

Wool Graft Copolymers Initiated by Azobisisobutyronitrile

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Synopsis

Grafting of methyl methacrylate onto wool fibers using azobisisobutyronitrile as initiator has been investigated under a variety of conditions. Increasing the monomer concentration caused a significant increase in the graft yields. The same holds good for initiator concentration and reaction time, but to a lower degree. The grafting reaction was favorably influenced considerably by the nature of solvent used; it follows the order methanol > dimethylformamide > benzene. For practical significance, a mixture of water:methanol:DMF (75:24:1) was found to be the most effective medium for grafting. Presence of lithium chloride in the polymerization system favors grafting during the later stages of reaction, whereas presence of ceric sulfate was effective for higher grafting in the initial stages of reaction. Reduction of wool prior to grafting enhanced its ability to grafting; the latter increases in proportion to the thiol content. The opposite holds true for acetylation. Alkali solubility measurements reveal that an interaction between wool and methyl methacrylate in presence of AIBN took place.

INTRODUCTION

The synthesis of graft and block copolymers is very often effected by a chain transfer initiation. This method of grafting generally consists of dissolving a polymer of one kind in the presence of a monomer of another kind and subjecting the mixture to polymerization conditions.

With azobisisobutyronitrile (AIBN), it is established that the grafting reaction proceeds via the production of a macroradical resulting from a chain transfer reaction between a growing chain and the polymer present in the solution. Grafting through a primary radical formed directly on the polymer backbone in the decomposition of AIBN was considered to be unlikely. This is due to the fact that the activation energy for the transfer reaction is higher than that for the propagation step. Thus, it was postulated that the addition of a vinyl monomer onto a primary radical proceeds much more easily than the abstraction of an atom from a polymer molecule.¹

This work was undertaken with the primary objective of studying the conditions affecting the grafting reaction of vinyl monomers with wool fibers under the influence of AIBN. Further, instead of carrying out the graft polymerization in the solvent media used for such type of reactions, it was carried out in a water/solvent mixture for practical significance.

EXPERIMENTAL

Materials

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

Reduction of wool was carried out using thioglycollic acid (TGA) (0.05–0.5*N*) for 24 hr at 25°C (liq. ratio 1:50). Acetylation of wool was carried out using a mixture of acetic anhydride and acetic acid using sulfuric acid as a catalyst.²

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

Procedure

A conditioned wool sample (1 g) was immersed in a 50-ml mixture of water:methanol:DMF (75:24:1) containing a known concentration of AIBN (0.01 mole/l.) at a specific temperature (60°C). The required quantity of freshly distilled MMA was then added (0.4–0.8 mole/l.). The flasks were immediately stoppered and kept in the thermostat for periods between 15 min and 6 hr. The operation was conducted in atmospheric oxygen.

During the reaction, the wool fibers were kept well immersed in the solution. The fibers were then removed, washed well, Soxhleted with acetone, and dried. Extraction with acetone and drying were repeated to constant weight. Calculation of the percentage grafting (i.e., weight add-on) was based on dry weight.

Treatment of wool with AIBN solution was carried out under conditions identical with those described above, except that MMA was absent.

Analysis

Thiol Content. The —SH content of reduced wool was estimated colorimetrically according to the modified Shinohara method.³

Acetyl Content. The acetyl content of acetylated wool was estimated volumetrically according to the procedure described by Elliott and Speakman.⁴

Alkali Solubility. The alkali solubility was carried out by treating wool samples (1 g) with 100 ml 0.1*N* NaOH solution for 1 hr at 65° with occasional shaking.⁵

RESULTS AND DISCUSSION

Previous studies have shown that AIBN could be used for inducing graft polymerization of styrene onto wool.⁶ However, studies were confined to the effect of the concentration of AIBN in solution. Hence, the

polymerization reaction of a vinyl monomer in the presence of wool was carried out under a variety of conditions to discover those optimal for grafting.

Reaction Medium

Attempts have been made to select the most suitable medium for the graft polymerization of MMA to wool fibers. Figure 1 shows the graft yields obtained when various solvents or water/solvent mixtures were used. It is clear that with the three solvents studied, i.e., methanol, dimethylformamide (DMF), and benzene, appreciable amount of graft formation was achieved. However, methanol was effective for high grafting because of the readiness of methanol to penetrate into the pores of wool fibers. As a result, swelling of the inner structure of wool occurred, thereby facilitating the diffusion of monomer, initiator, and growing chain into the wool. The ultimate effect on this certainly favors graft formation.

The lesser effectiveness of DMF and benzene might be traced back to the termination of the graft polymer radical and wool backbone radical via chain transfer to solvent, thus lowering the molecular size of the graft.^{7,8} Furthermore, because methanol is a nonsolvent of poly(methyl methacrylate) (PMMA), it is likely that acceleration phenomenon due to gel effect occurred.^{9,10} This is substantiated by the fact that DMF, which is also a nonsolvent of poly(methyl methacrylate), brings about a graft yield which is higher than that of benzene, which is a solvent of PMMA.

The effect of using water/solvent mixture as a medium for grafting is also shown in Figure 1. Although grafting occurred even in absence of solvent, yet the graft yield was quite low. This could be increased by using a water/solvent mixture containing more than 10% solvent. Regardless of the solvent employed, the grafting reaction proceeded in proportion to the ratio of solvent in the mixture. Here, too, water/methanol

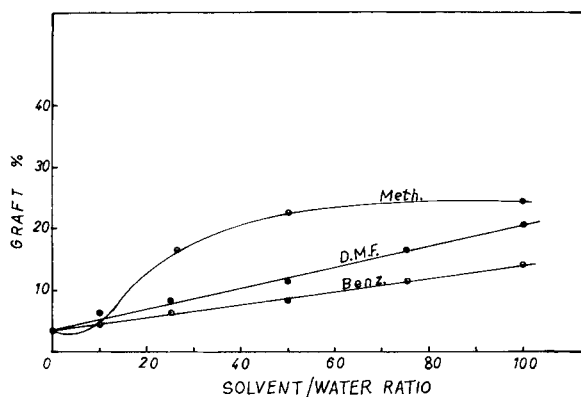


Fig. 1. Effect of type of solvent on grafting initiated by azobisisobutyronitrile (0.01 mole/l. AIBN; 0.4 mole/l. MMA; 60°C; 6 hr grafting; liquor ratio 1:50): (—●—) methanol; (—●—) dimethylformamide; (—○—) benzene.

mixture produces higher grafting than water/DMF and water/benzene mixture, particularly at higher water ratios.

Initiator and Monomer Concentration

It has been disclosed above that DMF is an effective initiator for graft polymerization of MMA to wool fibers in a water/solvent mixture. From the data given in Figure 1, one may conclude that a medium of 75 parts water and 25 parts methanol would prove of practical value. A more favorable medium was found to consist of 75 parts water, 24 parts methanol, and 1 part DMF; hence this is the composition of the medium for most of the results unless otherwise stated.

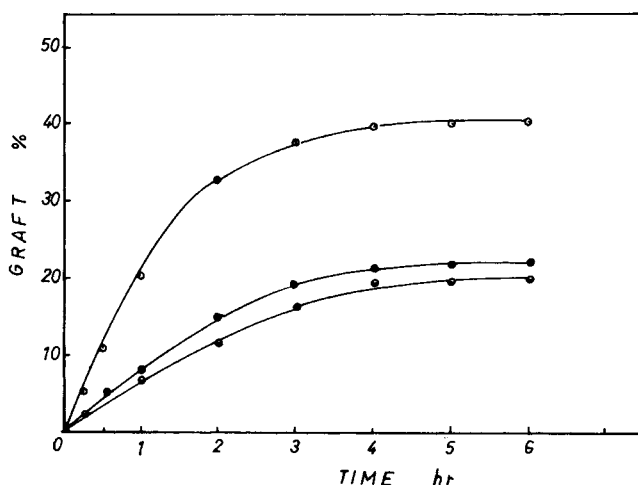


Fig. 2. Effect of monomer and initiator concentration on the graft yield. (60°C; 25% methanol; liquor ratio 1:50): (—○—) 0.4 mole/l. MMA, 0.01 mole/l. AIBN; (—●—) 0.4 mole/l. MMA; 0.02 mole/l. AIBN; (—○—) 0.8 mole/l. MMA; 0.01 mole/l. AIBN).

Figure 2 shows that the rate of grafting depends on the concentrations of initiator and monomer; and the higher the concentration, the greater the rate of grafting became. But the monomer concentration was more effective than the initiator concentration, showing that a small quantity of initiator is enough for efficient grafting.

Time of Polymerization

The graft per cent as a function of reaction time is shown in Figure 2. It is apparent that the extent of grafting increases as the time goes on, and then levels off. Leveling off of grafting could be attributed to a rapid fall in the concentration of monomer and initiator as well as to a decrease in the available sites for grafting on the wool molecule.

Addition of Lithium Chloride

It has been reported that the presence of lithium salts in the polymerization of acrylonitrile by AIBN has a pronounced effect on the polymerization, leading to an increase in the rate and the degree of polymerization.¹¹ Thus, it appears of interest to study the effect of lithium chloride on the grafting reaction. For this, a number of experiments were carried out where the graft polymerization of MMA to wool fibers was initiated by AIBN in the presence of various amounts of lithium chloride.

The dependence of the extent of grafting on the lithium chloride concentration is shown in Figure 3, where it is plotted versus the square root of lithium chloride concentration. The extent of grafting increases with

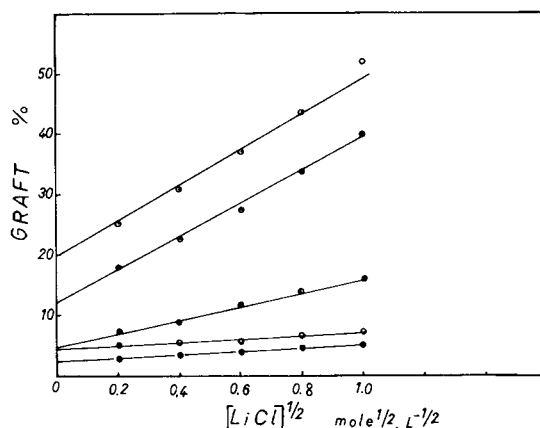


Fig. 3. Dependence of grafting initiated by AIBN on lithium chloride concentration (0.01 mole/l. AIBN; 0.4 mole/l. MMA; 60°C; liquor ratio 1:50, 25% methanol): (—●—) 15 min; (—●—) 30 min; (—●—) 1 hr; (—●—) 3 hr; (—○—) 4 hr.

increasing lithium chloride concentration only when the grafting reaction is allowed to proceed for a sufficient time. Little effect of lithium chloride on the extent of grafting was observed when the polymerization time was 30 min or less. The presence of lithium chloride in vinyl polymerization has been reported to cause an increase in the ratio of the rate of propagation/rate of termination.¹¹ Thus, it is likely that physical absorption of lithium chloride on wool fibers requires a time of at least 30 min. At this end, lithium chloride would be expected to open up more initiating sites on the wool backbone and may reduce the rate of termination of the growing polymer chain.

Addition of Ceric Sulfate

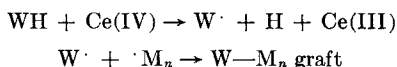
It has been reported that ceric sulfate and ceric ammonium nitrate are capable of initiating vinyl graft copolymerization to wool, and it was postulated that the grafting was initiated by a primary radical generated on the wool backbone perhaps via formation of chelate compound between wool

TABLE I
The Combined Effect of AIBN and Ce (IV) as Initiators on Graft Yield^a

Time of treatment, hr	AIBN (0.01 mole/l.)	Ce(IV) (0.05 <i>N</i>)	Combined catalysts (0.01 mole/l. AIBN + 0.05 <i>N</i> ceric)
1/4	2.0	11.6	14
1/2	5.2	12.6	30
1	6.6	14.4	36

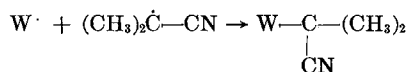
^a Grafting reaction was performed at 60°C, 0.4 mole/l. MMA, liquor ratio, 1:50.

and ceric ions.¹² With AIBN, on the other hand, it was established that grafting proceeds via a chain transfer reaction between a growing polymer chain and the polymer to be grafted.¹³ Thus, the presence of both initiators in a graft polymerization system would be worthy of studying because in a complex system like this, a variety of possibilities may occur. First, the primary free radicals formed on the wool backbone by the action of ceric ions may couple with a growing polymer chain brought about under the catalytic influence of AIBN. Consequently, an enhancement of the graft yield would be expected:

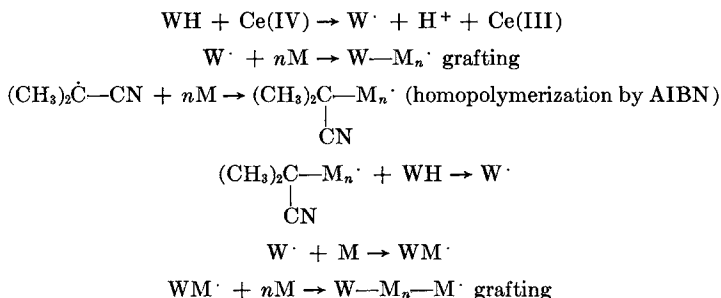


where WH is wool and M_n represents a growing polymer chain.

Secondly, the primary free radicals caused by ceric attack on the wool backbone may be terminated by the AIBN decomposition product:



This leads to a decrease in the graft formation. Third, the two initiators may act each in its own way, with a resultant graft yield equal to the total grafting obtained when the two initiators were used independently:



To check the validity of these assumptions, three runs of experiments were performed. In the first, the grafting reaction was initiated by AIBN. In the second, the use of ceric ion technique was employed.¹² The third experiment consists of initiating grafting by the utilization of AIBN together with ceric sulfate.

The data of graft yield shown in Table I validate only the first expectation where the graft yield under the combined catalytic effect of Ce(IV) and AIBN is higher than the total grafting obtained when the two initiators are used separately. However, the second possibility cannot be ruled out.

Pretreatment with Initiator

In these experiments, wool fibers were treated with the initiator solution for various intervals of time before addition of the monomer. After the desired pretreatment period, monomer was added and the grafting reaction was allowed to proceed for 3 hr. Results of these experiments are given in Figure 4. Increasing the pretreatment time up to 60 min caused an enhancement in the graft yield. Further increase in the pretreatment time lowered the graft yield.

During the time of pretreatment, there is a chance for the initiator to penetrate into the fibers and reach the proximity of wool molecules. Decomposition of the initiator in situ would be advantageous in producing primary radicals $[(\text{CH}_3)_2\dot{\text{C}}-\text{CN}]$ which attack the monomer after being added. As a result, polymer chains are initiated wherever the initiator decomposes. The effect of this is to bring about an increased amount of graft formation, since the growing polymer chains would be in the proximity of the wool molecules.

It appears that a pretreatment time of 60 min constitutes an optimum. Beyond it, vitiation of the primary free radicals resulting from the decomposition of AIBN seems to occur, thereby lowering the graft yield. However, these yields are still higher than that obtained when initiator, monomer, and wool are added together. For this reason, it was considered of

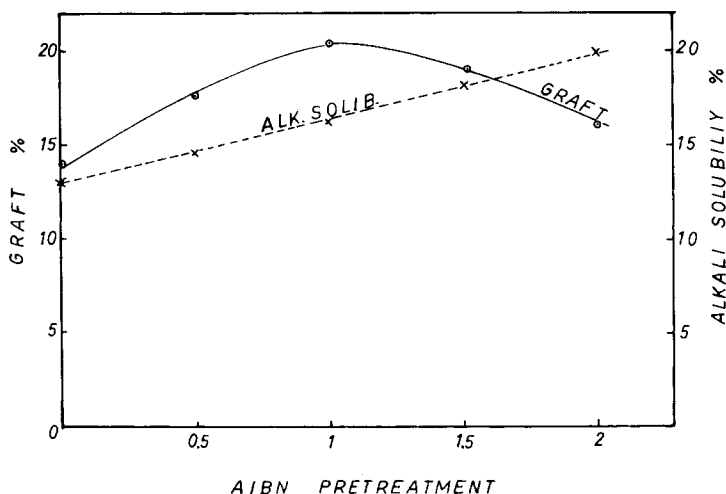


Fig. 4. Effect of time of pretreatment of wool with AIBN on graft yield and alkali solubility of wool: (—○—) grafting, 0.01 mole/l. AIBN; 0.4 mole/l. MMA; 60°C; 3 hr liquor ratio 1:50; (—×—) alkali solubility of pretreated wool.

importance to elucidate the degradative effect of AIBN on the wool fibers. Figure 4 shows the alkali solubility for wool treated with AIBN in the presence of atmospheric oxygen for different periods. Obviously, the degradation of wool, as measured by the alkali solubility, increases as the duration of AIBN treatment increases. This suggests that the AIBN being decomposed to free radicals, $(\text{CH}_3)_2\dot{\text{C}}-\text{CN}$, adds oxygen and attacks the wool molecules thereby causing wool degradation. However, the extent of degradation is much less than with other initiators.¹³

Chemical Modification of Wool

The effect on the graft polymerization reaction of the physical and/or chemical changes in the wool structure brought about by its reduction or acetylation was investigated. AIBN was used as initiator using the conventional method of grafting, i.e., initiator, monomer, water/methanol/DMF mixture (75:24:1), and wool were mixed simultaneously.

Reduction of wool with TGA is well known to increase considerably its thiol content ($-\text{SH}$ groups). The reduced wool would, therefore, be expected to acquire higher graft yields owing to the easy abstraction of the hydrogen atom of the $-\text{SH}$ group via a chain transfer process. In other words, the reduced wool is a very good transfer agent compared to the untreated wool. Indeed, the graft yields obtained with reduced wool are considerably higher than that of unreduced wool. This may be realized from Figure 5. The figure also shows that the graft yield increases with increase in the thiol content of wool. However, the influence of the relatively great swellability of reduced wool cannot be neglected.

Figure 6 shows the graft yield obtained with wool having different acetyl contents. It is apparent that as the acetyl content increases, the graft yields decrease. This is observed at various times of grafting. Introducing acetyl groups in the wool molecules has two effects: (a) blocking some of the amino and hydroxyl groups (possible sites for grafting) in the

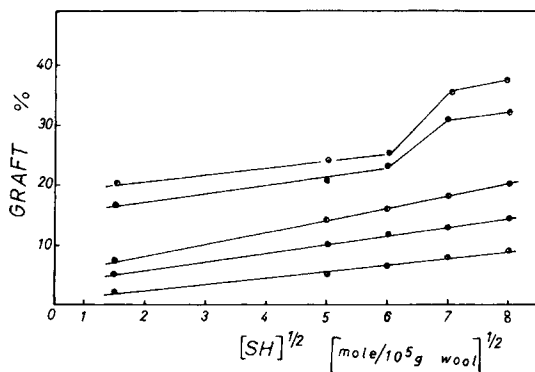


Fig. 5. Relationship between thiol content of reduced wool and graft yield (0.01 mole/l. AIBN; 0.4 mole/l. MMA; 60°C; liquor ratio 1:50; 25% methanol): (—●—) 15 min; (—●—) 30 min; (—●—) 1 hr; (—●—) 3 hr; (—○—) 4 hr.

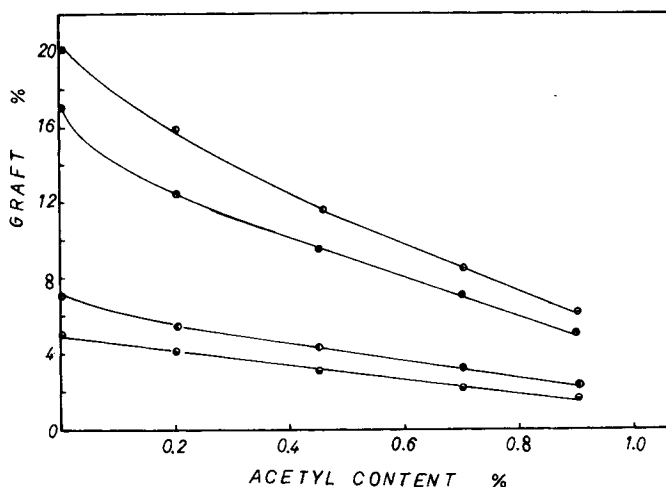


Fig. 6. Graft yield as a function of acetyl content of modified wool (0.01 mole/l. AIBN; 0.4 mole/l. MMA; 60°C; liquor ratio 1:50; 25% methanol): (—●—) 30 min; (—●—) 1 hr; (—●⊥) 3 hr; (—○—) 4 hr.

wool molecule, and (b) lowering the swellability of wool fibers. Both effects lead to decreased grafting.

Alkali Solubility

Figure 7 shows the rates of alkali solubility of poly(methyl methacrylate) grafted wool, untreated wool, and a physical mixture of wool and homopoly(methyl methacrylate). The alkali solubility was performed for various intervals of time by following a standard procedure.⁵ It is appar-

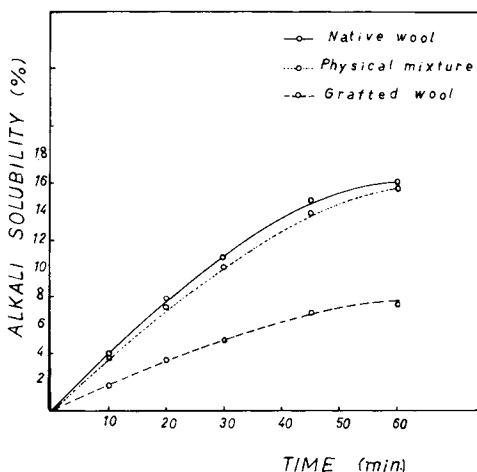


Fig. 7. Rate of alkali solubility of native wool, physical mixture of wool and homopoly(methyl methacrylate), and grafted wool (0.1N NaOH solution, 65°C; liquor ratio 1:100).

ent that the rates of the alkali solubility of the physical mixture and the untreated wool are comparable, whereas that of the grafted wool is significantly lower. This may be taken as an indication that an interaction has occurred between wool and methyl methacrylate in the presence of AIBN.

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Received August 23, 1972

Revised November 17, 1972