

Effect of Stirring on Cellulose Graft Copolymerization. III. Acrylic and Methacrylic Monomers

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Synopsis

Acrylate and methacrylate monomers were grafted onto dissolving pulp by the xanthate process. All the nine monomers tested showed a well-defined dependence of conversion on stirring speed. Total conversion and conversion to copolymer vs. agitator speed curves for each monomer were very similar in shape, but they varied widely from monomer to monomer. For the homologous series acrylate and methacrylate esters, optimum stirring speed was found to increase with increasing the size of the alkyl group. The breadth of the maximum also depended on the type of monomer. Monomers partially soluble in water forming water-insoluble polymers were found to be the most reactive.

INTRODUCTION

Graft copolymerization onto cellulose or wood pulp has been the subject of much research during the past two decades.¹ The effects of many variables (initiator type and concentration, pH, monomer type, temperature) have been studied in great detail, and some general rules have been established. Surprisingly, little attention has been paid to the role of stirring.

It is reasonable to expect that in a heterogeneous reaction such as grafting, where the growing chains are anchored to insoluble cellulose fibers, the effect of stirring would be important. Furthermore, one would expect that the rate of polymer formation would depend on monomer solubility in the reaction medium, as this would govern monomer supply to growing chains. Finally, the character of the growing chain (soluble vs. insoluble) should be also important.

Recent studies published by the present authors^{2,3} have given ample evidence that stirring is indeed important in graft copolymerization reactions. Apart from that, however, the results have been somewhat puzzling. Very similar conversion vs. stirring rate curves were obtained for two completely dissimilar monomers: the water-insoluble hydrophobic styrene and the water-soluble dimethylaminoethyl methacrylate (DMAEM). On the contrary, acrylonitrile and methyl methacrylate behaved quite differently. The present work was undertaken with the aim of elucidating this discrepancy by observing the graft copolymerization behavior of the homologous series of acrylates and methacrylates, and also acrylamide, as monomers.

EXPERIMENTAL

Materials

A dissolving pulp supplied by Zakłady Celulozy i Papieru, Swiecie, Poland, was used as the grafting substrate. The pulp was preserved in a freezer and thawed before use.

The monomers were: ethyl acrylate (EA) (Koch-Light); butyl acrylate (BA) (Koch-Light); ethyl methacrylate (EMA) (Koch-Light); butyl methacrylate (BMA) (Reachim); acrylic acid (AA) (Reachim); methacrylic acid (MAA) (Reachim); methyl methacrylate (MMA) (POCH); methyl acrylate (MA) (BDH); acrylamide (AM) (Serva). All monomers except acrylamide were purified by vacuum distillation and then stored in a refrigerator. All the other chemicals were used such as supplied by their manufacturers.

Polymerization

The xanthate grafting process^{4,5} was employed. All monomers except the two acids were grafted at initial pH 5.0.⁶ Acrylic acid and methacrylic acid were grafted at initial pH 1.2 using the method described by Puissant and Hornof.⁷ The emulsion xanthation process produced xanthated cellulose having $\gamma \cong 11$ (i.e., approximately 11 xanthate groups per 100 glucose units). The copolymerizations were conducted in a 1-L reactor similar to that described in previous work.³ The concentration of cellulose in the reaction mixture was fixed at 10 g/L. A reduced motor with adjustable speed was employed to drive the stirring assembly, and a strobe light was used to measure the number of revolutions of the stirrer.

Product Characterization and Analysis of Results

The homopolymer content of the reaction products was determined by a Soxhlet extraction of 3–4 g samples of the products with suitable solvents: chloroform for the polyacrylates and polymethacrylates, and methanol for polyacrylic and polymethacrylic acid. For the sake of simplicity, only two parameters were used to describe the reaction yield:

(1) Conversion to polymer (polymer yield)

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

represents the total amount of polymer formed (including both homopolymer and grafted polymer) in respect to the amount of monomer charged.

(2) Conversion to copolymer (copolymer yield)

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

represents the amount of polymer chemically bonded to the substrate (i.e., not removable by extraction), also with respect to the amount of monomer charged. In the expressions above, A = weight of dry products after

polymerization and extraction, B = dry weight of pulp charged (corrected for losses occurring during the xanthation and washing processes), C = weight of monomer charged, and D = dry weight of products isolated by filtration after the reaction has been terminated (before extraction).

RESULTS AND DISCUSSION

Acrylate and methacrylate monomers are ideally suited for the objective of this study. Both acrylic and methacrylic acid are water-soluble monomers, but their polymers have highly coiled conformations in the acidic reaction medium and tend to get occluded on the cellulosic substrate.⁷ For the sake of comparison, acrylamide was also used as an example of a monomer which is water-soluble in both monomer and polymer form.

Esters of acrylic and methacrylic acid all form polymers which are insoluble in water. The solubility of the monomeric esters decreases with increasing size of the alkyl radical. Methyl and ethyl acrylates and methacrylates are classified as slightly soluble in water, while the corresponding butyl esters are almost insoluble (0.2 g/dL for butyl acrylate in water). The monomers used in this work thus encompass a broad range of monomer and polymer solubility. Since the parameters reflecting polymer formation depend on how effectively the monomer is transported to the growing chains, it is likely that any dependence on stirring should also become evident from the results.

Figure 1 shows the results obtained with AM as the monomer. Only copolymer yield results are reported as the yield of the water soluble homopolymer was not determined. The conversion to copolymer rises sharply from 0 to 60 rpm and then remains almost constant up to 400 rpm. This is followed by a sharp drop in copolymer formation (400–450 rpm), which becomes more gradual at higher stirrer speed (450–700 rpm). This gradual decrease is similar to that observed with another water-soluble monomer (dimethylaminoethyl methacrylate) in a previous work.³

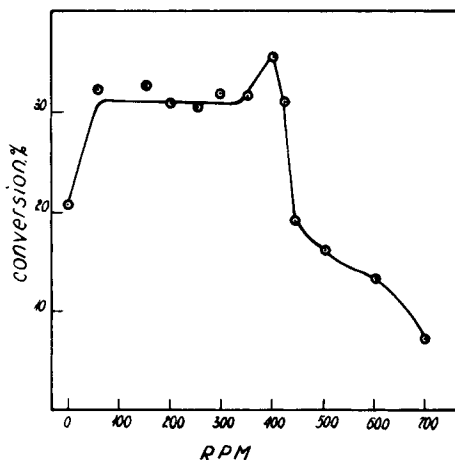


Fig. 1. Conversion of acrylamide to copolymer as a function of agitator speed. Temperature = 45°C; reaction time = 2 h; [AM] = 0.266 mol/L; [H₂O₂] = 0.49 mol/L.

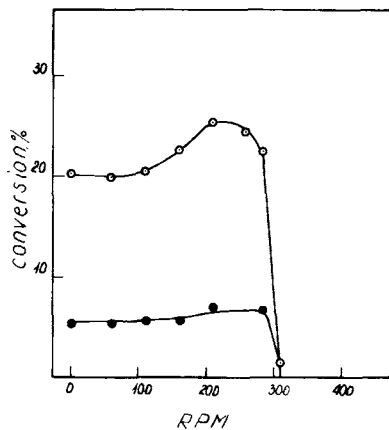


Fig. 2. Conversion of acrylic acid as a function of agitator speed. Temperature = 45°C; reaction time = 1 h; [AA] = 0.133 mol/L; [H₂O₂] = 0.049 mol/L; (○) polymer; (●) copolymer.

The conversion curves obtained for acrylic acid and methacrylic acid are displayed in Figures 2 and 3, respectively. The two sets of curves are not completely identical, although they do show a degree of similarity. A typical feature of these water-soluble monomers is that homopolymers are the predominant product. This is probably caused by the fact that initiation by the xanthate process involves the formation of free radicals ($\cdot\text{OH}$) in the homogeneous (water) phase, which can initiate homopolymerization in solution. The formation of copolymers is further hindered by the repulsive forces between the acid monomer and the similarly charged cellulose-polyacid copolymer.

The conversion curves for the three acrylate esters are shown in Figures 4-6. It is seen that the stirring speed required for maximum polymer for-

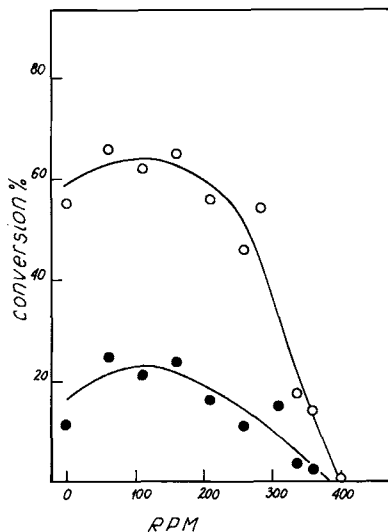


Fig. 3. Conversion of methacrylic acid as a function of agitator speed. Temperature = 45°C; reaction time = 1 h; [MAA] = 0.133 mol/L; [H₂O₂] = 0.049 mol/L; (○) polymer; (●) copolymer.

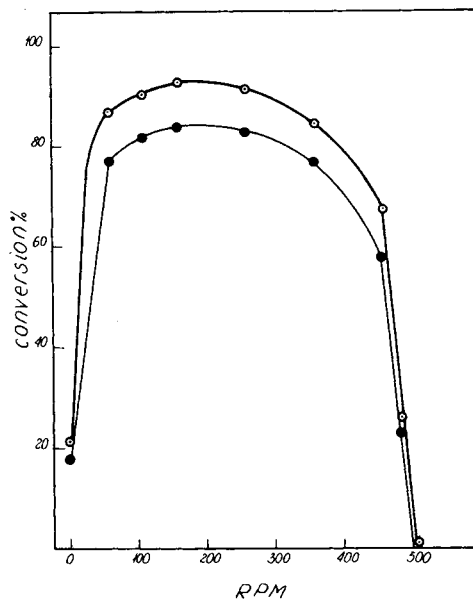


Fig. 4. Conversion of methyl acrylate as a function of agitator speed. Temperature = 25°C; reaction time = 30 min; [MA] = 0.133 mol/L; [H₂O₂] = 0.049 mol/L; (○) polymer; (●) copolymer.

It is interesting to note that MA and BA give curves which are essentially very similar in shape. Ethylacrylate, on the other hand, gives a narrower curve with a maximum at 210 rpm. This is somewhat higher than the

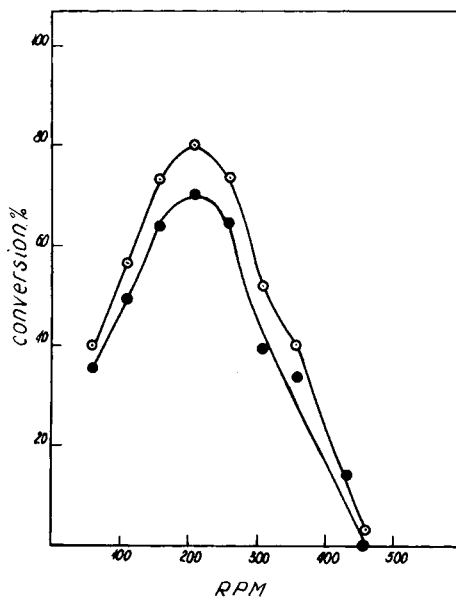


Fig. 5. Conversion of ethyl acrylate as a function of agitator speed. Temperature = 25°C; reaction time = 15 min; [EA] = 0.133 mol/L; [H₂O₂] = 0.0122 mol/L; (○) polymer; (●) copolymer.

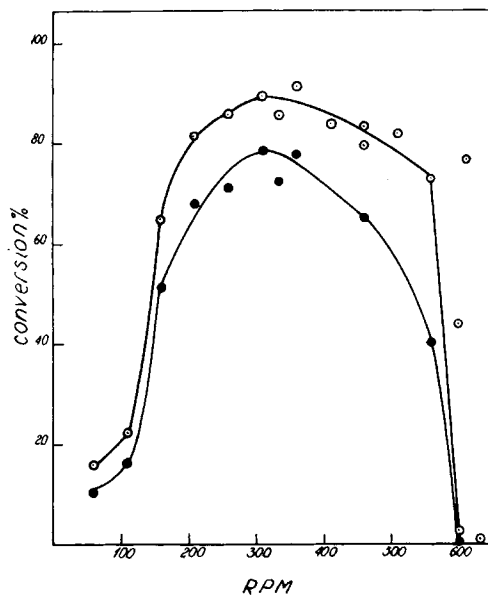


Fig. 6. Conversion of butyl acrylate as a function of agitator speed. Temperature = 25°C; reaction time = 1 h; [BA] = 0.133 mol/L; [H₂O₂] = 0.049 mol/L; (○) polymer; (●) copolymer.

maximum observed for MA (160 rpm) and considerably lower than the maximum observed for BA (310 rpm).

The methacrylate homologous series exhibits a very similar pattern. Once again, the methyl and butyl esters show very broad peaks with maxima at about 160 and 350 rpm, respectively; the ethyl ester shows a more narrow

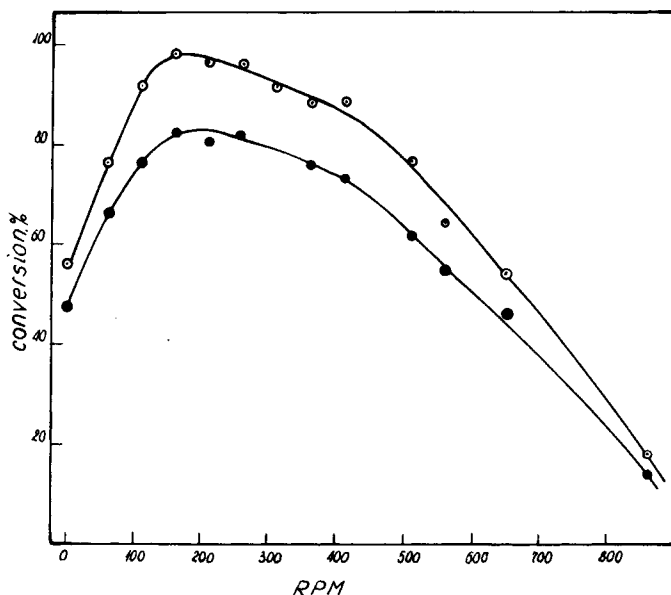


Fig. 7. Conversion of methyl methacrylate as a function of agitator speed. Temperature = 25°C; reaction time = 30 min; [MMA] = 0.133 mol/L; [H₂O₂] = 0.0245 mol/L; (○) polymer; (●) copolymer.

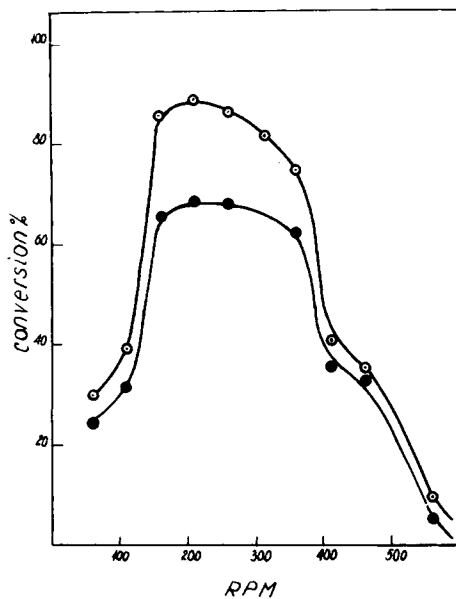


Fig. 8. Conversion of ethyl methacrylate as a function of agitator speed. Temperature = 25°C; reaction time = 30 min; [EMA] = 0.133 mol/L; [H₂O₂] = 0.0122 mol/L; (○) polymer; (●) copolymer.

peak with a maximum at approximately 210 rpm. The maximum is a bit broader with EMA than that obtained with EA, but other than that the two curves resemble each other quite closely.

Under the experimental conditions employed, the total conversion to

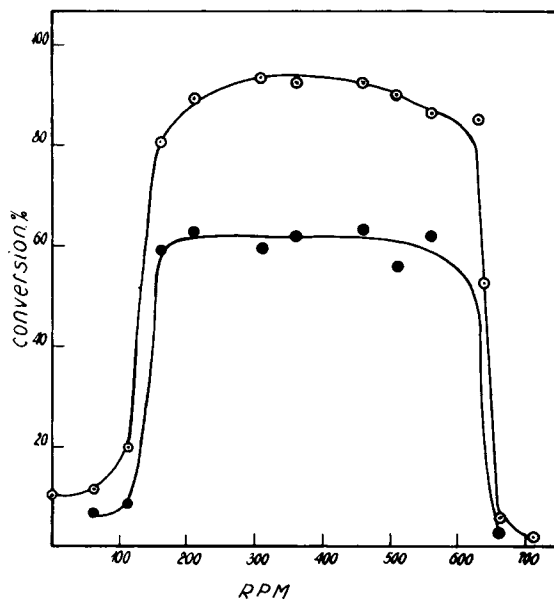


Fig. 9. Conversion of butyl methacrylate as a function of agitator speed. Temperature = 25°C; reaction time = 1 h; [BMA] = 0.133 mol/L; [H₂O₂] = 0.049 mol/L; (○) polymer; (●) copolymer.

TABLE I
Reactivity of Acrylic and Methacrylic Esters in Cellulose Grafting by the Xanthate Process^a

Monomers	Agitator speed ^b (rpm)	Conversion (%)
Methyl acrylate	160	49.3
Ethyl acrylate	210	82.0
Butyl acrylate	310	24.3
Methyl methacrylate	160	81.8
Ethyl methacrylate	210	85.8
Butyl methacrylate	350	9.8

^a Reaction conditions: temperature = 25°C; time = 15 min; [monomer] = 0.133 mol/L; [H₂O₂] = 0.0122 mol/L.

^b Estimated optimum agitator speed.

polymer approaches 100% at optimum stirring speeds (e.g., Figures 4, 6, 7, 8 and 9). The existence of a flat plateau on the curves could thus indicate that simply no more polymer can be formed in the system. The grafting reactivity of several acrylates and methacrylates has been studied previously for several initiation systems,⁸ but without taking into account the effects of stirring. In Table I, the reactivity of acrylate and methacrylate esters is compared. Much shorter reaction time and lower H₂O₂ concentration was used in these reactions in order to ensure that the reactivity of the individual monomers can be compared, and the reactions were conducted at the optimal stirring speeds determined above. It is evident that the reactivities vary widely, with the two water-insoluble monomers being the least reactive. The two ethyl esters and methyl methacrylate are the most reactive monomers, with methyl acrylate showing a lower conversion to polymer.

The foregoing results make it possible to make some general statements on the reactivity of acrylic monomers in graft copolymerizations initiated by the redox system involving partially xanthated cellulose and hydrogen peroxide. The two water-soluble monomer acids have low reactivity, and the predominant product is homopolymer. Among the monomers which are partially soluble in water, reactivity increases as solubility in water decreases (MA < EA, MMA < EMA). When the monomer becomes nearly insoluble in water however, reactivity drops sharply. The low conversion values for BA and BMA are possibly also due to longer induction periods observed with hydrophobic monomers.

Another factor which has been so far neglected is the interaction of grafted polymer chains with the aqueous reaction medium. It is expected, however, that the degree to which the growing chains are solvated in water would have an effect on the rate of polymerization. Further experiments are planned to look into this matter. At the moment, it would appear that the highest reactivity is observed in the case of monomers which are slightly water-soluble but yield water-insoluble, relatively hydrophobic polymer chains. This system ensures a ready supply of monomer to the active ends, but termination through an encounter with water-borne radicals is less likely. The mass transfer phenomena governing the copolymerization and homopolymerization process would undoubtedly be affected by stirring.

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