Effect of Stirring on Cellulose Graft Copolymerization. VI. Grafting of Methyl Acrylate by Ceric Salt

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INTRODUCTION

It was established by Graczyk and Hornof that stirring speed is an important variable in graft copolymerization onto cellulose. The effect of stirring was studied for a number of monomers and initiation systems.[1-4] The maximum of conversion on the conversion–stirring rate curve was observed followed by a drop of conversion to zero. The influence of agitation upon the conversion is the highest for graft copolymerization initiated with the xanthate–FE^{+2}–H_2O_2 and the xanthate–FE^{+2}–$K_2S_2O_8$ redox systems. The effect of stirring is much less significant for graft copolymerization initiated with FE^{+2}–H_2O_2 or FE^{+2}–$K_2S_2O_8$ and negligible for potassium persulfate.

Effect of stirring on graft copolymerization initiated with ceric ions was not studied by Graczyk and Hornof in detail. However, it was shown on the ground of one set of experiments that conversion in graft copolymerization of 2-dimethylaminoethyl methacrylate (DMAEM) initiated with ceric salt decreases steadily with an increase in stirring rate.[2]

These results are in accordance with Mansour and Nagaty,[5] who also observed that graft copolymerization initiated with ceric ammonium sulfate was strongly dependent on agitation. Unfortunately, the usefulness of their results is limited, because they used only two kinds of mixing: light hand shaking and intense agitation.

Recent publication of Fanta et al.[6] states that under their experimental conditions no large effect of stirring speed on the graft copolymerization of acrylonitryle and methyl acrylate onto starch and graft copolymerization of methyl acrylate onto cellulose initiated with ceric ions was observed. Their statements may be called in question especially with reference to cellulose because conversion of methyl acrylate was held at the level 95% and the effect of stirring was investigated only in a narrow range of agitator speed. It was established by the author that when the conversion is close to 100% the influence of stirring speed is very often much less significant even for monomers with a quite definite maximum.

The present work examines the graft copolymerization of methyl acrylate onto cellulose initiated with ceric salt in a broader range of agitator speed and concentration of reagents used.

EXPERIMENTAL

A dissolving pulp supplied by Zaklady Celulozy i Papieru in Swiecie, Poland was used as the grafting substrate. The pulp was preserved in a freezer and thawed before use. Methyl acrylate (MA) was purified by vacuum distillation. Ceric sulfate and sulfuric acid reagent grade were used.

Graft copolymerization was performed in a 1-L resin flask equipped with a Teflon paddle stirrer. Stirrer speeds were measured with photoelectric tachometer.

In a typical experiment the reactor was charged with a never-dry pulp and monomer followed by the addition of a suitable amount of water. The volume of the reaction mixture was adjusted every time to 450 mL independent of the amount of reagents charged as in experimental. Nitrogen, purified by passing through an alkaline pyrogallol solution, was continuously bubbled through the system at the rate 200 mL/min. After 15 min of swelling period the reaction was started by the addition of ceric sulfate with 15.3 mL $6N$ H_2SO_4 to adjust the concentration of sulfuric acid in the reaction mixture at the level 1%. The reaction was carried at 25°C (cellulose 30 g/L) or at 65°C (cellulose 10 g/L). The reaction was stopped by a addition of hydroquinone.

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

The grafting parameters were determined in the following manner:
1. Conversion to polymer
   $\% = (D - B)/ C \times 100$
2. Conversion to copolymer
   $\% = (A - B)/ C \times 100$
3. Grafting efficency
   $\% = (A - B)/(D - B) \times 100$

A, B, C, and D denote the weight of products after copolymerization and extraction, the weight of pulp and monomer charged in the reactor, and the weight of products isolated by filtration (unextracted), respectively.

RESULTS AND DISCUSSION

Recent publication by Graczyk and Hornof has stated that the shape of the conversion–stirring rate curve was strongly influenced by the concentration of cellulose and monomer.[7] For this reason two sets of experiments were carried out with a low (10g/L) and high (30 g/L) concentration of cellulose. The latter concentration of cellulose is even higher than that used by Fanta et al. (23.3 g/L). The concentration of methyl acrylate was also slightly higher than in Fanta's work (0.399 mol/L and 0.340 mol/L, respectively). The same size of reactor and the same geometry of stirrer were used to be able to compare experimental results in both papers. However, ceric sulfate instead of ceric ammonium sulfate was used in this study.

Fanta used a low concentration of ceric ion (1.42×10^{-3} mol/L) but carried out experiments in a relatively long period of time (2 h). It was established in preliminary experiments that the grafting reaction was very fast

in the presence of high concentration of cellulose and monomer. Thus, the time of reaction was limited only to 30 min.

Figures 1–3 show the results obtained for high concentration of cellulose (30 g/L) and methyl acrylate (0.399 mol/L) with a different concentration of ceric sulfate (10×10^{-3} mol/L, 2.5×10^{-3} mol/L, and 0.5×10^{-3} mol/L, respectively). It is seen that the shape of the conversion curve is extremely dependent on the concentration of initiator. In the first run, the conversion reaches about 93% and is independent of stirring speed in the range 0–460 rpm. This is followed by a dramatic drop of conversion from 93% to zero in a very narrow range of agitator speed (25 rpm). Thus, these results are in accordance with those of Fanta et al. However, these authors examined the phenomenon in too narrow a range of stirring speeds and were not able to observe a drop of conversion to zero.

The fourfold decrease in the concentration of ceric sulfate brings about a different shape of the curve. The conversion becomes dependent on the stirring rate especially in a low range of agitator speed. The broad maximum of conversion at 310 rpm is observed followed by the same dramatic drop of conversion to zero. However, the drop of conversion is slightly shifted to a higher range of stirring rate (460 and 535 rpm, respectively).

At a very low concentration of ceric sulfate (0.5×10^{-3} mol/L), the conversion of methyl acrylate is strongly dependent on agitator speed. The maximum is observed at 160 rpm and a characteristic phenomenon of a dramatic drop of conversion disappears. The conversion decreases to zero in a broader range of stirring speed (210–410 rpm).

The concentration of cellulose 10 g/L and methyl acrylate 0.133 mol/L was used in most of Graczyk and Hornof's papers. Therefore, it was interesting to examine the effect of stirring on graft copolymerization for these low concentrations of reagents. However, the temperature of the reaction had to be increased to 65°C in order to get a high degree of conversion.
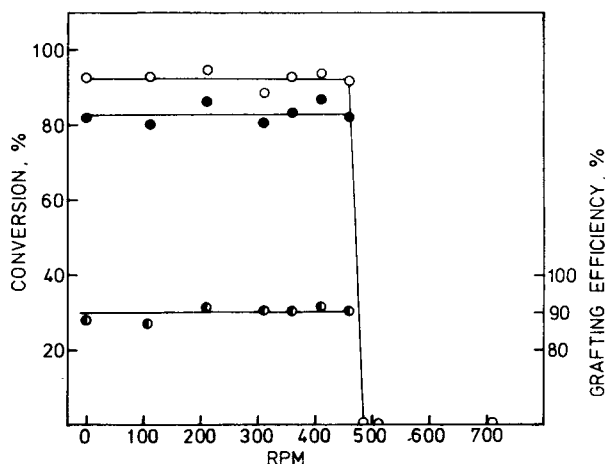
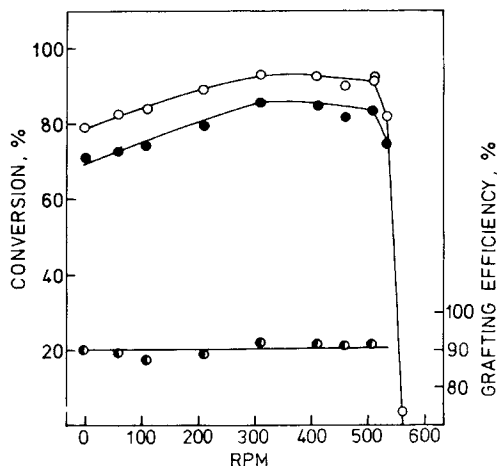

Fig. 1. Conversion of MA as a function of agitator speed: temperature = 25°C; time = 30 min; [cellulose] = 30 g/L; [MA] = 0.399 mol/L; [Ce(SO$_4$)$_2$] = 10×10^{-3} mol/L; (○) polymer; (●) copolymer; (◐) grafting efficiency.

Fig. 2. Conversion of MA as a function of agitator speed: temperature = 25°C; time = 30 min; [cellulose] =30 g/L; [MA] = 0.399 mol/L; [Ce(SO$_4$)$_2$] = 2.5 × 10^{-3} mol/L; (○) polymer; (●) copolymer; (◑) grafting efficiency.

The data obtained with three concentrations of ceric salt (the same as for the high concentration of cellulose and methyl acrylate) are plotted in Figures 4–6. It is to be seen that also for a low concentration of reagents the shape of conversion curves is strongly dependent on the concentration of ceric sulfate.

The maximum of conversion in the experiments with two higher concentrations of ceric sulfate is observed. The maximum is located at 310 and 360–380 rpm, respectively. In both cases, conversion drops sharply to zero in a narrow range of agitator speed.

At a low concentration of ceric sulfate the conversion reaches about 28% at zero revolutions per minute and then decreases steadily with increasing
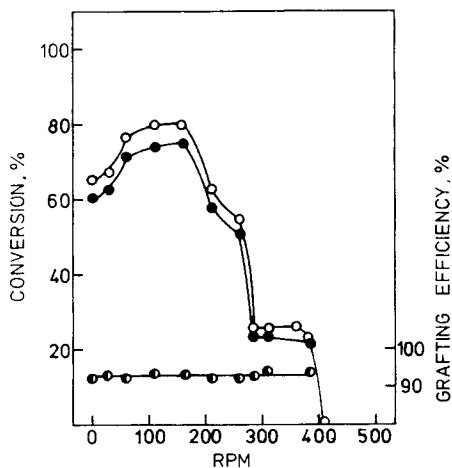

Fig. 3. Conversion of MA as a function of agitator speed: temperature = 25°C; time = 30; [cellulose] = 30 g/L; [MA] = 0.399 mol/L; [Ce(SO$_4$)$_2$] = 0.5 × 10^{-3} mol/L; (○) polymer; (●) copolymer; (◑) grafting efficiency.
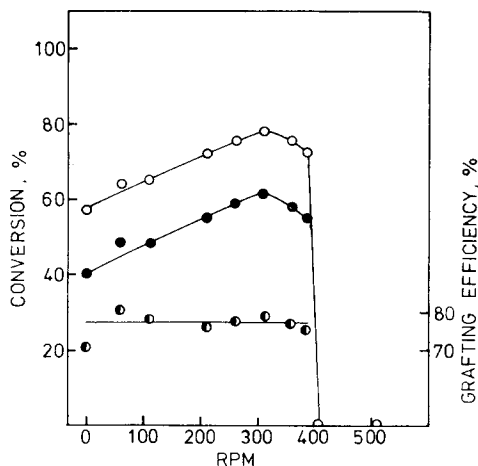
Fig. 4. Conversion of MA as a function of agitator speed: temperature = 65°C; time = 30 min; [cellulose] = 10 g/L; [MA] = 0.133 mol/L; [Ce(SO$_4$)$_2$] = 10 × 10^{-3} mol/L; (○) polymer; (●) copolymer; (◑) grafting efficiency.

agitator speed. Grafting was not observed beyond 300 rpm when the reaction time was equal to 30 min. This shape of the curve is qualitatively similar to the shape of curve for graft copolymerization of DMAEM initiated with ceric ammonium nitrate. Thus, the same shape of curve for water soluble DMAEM and only partly soluble in water methyl acrylate (5.2 g/100 cm^3) was received. The similarity of conversion curves for water-soluble DMAEM and hydrophobic styrene at the appropriate concentration of reagents in graft copolymerization initiated with the xanthate–FE^{+2}–H$_2$O$_2$ initiation system was also observed.[7]

Figure 6 presents also the results for grafting of methyl acrylate for 1 h. It is seen that twofold increase in the reaction time considerably changes
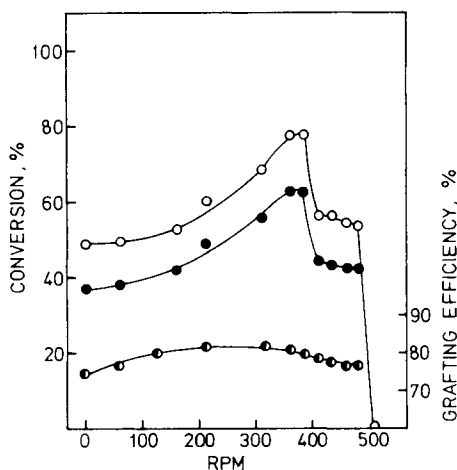

Fig. 5. Conversion of MA as a function of agitator speed: temperature = 65°C; time = 30 min; [cellulose] = 10 g/L; [MA] = 0.133 mol/L; [Ce(SO$_4$)$_2$] = 2.5 × 10^{-3} mol/L; (○) polymer; (●) copolymer; (◑) grafting efficiency.
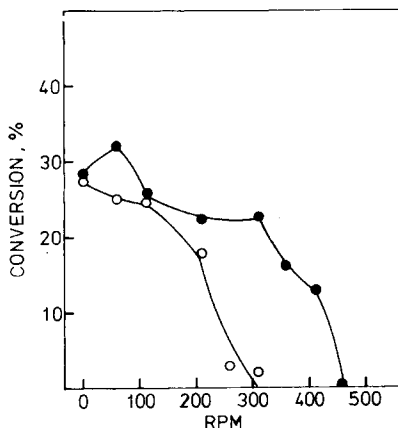
Fig. 6. Conversion of MA to polymer as a function of agitator speed: temperature = 65°C; [cellulose] = 10 g/L; [MA] = 0.133 mol/L; [Ce(SO$_4$)$_2$] = 0.5 × 10^{-3} mol/L; (○) time = 30 min; (●) time = 1 h.

the shape of conversion curve. The small maximum and fall to zero at 460 rpm is observed.

On the ground of presented results it is possible to conclude that graft copolymerization of methyl acrylate initiated with ceric salt is strongly influenced by agitation. Therefore, the shape of conversion curve is dependent on the conditions of the reaction in every case.

The details of the influence of reagent concentrations, reaction time and other variables on the effect of stirring in graft copolymerization of acrylates initiated with ceric salt is under investigation and will be presented in the next paper.

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