Grafting of Vinyl Monomers by the Xanthate Method

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Synopsis

The removal of oxygen from swollen pulp is very difficult. At least 1–2 h of purging with oxygen-free nitrogen or argon is required as well as efficient mixing and a low concentration of pulp (not higher than 1%). During the grafting reaction, in which the xanthate cellulose is a part of the redox system, the concentration of oxygen falls to zero and stabilizes at this level even if air is purged through the system or a higher rate of stirring is applied. Primary sulfur radicals created in the reaction of the xanthated groups with H_2O_2 are further oxidized by H_2O_2 or by particles of oxygen dissolved in the reaction mixture. The observed increase in reaction caused by an increase in stirring speed is due to the higher rate of diffusion of hydrophobic monomers as well as the diffusion of oxygen to active centers at high stirring speed. The low rate of grafting at lower agitation speeds is caused by agglomeration of monomer molecules to bigger particles and, as a result, decreased diffusion of monomer to active centers. Above 300 rpm, the effect of monomer diffusion diminishes and further increase in conversion is caused only by a higher rate of oxygen diffusion to active centers from reaction mixture or passing gas. However, above a certain level of oxygen, the effect of termination by oxygen prevails and the rate of reaction decreases. Additives increase the conversion in the lower range of agitation speed only. The application of additives and agitation are two equivalent methods, both of which lead to an increase in conversion in the lower range of stirring speed.

INTRODUCTION

Among the many methods of grafting vinyl monomers onto cellulose, the xanthate method has the highest potential for industrial application due to its high resistance to impurities (e.g., lignins), high conversion at ambient temperature, and the ability to carry out the reaction in the presence of air.[1] A number of papers have been published on the grafting of vinyl monomers by the xanthate method,[2-5] but little is known about the mechanism of the reaction and the parameters which govern the kinetics.

Graczyk and Hornof, in several papers,[6-9] showed that the reaction of grafting by the xanthate method is strongly affected by agitation. Maximum conversion on the conversion vs. stirring rate curve was observed, followed by a drop in conversion to zero in most cases. The shape of the curves was dependent on the concentration of reagents as well as the shape of stirrer and the geometry of the reactor. They found that the formation of polymer was almost completely inhibited by pure oxygen (only 6.2% conversion), while air only slightly slowed the reaction. These results were in accordance with other reports[10,11] that air does not significantly decrease conversion in comparison with reaction under nitrogen. It is well known that, depending on reaction conditions and the type of monomer, oxygen can act as an initiator or as an

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inhibitor of vinyl polymerization. It is a reasonable assumption that, at least at high stirring speed, a decrease in conversion could be caused by the termination of reaction by particles of oxygen, as has been documented in the case of the emulsion polymerization of vinyl monomers.[12,13]

Thus, comprehensive research was undertaken to study the effect of traces of oxygen and the combined effect of oxygen and stirring speed on conversion. For this purpose, different qualities of gases were used and the concentration of oxygen in the reaction mixture during the soaking period and reaction was studied.

In papers published by Graczyk and Hornof[6-9] the partly xanthated cellulose-Fe^{+2}-H_2O_2 redox system was studied. It was interesting to elucidate the separate influences of ferrous ion and xanthated cellulose on the kinetics of the reaction and the effect of stirring on conversion. For this purpose, the experiments were carried out with the following redox systems: cellulose xanthate-H_2O_2 ($K_2S_2O_8$) and cellulose xanthate-M^{+n} (where $M^{+n} = Fe^{+3}, V^{+5}$). For comparison with previous papers, these studies were limited to styrene as a monomer and commercial nitrogen of 99.9% purity.

Garnett et al.[14,15] established that additives considerably increase the rate of grafting styrene onto cellulose as well as grafting efficiency initiated by radiation. Vojnova et al.[16] also reported that additives such as hydroquinone or hydrazine accelerate the rate of grafting initiated by the Fe^{+2}-H_2O_2 redox system. The studies were undertaken in this paper to elucidate the influence of additives on conversion, especially in a lower range of stirring speed where the effect of agitation was considered important.

EXPERIMENTAL

Materials

A dissolving pulp supplied by Zaklady Celulozy i Papieru, Swiecie, Poland was used as the grafting substrate. Styrene (Zaklady Chemiczne Oswiecim, Poland), methyl acrylate (MA) (BDH), and methyl methacrylate (BMA) (REACHIM) were purified by vacuum distillation, and the middle fraction was stored in a refrigerator prior to use. All other chemicals were reagent grade.

Graft Copolymerization

Graft copolymerization was carried out in a 1-L glass reactor equipped with a teflon paddle stirrer, as described previously.[7] Stirrer speeds were measured with a photoelectric tachometer.

The emulsion method of xanthation employed gave $\gamma = 11$ (i.e., approximately 11 xanthate per 100 glucose units) as has been described previously.[17]

The reactions were carried out under positive inert gas pressure, which was purged at the rate of 12–15 L/h. Different qualities of gases and methods of adding initiation reagents were used, depending on reaction conditions.

Method 1

Oxygen-free nitrogen or argon was purged, usually for 1 h. Sulfuric acid and hydrogen peroxide were added from the funnels without opening the reactor at the same time, unless otherwise indicated.

Method 2A

Nitrogen of 99.9% purity was purged through the system. After a 15 min soaking period both H_2SO_4 and H_2O_2 were added at the same time by opening the reactor.

Method 2B

Nitrogen of 99.9% purity was purged through the system and a 15 min soaking period was applied, but H_2SO_4 was added 1 min earlier than H_2O_2 by opening the reactor, unless otherwise indicated.

Cellulose Xanthate–Fe^{+2}–H_2O_2 ($K_2S_2O_8$)

In the typical reaction, cellulose xanthate (10 g/L) with absorbed ferrous ions (presoaked in Mohr salt, washed, and filtered) was charged into the reactor with 0.06*M* monomer, 0.9 g Tween 80, and a suitable amount of distilled water to adjust the volume of reaction mixture to 450 mL. The reaction was started by adding 7.5 mL 0.2*N* sulfuric acid to adjust the initial pH to 5.0 and an oxidizing agent (H_2O_2 or $K_2S_2O_8$). The reaction was carried out for 1 h at 25°C unless otherwise indicated. The reaction was terminated by adding hydroquinone and the reaction products were quickly filtered and washed with 2 L of distilled water.

Additives in the reactions initiated by this method were added 10 min after the beginning of the swelling period, which lasted 15 min.

Cellulose Xanthate–H_2O_2 ($K_2S_2O_8$)

The same procedure and amount of reagents were applied as above. However, the soaking of cellulose in Mohr salt was omitted, and the reaction was carried out for 1 h at 65°C instead of 25°C.

Cellulose Xanthate–Fe^{+3} (V^{+5})

In a typical reaction, cellulose xanthate (10 g/L), 0.06M styrene, 0.9 g Tween 80, 0.924 g $Fe_2(SO_4)_3 \cdot 7H_2O$ (0.01*M*) or 1.0525 g NH_4VO_3 (0.01*M*) were adjusted to 450 mL by adding distilled water. After 15 min of swelling, the reaction was started by an addition of 7.5 mL 0.2*N* H_2SO_4 (xanthate–Fe^{+3}) or 45 mL 2*N* H_2SO_4 (xanthate–V^{+5}). The initial pH of the reaction was 5.0 or 1.0, respectively. The reaction was carried out at 45°C for 1 h and was stopped by an addition of hydroquinone.

Reaction Parameters

The percentage of conversion was calculated in the following manner:

1. Conversion to polymer (polymer yield):

$$\% = (D - B)/C \times 100$$

represents the total amount of polymer formed with respect to the amount of monomer charged.

2. Conversion to copolymer (copolymer yield):

$$\% = (A - B)/C \times 100$$

represents the amount of polymer chemically bounded to the substrate (i.e., not removed by extraction) also with respect to the amount of monomer charged.

3. Grafting efficiency:

$$\% = (A - B)/(D - B) \times 100$$

In the expressions above A, B, C, and D denote, respectively, dry weight of products after copolymerization and extraction, pulp charged into the reactor, monomer and products isolated by filtration (before extraction).

The homopolymer content in the reaction products was determined by soxhlet extraction of 3–4-g samples of products with acetone for 24 h.

Determination of Oxygen

The concentration of oxygen in the reaction mixture was determined in a 1-L standard reactor at 25°C. The same amount of reagent was used as in the reaction of grafting by the xanthate–Fe^{+2}–H_2O_2 redox system, if not otherwise indicated. The gases were purged at the rate of 15 L/h. An oxygenmeter TRS (West Germany) and probe were used.

RESULTS AND DISCUSSION

Oxygen Removal and Its Concentration during the Reaction

In papers published by Graczyk and Hornof[6-9] most experiments were carried out in 1-L reactors. It was interesting to measure how the removal of oxygen is dependent on stirring speed. The experiments were done according to Method 1 in the presence of oxygen-free argon. Figure 1 shows that oxygen removal rises considerably with an increase in agitation speed up to 400 rpm. Above this point, differences in the rate of oxygen removal become insignificant. At 310 rpm, the rate generally used in this experiment, 40–45 min was needed to decrease the concentration of oxygen below 0.1 ppm, and reproducibility of results was very good.

Figure 2 shows how the concentration of pulp influences oxygen removal. For the sake of comparison, data for oxygen removal from water are also included. The rate of oxygen removal from water and 1% concentration of cellulose is the same. The displayed oxygen concentration measured by the oxygen probe shows that the rate of oxygen removal increases as the concentration of pulp increases and is the highest for 3% cellulose. Of course, it is an artifact. The oxygen probe is clogged by cellulose fibers, and at the higher pulp concentration penetration of oxygen from the solution to the probe is prevented. The probe readout does not represent the actual concentration of oxygen in the pulp slurry but in close vicinity to the probe. It is clear from the

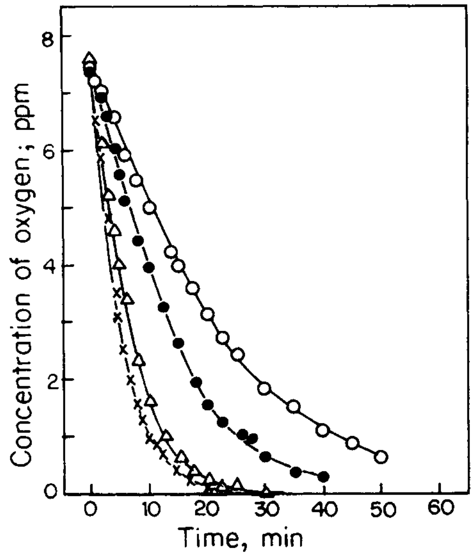


Fig. 1. Oxygen removal from the He reaction mixture as a function of stirring speed: oxygen-free argon; [cellulose] = 10 g/L; (○) 160 rpm; (●) 260 rpm; (△) 410 rpm; (×) 1000 rpm.

experiments in which the probe was immersed into the pulp slurry at the end of the oxygen removing period that a much higher stirring speed and a longer period of time is needed for oxygen removal when working with concentrations of pulp above 1%. Even at this concentration of pulp, efficient mixing and at least a 1 h oxygen removal period is needed. It will be shown later using the example of grafting styrene and BMA, that even as low concentra-

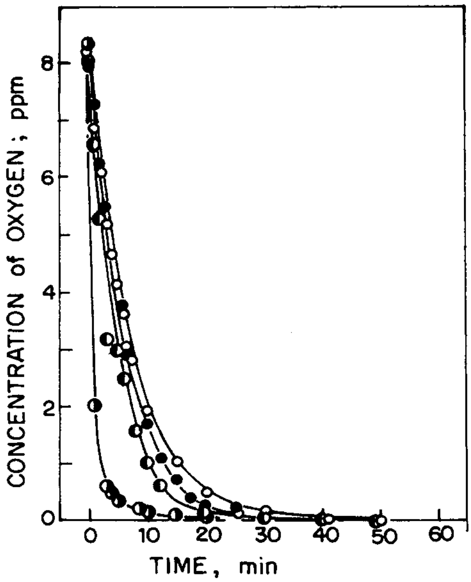


Fig. 2. Oxygen removal as a function of concentration of cellulose: oxygen-free argon; 310 rpm; (●) water; [cellulose]: (○) 10 g/L; (◐) 20 g/L; (◑) 30 g/L.

tion of oxygen as 0.1 ppm still has tremendous influence on the rate and kinetics of grafting.

In the experiments published by Graczyk and Hornof,[6-9] commercial nitrogen (99.9%) was used and the reaction was started according to Method 2B. Although oxygen was removed during a 15 min soaking period, a small amount of oxygen remained in the system (usually 1 ppm O_2). Figure 3 shows how the concentration of oxygen changes during the soaking and the reaction periods, at stirring speeds 160 and 310 rpm. It was observed that, at the moment of simultaneous addition of H_2SO_4 and H_2O_2 by an opening in the reactor, the concentration of oxygen rises to 2 ppm and later falls to zero. The drop in the concentration of oxygen to zero is faster at the lower stirring speed than at the higher one (160 and 310 rpm, respectively). It is just the opposite in the case of oxygen removal from the reaction mixture. The same pattern was observed when styrene was omitted from the reaction system. This means that viscosity of grafted pulp does not have any effect on the probe readout.

These observations confirm the reaction of xanthated cellulose with H_2O_2 without monomer in the presence of air (Fig. 4). At an air flow of 5 L/h, the concentration of oxygen also drops to zero as was seen, but a 50 min reaction period is needed. At a flow rate of 15 L/h (as is usually used), the concentration of oxygen drops to 1.5 ppm and, after 80 min, starts to rise with the decreasing concentration of xanthate groups as a result of their hydrolysis and oxidation.

Figure 5 shows that, in the presence of sulfuric acid alone, the concentration of oxygen does not decrease, though full hydrolysis of xanthated groups occurs. Only in the presence of both sulfuric acid and hydrogen peroxide does a drop in the concentration of oxygen occur. This phenomenon is also

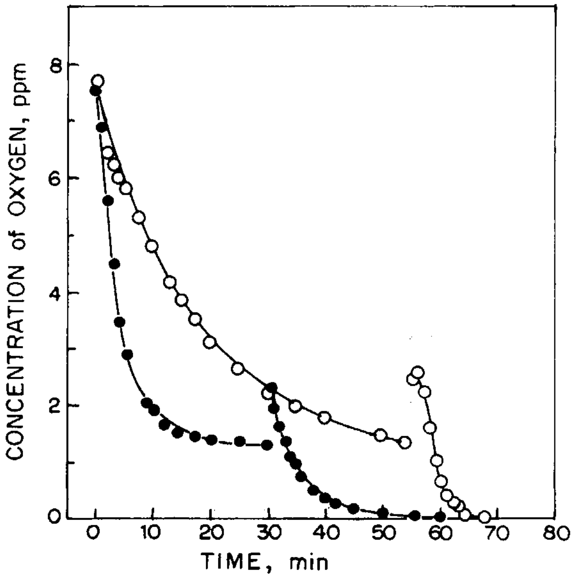


Fig. 3. Concentration of oxygen in the reaction mixture during soaking period and reaction of grafting styrene by the xanthated cellulose–Fe^{+2}–H_2O_2 redox system: nitrogen 99.9%; [cellulose] = 10 g/L; [styrene] = 0.133 mol/L; [H_2O_2] = 0.049 mol/L; (○) 160 rpm; (●) 310 rpm.

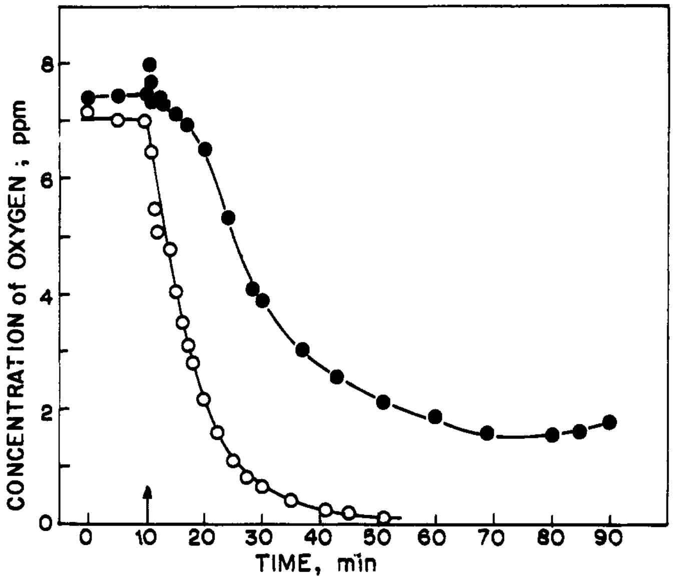


Fig. 4. Concentration of oxygen in the reaction of xanthated cellulose (saturated with Mohr salt) with H_2O_2 in the presence of air: [cellulose] = 10 g/L; $[H_2O_2]$ = 0.049 mol/L; $[H_2O_2]$ = 0.049 mol/L; $[H_2SO_4]$ = 0.0033 mol/L; air flow rate: (○) 5 L/h; (●) 15 L/h.

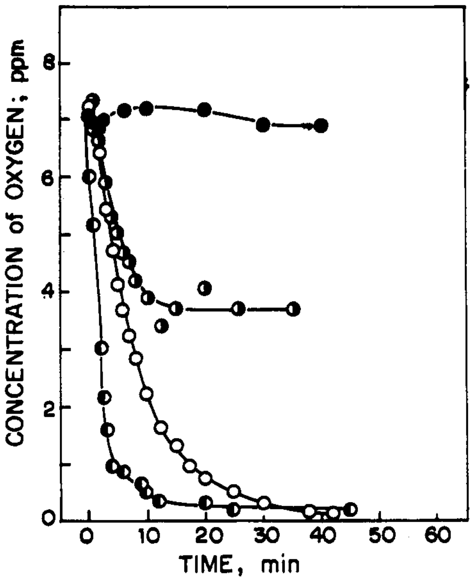


Fig. 5. Concentration of oxygen in the reaction of xanthated cellulose (saturated with Mohr salt) with H_2O_2 in the presence of air as a function of stirring speed: air flow rate = 15 L/h; [cellulose] = 10 g/L; $[H_2O_2]$ = 0.049 mol/L; $[H_2SO_4]$ = 0.0033 mol/L; (◐) 60 rpm; (○) 400 rpm; (◑) 800 rpm; (●) 400 rpm added H_2SO_4 only.

observed when air is purged through the system. At 60 and 400 rpm the drop in oxygen concentration to zero is possible, though at 800 rpm concentration of oxygen levels off at 3.7 ppm.

It is worth mentioning that, in the reaction of grafting initiated by ceric salt in the presence of traces of oxygen, no drop in oxygen concentration after an addition of the ceric salt is observed.[17]

The above results clearly show that xanthated cellulose is an oxygen scavanger in the reaction medium. The reaction is very fast and quantitative. It is able to consume all oxygen, though air is constantly purged through the system. Oxidized xanthated radicals still can initiate the grafting reaction, and this is the reason for the observed high conversion in the presence of air.[11]

Addition of Reagents

Initiation of the grafting reaction by the xanthation method occurs in two stages. In the first stage, xanthated groups are changed from a stable sodium salt to xanthogenic acid by the addition of acid. In the second stage, which follows immediately, added H_2O_2 creates radicals on unstable xanthate groups in the acid medium.

Better understanding of the reaction of initiation could have practical application. Water-soluble acrylic salts such as 2-dimethylaminoethyl methacrylate (DMAEM) and 3-dimethylaminopropyl methacrylamide (DMPMA) have the highest reactivity when they are in the form of salts. Since pK of these salts is below pH 7 (DMAEM pK = 4.25) during the soaking period in graft copolymerization by the xanthate method, Graczyk and Hornof[18] used them in partly neutralized form. Just before the reaction was started by an addition of H_2O_2, they were neutralized, and the pH of the reaction mixture was fixed at 4.0. The reaction of neutralization, and later of acidification, in pulp slurry is not an instant reaction, and at least 1 min is needed to stabilize the pH. Allowing time to elapse between an addition of acid and H_2O_2 will then influence the hydrolysis of xanthated cellulose, the subsequent creation of radicals, and, consequently, the rate of grafting.

In this set of experiments, commercial nitrogen was used and reagents were added according to Method 2. Figure 6 shows that at 310 rpm, which is really very efficient mixing, the same conversion to polymer is obtained when either both reagents (H_2SO_4, H_2O_2) are added at the same time or H_2SO_4 is added 5 min earlier. It appears that even slightly higher conversion is obtained when H_2SO_4 is added 1 min earlier than H_2O_2. Even when H_2SO_4 is added at the beginning of the soaking-oxygen removal period (first min) and H_2O_2 at the end of the soaking period (15 min), conversion is still high and reaches 72%.

At the lower range of agitation speed conversion reaches 30% when both reagents are added at the same time. Lower conversion of 15–18% is observed when H_2SO_4 and H_2O_2 are added at different times during the soaking period. Generally, differences caused by the method of reagent addition are small.

At a high stirring speed, conversion to polymer is strongly dependent on the method of reagent addition. The maximum conversion is observed at 310 rpm for reaction in which H_2SO_4 is added 1 or 5 min earlier than H_2O_2. When both reagents are added at the same time, the maximum shifts to higher stirring speed (400 rpm). In this case the conversion slowly falls as stirring speed

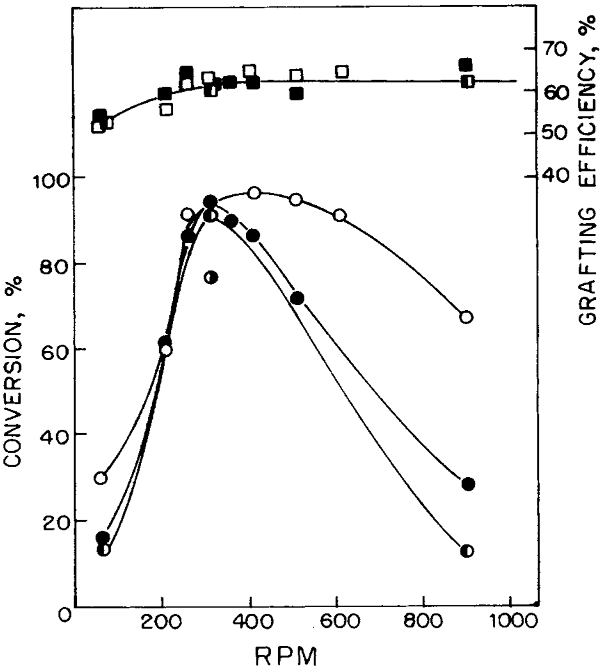


Fig. 6. Conversion of styrene to polymer and grafting efficiency as a function of stirring speed at different time of adding H_2SO_4 and H_2O_2: (○, ●, ◐, ◑) polymer; (□, ■, ◧, ◨) grafting efficiency; (○, □) H_2SO_4 and H_2O_2 added in 15 min; (●, ■) added: H_2SO_4—14 min; H_2O_2—15 min; (◐, ◧) added: H_2SO_4—10 min; H_2O_2—15 min; (◑, ◨) H_2SO_4—1 min; H_2O_2—16 min.

increases. When H_2SO_4 is added before H_2O_2, the maximum follows a dramatic drop in conversion. There is nearly no difference in the shape of curves for reactions in which elapsed time between an addition of H_2SO_4 and H_2O_2 is either 1 or 5 min.

The above results show that stirring speed has a tremendous effect on conversion when H_2SO_4 is added earlier than H_2O_2, e.g., 1 min earlier. Although one can presume, on the basis of a vortex creation in the reaction mixture (310 rpm), that efficient mixing of reagents occurs, it is not efficient to instant neutralization and later hydrolysis of the xanthate groups of cellulose. At 900 rpm, nearly full hydrolysis of xanthate groups occurs immediately, and the reaction slows considerably.

On the basis of the results presented, it is also possible to explain why Dimov and Pavlov[2] and Ehrnrooth[3] observed the highest initial rate of grafting of acrylonitile at pH 1.0, while overall conversion was the highest at pH 4.0–5.0. Dimov and others carried out their reactions without any mixing of reagents. Initiation of grafting by the xanthate method is a very fast reaction. Without mixing, hydrolysis of xanthated groups was relatively slow in the middle range of pH and, consequently, a low initial rate of grafting was observed. At a lower pH, over the same reaction time, more acid penetrated into cellulose fibers. Thus, hydrolysis of xanthated cellulose was faster and more radicals were created by hydrogen peroxide. Since diffusion of acid was considerably faster than that of monomer under these conditions, after the initially fast reaction conversion leveled off. This is due to the complete

TABLE I
Influence of the Method of Adding H_2SO_4 and H_2O_2 on Conversion to Polymer at a High Stirring Rate[a]

			Soaking period					
			Time of soaking period	Time of adding (min)				
No.	Gas	rpm	(min)	H_2SO_4	H_2O_2	Reaction time (min)	Conversion (%)	Grafting efficiency (%)
1	Argon purified	900	60	60	60	60	75.5	60.4
2		900	60	50	60	60	69.1	60.8
3		1300	60	60	60	60	77.9	67.1
4		1300	60	50	60	60	80.4	65.2
5	Nitrogen 99.9%	900	60	60	60	60	28.60	58.9
6		900	60	59	60	60	29.6	62.3
7	Nitrogen 99.9%	900	15	15	15	60	27.06	63.3
8		900	15	14	15	60	28.03	66.7

[a] Gas flow rate = 15 L/h; temperature = 25°C; [cellulose] = 10 g/L; [styrene] = 0.133 mol/L; $[H_2O_2] = 0.048$ mol/L.

hydrolysis of xanthated groups and recombination of formed radicals before a considerable amount of monomer penetrated into cellulose fibers.

All these differences take place in the presence of traces of oxygen. When oxygen was completely removed from the reaction system, even 10 min difference time between an addition of H_2SO_4 and H_2O_2 at a high stirring speed (e.g., 900 rpm) does not have any influence on conversion (Table I). For the sake of comparison in Table I data with nitrogen 99.9% are also included.

Influence of Soaking Period-Oxygen Removal Period on Conversion

Xanthated cellulose is an unstable substrate even if it is kept in the form of sodium salt (at pH 7) for longer periods of time. As was shown in the previous section, a period of at least 1 h was needed to lower the concentration of oxygen to below 0.1 ppm. Such a long soaking period could change the reactivity of xanthated cellulose. Two sets of experiments were carried out with different quality of gases to study this problem.

In the first set of experiments, commercial nitrogen 99.9% and Method 2A addition of reagents were applied. H_2SO_4 and H_2O_2 were added at the same time to avoid hydrolysis of cellulose before radicals were created.

During the soaking period, the reaction mixture was stirred at the rate of 310 rpm. Suitable stirring speed was adjusted 1–5 min before the reaction was started, so that any differences in conversion were caused by changes in the reactivity of xanthated cellulose and not by changes in the concentration of oxygen. Soaking periods of 15, 30, and 60 min were studied. As is shown in Figure 3, for this quality of nitrogen and 310 rpm, the concentration of oxygen stabilizes at the level of 1 ppm in 15 min.

Figure 7 shows that with an increase in the soaking period, conversion to polymer decreases, though the location of the maximum and the shape of

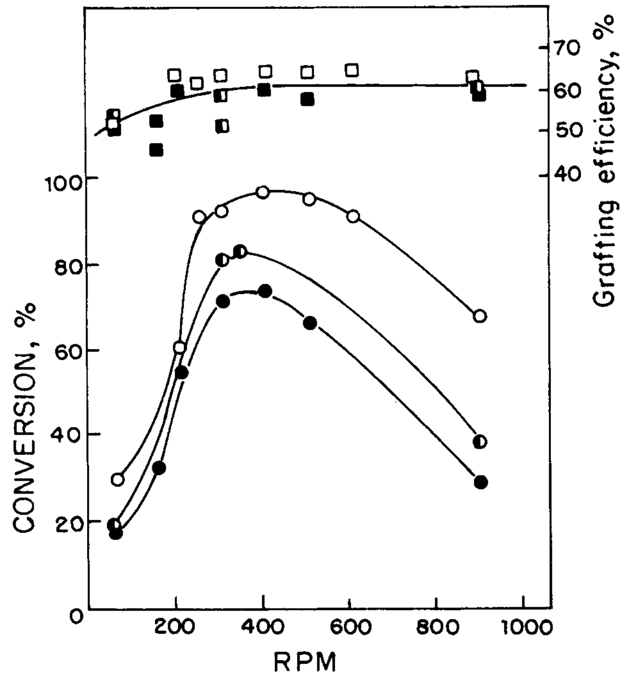


Fig. 7. Conversion of styrene to polymer and grafting efficiency as a function of stirring speed for different soaking periods: nitrogen 99.9%; H_2SO_4 and H_2O_2 added at the same time (Method 2A): soaking period: (○,□) 15 min; (◐, ◧) 30 min; (●,■) 60 min; (○, ◐,●) polymer; (□, ◧,■) grafting efficiency.

conversion curves for all three soaking periods remain the same. In comparison with a 15 min soaking period, conversion during a 1-h soaking period drops from 97% to 72%. However, reproducibility of experiments is very good if they are started after the same soaking period. Furthermore, grafting efficiency is independent of the oxygen removal period.

In the second set of experiments (Fig. 8), oxygen-free argon, Method 1 of addition reagents, and a 1-h oxygen-removal period were applied. In the middle range of the stirring rate (200–400 rpm), there are no differences in conversion between both gases. However, under oxygen-free argon conversion becomes independent of agitation speed up to 1300 rpm. An interesting phenomenon is observed when H_2SO_4 and H_2O_2 are added through an opening in the reactor. The conversion rises with an increase in the stirring speed, and a small maximum (conversion 90%) at 900 rpm is created followed by a slow fall in conversion. This is similar to the reaction with commercial nitrogen.

The same reactivity of xanthated cellulose after 1 h of soaking in the two sets of experiments means that changes in the reactivity of xanthated cellulose are not caused by traces of oxygen in the reaction mixture. Cornell[19] found that substitution of cellulose by xanthate groups during emulsion xanthation is not uniform. Probably during the soaking period, redistribution of xanthated groups occurs along the cellulose chain, with the most reactive group disappearing.

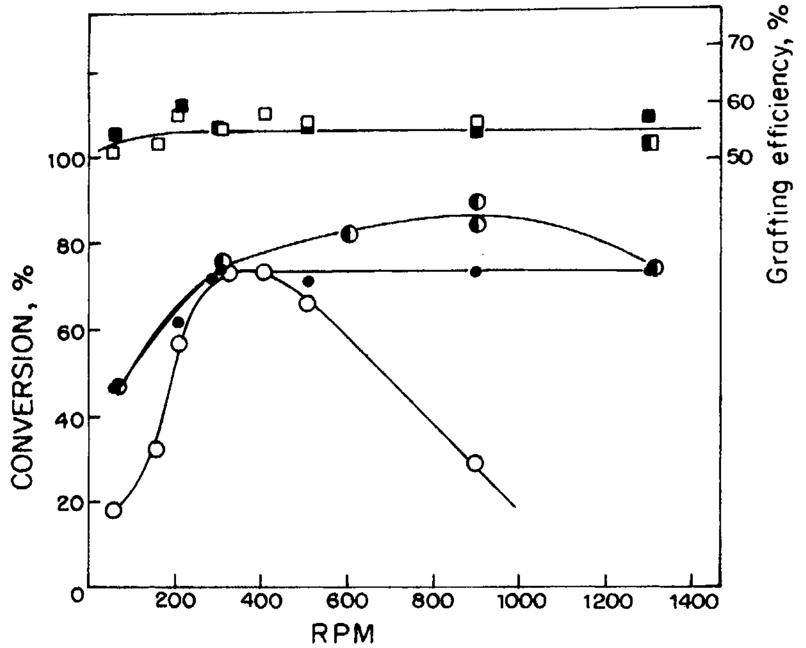


Fig. 8. Conversion of styrene to polymer and grafting efficiency for different purity of gases: H_2SO_4 and H_2O_2 added at the same time: (○, □) purification period = 60 min; nitrogen 99.9%, Method 2A; (●, ■) oxygen-free argon, Method 1; (◐, ◧) oxygen-free argon, Method 2A; (○, ●, ◐) polymer; (□, ■, ◧) grafting efficiency.

The nondependence for conversion on stirring rate at higher agitation speeds, as seen in Figure 8, is only apparent in the case of styrene. Figure 9 shows that it can also happen in the presence of commercial nitrogen (99.9%) and a 15-min soaking period when high concentration of reagents and a long reaction time are applied. For the sake of simplicity, data for conversion at a low rate of agitation speed in Figure 9 have been omitted. Any decrease in concentration of reagents and reaction time brings about a different pattern. For example, in the presence of nitrogen (99.9%) and with a 60-min soaking period, conversion increases steadily as stirring speed increases. Much lower conversion is observed during a 1-h soaking period in the presence of oxygen-free argon. Conversion reaches only 25–30% and slightly rises with an increase in stirring speed. After 2 h of oxygen removal, conversion is only 5% and becomes independent of the stirring rate. It is probable that, at longer oxygen removal periods, the reaction of grafting styrene will not occur at all. Hasan[20] recently found that the rate of emulsion polymerization of styrene is nearly zero when all reagents do not have any traces of peroxides and when oxygen has been carefully removed from the system (e.g., during 24 h of purging with oxygen-free argon). The results thus presented confirm that traces of oxygen are needed to initiate polymerization of styrene.

In the case of grafting BMA (Fig. 10), 2 h of oxygen removal are needed before conversion becomes independent of stirring speed. Once again, higher conversion is observed during a 15-min soaking period (traces of oxygen) than during 1 h (oxygen-free argon), although differences are lower than in the case

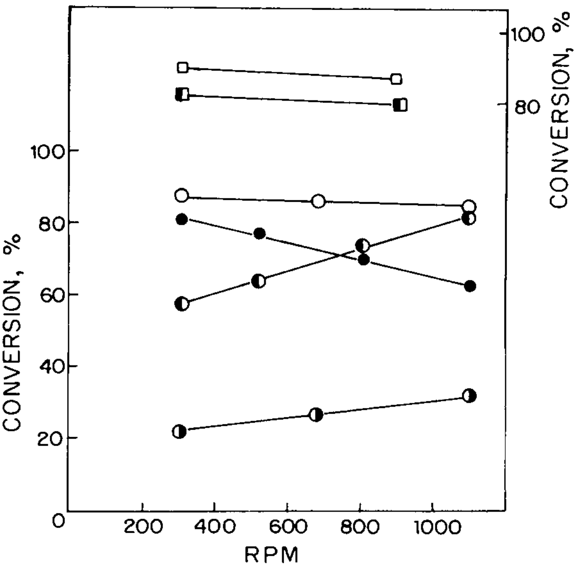


Fig. 9. Conversion of styrene to polymer as a function of stirring speed for different reaction conditions: (□, ◧) [H_2O_2] = 0.049 mol/L; time = 1 h; (○, ●, ◐, ◑) [H_2O_2] = 0.024 mol/L; time = 45 min; (●) soaking period 15 min, nitrogen 99.99%, Method 2B; (○, □) soaking period 15 min, nitrogen 99.99%, Method 2A; (◐, ◧) soaking period 60 min, nitrogen 99.99%, Method 2A; (◑) soaking period 60 min, oxygen-free argon, Method 1.

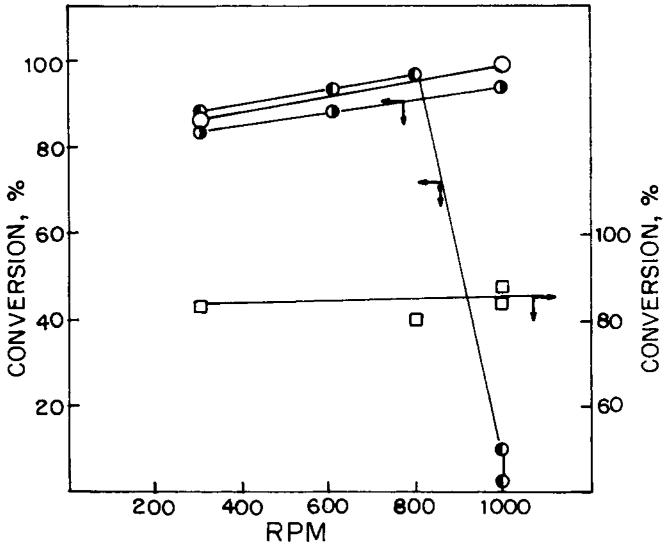


Fig. 10. Conversion of butyl methacrylate to polymer as a function of stirring speed for different oxygen removal periods: time = 15 min; [H_2O_2] = 0.0061 mol/L; (○) 15 min period, nitrogen 99.99%, Method 2A; (◐) 60 min period, nitrogen 99.99%, Method 2A; (◑) 60 min period, oxygen-free nitrogen, Method 1; (□) 120 min period, oxygen-free nitrogen, Method 1.

TABLE II
Influence of Agitator Speed in Soaking Period on Conversion to Polymer at a Low Range of Stirring Speed[a]

	Soaking period		Reaction		
No.	Time (min)	rpm	Time (min)	rpm	Conversion (%)
1	0–15	60	60	60	29.9
2	0–14	310	60	60	39.8
	14–15	60			
3	0–14	310	60	60	38.3
	14–15	60			
4	0–15	310	0–1	310	63.8
			1–60	60	

[a] Nitrogen 99.9%; flow rate = 15 L/h; temperature = 25°C; [cellulose] = 10 g/L; [styrene] = 0.133 mol/L; $[H_2O_2]$ = 0.049 mol/L; H_2SO_4 and H_2O_2 were added at the same time.

of styrene. Furthermore, experiments with a 1-h soaking period in the presence of 99.9% nitrogen show clearly that, with a higher stirring rate, small traces of oxygen can dramatically change the degree of conversion, causing it to drop to nearly zero in some cases.

Influence of Reaction Conditions on Conversion at Low Agitation Speed

Conversion of soluble monomers to polymers is only slightly dependent on agitation even at low stirring speeds, while for insoluble monomers a stirring rate of at least 300–400 rpm is required to obtain a high degree of conversion. For the latter, diffusion of monomers to active centers located onto cellulose is the rate determining process, which becomes negligible in the higher stirring speed (e.g., 300 rpm). Stirring speed influences not only the rate of monomer penetration into cellulose fiber but also the size of monomer droplets. With an increase in the stirring rate, the size of monomer droplets decreases. It is well known that the diffusion of monomer is faster from smaller particles than from bigger ones.[21]

Table II shows how changes in stirring speed in the low range during the soaking period influence conversion. Only when the reaction was carried out for the first minute at 310 rpm and later shifted to 60 rpm was a moderate conversion obtained (64%), still 30% lower than at the maximum. In two other cases, low conversion was also obtained. For example, when the stirring speed was shifted from 310 to 60 rpm 1 min before the reaction was started, the conversion was only 38% (35% lower than in the former case).

These experiments clearly show that low conversion at low agitation speed is caused by the low diffusion rate of monomer from big monomer droplets to the water phase rather than by the diffusion of monomer from the water phase into cellulose fibers.

Influence of Reaction Time on the Shape of Conversion vs. Stirring Speed Curve

As was demonstrated in the previous section, the dependence of styrene conversion on stirring speed at a high degree of conversion is not always

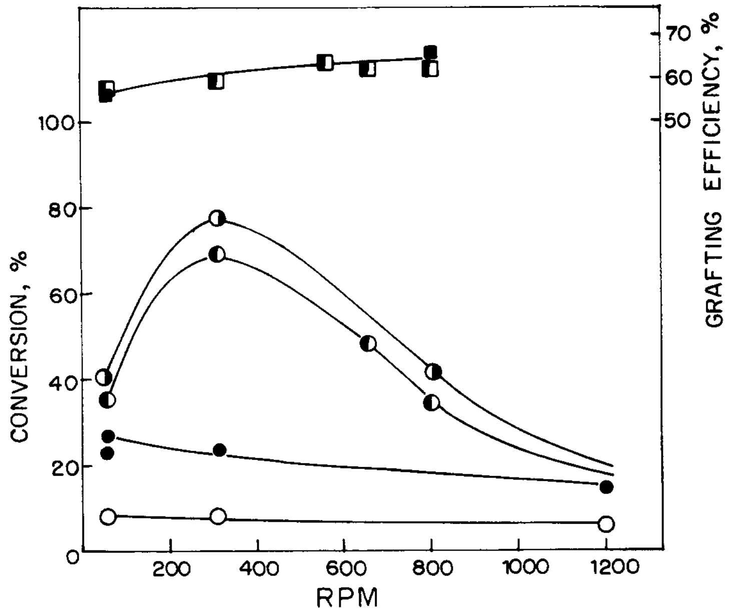


Fig. 11. Conversion of styrene to polymer and grafting efficiency as a function of stirring speed for different reaction times: nitrogen 99.9%, Method 2A; $[H_2O_2]$ = 0.024 mol/L; time: (○) 0.5 h; (●, ■) 1 h; (◐, ◧) 2 h; (◑) 3 h; (○, ●, ◐, ◑) polymer; (■, ◧) grafting efficiency.

evident. Thus, it is interesting to study how conversion is dependent on agitation at different reaction times. To allow for comparison, commercial nitrogen (99.9%) and Method 2A addition of reagents were used.

Figure 11 shows that, at the beginning of the reaction (0.5–1 h reaction period), conversion is only slightly dependent on stirring speed. Conversion is highest at a low range of agitation speed and no maximum is observed. By extending the reaction time to 2 h, conversion becomes strongly dependent on agitation speed, and a well-defined maximum is created. Longer reaction times do not generally change the shape of the curve, only increase its width.

The stage of grafting when the effect of agitation on conversion is not observed (till 20–30% conversion) can be compared with the first stage of emulsion polymerization, where nucleation occurs.[21] In the case of grafting onto cellulose, active centers on the cellulose backbone are created. In the second stage of emulsion polymerization, the number of loci stabilize, and the rate of emulsion polymerization is dependent on the transport of monomer from monomer droplets to the loci. The stage of grafting in which the effect of stirring on conversion is observed (above 20–30%) can be compared to the second stage of emulsion polymerization.

Dependence of pH of the Reaction Mixture on Reaction Conditions

During grafting onto xanthated cellulose, the pH of the reaction mixture is not stable but changes with reaction time.[3] For example, when the reaction is started at pH 5, the pH increases immediately to 6–6.5, and then falls gradually to 3.5–2.5. The maximum pH, the shape of the curve, and the final pH level are all a function of the cellulose gamma number and the concentra-

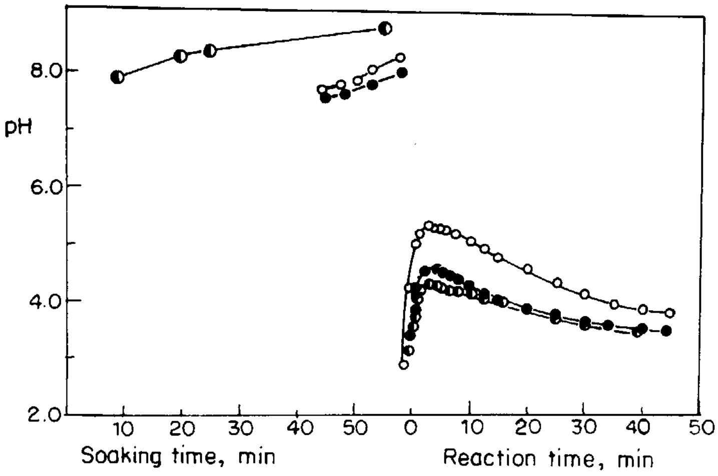


Fig. 12. The pH changes during the reaction of styrene grafting; nitrogen 99.99%, rpm = 1100; (○) 15 min swelling period, Method 2B; (●) 15 min swelling period, Method 2A; (◐) 60 min swelling period, Method 2A.

tion of hydrogen peroxide. With an increase in gamma number the final pH level decreases while the rate of change in pH rises with increasing initial H_2O_2 concentration.

For the present paper, the influence on the pH curve of changes in concentration of oxygen in the reaction mixture (different oxygen removal period) and method of reagent addition were studied. Two sets of experiments were carried out at 1100 and 310 rpm (Figs. 12 and 13, respectively). At 1100 rpm the highest peak is followed by a faster drop of pH when H_2SO_4 is added 1 min earlier than H_2O_2 (Method 2B). The difference between a 15- and a

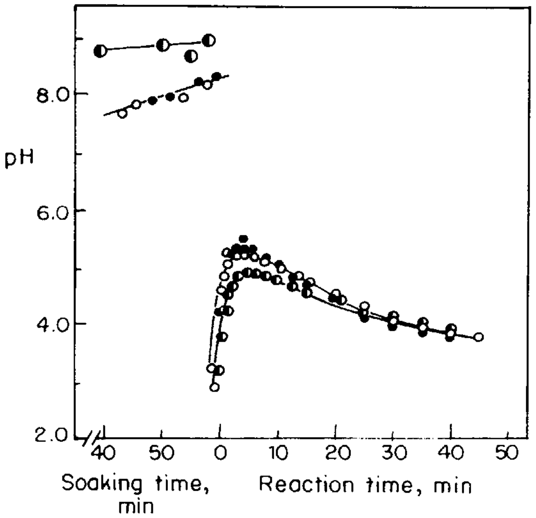


Fig. 13. The pH changes during the reaction of styrene grafting; nitrogen 99.99%, rpm = 310; (○) 15 min swelling period, Method 2B; (●) 15 min swelling period, Method 2A; (◐) 60 min swelling period, Method 2A.

60-min oxygen removal period is minimal. At 310 rpm the shape of the pH curves is influenced much less by the method by which the reaction is initiated.

At both stirring speeds the smallest differences between the initial and final pH's are observed when oxygen is nearly completely removed during a 1-h soaking period (nitrogen 99.99%). When H_2SO_4 is added earlier than H_2O_2 at the higher stirring speed (1100 rpm), hydrolysis and, subsequently, oxidation of xanthated groups by oxygen occurs faster than at 310 rpm. Some intermediate compounds are probably created during oxidation by oxygen and their presence increases the pH peak. However, the final pH level is independent of reaction conditions.

Cellulose Xanthate-Oxidizing Agent

Xanthated cellulose forms many redox systems, among which xanthate cellulose-Fe^{+2}-H_2O_2 ($K_2S_2O_8$) redox system is the most well known. This system has been described in the author's previous papers.[6-9] The set of experiments was carried out with several xanthate-oxidizing agent redox systems to elucidate the role of xanthated cellulose in complicated kinetic data for the xanthated method and indirectly the role of ferrous ion. For the sake of comparison with previous papers, nitrogen 99.9% and Method 2B reagents addition were used.

Figures 14 and 15 show results for grafting styrene by the cellulose xanthate-H_2O_2 and cellulose xanthate-$K_2S_2O_8$ redox systems, respectively.

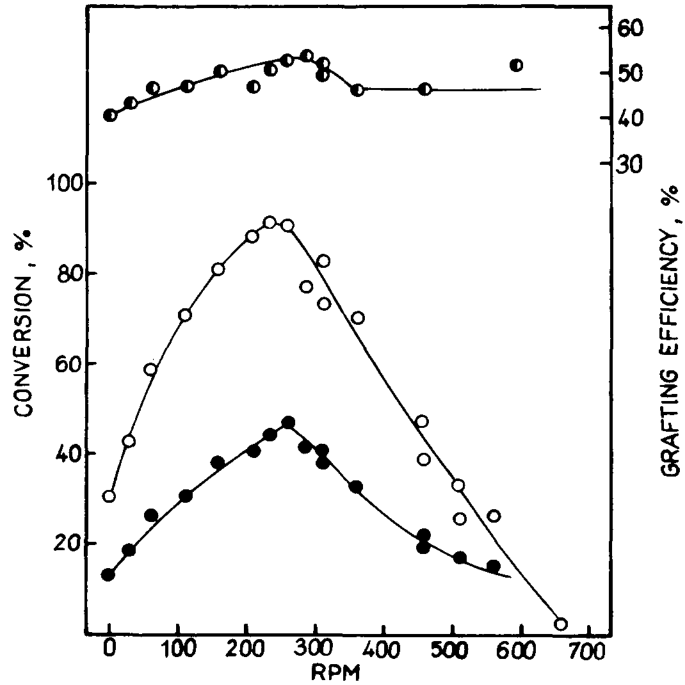


Fig. 14. Conversion of styrene as a function of stirring speed for the cellulose xanthate-H_2O_2 redox system at 65°C: (○) polymer; (●) copolymer; (◐) grafting efficiency.

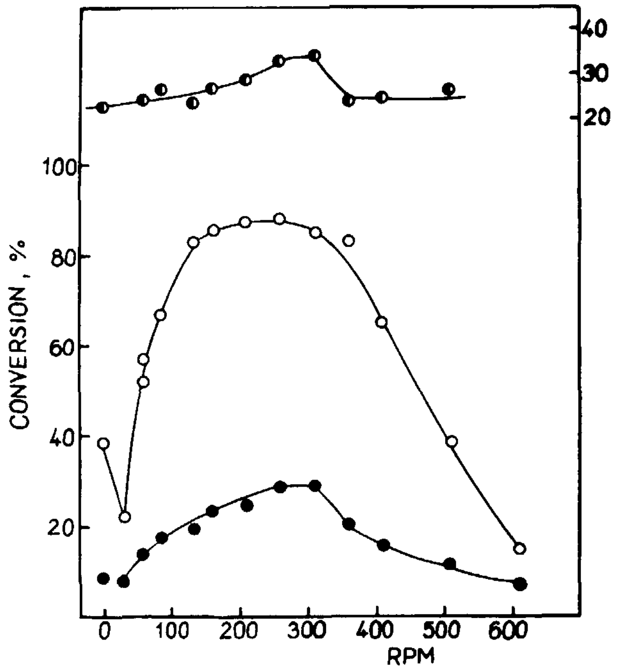


Fig. 15. Conversion of styrene as a function of stirring speed for the cellulose xanthate–$K_2S_2O_8$ redox system at 65°C; (○) polymer; (●) copolymer; (◐) grafting efficiency.

The temperature of the reaction had to be increased from 25 to 65°C to have significant conversion during 1 h. Both curves have broad maxima located at 260 rpm followed by a drop of conversion to zero. It is worth mentioning that in graft copolymerization initiated by the xanthate–Fe^{+2}–H_2O_2 and the xanthate–Fe^{+2}–$K_2S_2O_8$ redox systems the maxima were located at different stirring speeds (310 and 410 rpm, respectively). The drop in conversion on both curves is slow in comparison to the xanthate–Fe^{+2}–H_2O_2 ($K_2S_2O_8$) redox systems.

Grafting efficiency is moderately dependent on the stirring speed. Grafting efficiency increases from 40% at 60–110 rpm to 50–53% at the maximum for the xanthate–H_2O_2 redox system, while for the xanthate–$K_2S_2O_8$ redox system grafting efficiency is lower and changes from 22% at a low range of stirring to 35% at the maximum. Grafting efficiency for copolymerization of styrene by the xanthate–Fe^{+2}–H_2O_2 ($K_2S_2O_8$) redox system is independent of the type of oxidizing agent and is at a level of 50–58% at a low range of stirring speed and 65–68% at the maximum of conversion. Lower grafting efficiency in the presence of $K_2S_2O_8$ as an oxidizing agent (in comparison with H_2O_2) was caused by thermal decomposition of potassium persulfate at elevated temperatures, which led to homopolymerization.

Removing ferrous ion from the redox system decreases the rate and efficiency of grafting considerably. In the case of the xanthate–$K_2S_2O_8$ redox system, grafting efficiency drops nearly twofold.

Figure 16 shows conversion as a function of time for copolymerization of styrene initiated by the xanthate–H_2O_2 redox system. There is a 10-min induction period on the curve. The same shape of conversion curve is observed

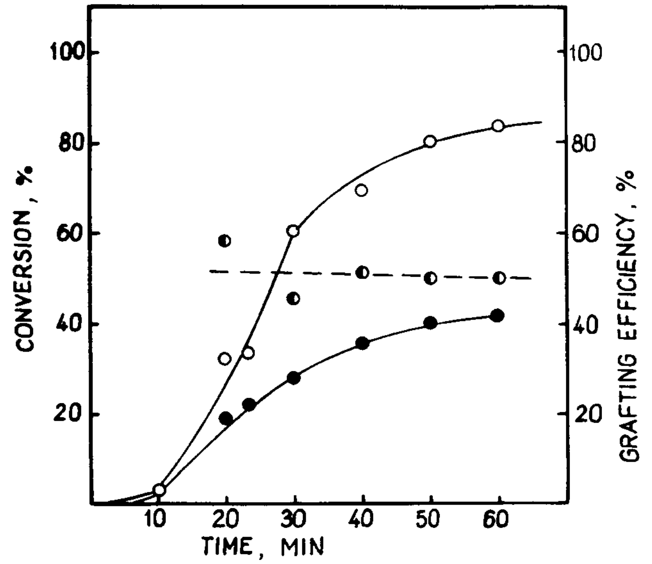


Fig. 16. Conversion of styrene as a function of time for the cellulose xanthate-H_2O_2 redox system at 65°C and 310 rpm; (○) polymer; (●) copolymer; (◐) grafting efficiency.

for the reaction initiated by the xanthate-$K_2S_2O_8$ redox system. However, the slow reaction period lasts 30 min.

As was presented in the experiments above, cellulose xanthate was the reducing agent while H_2O_2 or $K_2S_2O_8$ were the oxidizing agent. Rogovin et al.[22-24] have reported successful application of metals of changed valency for grafting onto cellulose, using the cellulose xanthate-M^{+n} redox system, where $M^{+n} = Fe^{+3}, V^{+5}, Cr^{+6}$ as an initiator. Xanthate groups of cellulose form with Fe^{+3} or V^{+5} high reduction potential, which prevents the formation of homopolymers.

It is pertinent to find out if the effect of agitation is observed when H_2O_2 or $K_2S_2O_8$ is replaced by metal salts. Metals are absorbed onto cellulose in close proximity to xanthate groups. Thus, the effect of stirring in the presence of metal salts may be different than when water-soluble oxidizing agents ($H_2O_2, K_2S_2O_8$) are used.

The concentration of cellulose and styrene was maintained at the same level as in the previous experiments described in this paper to allow comparison. The data obtained for the xanthate-Fe^{+3} redox system are shown in Figure 17. Conversion of styrene is low in these conditions. It is seen that conversion decreases steadily from 30% at 30 rpm to 10% at 400 rpm with declining trend at the highest stirring speeds. In the absence of agitation conversion to polymer is considerably lower than at 30 rpm. This means that a very low rate of mixing is needed to contact xanthate groups and absorbed metal to start copolymerization. Grafting efficiency is the highest at 0 rpm (65%) and decreases steadily to 45% at the highest stirring rate.

Conversion of styrene to polymer as a function of time is plotted in Figure 18. The induction period was not observed as it was in the case with the xanthate-H_2O_2-($K_2S_2O_8$) redox system.

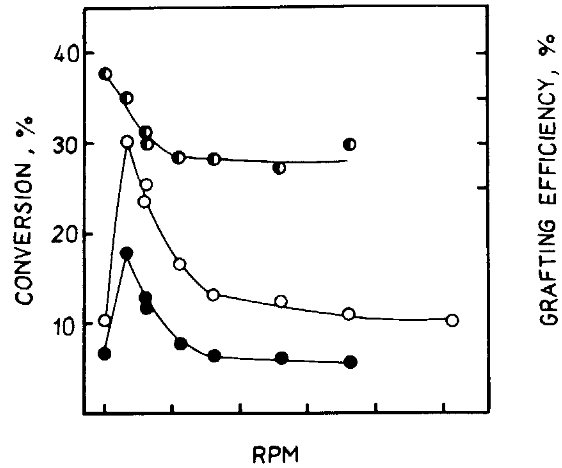


Fig. 17. Conversion of styrene as a function of stirring speed for the cellulose xanthate—Fe^{+3} redox system at 45°C; $[Fe_2(SO_4)_3\text{-}7H_2O] = 0.01$ mol/L; (○) polymer; (●) copolymer; (◐) grafting efficiency.

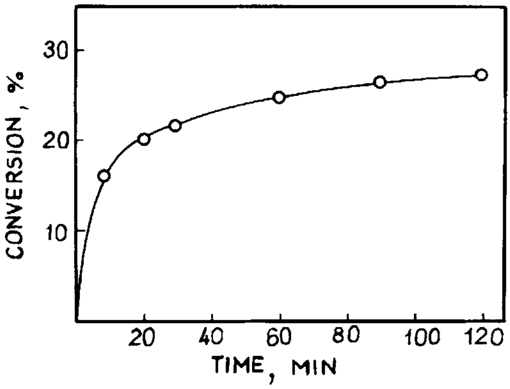


Fig. 18. Conversion of styrene to polymer as a function of time for the cellulose xanthate–Fe^{+3} redox system at 45°C and 60 rpm; $[Fe_2(SO_4)_3\text{-}7H_2O] = 0.01$ mol/L.

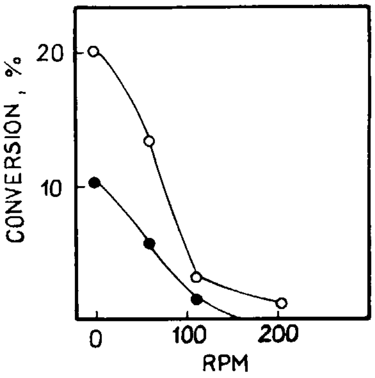


Fig. 19. Conversion of styrene to polymer and copolymer as a function of stirring speed for the cellulose xanthate–V^{+5} redox system at 45°C; $[NH_4VO_3] = 0.01$ mol/L; (○) polymer; (●) copolymer.

Vanadium salt is often used as an initiator of grafting onto cellulose. The conversion of styrene in graft copolymerization initiated by the cellulose xanthate V^{+5} redox system is displayed in Figure 19. The conversion is low, but it is possible to observe that both total polymer and copolymer decrease with increasing stirring rate and at 250 rpm conversion is nil.

Combined Effect of Stirring and Oxygen on Conversion

For all redox systems in which partly xanthated cellulose was used, the combined effect of stirring and oxygen on conversion was observed. On the conversion vs. stirring speed curve, it is possible to distinguish three stages (Fig. 20). In the first stage, the diffusion of monomer into cellulose fibers controls the conversion rate. With an increase in stirring speed, the size of monomer droplets decreases and the observed increase in conversion is caused by a higher diffusion rate of monomer from smaller droplets than from bigger ones. In the case of cellulose concentration of 1% and monomer concentration of 0.13 mol/L, above 300–350 rpm the effect of diffusion can be ignored.

In the second stage, a slight increase in conversion along with an increase in agitation is observed. The slope of the curve and the range of stirring speed are dependent upon the oxygen concentration in the reaction medium and in the purged gas. As stirring speed increases, more oxygen is dissolved in the reaction medium from the purged gas and penetrates to active centers.

Further, an increase in stirring speed leads to one of three variants in the third stage. In variant A, the concentration of oxygen in the reaction medium is so low that a higher dissolving rate of oxygen or a higher penetration to active centers causes a still higher degree of conversion. In variant B, the termination effect of oxygen prevails, and conversion falls with an increase in

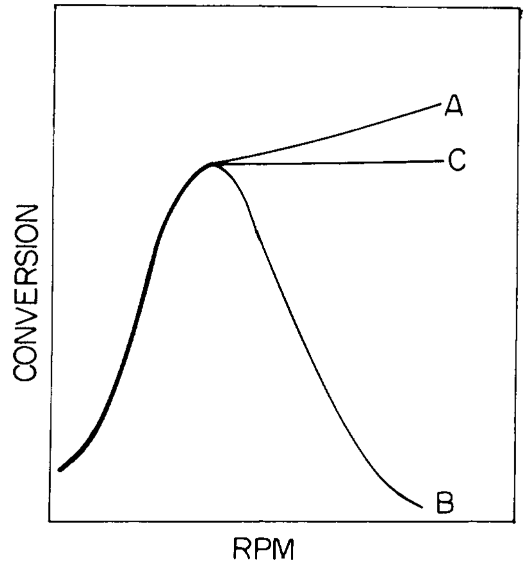


Fig. 20. Hypothetic curve conversion as a function of stirring speed for different reaction conditions.

stirring speed. In variant C, the termination effect of oxygen compensates for the accelerating effect of oxygen on conversion, and the reaction becomes independent of agitation speed.

In the case of oxygen-free argon, stage 3 can follow directly from stage 1, and the reaction becomes independent of the stirring speed. However, for xanthated cellulose a lower degree of conversion is observed in this case than in the reaction with a controlled amount of oxygen.

The positive effect of a controlled amount of oxygen on the rate of grafting, combined with a decrease in the reactivity of pulp with an increasing swelling period, leads to the conclusion that there is no reason to completely remove oxygen from the system. Furthermore, reproducibility of results is very good if the level of oxygen is kept constant. However, one has to take into account that experimental data will be strongly dependent on reaction conditions in every case. Comparative results will be doubtful unless all parameters of the reaction are known.

Reactivity of Monomers in Homologous Series

In the presence of a controlled amount of oxygen, when other reaction conditions are unchanged (e.g., how an initiator and sulfuric acid are added), the location of the maximum on the conversion vs. stirring speed curve for hydrophobic monomers is independent of the concentration level of hydrogen peroxide, though the shape of the curve is strongly dependent, especially at a higher stirring speed.

In the case of methyl acrylate, which is soluble in the reaction mixture, a completely different pattern is observed. Figure 21 shows how the conversion of MA and the maximum are dependent on agitation speed for three different concentrations of H_2O_2. At the highest H_2O_2 concentration studied (0.049

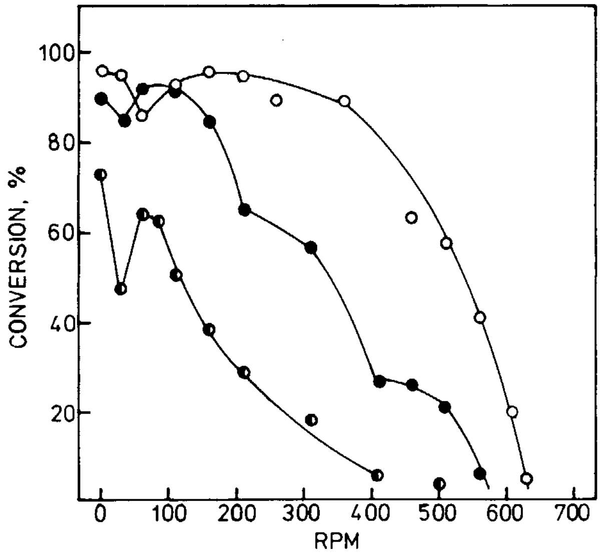


Fig. 21. Conversion of methyl acrylate to polymer as a function of agitation speed: nitrogen 99.9%; time = 30 min; (○) $[H_2O_2]$ = 0.049 mol/L; (●) $[H_2O_2]$ = 0.0244 mol/L; (◐) $[H_2O_2]$ = 0.0122 mol/L.

mol/L), the maximum is located at 160 rpm, while, at the lowest H_2O_2 concentration (0.012 mol/L), the highest conversion is observed in the reaction in which there has been no mixing.

For insoluble monomers, the effect of the diffusion of monomers into cellulose fibers is so strongly dependent on agitation that any changes in the concentration of H_2O_2 have no influence on the location of the maximum. Methyl acrylate is completely soluble under experimental conditions, and, when the effect of monomer diffusion into cellulose fibers becomes unimportant, the relative rate of oxygen concentration to H_2O_2 concentration starts to play an important role in the location of the maximum.

At a higher level of H_2O_2 concentration (0.049 mol/L) the reaction is fast, and the diffusion of monomer still has some influence, so that the maximum is located at 160 rpm. At a low concentration of H_2O_2 (0.012 mol/L) and a lower rate of reaction, the termination effect of oxygen prevails, with increasing agitation speed, and the highest conversion is observed in the reaction without agitation.

Graczyk and Hornof[8] found that for the homologous series of acrylates and methacrylate esters the optimum stirring speeds increases with an increase in the size of the alkyl group (Fig. 22). The reactivity of monomers was presented in the optimum stirring speeds, but in case of MA an incorrect stirring speed was recorded (160 rpm). Table III shows the reactivity of monomers with corrected data for MA. The conversion to polymer for methyl and ethyl esters, which are partly soluble in water is nearly the same at optimum agitation speed. Lower conversion for butyl esters may be due to the longer induction periods observed with hydrophobic monomers.

Once again, Figure 22 and Table III clearly show how important a suitable stirring speed is to the reaction of grafting onto cellulose xanthate. The maximum on the conversion vs. stirring speed curve is the place where the

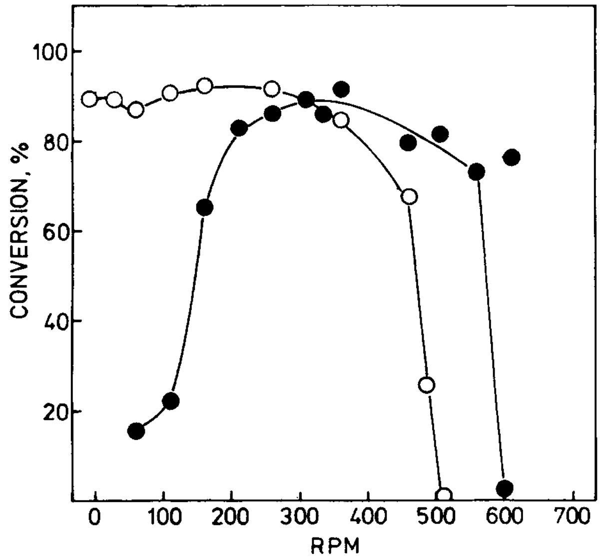


Fig. 22. Conversion of methyl acrylate and buthyl acrylate as a function of agitation speed; nitrogen 99.9%, flow rate 12 L/h; $[H_2O_2] = 0.049$ mol/L; (○) MA, time = 30 min; (●) BA, time = 1 h.

TABLE III
Reactivity of Acrylic and Methacrylic Esters in Cellulose Grafting by the Xanthate Method[a]

Monomer	Agitator speed[b] (rpm)	Conversion to polymer (%)
Methyl acrylate	0	72.0
Ethyl acrylate	210	82.0
Buthyl acrylate	310	24.3
Methyl methacrylate	160	81.8
Ethyl methacrylate	210	85.8
Buthyl methacrylate	350	9.8

[a] Reaction conditions: temperature = 25°C; time = 15 min; [monomer] = 0.133 mol/L; [H_2O_2] = 0.0122 mol/L.
[b] Estimated optimum agitator speed.

effect of conversion increases with increasing stirring speed, due to the higher diffusion rate of monomer and oxygen to active centers is compensated by the decrease in conversion caused by the higher rate of termination by oxygen at the higher stirring speed.

Influence of Additives

Garnett et al.[14,15] reported that graft copolymerization of styrene occurred much faster in a 30% solution of methanol than in water. Other alcohols in the homologous series also accelerate the rate of grafting initiated by radiation. It was interesting to investigate the influence of alcohols, especially methanol, on the rate of grafting and the shape of the conversion vs. stirring speed curve. For the sake of comparison with previous papers by the author, experiments were limited to the use of styrene as the monomer, the cellulose xanthate–Fe^{+2}–H_2O_2 ($K_2S_2O_8$) redox system, and nitrogen, 99.9% purity.

Figure 23 shows how conversion to polymer changes with the addition of 8 mL methanol, as compared to a standard reaction. The effect of methanol is significant only at a lower range of stirring speed. For example, at 60 rpm, conversion rises from 20 to 61% in the presence of methanol. Although the location of the maximum for the reaction with methanol shifts slightly to 360 rpm from 310 rpm, the degree of conversion at the maximum and the shape of the curve in the region of declining conversion are nearly the same. Furthermore, grafting efficiency is not affected by the addition of methanol.

In the experiments described above, methanol was added at a 10 min swelling period. The effect of the solvent was not observed when methanol was added together with styrene at the beginning of the swelling period or directly before starting the reaction by an addition of H_2O_2.

Figure 24 shows the effect of the addition of methanol on conversion at 60 rpm for two initiation systems, xanthated cellulose–Fe^{+2}–H_2O_2, and xanthated cellulose–Fe^{+2}–$K_2S_2O_8$. The conversion rises from 16–20% in the reaction without methanol to about 60% for the reaction with H_2O_2 and only to 40% for the redox system with $K_2S_2O_8$ in the presence of 6–7 mL methanol. From this point conversion becomes independent of the amount of methanol in both cases. This amount of methanol is nearly equal to the amount of

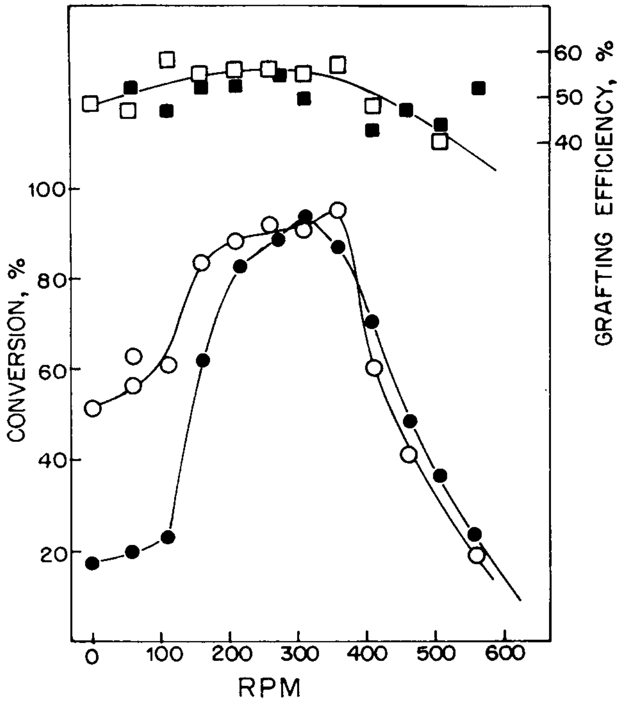


Fig. 23. Conversion of styrene to polymer and grafting efficiency as a function of stirring speed for reaction with and without methanol as an additive; nitrogen 99.9%; (○, □) with 8 mL methanol; (●, ■) without methanol; (○, ●) polymer; (□, ■) grafting efficiency.

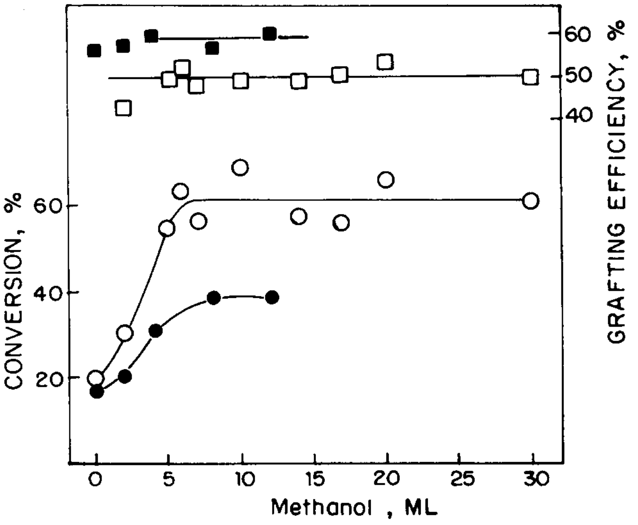


Fig. 24. Conversion of styrene to polymer and grafting efficiency as a function of amount of added methanol at 60 rpm; (○, □) H_2O_2; (●, ■) $K_2S_2O_8$; (○, ●) polymer; (□, ■) grafting efficiency.

TABLE IV

Grafting of Styrene in the Presence of Alcohols at 60 rpm[a]

No.	Alcohol	Conversion to polymer (%)	Grafting efficiency (%)
1	Methanol	61.3	49.6
2	Ethanol	48.2	45.6
3	*i*-Propanol	51.5	44.0
4	*n*-Butanol	60.4	49.8
5	*n*-Octanol	33.1	40.3
6	*i*-Propanol	33.3	41.1
7	Benzylalkohol	37.4	41.6
8	No alcohol	19.8	

[a] Reaction conditions: temperature = 25°C; time = 1 h; [cellulose] = 10 g/L; [styrene] = 0.133 mol/L; [H_2O_2] = 0.049 mol/L; amount of added alcohol = 8 mL.

styrene used in the reaction (6.9 mL). Grafting efficiency is not affected by the addition of methanol.

Table IV presents data for graft copolymerization of styrene initiated by the xanthate–Fe^{+2}–H_2O_2 redox system in the presence of (8 mL) several different alcohols. All alcohols tested increase the conversion of styrene. The influence is the greatest for *n*-butanol and *n*-propanol while *n*-octanol and *i*-propanol have the least influence. Grafting efficiency is not influenced by the type of alcohol used and is about the 45% level.

Conversion of styrene to polymer in the presence of a number of solvents during a 1 h reaction period is shown in Table V. Hydrophilic solvents increase the conversion of styrene to a higher degree than the hydrophobic. Dioxane, acetone, and ethyl acetate increase the conversion to the same level as methanol (48–64%). Chloroalkanes (CCl_4, chloroform) only slightly accelerate the rate of grafting. On the other hand, nitromethane and triethanola-

TABLE V

Grafting of Styrene in the Presence of Solvents at 60 rpm[a]

No.	Solvent	Conversion to polymer (%)	Grafting efficiency (%)
1	Dioxane	63.4	61.1
2	Acetone	52.0	51.6
3	Ethyl acetate	48.1	53.2
4	Dimethylformamide	50.7	50.4
5	Formamide	35.6	46.9
6	Carbon tetrachloride	36.4	36.0
7	Chloroform	26.0	45.7
8	Tetrachloroethylene	24.0	
9	Toluene	26.0	
10	Nitromethane	4.3	
11	Triethanolamine	2.0	

[a] Reaction conditions: temperature = 25°C; time = 1 h; [cellulose] = 10 g/L; [styrene] = 0.133 mol/L; [H_2O_2] = 0.049 mol/L; amount of added solvent = 8 mL.

mine retard graft copolymerization nearly completely. Both are known as inhibitors of radical polymerization.

Hydrophilic solvents such as alcohols, esters, and ethers are able to create intermolecular hydrogen bonds with cellulose. Thus, the number of intramolecular cellulose hydrogen bonds decreases or they are weaker and penetration of monomer into cellulose fibers is much easier. When solvent is added just before the reaction, intramolecular hydrogen bonds are not affected, and the rate of grafting is not changed.

Vojnova et al.[16] investigated the influence of reducing agents on the graft copolymerization initiated by the Fe^{+2}–H_2O_2 redox system. They found that conversion of 2-methyl-5-vinylpiridine (MVP) and MMA decreases steadily with an increase in hydroquinone concentration. The maximum conversion was observed for acrylamide and acrylonitrile. It was particularly broad in the case of the latter. El-Rafie et al.[25] recently studied the influence of hydrazine hydrate, sodium sulfite, sodium hydrosulfite, thiourea dioxide, and sodium sulfite on the reaction initiated by the xanthated method. Among all these additives only hydrazine hydrate increased conversion (only 10% at hydrazine concentration 8×10^{-3} mol/L).

Figure 25 shows the influence of an addition of hydroquinone on the conversion of styrene initiated by the xanthate–Fe^{+2}–H_2O_2 redox system at 60 rpm. Graft copolymerization of styrene in the presence of hydroquinone is faster than the standard reaction if the concentration of hydroquinone does not exceed 2.0 mmol/L. Above this concentration a slow fall in conversion is observed. In the range of 0.5–1 mmol/L hydroquinone concentration, the maximum is created and conversion is twice that achieved by reaction without hydroquinone. Grafting efficiency is only minimally affected by the addition of hydroquinone.

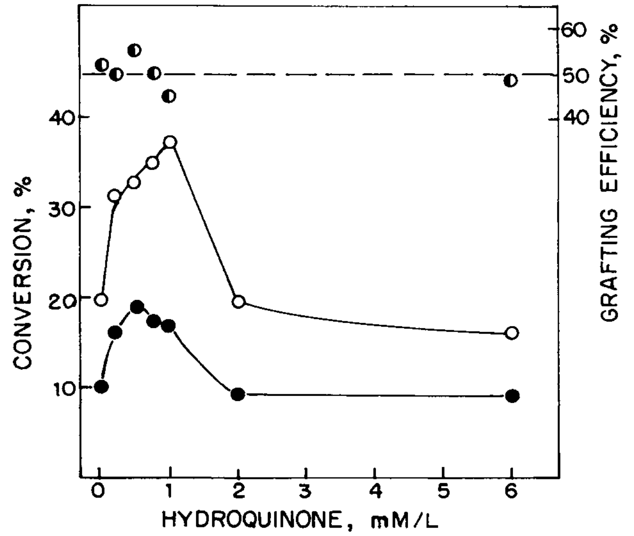


Fig. 25. Conversion of styrene as a function of added hydroquinone at 60 rpm; (○) polymer; (●) copolymer; (◐) grafting efficiency.

As was previously indicated, conversion in a low rate of stirring is only slightly influenced by the purity of the gases used. Thus, nearly the same correlation should be obtained in the presence of oxygen-free argon as for commercial nitrogen 99.9% purity.

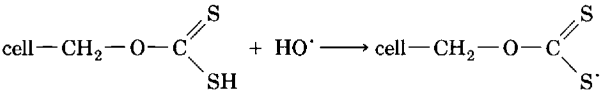
As observed, the increase in conversion caused by the addition of a solvent can be compared to the effect of stirring on conversion. In the case of styrene, methanol increases conversion to 61% at 60 rpm. The same level of conversion is obtained when the reaction is started at a higher stirring speed and after 1 min is shifted to 60 rpm.

The addition of a solvent or application of agitation are two equivalent methods leading to an increase in conversion. Stirring speed, by decreasing the size of monomer droplets, increases the diffusion of monomer to the water phase while solvents decrease intramolecular cellulose hydrogen bonds and in this way ease penetration of monomer to cellulose fibers. An increase of monomer solubility in the water/methanol phase may also play some role.

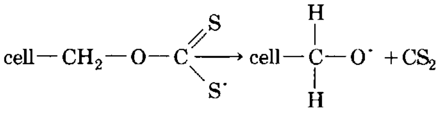
The Mechanism of Grafting by the Xanthate Method

The mechanism of grafting by the xanthated cellulose–Fe^{+2}–H_2O_2 redox system is shown in eqs. (1)–(10):

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + HO^- + HO^{\cdot} \qquad (1)$$

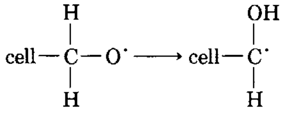


$$\text{cell}-CH_2-O-C\begin{array}{l}{}^{\diagup}S\\ {}_{\diagdown}SH\end{array} + HO^{\cdot} \longrightarrow \text{cell}-CH_2-O-C\begin{array}{l}{}^{\diagup}S\\ {}_{\diagdown}S^{\cdot}\end{array} \qquad (2)$$

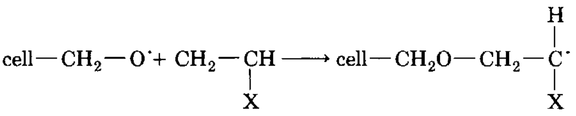


$$\text{cell}-CH_2-O-C\begin{array}{l}{}^{\diagup}S\\ {}_{\diagdown}S^{\cdot}\end{array} \longrightarrow \text{cell}-\underset{H}{\overset{H}{C}}-O^{\cdot} + CS_2 \qquad (3)$$

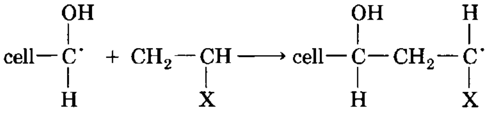
$$\text{cell}-CH_2-OH + HO^{\cdot} \longrightarrow \text{cell}-CH_2-O^{\cdot} + H_2O \qquad (4)$$



$$\text{cell}-\underset{H}{\overset{H}{C}}-O^{\cdot} \longrightarrow \text{cell}-\underset{H}{\overset{OH}{C^{\cdot}}} \qquad (5)$$

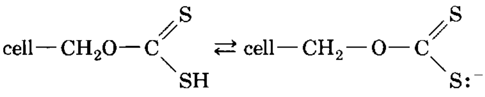


$$\text{cell}-CH_2-O^{\cdot} + CH_2-\underset{X}{CH} \longrightarrow \text{cell}-CH_2O-CH_2-\underset{X}{\overset{H}{C^{\cdot}}} \qquad (6)$$

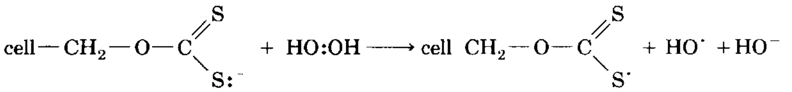


$$\text{cell}-\underset{H}{\overset{OH}{C^{\cdot}}} + CH_2-\underset{X}{CH} \longrightarrow \text{cell}-\underset{H}{\overset{OH}{C}}-CH_2-\underset{X}{\overset{H}{C^{\cdot}}} \qquad (7)$$

$$\text{cell}-CH_2-O^{\cdot} \longrightarrow \text{oxidation} \longrightarrow \text{stable products} \qquad (8)$$



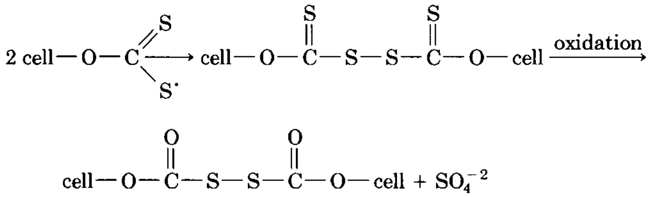
$$\text{cell}-CH_2O-C\begin{array}{l}{}^{\diagup}S\\ {}_{\diagdown}SH\end{array} \rightleftarrows \text{cell}-CH_2-O-C\begin{array}{l}{}^{\diagup}S\\ {}_{\diagdown}S:^-\end{array} \qquad (9)$$



$$\text{cell}-CH_2-O-C\begin{array}{l}{}^{\diagup}S\\ {}_{\diagdown}S:^-\end{array} + HO{:}OH \longrightarrow \text{cell}\ CH_2-O-C\begin{array}{l}{}^{\diagup}S\\ {}_{\diagdown}S^{\cdot}\end{array} + HO^{\cdot} + HO^- \qquad (10)$$

There is also a possible direct reaction between H_2O_2 and the xanthated groups as was postulated by Dimov and Pavlov.[2] Unstable microradicals on the sulfur atom probably decompose to form a cellulose macroradicals carrying the unpaired electron on the carbon or the oxygen atom. The macroradicals initiate polymerization and are also further oxidized to form stable products. However, a more complex kinetic scheme can be identified. Ehrnrooth[3] studied the concentration of sulfur in pulp and filtrate and found that the initial oxidate attack is very rapid. After a 1 min reaction period, only 10% of the initial concentration of the xanthated groups are unaffected and the total sulfur content of the system drops by half. The xanthate groups disappear completely during a 45 min reaction time, while the total sulfur content remains constant. By bubbling nitrogen through the system during the first 5 min of the reaction and immersing the outlet from the reactor in sodium ethoxide, sulfur did not leave the system in the form of carbon disulfide. This means that the reaction involving the simultaneous splitting of carbon disulfide represents no more than a minor reaction path overshadowed by other rapid oxidation reactions. Despite all the evidences, splitting of carbon sulfide is still considered as a major reaction path.[25,26]

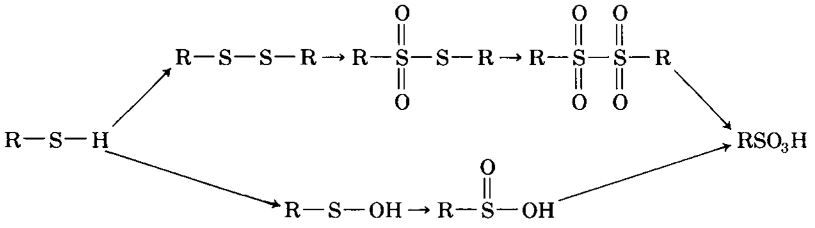
Since half of the total sulfur content remains in the system, it is likely that about one half of the sulfur macroradicals recombine very rapidly to form cellulose xanthide which are then slowly oxidized to cellulose monothiocarbonate disulfide and sulfate as shown:



$$2\,\text{cell}-O-C\overset{\displaystyle S}{\underset{\displaystyle S^{\cdot}}{\lessgtr}} \longrightarrow \text{cell}-O-\overset{\overset{\displaystyle S}{\|}}{C}-S-S-\overset{\overset{\displaystyle S}{\|}}{C}-O-\text{cell} \xrightarrow{\text{oxidation}} \quad (11)$$

$$\text{cell}-O-\overset{\overset{\displaystyle O}{\|}}{C}-S-S-\overset{\overset{\displaystyle O}{\|}}{C}-O-\text{cell} + SO_4^{-2}$$

There may also be a parallel path for oxidation through sulfinic acid, as shown below:

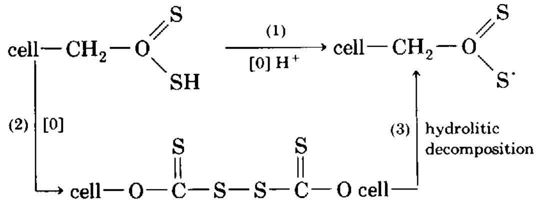


(12)

Sulfinic acid has been reported to be an efficient radical initiator of vinyl monomers.[27-30] Sulfinic acid can further be oxidized or decomposed[31,32] to sulfonic acid and disufoxide, according to

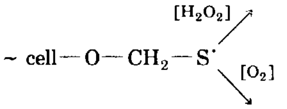
$$3RSO_2H \longrightarrow RS_2SR + RSO_3H + H_2O \quad (13)$$

It is also reasonable to assume that part of the xanthate groups are oxidized to disulfide and radicals are then created by homolytic decomposition, as shown below:


(14)

Independently of the reaction path, primary oxidized products are further oxidized to sulfonic acid, and its growing concentration causes a lowering of the final pH level. Secondary oxidized products have probably even higher ability to initiate grafting vinyl monomers than the primary oxidized products, as is shown in Figures 8–10.

It was found that the consumption of H_2O_2 increased exponentially with increasing concentration of xanthated groups in the pulp.[3] Molecular oxygen dissolved in the reaction medium can also oxidize sulfur products. Depending upon the relative concentration of H_2O_2 and oxygen, one of following paths prevails:


(15)

Oxidation by H_2O_2 is slower or the created products have a lower reactivity because a small amount of oxygen introduced into the system raises monomer conversion by about 20% (Fig. 9). At a concentration of H_2O_2 below 0.02 mol/L and nitrogen (99.9% purity), it is easy to see how important the influence of oxygen is on the degree of conversion. At higher concentrations of H_2O_2 (e.g., H_2O_2 0.05 mol/L) oxidation by H_2O_2 prevails, and, when the concentration of oxygen in the reaction medium is high enough, the termination effect of oxygen is observed.

In the reactions initiated by the redox systems in which thiourea[33,34] is the reducing agent, similar dependence of the reaction rate on the concentration of oxygen is observed. This is similar to the reaction initiated by the xanthate method. These redox systems can initiate polymerization in an oxygen-flushed closed system with a prolonged induction period. If oxygen is slowly bubbled into any of the systems, however, polymerization does not start. This means that when oxygen is present in a limited quantity, it is rather quickly consumed, resulting in products which probably do not inhibit the process. It was also found[34] that in reactions initiated by the redox systems with thiourea besides amino end groups, sulfonate end groups have also been detected in polymers. The concentration of sulfonate end groups rises with increasing acid concentration in the system.

Molecular weight of grafted polymers and homopolymers in graft copolymerization initiated by the xanthation method is low.[3,5,35] Ehrnrooth found that DP-grafted polymer diminishes with an increasing concentration of the initial xanthate groups and increasing H_2O_2 consumption. For the constant xanthate concentration, the peroxide consumption and DP of grafted polymer remains constant. This means that the chain terminator in the grafting reaction is a secondary xanthate oxidation product.

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