	6	8
	4	0	10		17	18	17
	8	0	29		33	35	34
	12	0	58		53	55	54
	20	6	148		97	83	84
	25	7	163		133	102	101
0.078[c]	1	0	1	—	6	9	8
	2	0	6	9	12	16	15
	4	0	14	21	25	29	27
	6	3	27	38	38	44	46
	8	4	37	42	44	53	57
	9	5	43	—	51	58	60
	10	4	47	52	54	62	65
	12	8	84	7	79	80	78
	15	10	118	134	101	91	93
	20	14	112	182	150	117	126

[a] All irradiations carried out in the presence of air at 25°C. Figures are mean values of four determinations.
[b] Fuel element source.
[c] ^{60}Co source.

The following specific observations and interpretations may be made of the detailed results.

Grafting in 10% Monomer Solutions

At low monomer concentrations, there is a long induction period and the grafting rate is very low. The grafting rate, in fact, is less than 1%/hr. at the maximum dose rate. At the lower dose rates, the induction period is much longer, and the diminishing grafting yields (Fig. 3) appear to be due to a predominance of homopolymerization in the solution.

This dose rate dependence may be ascribed to two factors. Firstly, an adequate concentration of cellulose radicals will need to be generated by irradiation so that grafting may eventuate unless transfer reactions and/or solvent radicals contribute to activation of the backbone polymer. The pertinent reactions involved in these processes can be represented by eqs. (1)–(5).
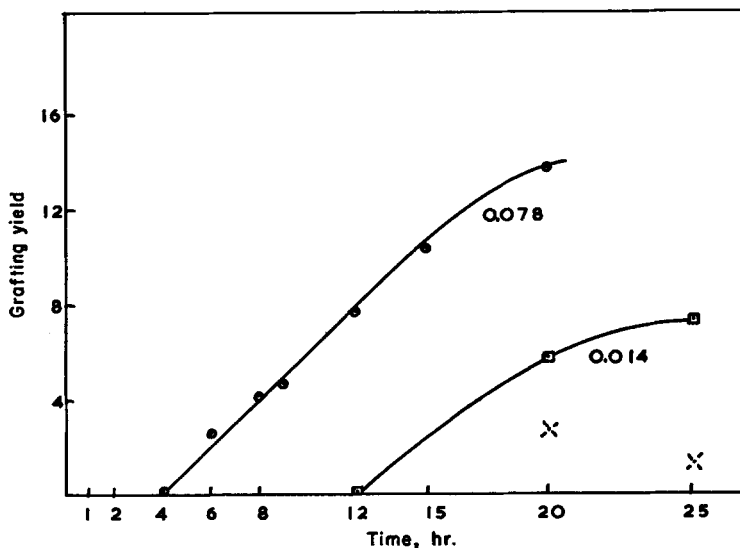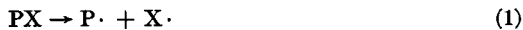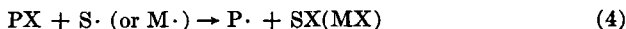
Fig. 3. Kinetic features of grafting to cellulose from 10% styrene in methanol at dose rates shown: (⊙) 0.078 Mrad/hr.; (⊡) 0.014 Mrad/hr.; (✕) 0.007 Mrad/hr.
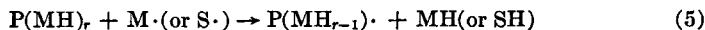
Initiation

$$PX \rightarrow P\cdot + X\cdot \tag{1}$$

$$MH \rightarrow M\cdot + H\cdot \tag{2}$$

$$SY \rightarrow S\cdot + Y\cdot \tag{3}$$

Transfer to Polymer:

$$PX + S\cdot \text{ (or } M\cdot) \rightarrow P\cdot + SX(MX) \tag{4}$$

Transfer to Copolymer:

$$P(MH)_r + M\cdot(\text{or } S\cdot) \rightarrow P(MH_{r-1})\cdot + MH(\text{or } SH) \tag{5}$$

Here PX, MH, and SY represent cellulose, monomer, and solvent molecules, respectively; $P\cdot$, $M\cdot$, and $S\cdot$ are the corresponding parent radicals formed by irradiation, while r is an integer indicating the chain length of the polymer.

Secondly, the value of G_{radicals} for the solvent which should be higher than that of the monomer for favorable grafting conditions, implies that in the absence of adequate monomer diffusion, the monomer concentration will be depleted in the immediate vicinity of the backbone polymer. Thus, a concentration barrier opposing grafting is established. This effect will be accentuated if monomer molecules are capable of scavenging solvent radicals as is postulated in detail later in the discussion.

Grafting in 30–50% Monomer Solutions

At higher monomer concentrations, the solvent-radical effect diminishes, and the monomer migrates to the grafting sites in the cellulose more readily.

The induction period is also reduced and the grafting rate accelerates, passing through maximum values for the system. Furthermore, this acceleration appears for smaller total radiation doses as the dose rate is reduced. Depending on the dose rate, the higher grafting rate may be sustained for a considerable time (Figs. 4 and 5).

In this range, a plot of grafting yield versus time is divided into two parts from the onset of the increasing grafting rate. The latter is also accompanied by increased swelling of the copolymer strip and precipitation of homopolymer from solution and is usually regarded as being indicative of a reduced termination rate.

For a monomer concentration of 40% (Fig. 4), the accelerated consumption of monomer also causes an early leveling off in the grafting yield at the higher dose rates, whereas this effect is not indicated in Figure 5.

Grafting in 70–90% Monomer Solutions

With these higher monomer concentrations, there are two effects to be seen in both Figures 6 and 7. The initial grafting rate is maintained for a period which is dependent upon the dose rate, then the grafting rate falls to a lower level. In both diagrams, it is observed that, with the exception of the 70% solution at the dose rate of 0.007 Mrad/hr., the change in the grafting rate is almost constant.

This result can be interpreted as a viscosity effect in which a reduction of termination and monomer diffusion cause a fall in the grafting rate.
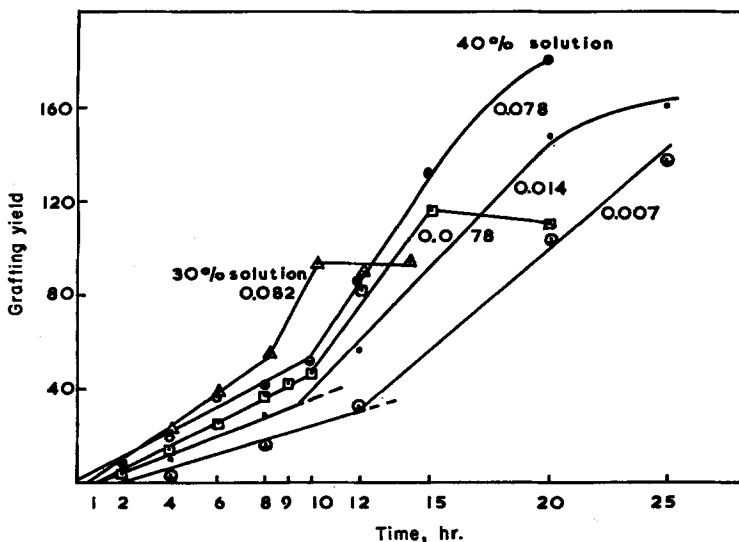

Fig. 4. Kinetic features of grafting to cellulose from 30 and 40% styrene in methanol at dose rates shown: (△) 0.082 Mrad/hr., 30% solution; (□) 0.078 Mrad/hr., 30% solution; (○) 0.078 Mrad/hr., 40% solution; (·) 0.014 Mrad/hr.; 30% solution; (◉) 0.007 Mrad/hr., 30% solution.
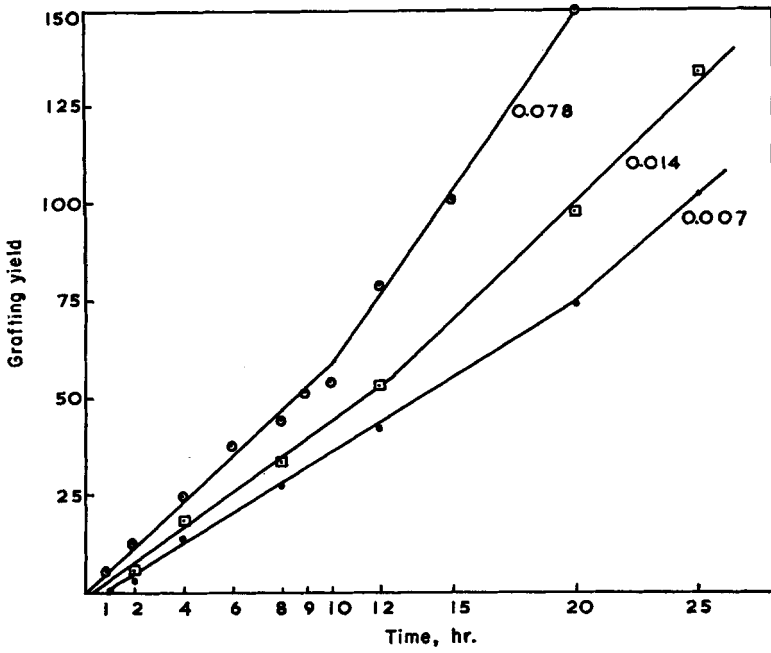
Fig. 5. Kinetic features of grafting to cellulose from 50% styrene in methanol at dose rates shown: (○) 0.078 Mrad/hr.;   (▣) 0.014 Mrad/hr.;   (●) 0.007 Mrad/hr.
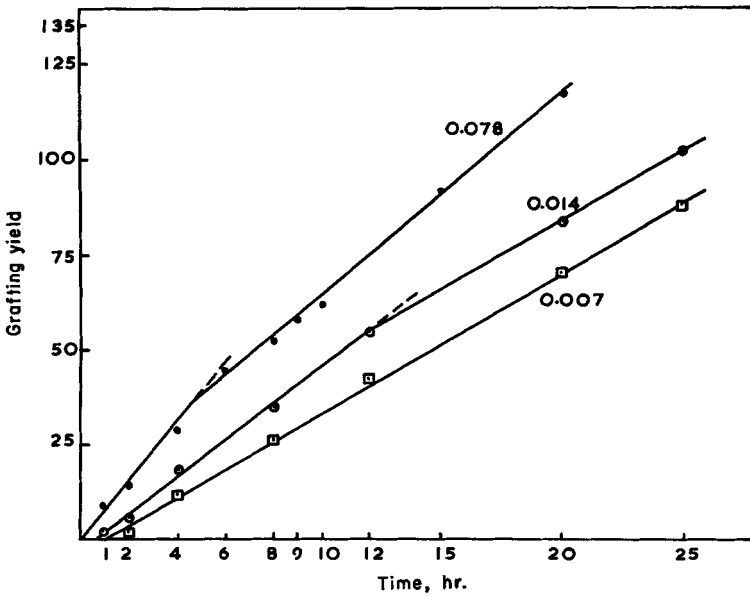

Fig. 6. Kinetic features of grafting to cellulose from 70% styrene in methanol at dose rates shown: (●) 0.077 Mrad/hr.;   (○) 0.014 Mrad/hr.;   (▣) 0.007 Mrad/hr.
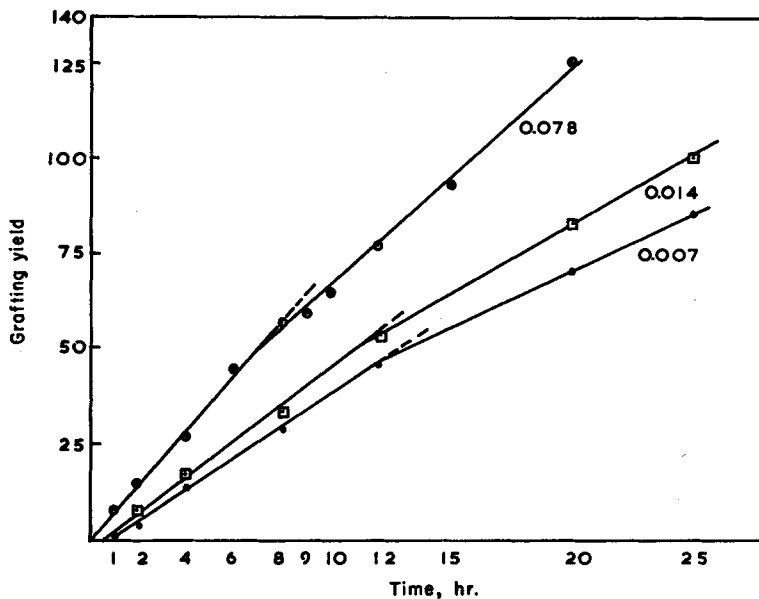
Fig. 7. Kinetic features of grafting to cellulose from 90% styrene in methanol at dose rates indicated: (⊙) 0.078 Mrad/hr.; (⊡) 0.014 Mrad/hr.; (●) 0.007 Mrad/hr.
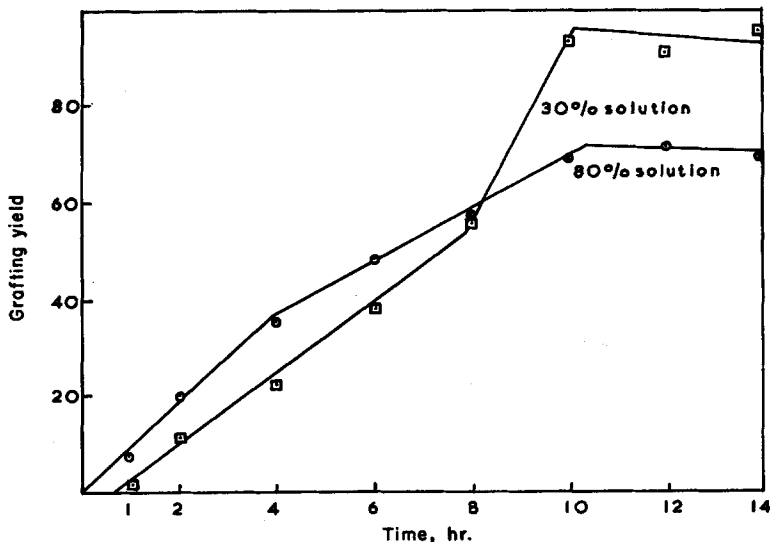

Fig. 8. Kinetic features of grafting to cellulose at a dose rate of 0.082 Mrad/hr.: (⊡) 30% styrene in methanol; (⊙) 80% styrene in methanol.

This is consistent with grafting throughout the later stages occurring in an unfavorable environment in viscous, homogeneous solutions. Thus, for each dose rate the onset of the effect divides the linear grafting rate curve into two components of differing slopes. However, at the lower concentration and dose rate of 0.007 Mrad/hr., the grafting yield is linear

TABLE II
Kinetic Data for Grafting in Styrene–Methanol Solutions

Time, hr.	Grafting yields, at various monomer concentrations, %[a]	
	30 vol.-%	80 vol.-%
1	1	8
2	11	20
4	22	35
6	38	48
8	55	57
10	93	69
12	91	71
14	95	69

[a] Dose rate 0.082 Mrad/hr. in air.   Figures are mean values of six determinations.

over the entire period (Fig. 6). Evidently, in this case, the conversion to polymer has not proceeded far enough for this viscosity effect to be observed. That the interpretation considered above represents a reproducible phenomenon is shown by the data of Table II and Figure 8 from another experiment. The same marked change in grafting rates is evident and consistent for the course of the reaction.

Odian et al.,[2–4] in an investigation of grafting to polyethylene and nylon with styrene–methanol mixtures have observed similar results directly attributable to a Trommsdorff-type effect. These authors developed the equation:
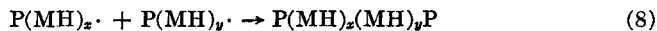
$$R_p = k_p(M)(R_i/2k_t)^{1/2}A \tag{6}$$

for grafting to polyethylene and nylon, assuming nonsteady-state conditions with regard to polymer radicals, based on the simplified kinetic scheme of equations (1), (7), and (8).

Propagation:

$$P\cdot + xMH \rightarrow P(MH)_x\cdot \tag{7}$$

Termination:

$$P(MH)_x\cdot + P(MH)_y\cdot \rightarrow P(MH)_x(MH)_yP \tag{8}$$

Here R_p and (M) are the moles of styrene grafted and absorbed, respectively, per liter of styrene–methanol–trunk polymer per second, R_i is the moles of free radicals produced in the trunk polymer per liter of styrene–methanol–amorphous trunk polymer per second, k_t and k_p are the rate constants for termination and propagation, respectively, and A is an exponential factor. The definitions and calculations assume that grafting occurs in the amorphous regions of the polymer, and that the volumes of the interacting components are additive.

In applying the above concepts to the cellulose system, it can only be assumed from the greater viscosity of the grafting solution that an increase in the magnitude of k_p^2/k_t actually occurs similar to that observed

with polyethylene and nylon, because in the absence of swelling data for cellulose in styrene–methanol mixtures, an analogous mathematical treatment cannot be made.

## Radical-Scavenging Mechanism of Copolymerization

The results of the present kinetic work may be utilized in the formulation of possible mechanisms for the grafting process. In conventional radical reactions, styrene is well known as a strong radical scavenger. In recent radiation chemistry studies of binary mixtures,[5–7] aromatic compounds such as benzene and styrene were shown to scavenge radolytically produced radicals, two type processes being identified: (1) addition [eq. (10)], which predominates, and (2) substitution [eq. (11)] reactions. In terms of this interpretation, the present cellulose system may be considered as the radiolysis of a binary mixture (methanol and styrene) in the presence of a heterogeneous additive (cellulose).
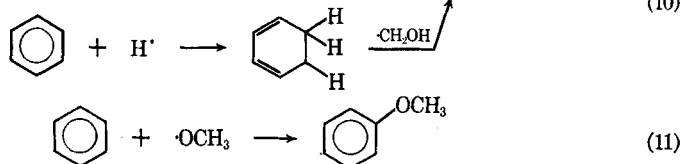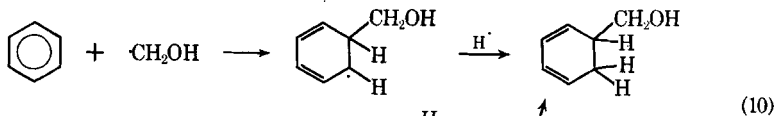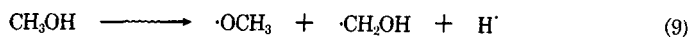

Thus, at low monomer concentrations (0–10%), the solvent will be in large excess, and the behavior of the system will essentially depend upon the radiation chemistry of methanol. Under these conditions, styrene will scavenge solvent radicals predominantly by an addition mechanism [eq. (10)], yielding essentially homopolymer at the expense of grafting, thus providing an additional explanation for the low grafting observed in Figure 1. Similarly, at high monomer concentrations (>70%), the relative amounts of methanol and styrene are not sufficient to prevent styrene scavenging other styrene radiolytic fragments yielding extensive homopolymerization again at the expense of grafting (Figs. 1 and 2). In the 30–70% monomer region, a compromise is attained where sufficient monomer is available to scavenge all methanol radicals, yet a slight excess of monomer is still available for grafting. The difference between reaction in this concentration region and the other two is that multiple scavenging by one styrene molecule is possible in the latter case, whereas this is minimized in the 30–70% concentration range.

The concept of radical scavenging in grafting reactions is also consistent with the charge-transfer theory recently proposed for bonding in copolymerized celluloses.[8] This theory relates the π-complex adsorption properties[9] of monomer and copolymers to radiolytically produced trapped radi-

cals in cellulose.[10-13] Radicals at the surface of the cellulose may form σ-bonds with π-complexed monomer or polymer whereas "inaccessible" radicals within the bulk of the cellulose may also contribute to bonding by charge-transfer effects [eq. (12)].

$$+ \ 2P^{\cdot} \longrightarrow \tag{12}$$
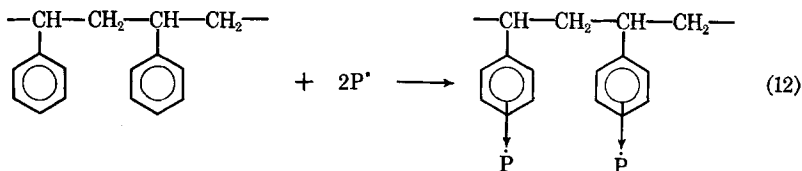
Charge-transfer bonding in the 20–70% monomer concentration range should also be influenced by cage effects, since there is now a greater probability of the slight excess of monomer radicals abstracting hydrogen from an adjacent hydrogen position in cellulose rather than dimerizing to give homopolymer. This would leave reformed monomer and a vacant site in the cellulose for grafting in the "cage" by charge-transfer bonding [eqs. (13) and (14)].

$$PH + \dot{M} \rightarrow MH + \dot{P} \tag{13}$$

$$MH + \dot{P} \rightarrow [MH \rightarrow \dot{P}] \tag{14}$$
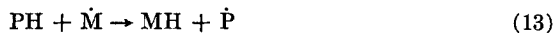
As has been previously mentioned,[1] it is not envisaged that grafting occurs exclusively by the above mechanisms in the radiation-induced cellulose–styrene–methanol system; however, available evidence does indicate that the proposed mechanism contributes significantly to the overall process. The concept of charge-transfer bonding is also consistent with the kinetic observations reported in the present paper. Future experiments will be designed to examine more fully the possible mechanistic implications of radical scavenging and charge-transfer bonding in radiation-induced grafting reactions with cellulose.

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Résumé

La cinétique des greffages induits par irradiation du styrène à la cellulose dans le méth-anol a été étudiée à l'air et à des vitesses de dose de 0.007, 0.014 et 0.078 Mrad/hr. dans une source de cobalt-60. Les variables affectant les vitesses de greffage incluent la concentra-tion en monomères, la vitesse de dose de radiation, la dose totale. Le greffage atteint un maximum de 60–70% par volume de méthanol dans le styrène. Les résultats ont été interprétés sur la base d'un mécanisme de greffage incluant des intermédiaires par trans-fert de charge; toutefois un traitement mathématique complet de ces données n'est pas possible à l'heure actuelle à cause de l'absence de données de gonflement appropriées dans des mélanges styrène/méthanol. Un greffage observé en solution jusqu'à 10% de mono-mère est attribué à la disparition des radicaux (principalement en provenance des sol-vants) par le monomère, ce qui amène à la formation de produits tels que le homopoly-mère non-greffé. La vitesse de greffage diminue pour des solutions au-dessus de 80–90% de concentration en monomères et la perte en radicaux par radical monomérique est de nouveau postulée pour expliquer le comportement observé.

Zusammenfassung

Die Kinetik der strahlungsinduzierten Aufpfropfung von Styrol auf Cellulose in Meth-anol wurde unter Luft bei einer Dosisleistung von 0,007, 0,014 und 0,078 Mrad/h in einer Cobalt-60-Quelle und einem erschöpften Brennstoffelement untersucht. Die Aufpfrop-fungsgeschwindigkeit wird durch die Monomerkonzentration, Strahlungsdosisleistung und Gesamtdosis beeinflusst. Die Aufpfropfung erreicht bei 60–70 Vol % Methanol in Styrol ein Maximum. Möglich erscheinende Pfropfmechanismen, darunter Ladungs-Übertragungs-Zwischenprodukte, wurden zur Deutung der Ergebnisse herangezogen; eine vollständige mathematische Behandlung der Ergebnisse ist gegenwärtig wegen des Fehlens geeigneter Quellungsdaten für Cellulose in Styrol-Methanolmischungen aber nicht möglich. Die in Lösungen mit bis zu 10% Monomerem beobachtete schlechte Aufpfrop-fung wird auf das Abfangen der vornehmlich aus dem Lösungsmittel stammenden Radi-kale durch das Monomere unter Bildung on Abfangprodukten einschliesslich von Homo-polymeren zurückgeführt. Die Aufpfropfungsgeschwindigkeit nimmt auch bei Lösun-gen mit mehr als 80–90% Monomerem ab und auch hier wird das Abfangen durch Mono-merradikale zur Erklärung herangezogen.