Effect of Stirring on Cellulose Graft Copolymerization

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Synopsis

Dissolving pulp was grafted with several monomers ranging from hydrophilic (dimethylaminoethyl methacrylate) to hydrophobic (styrene). The conversion of these monomers to polymer and copolymer was investigated in dependence on the number of revolutions of the agitator. The formation of grafted copolymer was found to be strongly influenced by stirring. For all the monomers employed, almost no copolymer was formed above 400 rpm. The formation of homopolymer was also severely reduced at higher stirring speeds. For some monomers, a maximum was obtained at about 200–300 rpm with both copolymer and homopolymer yields dropping off sharply at both lower and higher stirring speeds. The position of this maximum was affected by the size of the reactor. The behavior displayed by the xanthate–Fe^{2+}–H_2O_2, Fe^{2+}–H_2O_2, and ceric ion initiation systems was very similar. Also, monomer solubility in water seemed to have little importance in determining the general behavior.

INTRODUCTION

Recent work in this laboratory[1] gave evidence that stirring may be important in graft copolymerization reactions. While the effects of many other variables (type and concentration of initiator, pH, monomer type, temperature, etc.) have been investigated in great detail, there is almost no mention in the literature of the type and rate of stirring employed.[2] Yet, in a heterogeneous reaction such as grafting, it is reasonable to expect that stirring will play a significant role.

The investigations carried out in the previous work[1] were limited to one monomer only and to the xanthate grafting method. The aim of this paper is to establish whether the effects observed may be considered to be of a general character in a wide range of monomer types, initiation systems, and reactor geometries.

EXPERIMENTAL

Materials

The monomers used were styrene (Eastman Kodak), acrylonitrile (AN) (Eastman Kodak), methylmethacrylate (MMA) (Anachemia), and 2-dimethylaminoethyl methacrylate (DMAEM) (Eastman Kodak). All monomers were purified by vacuum distillation and then stored in a refrigerator. A dissolving pulp supplied by CIP Ltd. (Hawkesbury) was used as the grafting substrate.

Copolymerization Procedures

The copolymerization of DMAEM initiated with ceric ammonium nitrate was carried out in a 1-L reactor under nitrogen. The reactor was charged with 4.5 g of never-dry pulp (oven-dry weight) and 0.06 mol DMAEM which had been neutralized with nitric acid. The reaction mixture (pH = 5–6) was stirred for 15 min. The reaction was started by adding 1.48 g ceric ammonium nitrate $(NH_4)_2Ce(NO_3)_6$. The pH of the mixture dropped to 1.6 upon addition of the initiator. In the zero rpm experiment, the reaction mixture was stirred for 5 min at 60 rpm immediately after the initiator was added, and then about 20 s each 10-min interval. The reaction was terminated after 2 h by an addition of hydroquinone.

The copolymerization of styrene by the $Fe^{2+}–H_2O_2$ redox system was also carried out in the 1-L reactor under nitrogen. The pulp (4.5 g) was presoaked in 150 mL of 0.004% ferrous ammonium sulfate. It was subsequently washed with 350 mL of distilled water and then charged into the reactor together with 0.06 mol of styrene and 200 mL of distilled water. After a 15-min swelling period 0.15 g of hydrogen peroxide (0.11 mol/L) was added and the volume of the reaction mixture was adjusted to 450 mL. The reaction was carried out at 75°C for 2 h, and it was stopped by an addition of hydroquinone.

The xanthate process used for grafting cellulose with AN, MMA, and styrene has been described earlier.[3,4] The emulsion method of xanthation employed gave $\gamma \cong 11$ (i.e., approximately 11 xanthate groups per 100 glucose units).

Reactors

Standard pyrex resin kettles (1 and 2 L volume) were used. The reactor lid was equipped with a ground glass shaft to guide a Pyrex stirrer rod. A teflon impeller was used in both reactors, the ratio of impeller diameter to reactor diameter being 0.8 in both cases. A reduced motor with adjustable speed was used to drive the stirrer assembly and a strobe light was employed to measure the number of revolutions.

Extraction

The homopolymer content in the reaction products was determined by Soxhlet extraction of 3–4 g samples of the products with suitable solvents: acetone for polystyrene, chloroform for poly(methyl methacrylate) and dimethylformamide for polyacrylonitrile. The extraction of polyacrylonitrile was carried out under vacuum (20–30 mm Hg) in order to minimize degradation.

Reaction Parameters

For the sake of simplicity, only two parameters are used to characterize the reactions:

(1) conversion to polymer (polymer yield)

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

represents the total amount of polymer formed in respect to monomer charged;

(2) conversion to copolymer (copolymer yield)

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

represents the amount of polymer formed which is bound to the substrate (i.e., it is not removed by extraction), also in respect to monomer charged.

In the expressions above, A = dry weight of products after copolymerization and extraction; B = dry weight of pulp charged in the reactor (corrected for losses due to xanthation and washing); C = weight of monomer charged; D = dry weight of products isolated by filtration (before extraction).

RESULTS AND DISCUSSION

The four monomers chosen for this work include two water-insoluble monomers (styrene, MMA), a water-soluble monomer giving a water-soluble polymer (DMAEM) and a water-soluble monomer giving a water-insoluble polymer (AN). It is evident that the solubility of the monomer will influence the supply of monomer to the growing chains. It has been shown[1,5,6] that water-soluble monomers give more homopolymer, probably due to transfer by monomer and/or to the initiation of polymerization in the aqueous phase. On the other hand, the copolymer/homopolymer ratio can be somewhat controlled by a judicious choice of surfactant used to solubilize the monomer and of the initiating system. As a consequence, one would expect that both total monomer conversion and the copolymer/homopolymer ratio would be influenced differently by the stirring rate for the two types of monomers. However, this expectation is not quite borne out by the results of this work.
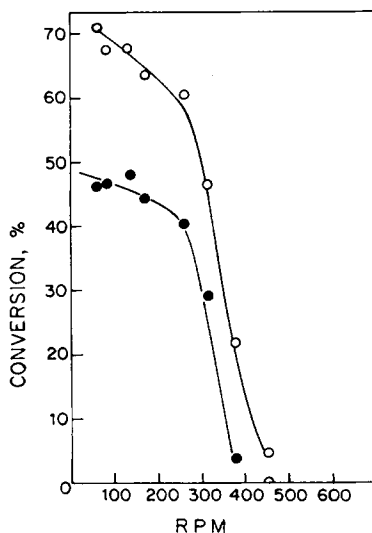

Fig. 1. Conversion of AN as a function of agitator speed for a 1-L reactor: [AN] = 0.133 mol/L; [H$_2$O$_2$] = 0.098 mol/L; (O) polymer; (●) copolymer.
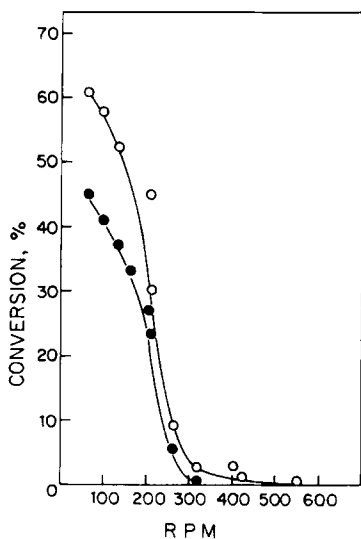
Fig. 2. Conversion of AN as a function of agitator speed for a 2-L reactor: [AN] = 0.133 mol/L; [H_2O_2] = 0.098 mol/L; (O) polymer; (●) copolymer.

Figures 1 and 2 show the conversion of AN to polymer ("polymer yield") and conversion to copolymer ("copolymer yield") as a function of the number of revolutions of the agitator. It is seen that the curves are qualitatively similar for the 1-L and 2-L reactors, although the absolute values of conversion differ. In both reactors, polymer yield and copolymer yield drop sharply as a result of increasing agitator speed. Unlike the results obtained with DMAEM as the monomer,[1] no maximum is observed on either curve. However, there appears
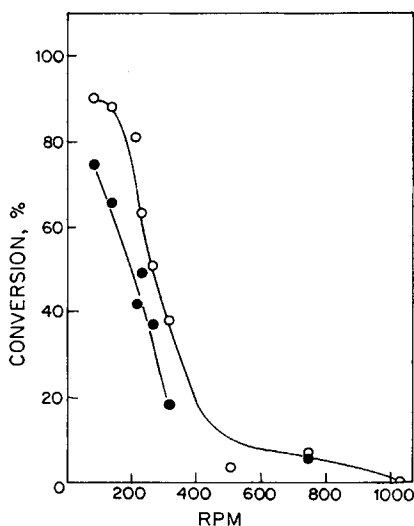

Fig. 3. Conversion of MMA as a function of agitator speed for a 2-L reactor: [MMA] = 0.133 mol/L; [H_2O_2] = 0.049 mol/L; (O) polymer; (●) copolymer.
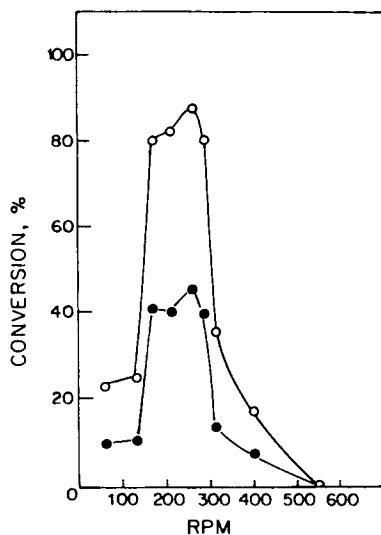
Fig. 4. Conversion of styrene as a function of agitator speed for a 1-L reactor: [styrene] = 0.133 mol/L; [H_2O_2] = 0.049 mol/L; (O) polymer; (●) copolymer.

to be a small difference as to the position of the inflection point on the conversion curves. In the 1-L reactor (Fig. 1), this point is located at about 300–350 rpm while, in the 2-L reactor, it appears in the range 180–220 rpm. This difference between the two reactors is in qualitative agreement with the observations made when DMAEM was employed as the monomer. Also, the conversions are somewhat different for the two reactor sizes.

Figure 3 displays the data obtained with MMA as the monomer in the 2-L reactor. The same pattern is obtained as in the previous two figures. Both total
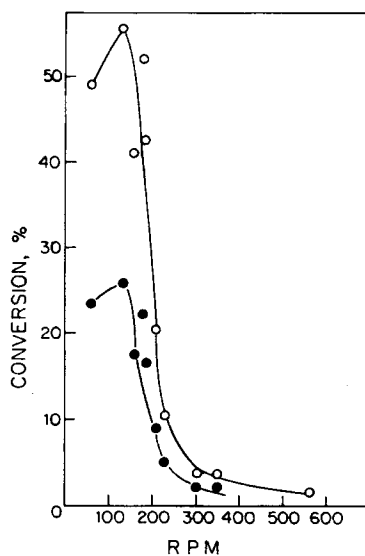

Fig. 5. Conversion of styrene as a function of agitator speed for a 2-L reactor: [styrene] = 0.133 mol/L; [H_2O_2] = 0.040 mol/L; (O) polymer; (●) copolymer.
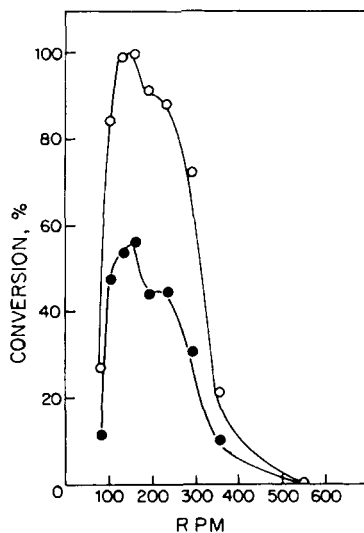
Fig. 6.   Conversion of styrene as a function of agitator speed for a 2-L reactor (amount of reagents doubled):   [pulp] = 9.0 g; [styrene] = 0.266 mol/L; $[H_2O_2]$ = 0.098 mol/L; (O) polymer; (●) copolymer.

polymer yield and copolymer yield decrease rapidly with increased revolutions and similar to acrylonitrile; very little copolymer formation is observed beyond about 400 rpm.

Figures 4 and 5 show the behavior of the most hydrophobic monomer among those tested, i.e., styrene.   Surprisingly, the curves obtained resemble closely those observed with the water-soluble DMAEM.[1]   Both polymer yield and co-
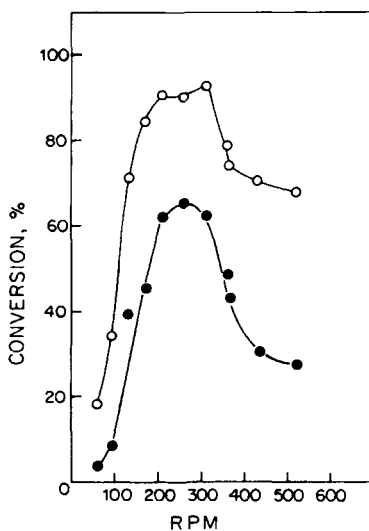

Figure 7.   Conversion of styrene initiated by ferrous ion–hydrogen peroxide as a function of agitator speed for a 1-L reactor at 75°C: [styrene] = 0.133 mol/L; $[H_2O_2]$ = 0.011 mol/L; (O) polymer; (●) copolymer.
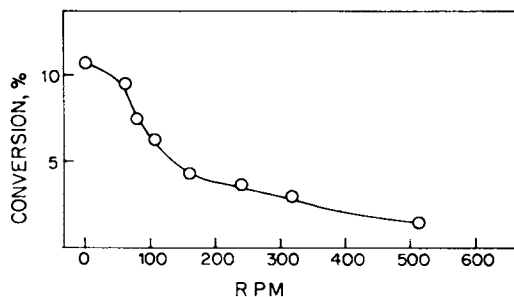
Fig. 8. Conversion to copolymer of DMAEM initiated by ceric ammonium nitrate as a function of agitator speed for a 1-L reactor: DMAEM = 0.133 mol/L; $(NH_4)_2Ce(NO_3)_6$ = 0.006 mol/L.

polymer yield curves show a well-defined maximum which is located at 250 rpm and 150 rpm for the 1-L and 2-L reactors, respectively. Figure 4 shows that, with the 1-L reactor, conversion increases dramatically with the number of revolutions of the agitator in the range 100–200 rpm. Thus an increase from 130 to 170 rpm brings about a rise in total polymer yield from 25% to 81%. A narrow plateau is then obtained (200–300 rpm) followed by a precipitous drop in polymer formation above 300 rpm. The 2-L reactor shows similar results, although the position of the maximum is shifted to lower rpm and the rise in polymer yield at low agitator speeds is not so clearly in evidence. The conversions obtained in the 2-L reactor are considerably lower than those observed in the 1-L reactor, and there is very little copolymer formation beyond about 200 rpm agitator speed.

Both the results with styrene and with DMAEM as monomers indicate that the size of the reactor plays a very important role. It should be noted that the volume of the reaction mixture was the same in both reactors. Since the two reactor kettles differ in diameter, the height of liquid was also different in each reactor (73 mm in the 1-L reactor and 48 mm in the 2-L reactor). In the next series of experiments, the volume of the reaction mixture in the 2-L reactor was doubled by using twice the original amount of all reagents. Thus, this new system was roughly geometrically similar to the 1-L reactor.

The conversion data obtained with the above system are plotted in Figure 6. Comparing these curves with those shown in Figure 5, it is evident that the volume of reagents and, consequently, the height of liquid in the reactor plays a significant role in determining polymer and copolymer yield, and has also an effect on the position of the maximum. The conversion values are almost twice as high as those obtained in the 2-L reactor using the normal amount of reagents, and they are comparable to the conversion values obtained in the 1-L reactor. Also the shape of the curves resembles more the shape of the curves shown in Figure 4 than of those in Figure 5.

The results presented so far have been obtained using the xanthate initiation system. It appeared interesting to find out if other initiators would be also influenced by the number of revolutions of the agitator. For this purpose, two sets of experiments were carried out in the 1-L reactor.

In the first set of experiments, styrene was copolymerized with cellulose using the $Fe^{2+}-H_2O_2$ redox initiator system. The results are shown in Figure 7. A comparison of these results with those shown previously in Figure 4 gives clear

evidence that the xanthation step does not affect the dependence of the reaction on stirring. In fact, both polymer and copolymer yield curves have a shape almost identical with that obtained when the xanthated pulp was used.

The ceric ion initiation system was employed in the other set of experiments. Very low grafting was observed with styrene as a monomer so DMAEM was used instead. As evident from Figure 8, the conversion was very low with this monomer as well, recording a maximum copolymer yield of 10.8% at zero revolutions per minute. The yield then decreases steadily with increasing agitator speed. Although these results are obviously subject to a large error due to the very low conversion, the authors believe that the trend observed represents the true behavior of the system.

CONCLUSION

All of the systems investigated in this work have a common feature in that a rapid decrease in polymer and copolymer yield is observed beyond a certain limiting number of revolutions of the agitator. A distinct maximum is present for some of the systems, which is preceded by an interval in which polymer production increases sharply with increasing agitator speed. The position of this maximum depends on a number of parameters including the type of monomer, initiator, and reactor used. The fact that the maximum was present in the case of styrene and DMAEM and was absent in the case of AN and MMA would indicate that the polarity (and solubility in water) of the monomer has little or no effect. The main conclusion to be drawn from this work is that one must be very careful when comparing grafting data found in the literature. Unless parameters such as agitator speed and reactor shape are known, such comparisons may not be warranted.

References

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