

# Effect of Stirring on Cellulose Graft Copolymerization. V. Influence of Reaction Parameters

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## Synopsis

Styrene was grafted onto dissolving pulp by the cellulose xanthate- $\text{Fe}^{2+}$ - $\text{H}_2\text{O}_2$  system. Reaction parameters were found to have strong influence on conversion to both copolymer and total polymer, as well as on the dependence of polymerization on stirring. The formation of polymer was almost completely inhibited by pure oxygen, while air only slowed down the reaction. Under inert atmosphere, the effect of agitator speed was found to be strongly dependent on monomer and substrate concentration as well as on the concentration of emulsifier. The location of the maximum on the conversion vs. agitator speed curve was strongly affected by the shape of the stirrer. The presence of emulsifier had a relatively small effect on copolymer formation in the case of acrylamide, a water-soluble monomer. Also the effect of stirring was less marked in the case of acrylamide. In all the systems investigated, the conversion to copolymer and total polymer was found to drop rapidly above a certain limiting agitator speed. The latter was different and characteristic for each system. No polymer formation was observed beyond 1000 rpm regardless of all other reaction conditions.

## INTRODUCTION

Considerable attention has been paid during the last two decades to the problems of graft copolymerization of vinyl monomers with cellulose and wood pulp.<sup>1</sup> It has been recently established by these authors that stirring plays a very important role in such reactions. These effects have been observed and studied for several different monomers and initiation systems.<sup>2-5</sup> Plots of conversion (to either copolymer or total polymer) vs. stirring rate generally showed well-defined maxima, the location of which depended on reaction conditions. The objective of the present work is to investigate in more detail the influence of various reaction parameters in a system involving styrene as the monomer and the cellulose xanthate- $\text{Fe}^{2+}$ - $\text{H}_2\text{O}_2$  initiation system.

## EXPERIMENTAL

The experimental procedures related to monomer and pulp preparation, and to copolymerization have been described in a previous paper.<sup>5</sup> Once again, a standard 1-L Pyrex resin kettle was employed to conduct the grafting experiments. Two types of stirrer were used: a Teflon paddle stirrer (ratio of paddle diameter to reactor diameter equal to 0.8) and an anchor stirrer. The arms of the latter were made to reach 1 cm below the surface

of the reaction mixture. The total volume of the reaction mixture was 450 mL in all experiments.

The grafting parameters are defined as follows:

1. Conversion to polymer (polymer yield)

$$\% = \frac{D - B}{C} = 100$$

2. Conversion to copolymer (copolymer yield)

$$\% = \frac{A - B}{C} \times 100$$

3. Grafting efficiency

$$\% = \frac{A - B}{D - B} \times 100 = \frac{\text{conversion to copolymer}}{\text{conversion to polymer}} \times 100$$

In the formulas above,  $A$  = dry weight of products after copolymerization and extraction,  $B$  = dry weight of pulp charged into the reactor corrected for pulp losses during the process,  $C$  = weight of the monomer charged, and  $D$  = dry weight of products isolated by filtration (before extraction).

A dissolving pulp (referred to in the text as "pulp") supplied by the Zaklady Celulozy i Papieru at Swiecie, Poland, was used as the grafting substrate. Styrene was distilled under vacuum and stored in a refrigerator before use. All the chemicals used were reagent quality.

## RESULTS AND DISCUSSION

### Effect of Oxygen

It is well known that, depending on reaction conditions and on the type of monomer, oxygen can act both as an initiator or as an inhibitor of vinyl polymerization. Hornof et al.<sup>6</sup> grafted several monomers onto graft semi-bleached softwood pulp by the xanthation process and found that conversion of some monomers (e.g., styrene) was at the same level or even higher in the presence of air. Other monomers (e.g., acrylamide) required an inert atmosphere, and the presence of air caused the conversion to drop considerably.

This effect was studied in more detail in the present work. Grafting of styrene was conducted while the reactor was being purged with either oxygen, air, or nitrogen at 200 mL/min. The results are shown in Figure 1 as a function of agitator speed. It is evident that, under pure oxygen, the conversion of styrene is very low. It is only 6.5% at 0 rpm and it declines steadily with increasing agitator speed, reaching zero at 210 rpm.

A similar set of reactions carried out under nitrogen produced a characteristic bell-shaped curve expected for styrene. The total conversion rises

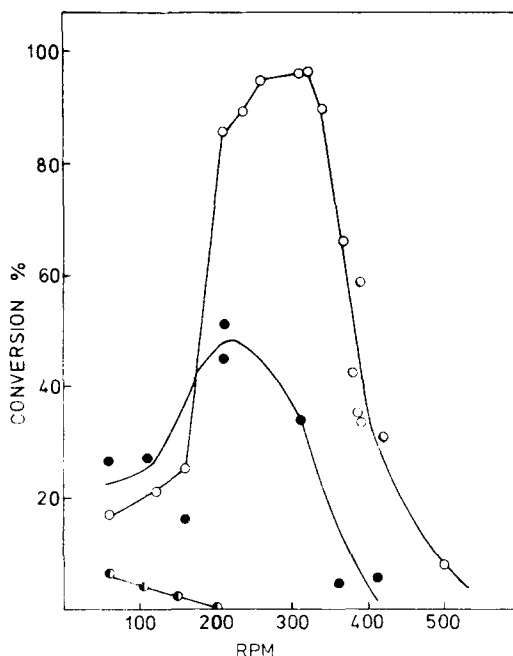


Fig. 1. Conversion of styrene to polymer as a function of agitator speed: temperature = 45°C; time = 1 h; [pulp] = 10 g/L; [styrene] = 0.133 mol/L; [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; gas flow rate = 200 mL/min; (○) nitrogen; (●) air; (●) oxygen.

dramatically with increasing agitator speed from 25% at 160 rpm to 87% at 210 rpm. The maximum situated at 320 rpm is followed by a sharp drop in conversion (down to near zero conversion at above 500 rpm).

A similar pattern is observed when nitrogen is replaced by air. However, the increase in conversion with rising agitator speed is not so sharp, viz., only about twofold compared with a sixfold increase under nitrogen. Also, the maximum occurs at a lower agitator speed (220 rpm). It would thus appear that the presence of oxygen plays a rather complex role and its effect depends both on the partial pressure of oxygen above the reaction mixture and on agitator speed. All the subsequent experiments were conducted under nitrogen atmosphere.

### Effect of Hydrogen Peroxide

Graft copolymerization initiated by the [partial cellulose xanthate-Fe<sup>2+</sup> - H<sub>2</sub>O<sub>2</sub>] system is expected to be influenced by the individual concentrations of the components. Hirabayashi<sup>7</sup> found that the effect of the concentration of Mohr salt (source of Fe<sup>2+</sup> ions) is very small. This effect can be neglected under the conditions prevailing in the present work. The effect of H<sub>2</sub>O<sub>2</sub>, however, has been found to be very important.<sup>8</sup> Figure 2 shows the conversion of styrene to polymer to be strongly dependent on the initial concentration of hydrogen peroxide in the reaction mixture. It is in particular the duration of the induction period which is affected. At 0.0061 mol/L of

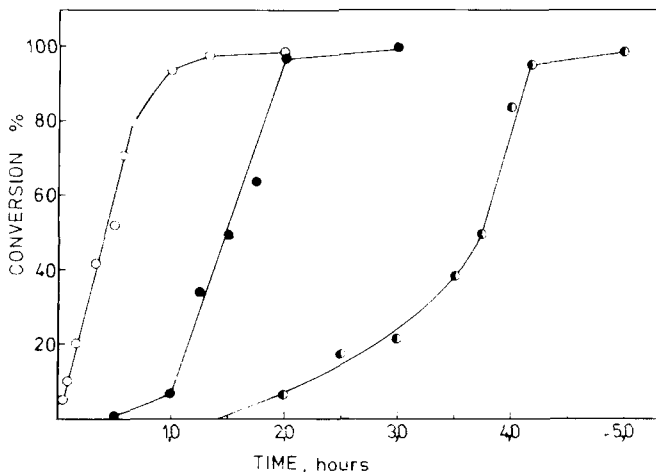


Fig. 2. Conversion of styrene to polymer as a function of reaction time: rpm = 310; temperature = 45°C; [pulp] = 10 g/L; [styrene] = 0.133 mol/L; (○) [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; (●) [H<sub>2</sub>O<sub>2</sub>] = 0.0122 mol/L; (●) [H<sub>2</sub>O<sub>2</sub>] = 0.0061 mol/L.

H<sub>2</sub>O<sub>2</sub> a nearly 1.5 h induction period is observed, followed by a prolonged acceleration period up to 50% conversion. Both the induction and acceleration period are much shorter at 0.0122 mol/L H<sub>2</sub>O<sub>2</sub> and they disappear completely at 0.049 mol/L H<sub>2</sub>O<sub>2</sub>.

It is very interesting to note that the maximum apparent polymerization rate, as reflected by the slope of the conversion curve at the point of inflection, is almost identical in all three cases.

Figures 3 and 4 show the conversion of styrene to polymer and to copolymer, respectively, as a function of agitator speed. It is evident that the concentration of hydrogen peroxide does not have any influence on the location of maximum conversion. These reactions were terminated after only 2 h reaction time so that the experiments with the lowest concentration of H<sub>2</sub>O<sub>2</sub> (0.0061 mol/L) show very low conversions (8%) with no discernible maximum. Grafting efficiency also appears to be not affected by H<sub>2</sub>O<sub>2</sub> concentration, although it is somewhat dependent on agitator speed. For both concentrations of H<sub>2</sub>O<sub>2</sub>, the grafting efficiency is 10–15% higher in the range of agitator speed corresponding to maximum polymer formation (60–68% vs. 47–55% at either below or above the optimum stirring).

### Effect of Substrate and Monomer Concentration

In the experiments discussed above, the concentration of pulp was fixed at 10 g/L while the concentration of styrene was 0.133 mol/L. It was interesting to find out how a change in the concentration of pulp, styrene, or both would affect the shape of the conversion-stirring rate curve and the position of the maximum.

The conversion curves obtained with pulp concentrations 20 and 30 g/L are displayed in Figures 5 and 6, respectively. It is seen that the maximum of conversion shifts to a higher range of agitator speed (460 and 510 rpm, respectively, compared with 320 rpm at 10 g/L of pulp). Comparing Figures 3, 5, and 6, it is apparent that pulp concentration has the largest effect at

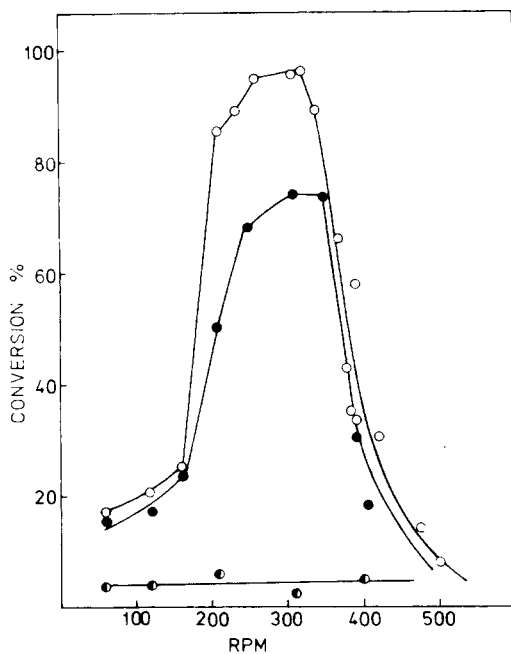


Fig. 3. Conversion of styrene to polymer as a function of agitator speed: temperature = 45°C; time = 1 h; [pulp] = 10 g/L; [styrene] = 0.133 mol/L; (○) [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; (●) [H<sub>2</sub>O<sub>2</sub>] = 0.0122 mol/L; (●) [H<sub>2</sub>O<sub>2</sub>] = 0.0061 mol/L.

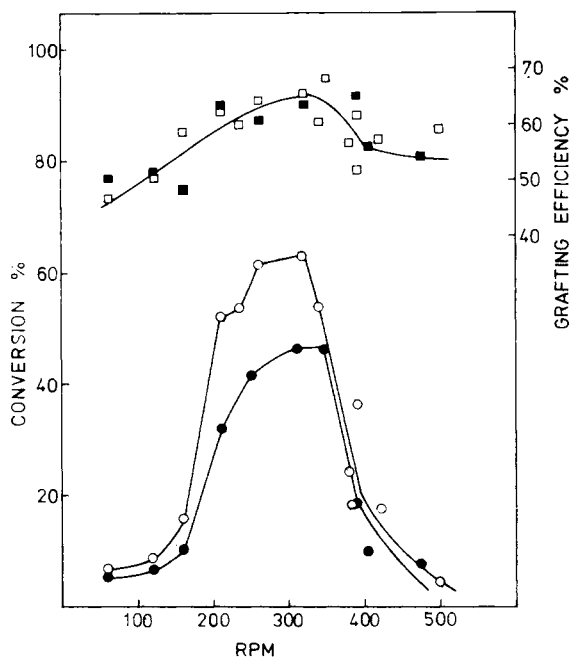


Fig. 4. Conversion of styrene to copolymer and grafting efficiency as a function of agitator speed: temperature = 45°C; time = 1 h; [pulp] = 10 g/L; [styrene] = 0.133 mol/L; (○) (□) [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; (●) (■) [H<sub>2</sub>O<sub>2</sub>] = 0.0122 mol/L; (○) conversion to copolymer; (□) grafting efficiency.

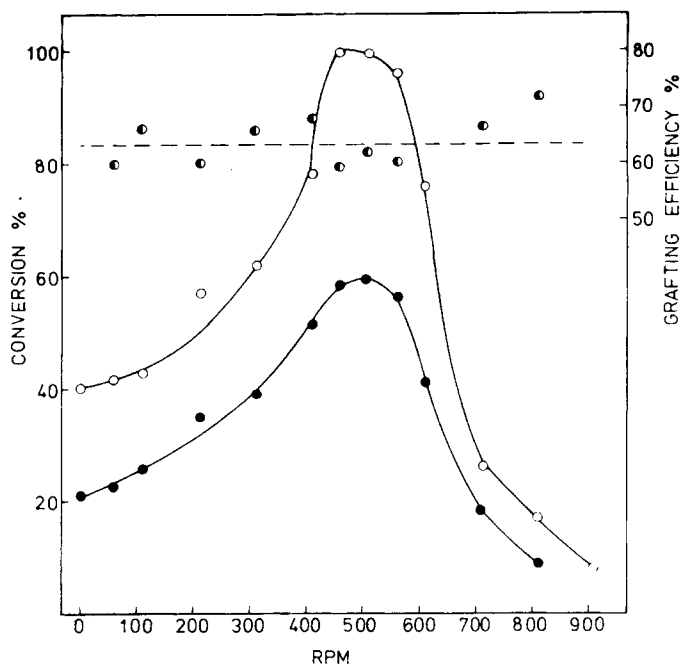


Fig. 5. Conversion of styrene as a function of agitator speed: temperature = 45°C; time = 1 h; [pulp] = 20 g/L; [styrene] = 0.133 mol/L; [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; (○) polymer; (●) copolymer; (●) grafting efficiency.

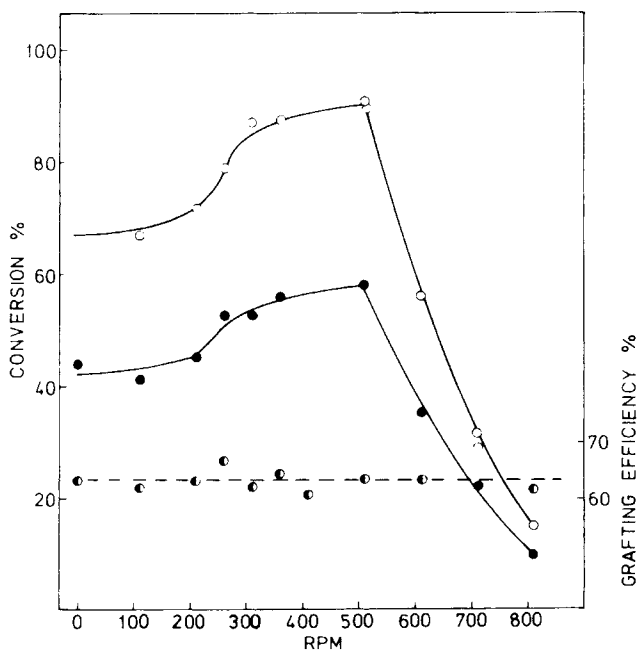


Fig. 6. Conversion of styrene as a function of agitator speed: temperature = 45°C; time = 1 h; [pulp] = 30 g/L; [styrene] = 0.133 mol/L; [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; (○) polymer; (●) copolymer; (●) grafting efficiency.

agitator speeds below that corresponding to maximum conversion. Thus total conversions amounting to 20, 40, and 60% are observed in this region for pulp concentrations of 10, 20, and 30 g/L. The total conversion of styrene at maximum, on the contrary, remains the same in all three experiments.

An associated phenomenon which probably plays an important role in these reactions is the formation of a vortex. At 10 g/L of pulp, a vortex appears at a very low stirring rate ( $\approx 60$  rpm). An increase in pulp concentration shifts the onset of vortex formation to higher revolutions, viz., to 200–300 rpm at 20 g/L and to 350–400 rpm at 30 g/L of pulp. In all three systems, formation of the vortex occurred at an agitator speed below that required for maximum conversion. Grafting efficiency is about 64% at both concentrations of cellulose and is independent of agitator speed.

On the other hand, a threefold increase in monomer concentration influences very strongly the dependence of grafting efficiency on agitator speed (Fig. 7). At 0.399 mol/L initial concentration of styrene, the grafting efficiency maximum (70%) coincides with maximum conversion observed at 110 rpm. At higher revolutions, grafting efficiency drops rapidly and reaches 35% at 450 rpm. The total conversion reaches only about 60% at maximum.

Figure 8 plots the data obtained when both pulp and styrene concentrations were increased (to 30 g/L and to 0.399 mol/L, respectively). It is evident that, in this particular case, conversion to either copolymer or total polymer is only little dependent on stirring in the low range of agitator speed (0–300 rpm). The maximum observed at 410 rpm is not very prominent, and the subsequent conversion drop at higher revolutions takes place more gradually. It is interesting to observe that this general behavior is somewhat similar to that encountered when using water-soluble monomers.<sup>2,4</sup>

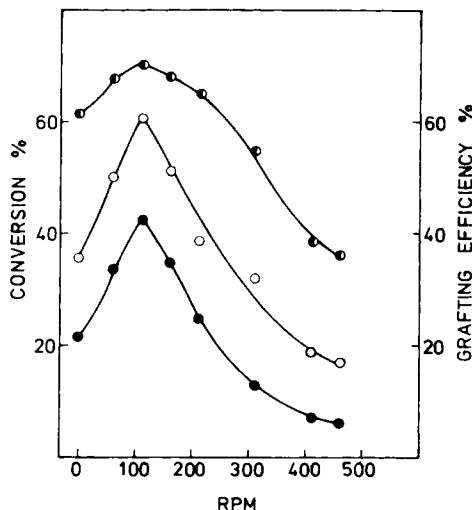


Fig. 7. Conversion of styrene as a function of agitator speed: temperature = 45°C; time = 1 h; [pulp] = 10 g/L; [styrene] = 0.399 mol/L; [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; (○) polymer; (●) copolymer; (◐) grafting efficiency.

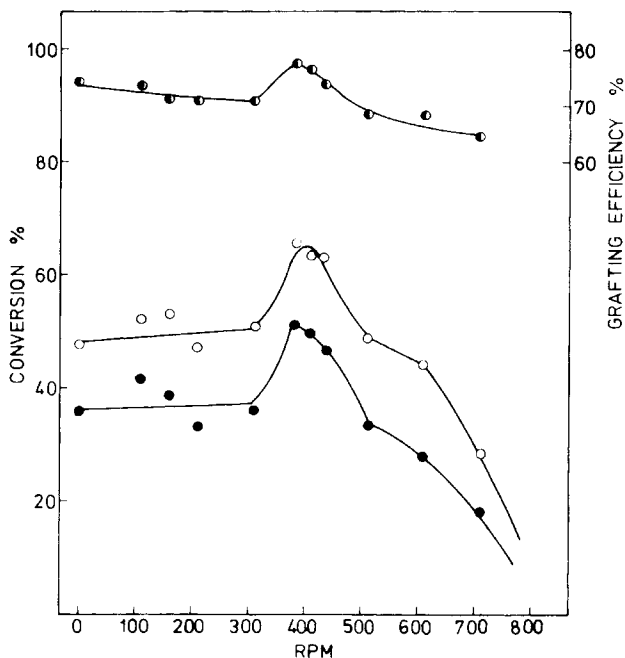


Fig. 8. Conversion of styrene as a function of agitator speed: temperature = 45°C; time = 1 h; [pulp] = 30 g/L; [styrene] = 0.399 mol/L; [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; (○) polymer; (●) copolymer; (●) grafting efficiency.

### Effect of the Type of Stirrer

The Teflon paddle stirrer used in the experiments described above is not very efficient in stirring heterogeneous mixtures such as the fibrous suspension of cellulose or wood pulp. At low revolutions, it produces a vortex in the middle of the reactor while little agitation takes place in the proximity of the reactor wall. At higher revolutions, especially when the pulp consistency is high, the whole mass of the reaction mixture tends to rotate with the agitator. In either case, the mixing is irregular and inefficient.

An anchor stirrer was employed in the next two series of experiments. This type of stirrer performs much better as regards the mixing of reagents close to the reactor wall. Figure 9 shows the results obtained with the low concentration of both substrate and monomer ([styrene] = 0.133 mol/L; [pulp] = 10 g/L) while the results obtained with the high concentrations of these reagents ([styrene] = 0.399 mol/L; [pulp] = 30 g/L) are plotted in Figure 10. A comparison with the previous results obtained using the Teflon paddle stirrer shows that the use of an anchor stirrer has three important effects. First, it shifts the maximum conversion to both total polymer and copolymer to much lower agitator speeds. Second, the peak becomes very small, particularly in the high concentration system. Last, the subsequent decrease in conversion when going towards higher agitator speed is much less abrupt. This is especially apparent in the high concentration system; in this case, the grafting efficiency also shows a decreasing trend with rising



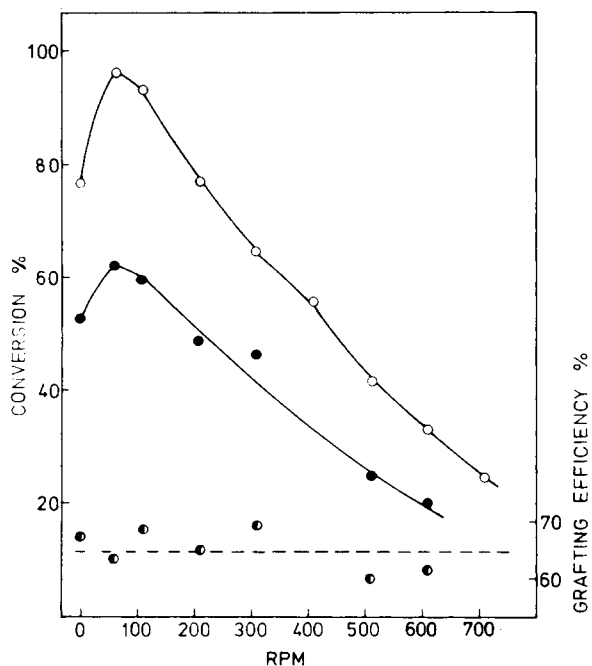


Fig. 9. Conversion of styrene as a function of agitator speed (anchor stirrer): temperature = 45°C; time = 1 h; [pulp] = 10 g/L; [styrene] = 0.133 mol/L; [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; (○) polymer; (●) copolymer; (◐) grafting efficiency.

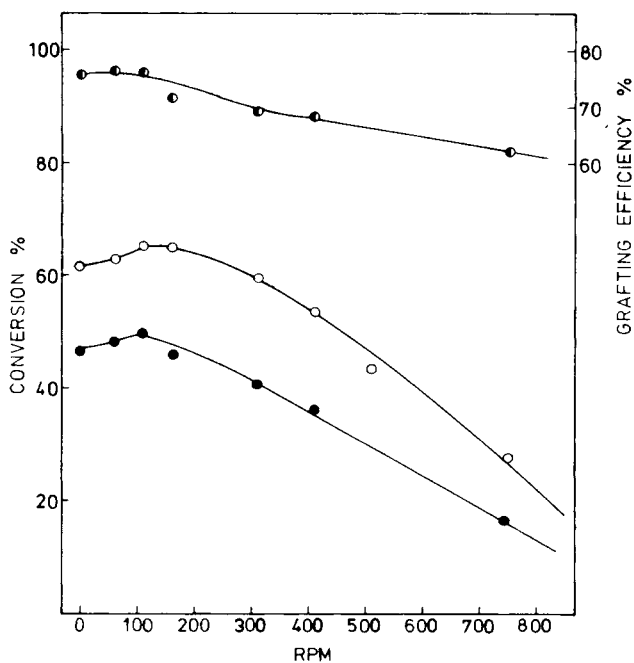


Fig. 10. Conversion of styrene as a function of agitator speed (anchor stirrer): temperature = 45°C; time = 1 h; [pulp] = 30 g/L; [styrene] = 0.399 mol/L; [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; (○) polymer; (●) copolymer; (◐) grafting efficiency.

agitator speed. Stirring seems to have no effect on grafting efficiency in the low concentration system. In both systems, the maximum conversion is coincident with the onset of vortex formation. Interestingly, no polymer is formed when the agitator speed is very high (above 700–800 rpm) regardless of all other reaction conditions.

### Effect of Surfactant

The polymerizations described so far were carried out in the presence of 0.2% of a nonionic surfactant, Tween-80. Reactions conducted without surfactant at 45°C, which has been the temperature normally used in the other experiments, were characterized by near-zero conversion of the monomer after 1 h reaction time. Figure 11 shows the results of experiments in which the temperature was raised to 65°C. It is seen that the general shape of the conversion vs. agitator speed curve is quite similar to those obtained in the presence of Tween-80; only the location of the maximum is shifted to a higher agitator speed (450 rpm). To the left of the maximum, there is a relatively broad plateau located between 260 and 400 rpm.

Agitator speed influences graft copolymerization of acrylamide in a different manner from copolymerization of styrene.<sup>4</sup> As a water-soluble monomer, acrylamide is readily transported to the growing chains of both homopolymer and copolymer, and one would expect that its polymerization would be independent of surfactant. This is borne out by the results displayed in Figure 12. It is evident that the conversion to copolymer is only

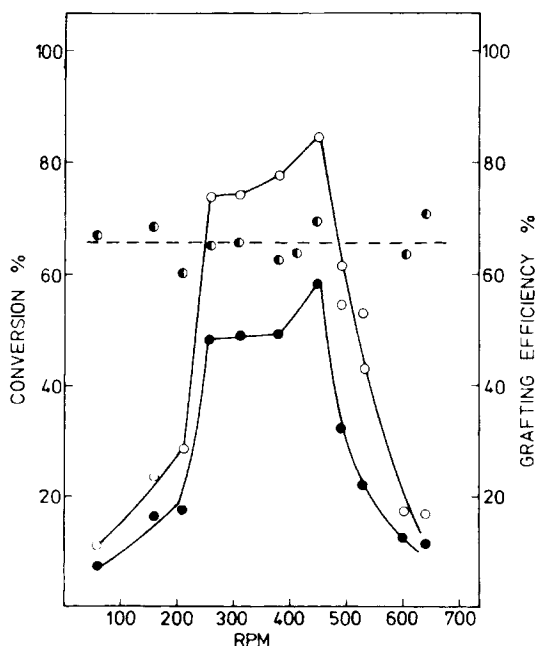


Fig. 11. Conversion of styrene as a function of agitator speed without an emulsifier: temperature = 65°C; time = 2 h; [styrene] = 0.049 mol/L; [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; (○) polymer; (●) copolymer; (●) grafting efficiency.

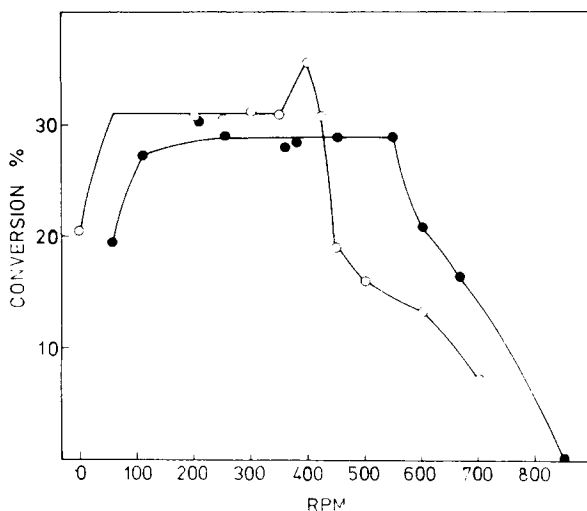


Fig. 12. Conversion of acrylamide to copolymer as a function of agitator speed: temperature = 45°C; time = 2 h; [acrylamide] = 0.266 mol/L; [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; (○) with Tween-80 as an emulsifier; (●) without Tween-80.

weakly influenced by the presence of Tween-80; furthermore, the surfactant does not have much effect on the dependence of copolymer yield on agitator speed. The only effect seems to be the somewhat broadened conversion plateau in the absence of surfactant.

In the case of styrene on the other hand, the concentration of surfactant is important. As shown in Figure 13, the conversion of this water-insoluble monomer is strongly dependent on surfactant concentration. The emulsifier apparently facilitates the transport of the monomer to the growing centers thus increasing reaction rate.

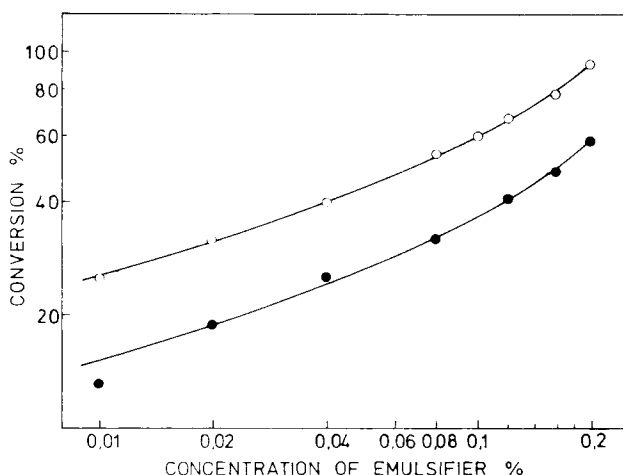


Fig. 13. Conversion of styrene as a function of concentration of Tween 80: temperature = 45°C; time = 1 h; [styrene] = 0.133 mol/L; [H<sub>2</sub>O<sub>2</sub>] = 0.049 mol/L; (○) polymer; (●) copolymer.

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