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Radiation-Induced Reactions with Cellulose. XV. Effect of Mineral and Organic Acids on Grafting of Monomers Using Ionizing Radiation

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Radiation-Induced Reactions with Cellulose. XV. Effect of Mineral and Organic Acids on Grafting of Monomers Using Ionizing Radiation

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ABSTRACT

The effect of a range of inorganic and organic acids on the radiation-induced grafting of styrene in methanol to cellulose is discussed using the simultaneous method. Sulfuric acid is the most effective acid for increasing the grafting yield, hydrochloric being the next most efficient. Acetic acid retards the copolymerization. Under the most favorable radiation conditions, inclusion of sulfuric acid (up to 1.1 M) produces a twentyfold increase in graft. The presence of mineral acid also 1) enhances the intensity of a Trommsdorff peak if already present in the grafting solution and 2) induces a peak if none were previously present without acid. A mechanism for the enhanced acid effects in these grafting reactions is proposed involving charge-transfer intermediates.

INTRODUCTION

In the radiation-induced grafting of monomers to cellulose using the simultaneous technique [1-9], the efficiency of the process depends predominantly upon four parameters. These include the radiation total dose and dose rate, the structure of the monomer, and the concentration of monomer in a particular solvent. The nature of the solvent is important since swelling or wetting materials, such as the low molecular weight alcohols, enhance the grafting reaction [4] whereas nonpolar, nonwetting compounds like benzene and cyclohexane significantly reduce grafting [4]. Professor Stannett, one of the pioneers in this field, has reviewed the effect of the above variables on the grafting process [1].

In the simultaneous grafting procedure where the trunk polymer is irradiated in contact with a solution of the monomer in solvent, a concentration phenomenon is observed which is usually attributed to the Trommsdorff or gel effect. Hence at a particular monomer concentration in certain solvents, accelerated copolymerization is found, the chain lengths of the grafted polymer usually being highest at the Trommsdorff peak concentration. From both fundamental and practical considerations, it is therefore important to establish whether a gel effect occurs in a particular grafting system and, if so, the variables effecting the optimization of such an accelerated effect. Solvents that are suitable for swelling cellulose and demonstrating Trommsdorff effects are the lower alcohols, particularly methanol. For the mechanism of this gel effect in radiation grafting reactions in these solvents, particularly involving cellulose [4], hydrogen atom scavenging has been invoked [4]. In related studies of the radiolysis of solvent methanol alone, it has been shown that the yield of the main product, hydrogen, is enhanced if mineral acid is present [10-13]. This increase in hydrogen yield from the radiolysis of methanol has been attributed to increased hydrogen atom production. Since methanol is an important solvent in radiation grafting, it is of interest to discover whether analogous acid effects are observed in copolymerization reactions involving this alcohol.

In the present paper, the effect of both mineral and organic acids on the radiation-induced grafting of styrene in methanol to cellulose is discussed. In particular, the influence of these acids in determining the magnitude and position of the Trommsdorff peak is considered. The possible mechanistic role of hydrogen atom scavenging in these acid grafting solutions is examined and related to general acid effects in the radiolysis of methanol.

A preliminary communication of these results has been published [14].

EXPERIMENTAL

All chemicals were of high purity. However, where necessary, further purification was achieved either by recrystallization or redistillation. Commercial styrene was donated by Monsanto (Australia) Ltd.

Preparation of Monomer Solutions

Inhibitor in the commercial styrene was removed by washing with dilute sodium hydroxide. This styrene was then distilled under reduced pressure, the middle 80% fraction collected and stored at -2°C on fused calcium chloride. The monomer was redistilled under reduced pressure immediately prior to use and the purity checked by gas chromatography.

Methanol (Allied Chemicals, acetone-free, ACS reagent) was further fractionated twice (in the presence of 2,4-dinitrophenylhydrazine and concentrated sulfuric acid) through a column (1 m) filled with glass helices. The fractionation was performed in a dry atmosphere, as previously described [11], because of the effect that trace impurities have on the radiolysis yields in methanol [11].

Irradiation of Solutions

For the grafting experiments, strips (5×4 cm) of cellulose (Whatman No. 41 double acid washed chromatography paper) were equilibrated at 65% r.h. for 24 hours at 23°C , folded, and added to test tubes (16×1.2 cm). Monomer solution (6 ml, freshly prepared immediately prior to use) containing the acid to be tested was then added to each tube. For the actual irradiations, tubes were sealed off at 10^{-3} Torr after three freeze-thaw cycles. Measurements were made initially in quadruplicate; however, due to the exceptionally good reproducibility of these data, duplicates were only needed for later runs.

Two sources were used for the irradiations. The first was a large ^{60}Co pond facility at the Australian Atomic Energy Commission Research Establishment while the second was a spent fuel element facility at the same center. For dose rates above 0.40×10^6 rad/hr, the ^{60}Co source only was used. Radiation dose rates and total doses were determined by the ferrous sulfate dosimeter, assuming $G(\text{Fe}^{3+}) = 15.6$.

After irradiation was completed, the cellulose strips were removed from the irradiation vessels and washed several times with cold

methanol to remove residual free acid. Failure to wash at this stage can lead to severe charring of the strips during the subsequent Soxhlet extraction since acid can concentrate in the cellulose and chemically degrade it. After washing, the strips were extracted in benzene in a large Soxhlet for 100 hr, dried, humidified to 65% r.h. at 23°C for 24 hr, then weighed to determine the grafting yield. The increase in weight was calculated as a percentage of the conditioned weight of the original paper. Dilli and Garnett [15] have shown that this technique is satisfactory for the complete extraction of the homopolymer and remaining monomer.

Procedure for Sample Pretreatment Experiments

In the pretreatment technique, a modification of the original Staudinger and Eicher [16] "inclusion method" was used. This involves treating the cellulose with a swelling solvent, then slowly replacing this material with pure monomer prior to irradiation. For the present work, methanol, water, and acidified solutions of these solvents were used to pretreat the cellulose. The procedure involved immersing the cellulose strip in the required solution for 30 min, then draining off the liquid. Pure styrene was then added and drained off a number of times before a final volume (6.0 ml) of the pure monomer was added to the cellulose, the tube evacuated, sealed off at 10^{-3} Torr after two freeze-thaw cycles, and irradiated as described above.

RESULTS

The effect of including different concentrations of sulfuric acid on the radiation-induced grafting of styrene in methanol to cellulose is shown in Table 1. It will be observed that at all acid concentrations there is at least one particular concentration of styrene in methanol where there is a significant enhancement in copolymerization when compared with the blank containing no acid. If these data are plotted as in Fig. 1 (higher acidities) and Fig. 2 (lower acidities), it is obvious that a Trommsdorff peak has been induced into the system by the inclusion of acid. Under the irradiation conditions used, it will be observed that there is no gel effect without acid. If the data are graphed as in Fig. 3, it is clear that the largest graft occurs with the 20% solution of styrene in methanol at a sulfuric acid molarity of 1.1. However, the greatest percentage increase with inclusion of acid occurs in the 10% solution, from 1.2% (no acid) to 21.2% (1.1 M).

If radiation conditions are chosen where there is a Trommsdorff peak already present in the blank without acid, then inclusion of acid

TABLE 1. Effect of Mineral Acid on Radiation-Induced Grafting of Styrene in Methanol to Cellulose^a

%Styrene (by volume)	Graft (%) in concentration (M) of sulfuric acid							
	0.0	1.1×10^{-3}	5.4×10^{-3}	1.1×10^{-2}	5.4×10^{-2}	1.1×10^{-1}	5.4×10^{-1}	1.1
10	1.2	5.4	15.1	7.5	8.8	11.0	19.4	21.2
20	8.9	22.6	28.6	28.7	38.4	48.2	58.5	74.7
30	13.9	41.0	lost	44.7	47.5	49.6	39.3	27.0
40	16.3	27.5	37.1	17.8	34.0	30.2	20.2	16.1
60	29.8	31.2	28.0	29.1	26.8	23.0	16.5	15.1 ^b
80	34.1	24.8	21.7	26.5	19.3	21.3	12.4 ^b	10.1 ^b

^aDose rate = 2.78×10^4 rad/hr. Total dose = 0.20×10^6 rad.

^bPhase separation observed.

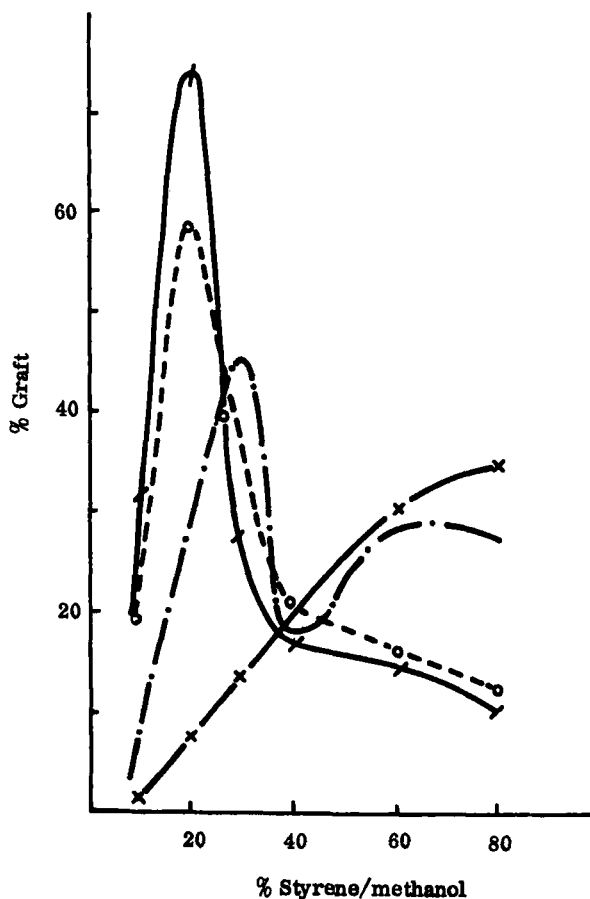


FIG. 1. Induced Trommsdorff peak in the presence of relatively high acid concentrations in the radiation grafting of styrene in methanol to cellulose (radiation conditions as in Table 1). (x) 0.0 M H_2SO_4 ; (- · -) 1.1×10^{-2} M H_2SO_4 ; (o) 5.4×10^{-2} M H_2SO_4 ; (—) 1.1 M H_2SO_4 .

enhances the intensity of this peak (Table 2). This trend in the data is more clearly evident if the results are plotted (Fig. 4). Further, if the data are graphed in a fashion similar to Fig. 3, then the largest acid effect occurs with the 25% monomer solution (Fig. 5). The other essential difference between the results in Tables 1 and 2 is the dose rate and total dose. If the dose rate and total dose are lowered for the styrene-methanol system from 2.73×10^4 rad/hr and 0.2×10^6 rad

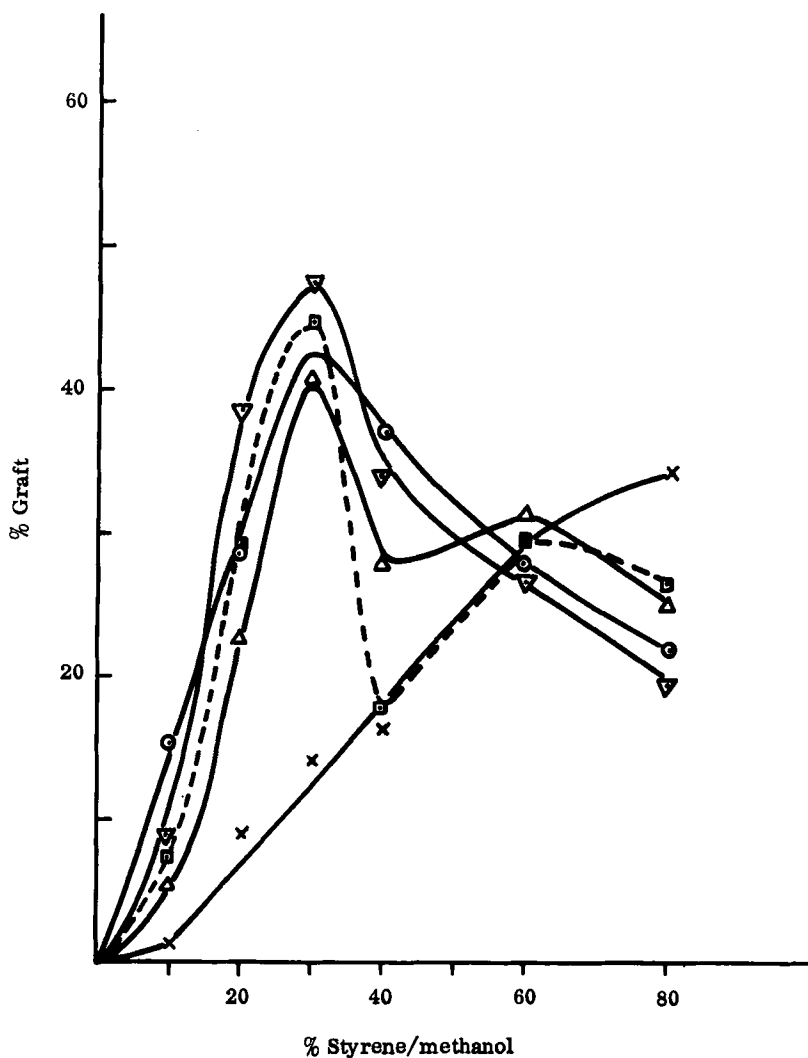


FIG. 2. Induced Trommsdorff peak in the presence of relatively low acid concentrations in the radiation grafting of styrene in methanol to cellulose (radiation conditions as in Table 1). (x) 0.0 \underline{M} H_2SO_4 ; (Δ) 1.1×10^{-3} \underline{M} H_2SO_4 ; (\odot) 5.1×10^{-3} \underline{M} H_2SO_4 ; (\boxplus) 1.1×10^{-2} \underline{M} H_2SO_4 ; (∇) 5.4×10^{-2} \underline{M} H_2SO_4 .

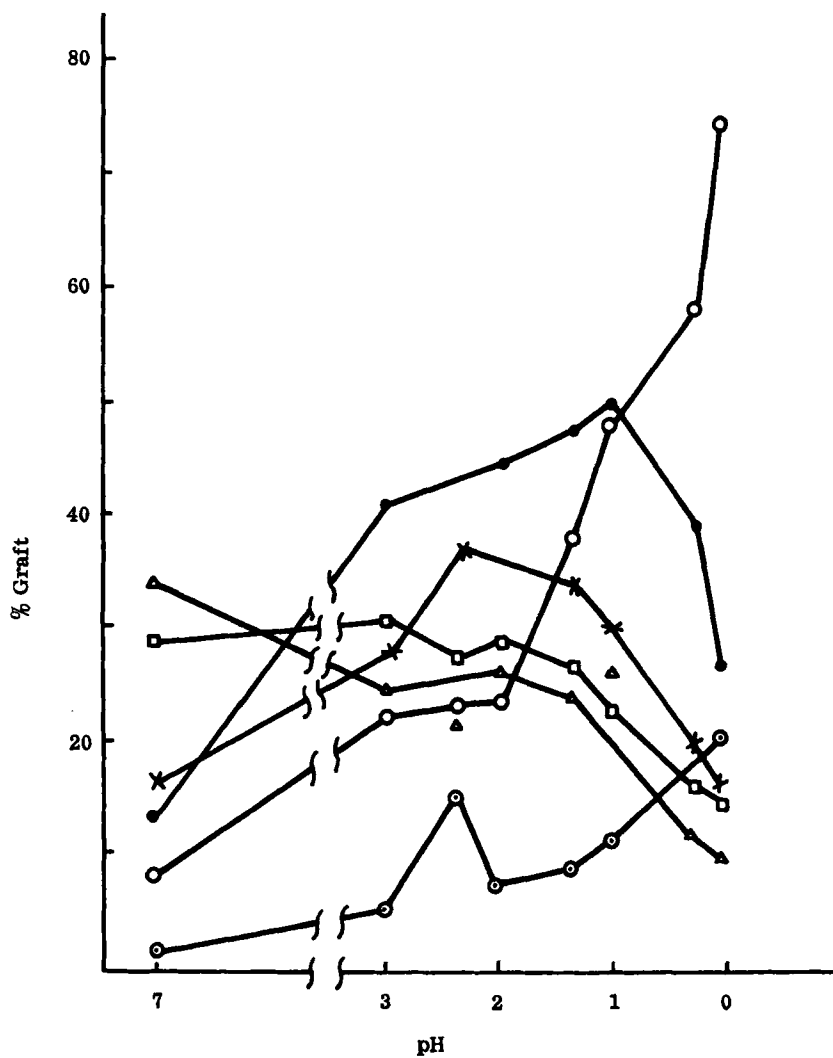


FIG. 3. Effect of pH on grafting yield to cellulose for various concentrations of styrene in methanol when induced Trommsdorff effect is observed. Radiation conditions as for Fig. 1. Concentrations: (●) 10%; (○) 20%; (●) 30%; (×) 40%; (□) 60%; (△) 80%.

TABLE 2. Effect of Mineral Acid on Trommsdorff Effect in Radiation-Induced Grafting of Styrene in Methanol to Cellulose^a

% Styrene (by volume)	Graft (%) in concentration (M) of sulfuric acid				
	0.0	0.9×10^{-4}	0.9×10^{-3}	0.9×10^{-2}	0.7×10^{-1}
15	35.1	38.4	31.5	50.8	78.7
20	61.9	69.3	65.6	87.2	109.8
25	99.3	112.5	110.8	123.3	162.7
30	104.5	113.9	98.8	109.6	Very high
35	100.9	102.8	80.0	90.7	124.0
45	80.5	52.6	42.0	48.4	82.5

^aDose rate = 6.77×10^3 rad/hr. Time of irradiation = 17 hr.

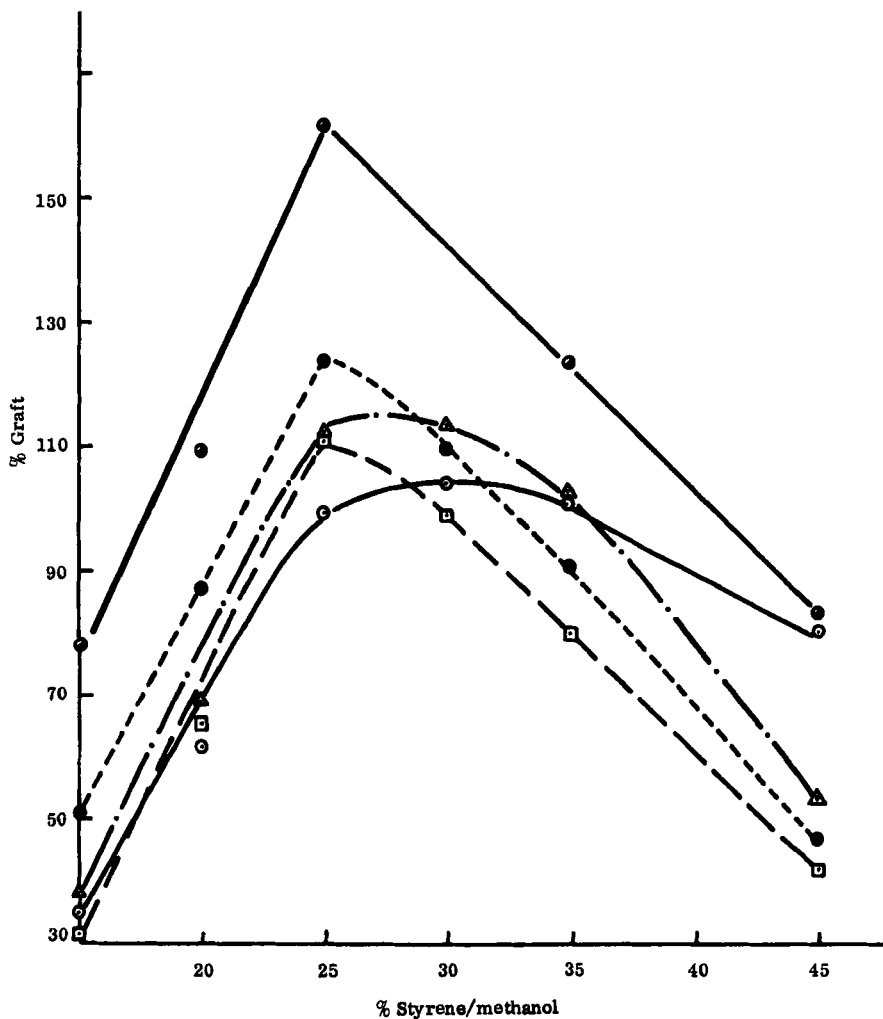


FIG. 4. Enhanced Trommsdorff peak in presence of acid for radiation grafting of styrene to cellulose. Radiation conditions as in Table 2. (○) 0.0 M H₂SO₄; (△) 0.9 × 10⁻⁴ M H₂SO₄; (□) 0.9 × 10⁻³ M H₂SO₄; (●) 0.9 × 10⁻² M H₂SO₄; (●) 0.7 × 10⁻¹ M H₂SO₄.

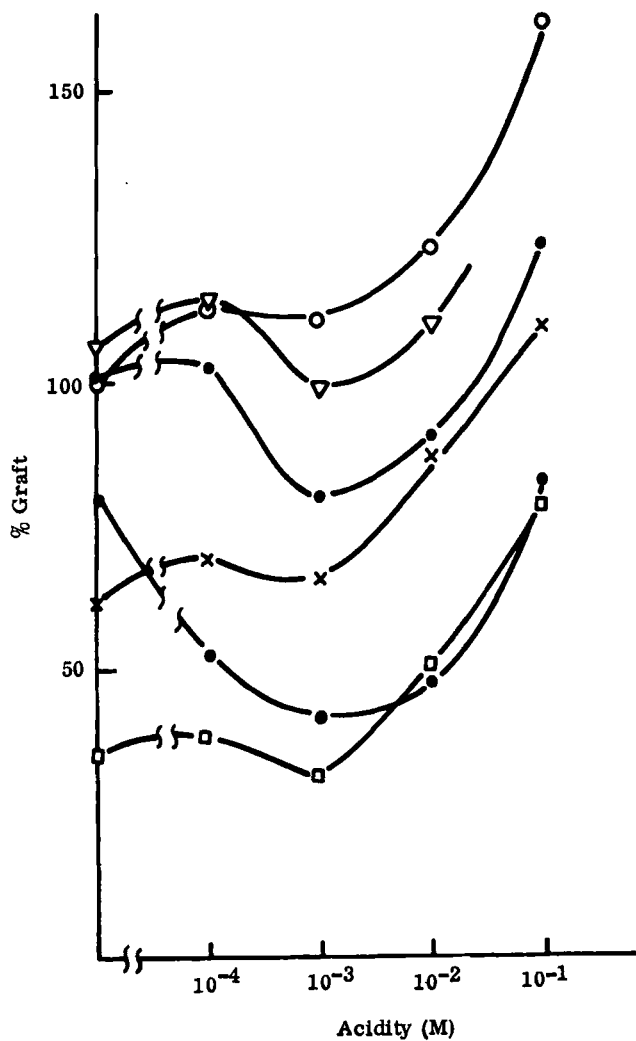


FIG. 5. Effect of acidity on radiation grafting under enhanced Trommsdorff effect conditions. Data from Table 2. (□) 15%; (×) 20%; (○) 25%; (▽) 30%; (●) 35%; (⊙) 45%.

(Table 1) to 6.77×10^3 rad/hr and 0.12×10^6 rad (Table 2) respectively, then both an increase in total graft and an induced Trommsdorff peak are observed at the lower dose and dose-rate conditions, consistent with a previous report [4].

The effect of varying the nature of the acid is shown in Table 3, both mineral and organic acids having been studied. Sulfuric acid is the best of all acids with hydrochloric acid the next most effective, particularly at the 10% monomer concentration. At no monomer concentration does acetic acid show an improved graft. Phosphoric acid shows slight enhancement in copolymerization at 10% monomer concentration, and nitric acid at 0.02 M is similar. However, at 2 M, nitric acid radically reduces the graft. The trends in these data can again be more clearly followed if the results are graphed (Fig. 6).

The role of water as a swelling solvent in the radiation-induced grafting of monomers to relevant trunk polymers has previously been discussed by a number of authors [1, 4]. In the present styrene-methanol system, without acid, inclusion of water at low concentrations leads to a progressive decrease in graft with increasing water content (Table 4, Fig. 7). If these data are plotted as in Fig. 8, it is obvious that at each specific water concentration there is an increase in grafting efficiency only when acid is added. The magnitude of this increase decreases as the water content increases. There is also a Trommsdorff effect with increasing acidity at those particular water concentrations where sufficient data are available (1, 3, 5, and 8% H₂O). Again, the magnitude of this effect decreases with increasing water content. The actual acidity at which the peak is optimized also decreases with increasing water. In all of these water solutions, it is significant that a large excess of methanol is also present.

If, instead of acid, alkali is included in the grafting solution, styrene copolymerization to cellulose is reduced, the magnitude of the reduction being directly proportional to the base added (Table 5, Fig. 9). If plotted in the alternate form (Fig. 10), it is obvious that the gel effect is also evident in grafting in alkaline solutions.

The effect of pretreatment of the cellulose with acidic solutions on the radiation-induced grafting of styrene by the "inclusion technique" [16] is shown in Table 6. Only with methanol and at the specific dose rate of 1.95×10^4 rad/hr is an enhancement in grafting achieved in the presence of acid. These data also confirm the importance of polar solvents, such as water and methanol that can swell the cellulose, on the efficiency of grafting by the inclusion method.

DISCUSSION

Effect of Inorganic Versus Organic Acids on Grafting

The data in Tables 1 to 3 and Figs. 1 to 6 show that the mineral acids, particularly sulfuric, are significantly better than the organic acid, acetic, for enhancing the radiation-induced grafting of styrene in

TABLE 3. Effect of Mineral and Organic Acid Structure on Radiation-Induced Grafting of Styrene in Methanol to Cellulose^a

% Styrene (by volume)	Graft (%) in							
	No acid	H ₂ SO ₄ , 1 M	HCl, 2 M	HNO ₃ , 2 M	HNO ₃ , 0.02 M	AcOH, 2 M	H ₃ PO ₄ , 0.67 M	
10	6.2	27.8	26.5	1.0	7.4	5.8	8.5	
20	30.3	82.7	_b	7.5	29.1	23.2	25.8	
30	41.3	33.7	18.3 ^b	9.1	37.4	38.8	30.6	
40	-	19.7	19.1 ^b	11.2	30.6	36.8	28.7	
50	38.6	-	-	-	-	-	-	
60	-	25.5 ^b	15.1 ^b	20.6	34.8	42.5	30.4	
80	56.1	20.6 ^b	8.6 ^b	8.0	28.5	42.2 ^b	31.5	

^aDose rate = 2.64×10^4 rad/hr. Total dose = 0.20×10^6 rad.^bPhase separation observed.

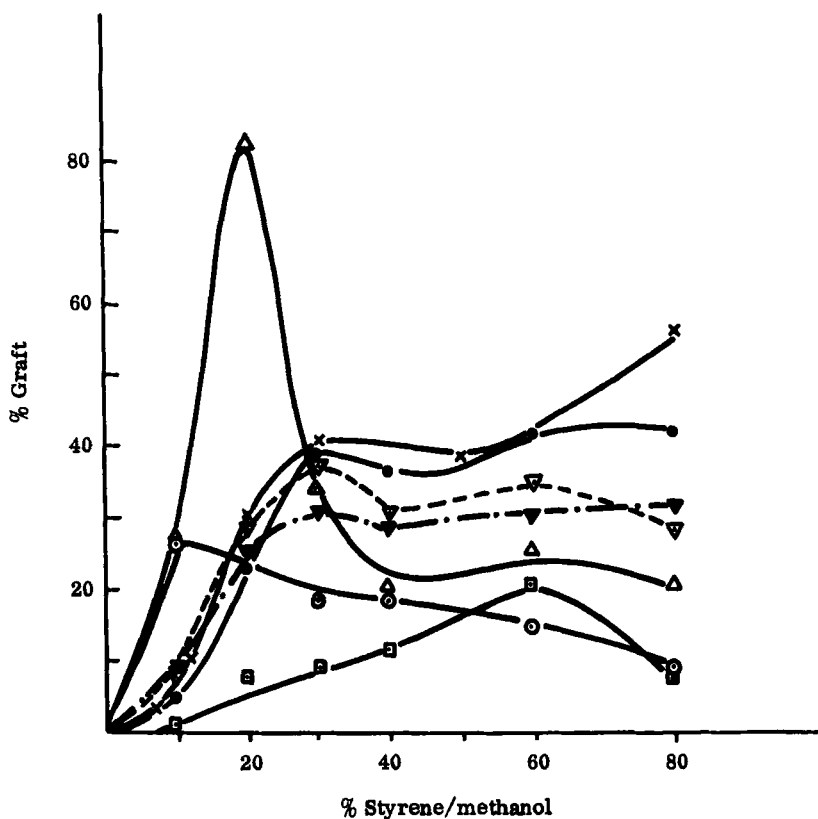


FIG. 6. Effect of acid structure on radiation grafting of styrene in methanol to cellulose. Conditions as in Table 3. (x) 0.0 M H₂SO₄; (Δ) 1 M H₂SO₄; (⊙) 2 M HCl; (□) 2 M HNO₃; (∇) 0.2 M HNO₃; (●) 2 M AcOH; (▽) 0.67 M H₃PO₄.

methanol to cellulose under vacuum irradiation conditions. Acetic acid has previously been used by Huang and Rapson [8] as a swelling agent for the radiation grafting of styrene to cellulose. Poor grafting was observed by these authors in all experiments when rayon was swollen with acetic acid up to 200% by weight of dry rayon. Present data are consistent with these earlier findings. The fact that the nitric acid results are so poor, especially at 2 M concentration (Table 3), suggests that the mineral acid effect is a compromise between enhancement at the higher acidities and oxidation leading to degradation of the trunk polymer. With nitric acid, oxidation is obviously very extensive, particularly at the higher molarity.

TABLE 4. Effect of Water on Radiation-Induced Grafting of Styrene in Methanol to Cellulose in Acidified Solution^a

Sulfuric acid (M)	Graft (%) in concentration of water (volume %)								
	0	1	2	3	3.5	4	5	7.5	8
0.0	129.0	110.5	41.5	37.0 ^b	-	-	30.0 ^b	-	21.9
2.1×10^{-3}	-	140.7	-	69.9	-	-	35.7	-	22.4
2.1×10^{-2}	-	153.0	-	80.1	-	-	31.4	-	17.7
2.1×10^{-1}	-	181.2	-	78.1	-	-	31.9	17.8	
2.1	-	36.3	33.3	31.5	29.7	32.8			

^aDose rate = 1.11×10^4 rad/hr. Total dose = 0.20×10^6 rad. Concentration of styrene in methanol (30% by volume).

^bBy interpolation.

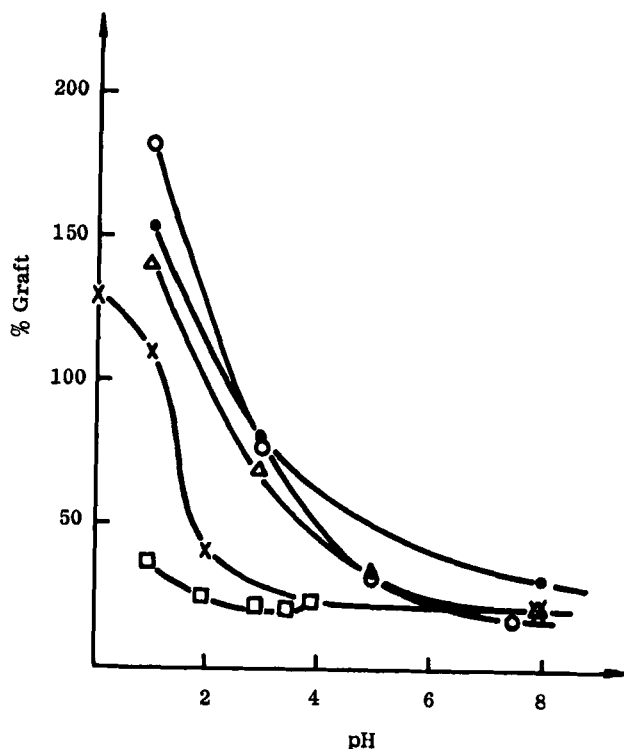


FIG. 7. Effect of water on radiation-induced grafting of styrene in methanol to cellulose in acidified solution. Conditions as in Table 4. (x) 0.0 M H₂SO₄; (Δ) 2.1 × 10⁻³ M H₂SO₄; (●) 2.1 × 10⁻² M H₂SO₄; (○) 2.1 × 10⁻¹ M H₂SO₄; (□) 2.1 M H₂SO₄.

General Acid Effect

Physical properties such as swelling and diffusion are frequently invoked to explain complex phenomenon associated with grafting. When acid is used as additive as in the present studies, physical factors alone do not satisfactorily explain the large enhancement in graft observed, especially with low concentrations of sulfuric acid. The suggestion that the favorable effect of acid is due exclusively to improved accessibility of styrene to the cellulose structure is also not tenable since hydroxide ion also possesses the same property and grafting is retarded in the presence of alkali (Table 5). Thus the acid and alkali grafting results indicate that the acid enhancement is of a

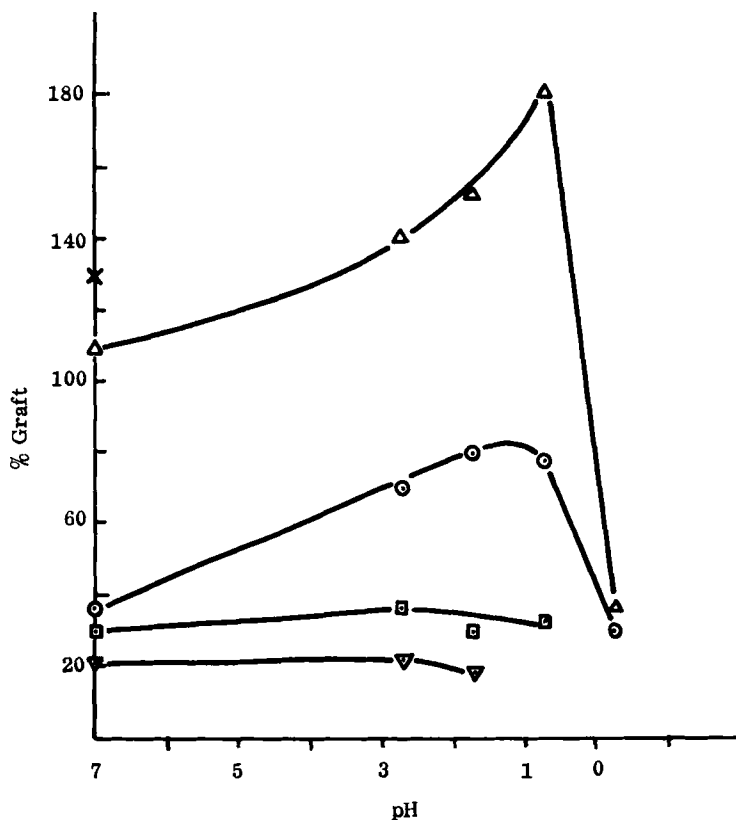


FIG. 8. Effect of water on Trommsdorff peak in radiation grafting of styrene in methanol to cellulose in acidified solution. Conditions as in Table 4. (x) 0% H₂O; (Δ) 1% H₂O; (⊙) 3% H₂O; (⊞) 5% H₂O; (∇) 8% H₂O.

predominantly chemical nature. Swelling and accessibility of acid probably make a small contribution to the increased acid graft since acid is known to promote uncoiling of the cellulosic chains during hydrolysis [17].

The observed acid effects in the present grafting reaction thus appear to be predominantly due to a radiation chemistry phenomena. It is apparent that the acid additive interferes with the precursors of the radicals produced from radiolysis of the grafting system. In terms of this proposed model, acid additives, if present in sufficiently high concentration, i.e., the levels reported in the present work, should

TABLE 5. Effect of Alkali on Radiation-Induced Grafting of Styrene in Methanol to Cellulose^a

% Styrene (by volume)	Graft (%) in sodium hydroxide solution (M)			
	0.0	10 ⁻³	10 ⁻²	10 ⁻¹
10	6.2	-	-	-
20	30.3	17.8	10.1	6.5
30	41.3	26.9	11.7	7.7
50	38.6	31.1	12.0	2.7
80	56.1	29.4	2.8	0.9

^aDose rate = 2.64×10^4 rad/hr. Total dose = 0.20×10^6 rad.

advantageously affect both the propagation rate of the styrene polymerization and also the number and nature of the sites in the cellulose available for grafting. Where the cellulose samples were pretreated with acidified methanol and water, as in the "inclusion technique" (Table 6), the concentration of acid in the final polymerization solution, after numerous styrene extractions when acid is lost each time, was so small that the effect of acid on the propagation rate was negligible. The fact that acid can affect the grafting reaction by interfering with the precursors of the products of the radiolysis of methanol, and/or cellulose, is consistent with the proposed role of styrene in these reactions. Thus this monomer is known to be a very effective radical scavenger in radiation copolymerization [4], grafting occurring when styrene reacts with cellulose macroradicals.

Role of Solvent in Mechanism of the Acid Effect

The effect of high-energy radiation on cellulose is to produce macroradicals capable of acting as grafting sites [4]. Styrene, being aromatic in structure, should be more radiation stable than the solvent, methanol. A summary of the relevant radiation chemistry of the three components in the present system, viz., cellulose, methanol, and styrene, is therefore necessary for a mechanistic discussion of the process. The interaction of gamma rays with methanol leads to the formation of ions, free radicals, and excited molecules. It has been suggested, particularly for polymerization work, that the lifetime of the excited states and of ions in a liquid medium is so short

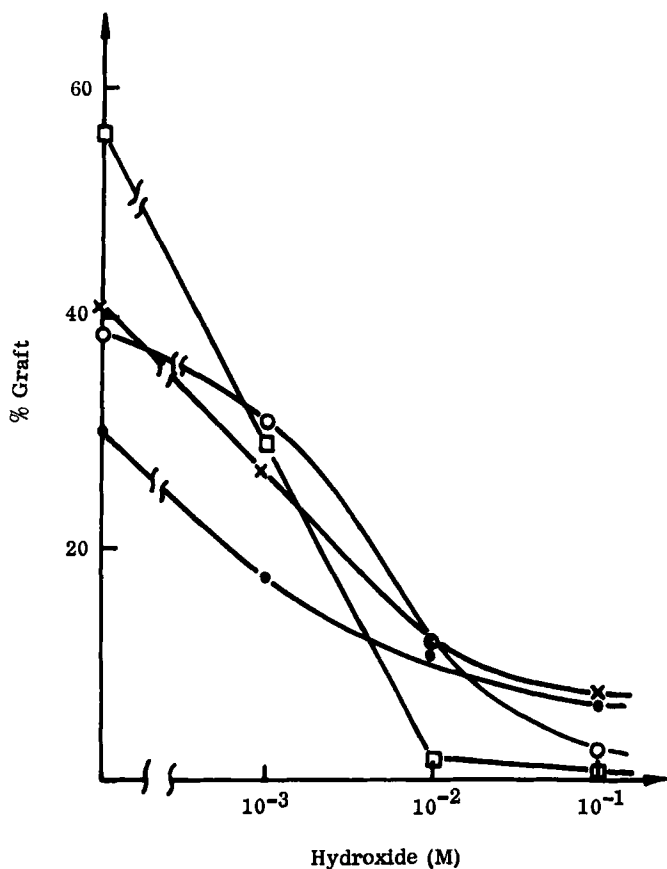


FIG. 9. Effect of alkali on radiation-induced grafting of various concentrations of styrene in methanol to cellulose. Conditions as in Table 5. (●) 20%; (○) 30%; (×) 50%; (□) 80%.

that only radicals, produced by the fast decomposition of excited states, are predominantly responsible for subsequent reactions. However, pulse radiolysis work [18] has shown that the lifetime of ions can be extended in alcohols sufficient for ionic processes to occur.

For methanol, irradiation yields the protonated species in Eqs. (1) to (3):



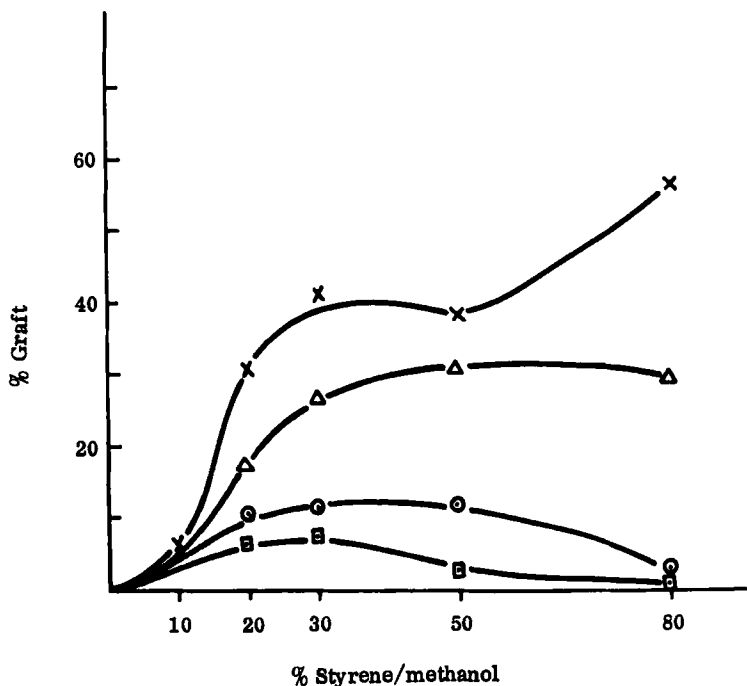
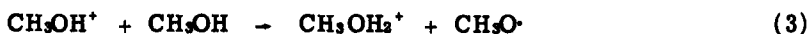
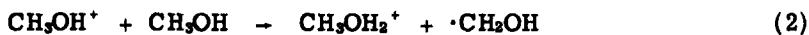
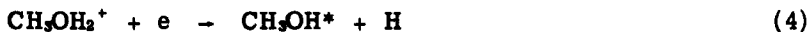


FIG. 10. Effect of alkali on Trommsdorff peak for radiation grafting of styrene in methanol to cellulose. Conditions as in Table 5. (x) 0.0 M NaOH; (Δ) 10^{-3} M NaOH; (\odot) 10^{-2} M NaOH; (\boxplus) 10^{-1} M NaOH.



Baxendale and Sedgwick [19] have suggested that the CH_3OH_2^+ species are the only ions present in methanol vapor before neutralization by electron capture:



resulting in excited molecules and hydrogen atoms. Excited methanol molecules then decompose to give radicals and molecular products:

TABLE 6. Effect of Acid Pretreatment of Cellulose on Radiation-Induced Grafting of Styrene^a

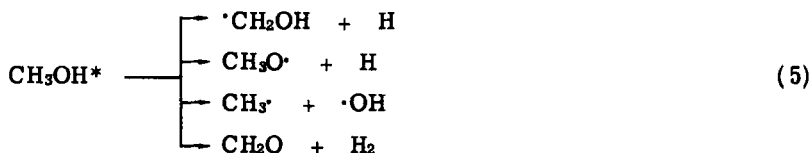
Pretreatment solution	Graft (%) at dose rate (rad/hr × 10 ⁻⁴)			
	1.95 ^c	1.95 ^d	2.64 ^c	40.4 ^c
Control	1.0	0	0	0.8
Methanol	42.9	3.5	-	67.0
Methanol + acid ^b	74.2	6.4	19.5	33.8
Water	53.9	41.8	-	77.1
Water + acid ^b	41.7	30.5	29.6	51.6

^aTotal dose = 0.20 × 10⁸ rad.

^bPretreatment solutions acidified with H₂SO₄ (1.1 M).

^cExtraction with styrene (2×) after pretreatment.

^dExtraction with styrene (4×) after pretreatment.



It has also been shown that solvated electrons produced in methanol are sufficiently long lived to react with solute at low concentrations [18]. Sulfuric acid has a significant effect on the yields of radiolysis products from methanol [10-13]. These results have been interpreted in terms of the affinity of hydrogen ions for the solvated electron [10-13]. The increase in G(H₂) found with the addition of sulfuric acid during methanol radiolysis is consistent with electron scavenging by hydrogen ions:



In particular, in the radiolysis of methanol, addition of sulfuric acid increases the G(H₂) yield, presumably by increasing G(H) via reactions such as Eq. (6).

The addition of acid also facilitates the formation of the protonated species CH₃OH₂⁺ (Eq. 7), and hence accelerates the production of excited states, radicals, and molecular products as shown in Eqs. (4) and (5).



There is thus a considerably higher concentration of excited states, radicals, and ions, in particular hydrogen atoms, when the acid concentration is increased in the methanol-styrene radiation grafting solution. Most of these species originate from the methanol radiolysis, since styrene is more radiation stable than the solvent. However, the styrene, being a strong radical scavenger, will scavenge the species above, particularly H atoms, leading to a higher rate of polymerization and ultimately grafting.

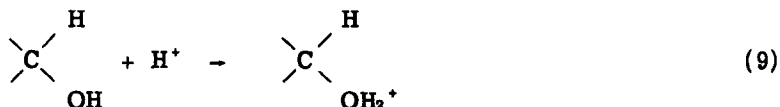
Effect of Acid on Radical Formation in Cellulose

Dilli and Garnett [4, 20] have stressed the importance of radiolytically produced hydrogen atoms in the mechanism of styrene grafting to cellulose in the presence of methanol. These authors have discussed the formation of cellulose macroradicals by hydrogen atom abstraction:

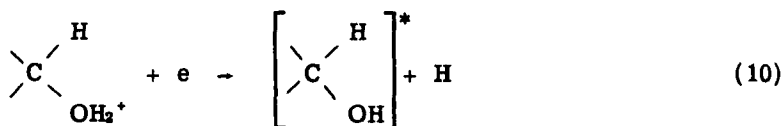


(where Ce = cellulose). Additional radicals which are potential grafting sites can also be formed in cellulose by other primary radiation processes. Electron spin resonance studies [21-24] indicate the nature of these additional types of macroradicals.

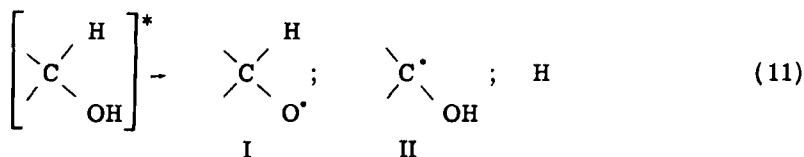
Addition of mineral acid to the grafting solution will lead to strong hydrogen ion adsorption on the surface of the cellulose (and also within the bulk, if the cellulose is swollen as in methanol), followed by protonation:



The capture of secondary electrons by the charged species in Eq. (9) leads to hydrogen atom formation and excited cellulose molecules:



The decomposition of such excited cellulose molecules yields macro-radicals for further grafting and also additional hydrogen atoms:



The process in Eq. (11) depicts one radiolysis pathway for the formation of alkoxy radical sites (I) for copolymerization whereas alkyl radicals (II) are usually obtained preferentially by energetic hydrogen abstraction reactions. It is thus obvious how inclusion of acid in the grafting solution can increase the sites available in cellulose for radiation copolymerization, particularly due to reactions involving hydrogen atoms.

Effect of Acid on Trommsdorff Peak

The effect of an increase in $G(H)$ with inclusion of acid on the grafting reaction is also evident from the acid dependency of the Trommsdorff peak. The gel or Trommsdorff effect [4] is associated with a change in viscosity of the medium as the polymerization proceeds, thus at higher viscosities bimolecular chain termination of the radical chains is hindered. In contrast, other steps in the polymerization such as initiation, propagation, and radical transfer are not affected to the same degree by an increase in viscosity, since the molecules involved are smaller and more mobile. The Trommsdorff effect thus leads to rapid consumption of monomer and high molecular weights. From previous studies with radiation grafting to cellulose [4], the most important parameters determining the position of the Trommsdorff peak in these reactions are radiation dose and dose rate, concentration of monomer in solvent, and structure of both monomer and solvent.

In this earlier work, evidence was also accumulating to indicate that the actual mechanism of the Trommsdorff effect in radiation grafting was predominantly due to H atom scavenging. Thus any method for increasing $G(H)$ in the copolymerization system should theoretically enhance the intensity of the gel peak if already present in the system. Data in Figs. 4 and 5 are consistent with this prediction. Furthermore, it is also found that addition of acid can induce a Trommsdorff effect where none was previously present (Figs. 1 and 2), again presumably due to an increase in $G(H)$ in the system

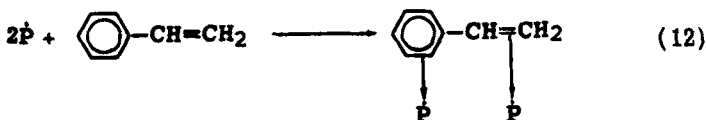
from interaction between hydrogen ions and secondary electrons of the type discussed in the preceding section.

Specific Mechanism for Acid Enhancement of Grafting

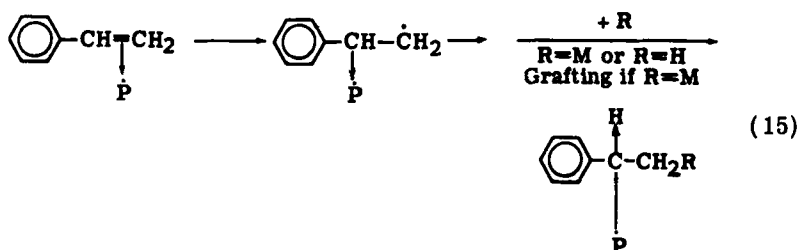
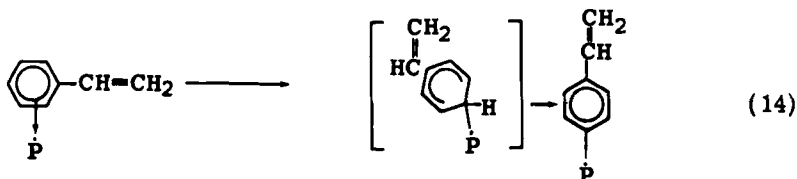
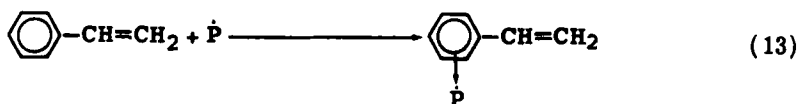
Dilli and Garnett [4, 15] have suggested that for the radiation grafting of styrene in methanol to cellulose in the absence of acid, the copolymerization at low monomer concentrations depends essentially on the radiation chemistry of the solvent methanol whereas at high monomer concentrations the radiation chemistry of the monomer determines the reaction pathway. Swelling of cellulose by methanol is considered to be appreciable in both concentration regions. The interpretation of the Trommsdorff effect is also consistent with this relatively simple model.

From this work, Dilli and Garnett [20] developed a charge-transfer theory for grafting which was applicable to the copolymerization of a wide range of monomers to trunk polymers, particularly cellulose. The theory was also relevant to grafting by initiating methods other than radiation-induced processes. Subsequently, Gaylord [25] also discussed a theory involving charge-transfer bonded species in grafting reactions. Gaylord's theory [25] and the original charge-transfer concept [20] are very similar.

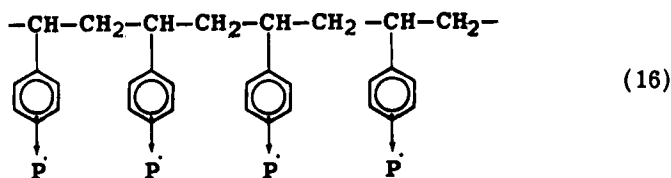
It is important to summarize the significant features of the earlier charge-transfer theory [20] since the present acid effect is consistent with the theory. The basic principle of the theory is that radiation-induced trapped radicals are available for bonding in the trunk polymer. Thus charge-transfer adsorption of monomer or growing polymer to the trunk polymer (Eq. 12) facilitates subsequent copolymerization.



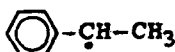
Using styrene and irradiated cellulose as representative model, the complex in Eq. (12) shows the delocalized Π -bonding between styrene and free valencies of irradiated cellulose. From this intermediate charge-transfer complex, a number of specific grafting mechanisms are possible. For radical sites that are easily accessible at the surface, the Π -complex may react further by a Π - σ conversion with either the ring (Eqs. 13 and 14) or side-chain (Eq. 15) to give σ -bonded species.



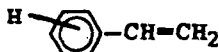
Where the mobility of the polystyrene chains and radicals is impeded, Π - σ conversion processes are restricted; however, grafting could still occur through charge-transfer bonding of the type shown in Eq. (16). Such bonding would keep homopolymer locked between the chains as "graft" and could explain the apparent anomalies observed when homopolymer is extracted from copolymerized celluloses.



These mechanisms, particularly that shown in Eq. (16), can be developed further because of recent fundamental studies of the pulse radiolysis of styrene and styrene solutions [26]. This work shows that under certain radiolysis conditions hydrogen atoms can add with equal probability to either the side chain or ring of styrene to give species such as III and IV:



III



IV

This result suggests that styrene in grafting reactions can be copolymerized via a mechanism analogous to Eq. (16) involving π -olefin complexing through the side chain with multiple cross-linking through the radical sites on the aromatic rings.

The present charge-transfer theory is also satisfactory for interpreting the acid effects that have been observed in the current work. Thus, through the increase in $G(H)$ yield in the presence of acid, increased grafting sites in cellulose can be obtained by hydrogen atom abstraction processes. These additional hydrogen atoms in the acidic solutions in the low monomer concentration where the Trommsdorff peaks are observed can also explain both the induced and enhanced gel effects found in acid. In this low monomer concentration region, more hydrogen ions would be outside the cellulose in solution than the analogous situation at high monomer concentration ($\approx 80\%$) where no gel effect is observed. This increase in the number of hydrogen ions would lead to more hydrogen atoms, increased scavenging by styrene in solution, and a buildup of polymer chain length prior to grafting in the concentration region where the Trommsdorff peak is found. This interpretation is consistent with the observed results, especially at low conversion where the increase in grafting yields at the Trommsdorff peak as the acid concentration is increased to ≈ 1 M, parallels Sherman's [12] data for the effect of acidity on $G(H_2)$ from the radiolysis of methanol.

The possibility that energy transfer and ionic mechanisms contribute to the present acid effects in radiation grafting cannot be overlooked. Present evidence [27] suggests that any such contribution of these competing processes will be minimal. However, current work is in progress to clarify this situation [27].

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