The Combined Effect of Stirring and Oxygen on the Graft Copolymerization of Methyl Methacrylate onto Cellulose

A. HANNA and V. HORNOF, *Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4*

Synopsis

Methyl methacrylate was grafted onto bleached kraft pulp using ceric ammonium nitrate as initiator. The effect of stirring on the conversion to polymer and copolymer was strongly influenced by the presence of oxygen. In an oxygen-free system, the conversion was found to first increase rapidly with rising stirrer speed and then level off. No decrease in conversion was observed even at very high stirrer speeds (up to 1000 rpm). Inclusion of oxygen resulted in the appearance of a maximum on the conversion versus stirring speed curve, followed by a decrease in conversion at more intense agitation. The presence of oxygen also adversely affected the grafting efficiency.

INTRODUCTION

Graft copolymerization of various monomers onto cellulose and wood fibers has been studied extensively during the last three decades.[1] As in any heterogeneous process, it is reasonable to expect that stirring should play an important role. Recent papers published by Graczyk and Hornof[2-5] have shown that this is indeed so, although some other factors, such as monomer solubility, the type of initiation system, and reactor geometry, were also important. They also noted[6] that the effect of stirring was strongly dependent on whether the reaction was conducted in the presence or absence of oxygen. It was therefore decided to study the combined effect of oxygen and stirring on grafting in more detail. The ceric ion method was employed because of its relative simplicity in comparison with other initiation methods.

EXPERIMENTAL

Reactants

Never dried hardwood bleached kraft pulp supplied by Thurso Pulp and Paper (Thurso, Quebec) was used as the grafting substrate. The pulp was washed with distilled water and stored in a freezer before use.

Methyl methacrylate monomer was supplied by Scientific Polymer Products, Inc. (Ontario, New York). It was purified by passing the monomer, dropwise, through a molecular sieve column packed with HR-4 supplied by the same company.

Ceric ammonium nitrate used as the initiator was supplied by Fisher Scientific (reagent grade). Hydroquinone (reagent grade) used to terminate the

polymerization was supplied by J. T. Baker. Nitrogen and oxygen cylinders as well as cylinders containing made-to-order mixtures of nitrogen and oxygen were supplied by Air Products and Chemicals Inc.

Equipment

The reaction was conducted in a 2-L Pyrex resin kettle equipped with a Teflon stirrer driven by a variable-speed electric motor. A General Radio 1538-A Strobotac strobe light was used to measure the number of revolutions of the stirrer. The reactor was placed in a constant temperature bath. The temperature of the bath was controlled by a precision temperature controller Model 245 supplied by Bailey Instrument Company within $\pm 0.5°C$ of the desired temperature.

Dissolved oxygen measurements in the reaction mixture were taken using a YSI Model 54 ARC oxygen meter supplied by Yellow Springs Instrument Co.

Procedures

An amount of wet pulp of predetermined consistency, corresponding to 20 g dry matter, was charged in the reactor with distilled water. A nitrogen-oxygen mixture of a desired ratio was then bubbled in the reaction mixture, under continuous stirring, for about 4 h. A solution of 6.07 g ceric ammonium nitrate was then charged into the reactor. Then, 1 min later, 25.66 g of methyl methacrylate was also injected into the reactor. The reaction was assumed to have started the moment the monomer was injected. The reaction was then allowed to proceed at 45°C and constant stirring speed for 1 h; it was then terminated by injecting the solution of 1.7 g hydroquinone in distilled water. The total volume of the reaction mixture was approximately 2000 mL.

The reaction products (graft copolymer and homopolymer) were filtered and thoroughly washed with distilled water, then dried to constant weight in a vacuum oven and weighed. The homopolymer was subsequently removed by Soxhlet extraction with acetone for about 48 h. The reaction parameters were then calculated as follows:

$$\% \text{ polymer yield (conversion to polymer)} = \frac{D - B}{C \times 100}$$

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

$$\% \text{ grafting efficiency} = \frac{A - B}{D - B} \times 100$$

where: A = dry weight of products after reaction and extraction
B = dry weight of pulp charged in the reactor
C = weight of monomer charged in the reactor
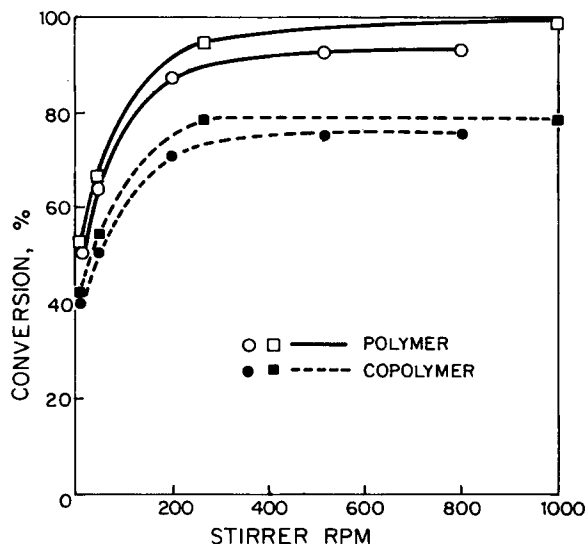D = dry weight of products after reaction

Fig. 1. Conversion as a function of stirrer speed for reactions conducted under pure nitrogen: ○ ●, commercial nitrogen (1 ppm O_2); ☐ ■, as above, passed over copper shavings.

RESULTS

The main objective of this study was to investigate the effects of stirring rate on grafting at different concentrations of oxygen in the reactor atmosphere. All the other reaction parameters were therefore maintained at constant values. The stirrer was designed to provide efficient mixing of all reactants, and it could be driven at constant speeds ranging from as low as 10 rpm to as high as 1000 rpm.

In the first set of experiments, a special purity commercial nitrogen characterized as having less than 1 ppm O_2 was used. The dissolved oxygen (DO) concentration in the reaction mixture was found to be 0.5 ppm, probably due to oxygen originally present in the solution and in the pulp. The conversion results are shown in Figure 1. Both conversion to polymer and conversion to copolymer show an initial increase with rising stirring speed up to about 350 rpm and then remain constant. There is no decrease in conversion observed even at stirring speeds as high as 800 rpm. The maximum polymer yield obtained is just over 90%.

Special precautions to remove all oxygen were taken in the second set of experiments. The nitrogen used in set 1 was further purified by passing it through a heated column (450°C) packed with copper shavings. Furthermore, the monomer and initiator solutions were deoxygenized by bubbling the purified nitrogen through them for about 2 h prior to the reaction. The amount of oxygen dissolved at the start of the reaction was undetectable by the oxygen meter used in this study. The conversion results, also shown in Figure 1, are very similar to the results of the first set, except that a polymer yield of almost 100% was obtained at high stirring speeds. The grafting efficiency obtained in both sets was about 80%, and it was independent of stirring speed.
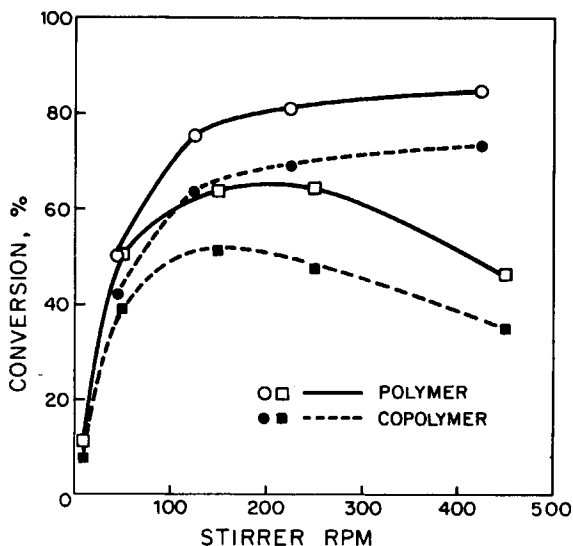
HANNA AND HORNOF

Fig. 2. Conversion as a function of stirrer speed for reactions conducted under 99 and 95% nitrogen: ○ ●, 99% nitrogen-1% oxygen mixture; □ ■, 95% nitrogen-5% oxygen mixture.

The third set of experiments was carried out under an atmosphere of 99% nitrogen and 1% oxygen (by mole). The dissolved oxygen concentration in the reaction mixture was found to be 0.6 ppm. The left-hand sides of the conversion curves shown in Figure 2 remain similar to those of sets 1 and 2, but the maximum polymer yield is only about 80%. A small decrease in conversion is observed at high rpm. It is interesting to note that the grafting efficiency obtained in this set is higher than in the two previous sets (85%), and it appears to be independent of stirring speed.
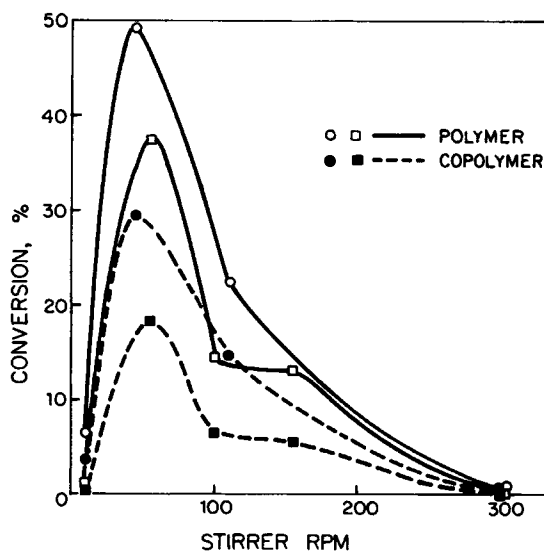

Fig. 3. Conversion as a function of stirrer speed for reactions conducted under 90 and 70% nitrogen: ○ ●, 90% nitrogen-10% oxygen mixture; □ ■, 70% nitrogen-30% oxygen mixture.

The conversion behavior observed with set 3 is augmented in set 4 using a gas mixture containing 95% nitrogen and 5% oxygen (Fig. 2). The dissolved oxygen concentration was found to be 3 ppm. Here the polymer yield increases up to about 65% at 200 rpm and then starts to decrease. The grafting efficiency, however, is lower than in the previous three sets, increasing from 62% at 10 rpm to 77% at 970 rpm.

Further increases in oxygen concentration only amplified the general features that began to appear in sets 3 and 4. The fifth set (Fig. 3) was conducted using a 90% nitrogen–10% oxygen gas mixture (DO = 5.5 ppm). The maximum polymer yield obtained is just under 50% at 45 rpm; the conversion then decreases dramatically with increasing stirring speed and becomes nil at 300 rpm. In the sixth set (Fig. 3), using a gas mixture containing 30% oxygen (DO = 9.2 ppm), the maximum polymer yield is further depressed to about 38% at 55 rpm and very low conversions are observed at stirring speeds above 100 rpm.

It should be noted that the grafting efficiency values obtained in sets 5 and 6 were considerably lower than in the previous four sets. In set 5, the grafting efficiency increases from 54% at 10 rpm to 65% at 100 rpm. In set 6, a very low grafting efficiency of 39% is recorded at 10 rpm, which increases to 49% at 55 rpm and then decreases again to 45% at 100 rpm.

DISCUSSION

The data indicate that when the reaction mixture and atmosphere were completely deoxygenized, the effect of stirring speed was confined to an initial dramatic increase of conversion with increased stirrer rpm, followed by a levelling off of the conversion versus stirring speed curve. The conversion then did not decrease even when the stirring speed was increased to as high as 1000 rpm, which was the physical limit of the system. The initial increase in conversion can be attributed to the enhanced mixing, and thence improved mass transport, associated with an increase in stirrer rpm. Efficient mixing is very important here because the reaction system is heterogeneous and the monomer is only partially soluble in water. The polymer yield data are replotted as a function of dissolved oxygen concentration in Figure 4 for 150 and 300 rpm stirring speed. It is seen that conversion decreases almost linearly with the dissolved oxygen concentration up to 5.5 ppm. At this point the polymer yield is just above 10% at 150 rpm and zero at 300 rpm, and no change is observed when the dissolved oxygen concentration is further increased.

It is thus evident that the concentration of oxygen present strongly influences the magnitude of the effect of agitation on a polymerization. The bell-shaped conversion versus stirring speed curve obtained in the presence of oxygen can be explained in the following manner:

1. The initial increase of conversion with increased stirrer speed is due to better mixing, resulting in improved transport of the monomer to the growing radicals.

2. As the stirrer speed is increased further, the rate of oxygen transport from the reaction atmosphere into the reaction mixture also increases and a point is reached at which the two factors balance each other (a maximum on the conversion versus stirrer speed curve).
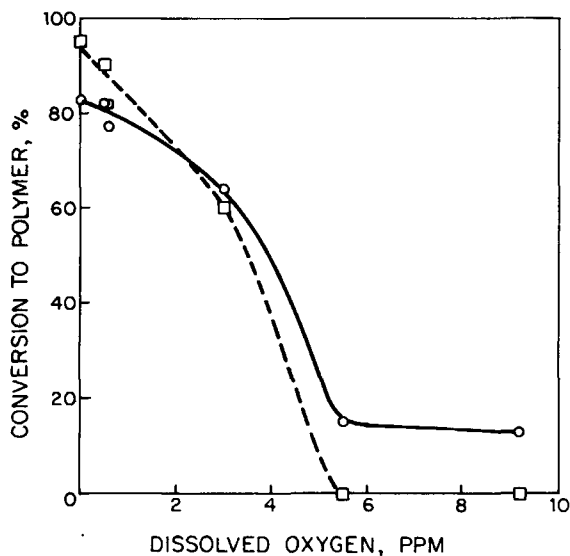
Fig. 4.   Conversion to polymer as a function of dissolved oxygen concentration: ○, at 150 rpm; □, at 300 rpm.

3. If the stirrer speed is increased even higher, any increase in the rate of propagation is far outweighed by the increased inhibition or retardation effects of the oxygen being transported into the reaction mixture.

This scheme is supported by the fact that the position of the maximum shifts to lower rpm when the concentration of oxygen in the reaction atmosphere is increased and that no decrease in conversion at higher stirring speed is observed when the reaction is conducted under pure nitrogen. It is thus possible that the more or less dramatic drop of conversion at higher stirring speeds observed previously[2-5] was at least partly due to small amounts of oxygen introduced into the system in nondegassed pulp and other components of the reaction mixture and by flushing the system with commercial nitrogen of 99.99% purity. Other factors, such as monomer solubility and type of initiator, also play an important role, as is evident from the different shape of conversion versus stirring speed curves obtained in different systems. It should be noted in this context that Mansour and Nagaty[7] observed reduced grafting yields of vinyl monomers under intense agitation even under carefully purified nitrogen. Similar behavior has been reported by Nomura and coworkers[8] for the emulsion polymerization of styrene. In grafting systems of relatively high consistency, such as the system studied here, the actual intensity of agitation probably does not much increase at very high stirring speeds as the whole mass of the reaction mixture tends to rotate with the stirrer paddle. This last effect was reduced but not completely eliminated in the present work by using a special stirrer design that ensured some degree of axial pulp movement at high stirring speeds. Also, the work described here involves only one particular initiation system, and it is doubtful whether it is possible to extend these conclusions to other systems. The work currently in progress is hoped to provide a better understanding of these problems.

References

1. A. Hebeish and J. T. Guthrie, *The Chemistry and Technology of Cellulosic Copolymers*, Springer-Verlag, New York, 1981.

2. T. Graczyk and V. Hornof, *Polym. Prepr.*, **23**(2), 124 (1982).

3. T. Graczyk and V. Hornof, *J. Appl. Polym. Sci.*, **28**, 1371 (1983).

4. T. Graczyk and V. Hornof, *J. Appl. Polym. Sci.*, **29**, 4247 (1984).

5. T. Graczyk and V. Hornof, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 851 (1985).

6. T. Graczyk and V. Hornof, *J. Appl. Polym. Sci.*, **30**, 4175 (1985).

7. O. Y. Mansour and A. Nagaty, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 141 (1974).

8. M. Nomura, M. Harada, W. Eguchi, and S. Nagata, *J. Appl. Polym. Sci.*, **16**, 835 (1972).