Graft Polymerization of Methyl Methacrylate onto Wool Using Dimethylaniline/Copper(II) System

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Synopsis

Dimethylaniline (DMA)/Cu^{II}-induced grafting of methyl methacrylate (MMA) onto wool fibres was studied under different conditions. The grafting reaction was found to be influenced by Cu^{II}, DMA, and MMA concentrations as well as polymerization temperature, reaction time, and polymerization medium. While the graft yield increased by increasing the amount of MMA from 100 to 500 mmol/L, maximum grafting occurred at 0.5 mmol/L $CuSO_4$, 10 mmol/L DMA. The graft yield increased by increasing the reaction time from 15 to 150 min and by raising the polymerization temperature from 60 to 80°C. Using dimethylformamide/water and ethyl alcohol/water mixture as a medium for grafting decreased the graft yield, while using isopropyl alcohol/water mixtures increased the graft yield as compared to pure aqueous medium.

INTRODUCTION

Graft polymerization of vinyl monomers onto wool or in the interior of the fiber can be initiated through formation of free radicals on wool backbone. Irradiation methods as well as chemical methods have been used for inducing vinyl grafting onto and deposits of ungrafted polymer in wool.[1-4] Formation of radicals that are capable of initiating polymerization could be achieved by irradiation of wool by high-energy radiation[4-7] or low-energy radiation in the presence and absence of sensitizers.[7-13] Radicals are also formed when wool is present in a polymerization medium containing redox systems,[14-17] ceric ions,[18,19] periodate ions,[20] acetonylacetonato–Cu^{II}–trichloroacetic acid complexes,[21-24] potassium permanganate,[25,26] benzoyl peroxide,[27] or azobisisobutyronitrile.[28]

Dimethylaniline (DMA) has been used as a catalyst with cupric nitrate,[29] benzoyl peroxide,[30] or benzyl chloride[31] for polymerization of vinyl monomers. The use of the DMA–Cu^{II} system as initiator for graft polymerization of methyl methacrylate (MMA) onto nylon[32] and viscose[33] has been reported by us. The ability of this system to induce graft polymerization of MMA onto wool is presented in this article.

EXPERIMENTAL

Materials

Merino wool fibers were Soxhlet extracted with acetone for 24 h, followed by washing with cold, distilled water and dried at ambient conditions.

Methyl methacrylate (MMA) was washed successively with 5% NaOH solution and water, then dried with anhydrous sodium sulfate, and distilled under reduced pressure in nitrogen before use.

Dimethylaniline (DMA) Merck, free from monoethylaniline, was distilled under vacuum in nitrogen atmosphere. The colorless product was preserved under nitrogen in a dark bottle.

Ethyl alcohol, isopropyl alcohol, and dimethylformamide were pure-grade chemicals.

Copper sulfate was B.D.H.-grade chemical.

Procedure

Unless otherwise stated, the graft polymerization reaction was carried out as follows: A conditioned wool sample (0.5 g) was introduced in a 70-ml stoppered Erlenmeyer flask containing 50 ml of a solution at pH 8.3 consisting of water, copper sulfate, DMA, and MMA at a specific temperature. The flasks were immediately stoppered and kept in a thermostat for prescribed times. During the reaction, the wool was kept well immersed in the solution. The fibers were then removed, thoroughly washed, repeatedly Soxhlet extracted with acetone, and dried to constant weight.

The percentage graft yield was calculated from the following equation:

$$\% \text{ graft yield} = \frac{\text{weight of grafted polymer}}{\text{dry weight of original wool sample}} \times 100$$

RESULTS AND DISCUSSION

Cupric Ion Concentration

Previous reports have disclosed that (a) substantial grafting occurred on nylon 6[32] and viscose[33] when both substrates were independently present in a polymerization system containing DMA, MMA, and water; (b) auto-oxidation of DMA via a free radical intermediate is responsible for initiation of grafting; and (c) inclusion of Cu^{II} at certain concentrations in the polymerization system enhances grafting significantly.

When wool fibers were introduced in an aqueous polymerization system containing DMA and MMA (400 mmol/L) at a material-to-liquor ratio of 1:100 and the reaction was allowed to proceed at 70°C for 1 h, neither grafting nor homopolymerization occurred. This is in contrast with the results for nylon 6 and viscose.[32,33]

To achieve grafting on wool, addition of copper sulfate to the DMA/MMA/water system was essential. Thus, copper sulfate at different concentrations was incorporated in the polymerization by two techniques. The first involved addition of copper sulfate to the polymerization system, whereas the second technique entailed impregnation of wool fibers in copper sulfate solution at room temperature for 15 min using a material-to-liquor ratio of 1:100 followed by washing and drying. The copper sulfate-treated wool so obtained was then introduced in the polymerization system.

Figure 1 shows the effect of Cu^{II} concentration on grafting when the latter was performed according to the first technique, whereas results of the graft polymerization obtained with the second technique are shown in Figure 2. It is clear that regardless of the technique employed, inclusion of Cu^{II} in the polymerization
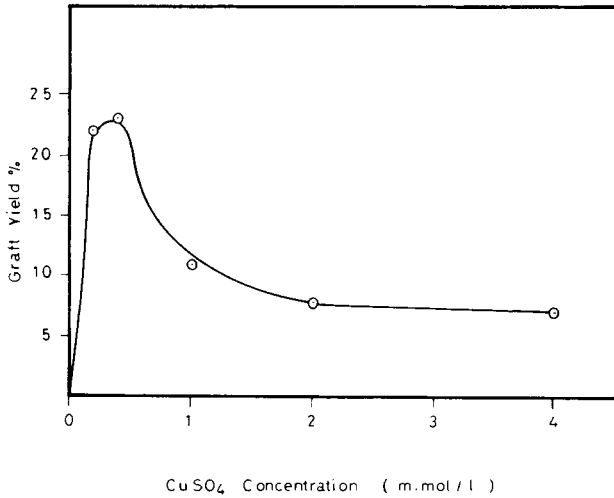
Fig. 1. Variation of percentage graft yield with copper sulfate concentration: MMA, 400 mmol/L; DMA, 10 mmol/L; time, 60 min; temp., 70°C; material:liquor, 1:100.

system enables the DMA to initiate grafting of MMA onto wool fibers. It is also seen that the concentration of Cu^{II} determines the magnitude of grafting. Increasing the Cu^{II} concentration up to 0.5 mmol/L is accompanied by a significant enhancement in the magnitude of grafting when the first technique was used. Thereafter, grafting falls sharply upon further increase in the Cu^{II} concentration. The same situation is encountered with the second technique, except that no sharp decrease in the magnitude of grafting is observed by increasing the Cu^{II} concentration within the range studied. The difference in shape of the dependence of grafting on Cu^{II} concentration may be associated with the different pH of the two Cu^{II} solutions and with the formation of hydrolyzed species in the first technique where the pH is presumably higher.
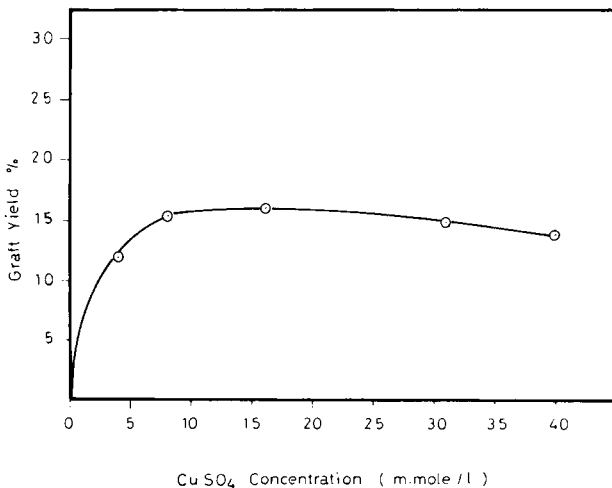

Fig. 2. Effect of pretreatment with different copper sulfate concentrations on percentage of grafting: MMA, 400 mmol/L; DMA, 10 mmol/L; time, 60 min; temp., 70°C; material:liquor, 1: 100.

That grafting occurs only in the presence of Cu^{II} demonstrates the role of Cu^{II} in graft initiation.   It is very reasonable to assume that the presence of Cu^{II} together with DMA can bring about different free radical species in the polymerization system.   Methylanilinomethyl radical can be created as a result of reaction of Cu^{II} with DMA.[29]   In addition to the methylanilinomethyl radical, other radical intermediates formed in the reoxidation of cuprous ion by atmospheric oxygen may participate in the initiation of polymerization.[34–36]

The finding that there is a critical concentration of Cu^{II} for achieving maximum grafting suggests that, besides participation in grafting initiation, the Cu^{II} does take part in the termination of the growing polymer chain of the graft and wool radical, in accordance with the results obtained previously with nylon 6 and viscose.[32,33]

DMA Concentration

Figure 3 shows that no grafting occurs when the concentration of DMA is less than 5 mmol/L.   Above this concentration the graft yield increases significantly when the DMA concentration is increased up to 10 mmol/L, then decreases sharply upon further increase in DMA concentration.   In other words, a DMA concentration of 10 mmol/L constitutes the optimal concentration for grafting MMA onto wool using the DMA–Cu^{II} system.   A similar trend has been noted by us in the DMA–Cu^{II} system-initiated graft polymerization of MMA onto nylon 6 and viscose.[32,33]   However, with the latter two substrates, i.e., nylon 6 and viscose, the optimal DMA concentration amounts to 20–40 and 80 mmol/L, respectively.[32,33]   This again signifies the differences in nature between wool, nylon 6, and viscose which, in turn, are reflected in their amenability to grafting using the polymerization system in question.

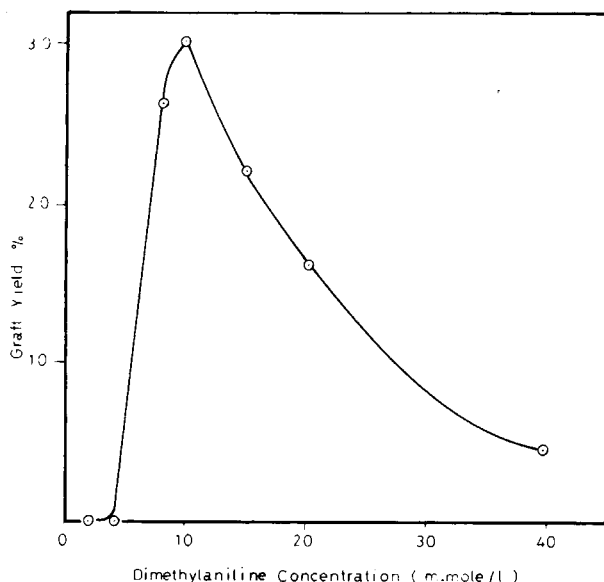The enhancement in grafting by increasing DMA concentration (Fig. 3) con-

Fig. 3. Variation of percentage of grafting with dimethylaniline concentration: MMA, 400 mmol/L; copper sulfate, 0.4 mmol/L; time, 90 min; temp., 70°C; material:liquor, 1:100.
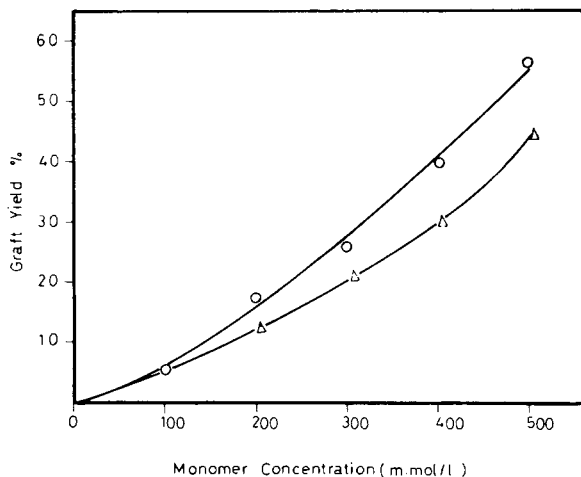
Fig. 4. Variation of percentage of grafting with the amount of monomer: (O) in presence of 20 mmol/L acetic acid; (△) in absence of acetic acid; DMA, 10 mmole/l; CuSO$_4$, 0.4 mmole/L; time, 90 min; temp., 70°C; material:liquor, 1:100.

stitutes direct evidence for participation of the methylanilinomethyl radical in grafting initiation, whereas the decrement in grafting upon using higher DMA concentrations is evidence for involvement of the methylanilinomethyl radical in the termination of grafting. It is also likely that at higher DMA concentration, there is an abundance of methylanilinomethyl radicals, a situation which assists termination by coupling of these particular radicals thereby decreasing grafting.

Amount of Monomer

Figure 4 shows the graft yield vs. MMA amount. It is seen that the graft yield increases outstandingly as the amount of MMA increases (from 100 to 500 mmol/L) within the range studied. This is rather in accordance with previous reports.[32,33]
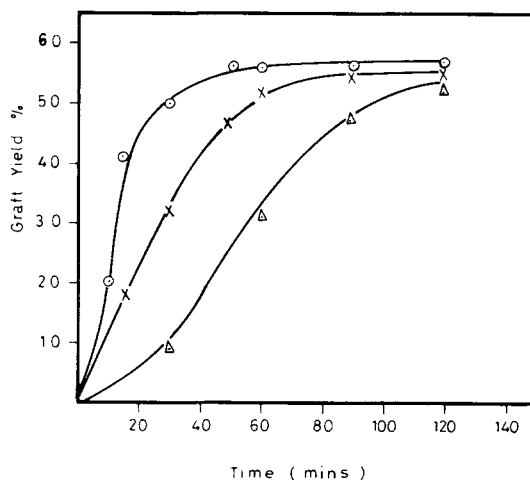

Fig. 5. Effect of temperature on rate of grafting: DMA, 10 mmol/L; CuSO$_4$, 0.4 mmol/L; isopropyl alcohol, 20%, MMA, 200 mmol/L; material:liquor, 1:100, (△) 60°C; (×) 70°C; (O) 80°C.
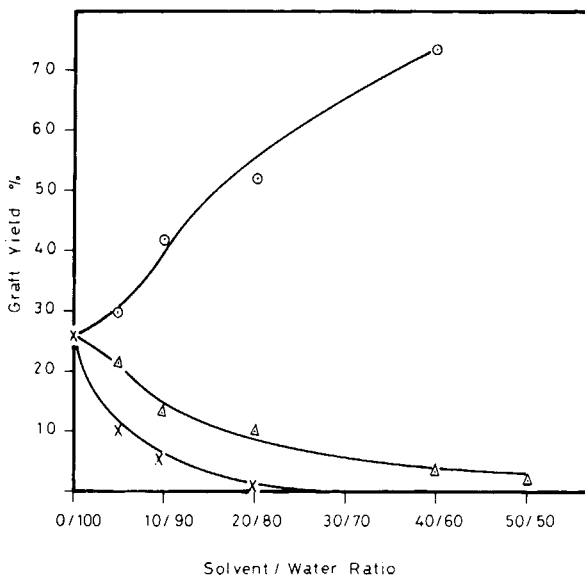
Fig. 6. Variation of graft yield percentage with solvent/water ratio: MMA, 200 mmol/L; DMA, 10 mmol/L; $CuSO_4$, 0.4 mmol/L; time, 60 min; temp., 70°C; material:liquor, 1:100, (O) isopropyl alcohol; ($\triangle$) ethyl alcohol; ($\times$) dimethylformamide.

An interesting feature (Fig. 4) is that incorporation of acetic acid at a concentration of 20 mmol/L in the polymerization system enhances grafting considerably, particularly at monomer concentrations higher than 200 mmol/L. This could be ascribed to the ability of acetic acid to speed up the auto-oxidation of DMA, via hydrogen-bonded complex formation, to yield aminohydroperoxides which function as chain carriers in the autooxidation.[37]

Polymerization Temperature

Figure 5 shows the effect of polymerization temperature on grafting of wool with MMA using DMA–Cu^{II} system as initiator. Obviously, the extent and rate of grafting is higher the higher the temperature, particularly during the initial stages of grafting reaction within the range studied (60–80°C).

It is as well to point out that isopropyl alcohol was included in studying the effect of polymerization temperature. As shown later, using isopropyl alcohol/water mixtures improves the graft yield substantially.

Reaction Time

The effect of reaction time on the graft yield obtained upon grafting of MMA onto wool fibers using the DMA–Cu^{II} system is shown in Figure 5. It is evident that increasing the reaction time causes a significant enhancement in the graft yield, though this enhancement is not so striking during the later stages of the reaction.

Reaction Medium

Figure 6 shows the graft yields obtained when the grafting reaction was carried out in different media. It is seen that using ethyl alcohol/water and dimethyl-formamide (DMF/water) mixtures as media for grafting decreases the graft yield, the decrease being more at higher solvent-to-water ratio. Indeed, using DMF/water at a ratio of 30:70 offsets grafting. The opposite situation is encountered when isopropyl alcohol/water mixtures were used at different ratios within the range studied. The higher graft yields obtained upon using isopropyl alcohol in admixture with water suggest that this particular mixture favors wool swellability and monomer miscibility. In fact, isopropyl alcohol probably increases the grafting by opening up previously inaccessible parts of the wool structure and rendering them accessible to an MMA/isopropyl alcohol mixture.

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