

## Azobisisobutyronitrile-Induced Vinyl Graft Polymerization onto Nylon 66

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### Synopsis

The presence of nylon 66 during polymerization of methyl methacrylate (MMA) under the influence of azobisisobutyronitrile (AIBN) produces a nylon-PMMA graft copolymer. The copolymerization reaction is greatly influenced by the reaction medium, temperature and time of the reaction, concentration of MMA, and addition of metallic ions. Polymerization in pure organic solvents brings about little or no grafting. Incorporation of water into the polymerization system enhances grafting significantly. A reaction medium of a water/solvent mixture in a ratio of 75:25 constitutes the most favorable medium for the grafting reaction in question. Of the solvents examined, methanol, ethanol, propanol, isopropanol, and acetone work extremely well. Increase in reaction time is accompanied by an increase in the graft yield. The same holds true for the reaction temperature; the graft yield is much higher at 70 than at 50°C and follows the order 70°C > 60°C > 50°C. Increasing MMA concentration also causes considerable enhancement of the graft yield. The presence of 0.01M cupric sulfate in the polymerization system brings about an eightfold increase in the graft yield, whereas the presence of ferric sulfate at the same concentration causes a sixfold increase. The mode of initiation of grafting seems to be different in the presence of metallic ions than in their absence. A mechanism for the reactions involved in both cases has been proposed.

### INTRODUCTION

The use of azobisisobutyronitrile (AIBN) as initiator for vinyl graft polymerization onto cellulose and modified celluloses<sup>1-4</sup> as well as wool<sup>5</sup> has been reported. The grafting reaction has been postulated to proceed through production of macroradicals resulting from a chain transfer reaction between a growing vinyl homopolymer chain and the substrate present in the polymerization solution. However, grafting onto nylon with AIBN as initiator has not been reported to the authors knowledge.

This work presents the results of studies of the grafting of methyl methacrylate (MMA) onto nylon 66 induced by AIBN. Furthermore, the influence of metallic ions, namely, ferric ions and cupric ions, on the grafting reaction is examined.

### EXPERIMENTAL

Nylon 66 fibers, kindly supplied by the Artificial Silk Company, Alexandria, were used as received without further purification.

Methyl methacrylate (MMA) was purified in a manner similar to that previously described.<sup>4,6</sup> Azobisisobutyronitrile (AIBN) was also purified as described elsewhere.<sup>5</sup> The copper sulfate and ferric sulfate used were analytical grade.

Unless otherwise stated, the polymerization reaction was carried out as follows. The nylon sample (1 g) was introduced into an erylenmeyer flask containing 100 ml of the reaction solution. The latter consisted of solvent, water, monomer, and AIBN. The flask was stoppered and kept in a thermostate and the contents stirred occasionally during polymerization. The experimental conditions are detailed in the text. The grafting product was thoroughly washed with water, given a light soaping to remove the loosely adhered homopolymer, and dried in an oven at 105°C. The dried samples were then repeatedly Soxhlet extracted with benzene until constant weight. The graft yield (increase in weight) was based on the dry weight of the nylon backbone.

## RESULTS AND DISCUSSION

Previous studies in this laboratory have indicated that grafting onto cellulosic materials<sup>4</sup> and wool<sup>5</sup> using AIBN as initiator can be carried out in a solvent/water mixture. These studies<sup>4,5</sup> have also revealed that the magnitude of grafting varies significantly with the type and the amount of solvent used.

Table I shows the graft yields obtained with nylon 66 when the grafting reaction was initiated by AIBN in different solvent/water mixtures. It is clear that regardless of the solvent used, an increase in the amount of solvent in the solvent/water mixture is accompanied by a decrease in the graft yield. Except in the case of butanol, substantial grafting occurred with a water/solvent mixture containing 25% of ethanol, propanol, isopropanol, or acetone. The graft yield was quite poor when a solvent/water mixture of 75:25 was employed. Indeed, a solvent/water mixture containing 25% of any of the mentioned alcohols or acetone constitutes the optimal reaction medium. In the latter the monomer and initiator seem to be completely miscible and the swelling of nylon by water is not hindered by the presence of the solvents. As a result, access to and diffusion of monomer and initiator are simplified, thus favoring grafting. The significant fall in the graft yield upon using a greater amount of the solvent in the reaction medium support this.

‡ An acetone/water mixture produced graft yields comparable with those of the alcohols. This is expected since the structure of acetone, because of the keto-

TABLE I  
Effect of Reaction Medium on Grafting Methyl Methacrylate onto Nylon

Solvent	Graft yield, %		
	Solvent/water: 25:75	50:50	75:25
Methanol	13.5	10.0	3.5
Ethanol	14.0	8.5	3.0
Propanol	14.0	8.0	3.6
Isopropanol	15.0	10.0	3.2
Acetone	13.8	9.0	4.0
Butanol	7.2	1.6	0.0

AIBN, 0.01M; MMA, 3%; material/liquor ratio, 1:100; temperature, 60°C; reaction time, 3 hr.

enol tautomerism, is somewhat similar to the structure of the alcohols. The failure of butanol to bring about substantial grafting could be associated with its hydrophobic character, compared to the other alcohols, which adversely affects the swelling of nylon by water. This certainly hinders monomer access to reactive sites on the nylon backbone.

### Monomer Concentration

Figure 1 shows the graft yields obtained with nylon at different concentrations of MMA. Obviously, for a given reaction time the extent of grafting is higher at higher MMA concentration. For instance, graft yields of 4 and 8.3% were achieved after 3 hr with a monomer concentration of 1 and 2%, respectively. However, a graft yield of 14% was achieved when 3% MMA was used under the same conditions.

The significant enhancement of grafting with the use of high monomer concentration could be associated with the favorable effect of the monomer concentration on producing a larger number of growing polymer chains, which in turn increases the possibility of hydrogen abstraction from nylon via chain transfer to give rise to nylon macroradicals. This and the availability of monomer in the vicinity of nylon would certainly facilitate grafting. It is also very likely that at higher MMA concentration, complexation of nylon with MMA occurs. Such complexation causes an enhancement in MMA reactivity due to formation of a donor-acceptor complex in which the uncomplexed MMA, though normally an electron acceptor, behaves as a donor relative to the complexed MMA which was converted to a stronger acceptor.<sup>7</sup> In addition, the gel effect which is brought about at high monomer concentration because of the solubility of PMMA in its own monomer seems to play a significant role here. The role of the gel effect<sup>4</sup> is to promote grafting through hindrance of the termination of the growing polymer chain radicals by coupling as well as increasing the swellability of nylon. The effect of increasing nylon swellability is to assist diffusion of low molecular weight growing homopolymer chains to the interior of nylon for a transfer reaction. It also facilitates diffusion of monomer to the growing grafted chains and active sites on nylon backbone, thereby leading to higher grafting.

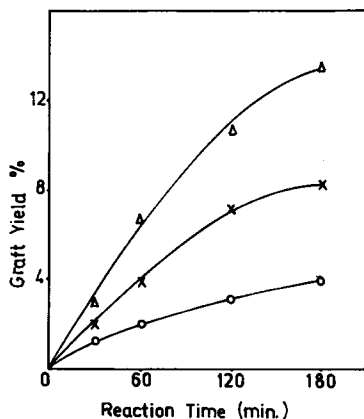


Fig. 1. Variation of the graft yield with monomer concentration and reaction time: (○) 1% MMA; (×) 2% MMA; (△) 3% MMA; AIBN, 0.01M; methanol/water, 25:75; temperature, 60°C; material/liquor, 1:100.

### Initiator Concentration

The effect of AIBN concentration on the graft yield was investigated over a range of 0.005–0.03*M*. It was found that within this range the AIBN concentration has practically no effect on the graft yield. This is in contrast with grafting onto cellulose<sup>4</sup> but tallied, to a considerable extent, with grafting onto wool.<sup>5</sup>

### Reaction Time

The effect of reaction time on grafting nylon with MMA is to bring about a considerable increase in the graft yield, as shown in Figures 2 and 3. The increased grafting by prolongation of the polymerization reaction could be anticipated in view of the favorable effect of duration on: (a) decomposition of AIBN, (b) diffusion and adsorption of the monomer on nylon fibers, (c) number of the growing homopolymer chains in the vicinity of nylon, (d) diffusion of low molecular weight growing homopolymer chains, (e) termination of the homopolymer chain radicals by abstraction of hydrogen atom from nylon to create

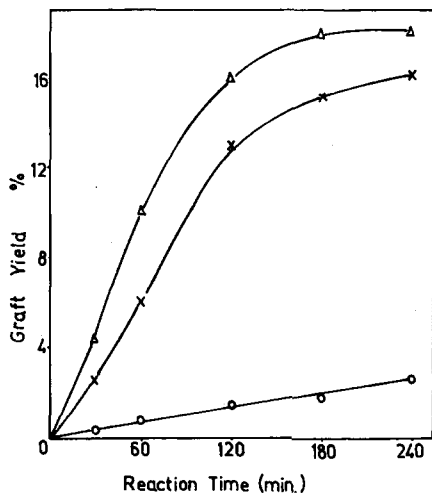


Fig. 2. Effect of temperature on grafting MMA onto nylon: (○) 50°C; (×) 60°C; (Δ) 70°C; AIBN, 0.01*M*; MMA, 3%; isopropanol/water, 25:75; material/liquor, 1:100.

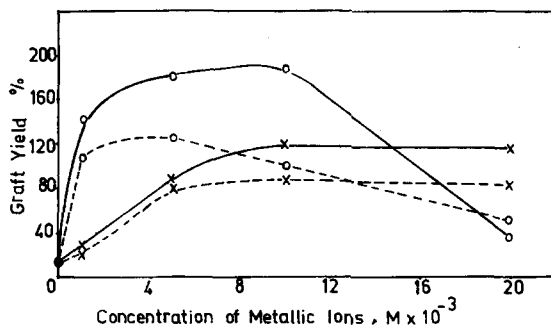


Fig. 3. Effect of metal ions on grafting MMA onto nylon with AIBN as initiator: (—) method I; (---) method II; (●) in absence of metal ions; (○) in presence of  $Cu^{2+}$ ; (×) in presence of  $Fe^{3+}$ ; AIBN, 0.01*M*; MMA, 3%; temperature, 70°C; isopropanol/water, 25:75; reaction time, 3 hr; material/liquor, 1:100.

active sites on the latter, and (f) initiation and propagation of the graft. The combined effect of increasing such parameters is definitely higher grafting.

### Reaction Temperature

Figure 2 shows the effect of temperature of the polymerization reaction on the rate of grafting of MMA onto nylon. At 50°C the rate of grafting is very low and the maximum graft yield obtained, within the range studied, is quite poor. A marked increase in the grafting rate as well as the maximum graft yield may be achieved by raising the polymerization temperature to 60°C. Further increase in both the rate of grafting and the maximum graft yield is brought about at 70°C. Moreover, at 60 and 70°C the rate of grafting is characterized by an initial fast rate followed by a slower rate, whereas at 50°C the graft yield increases gradually as the reaction time increases. These findings are again in contrast with those reported for grafting MMA onto cellulose using AIBN as initiator.<sup>4</sup>

The low graft yields obtained at 50°C suggest that nylon is a very poor transfer agent at this temperature. However, the relatively slow rate of AIBN decomposition at 50°C cannot be completely ruled out. On the other hand, the enhancement of grafting as the temperature increases could be attributed to accentuation in swelling of nylon, an increment in the solubility of the monomer and its diffusion into nylon fibers, the faster rate of AIBN decomposition, favorable chain transfer reaction between growing homopolymer chain and nylon, and initiation and propagation of the graft.

An additional point of interest is that the slower rate of grafting in the later stage of the reaction at 60 and 70°C suggests that termination at this stage of the growing homopolymer chains occurs essentially by means other than abstraction of hydrogen from nylon. This and the depletion in monomer and initiator concentration as the reaction proceeds would account for the leveling off of grafting, particularly at 70°C.

### Effect of Metallic Ions

It has been reported that the presence of cupric ions during grafting of MMA onto cellulose<sup>7-9</sup> and wool<sup>10</sup> significantly improves the graft yield when the polymerization is initiated via a free-radical mechanism using redox systems. In order to see whether this would also be the case when the grafting reaction is induced by a chain transfer mechanism, the influence of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  ions on grafting nylon 66 with MMA with AIBN as initiator was examined. Incorporation of the said metallic ions in the polymerization system was carried out according to the methods given below.

#### *Method I*

The nylon sample (1 g) was immersed in 100 ml of an isopropanol/water mixture (25:75) containing a known concentration of either cupric sulfate or ferric sulfate for 20 hr at room temperature. The MMA monomer (3 g) and AIBN (0.01M) were then added and the grafting reaction was allowed to proceed at 70°C for 3 hr.

#### *Method II*

In this method nylon, MMA, AIBN, and the metallic ions were admixed and they were used at concentrations identical to those used in method I. The

graft polymerization reaction was also conducted for 3 hr at 70°C. The results obtained are shown in Figure 3.

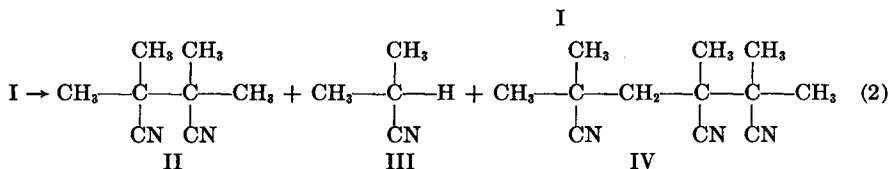
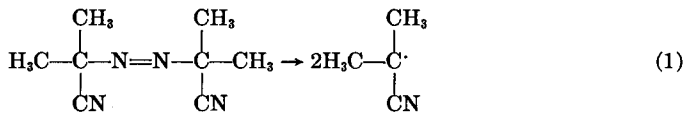
It is clear (Fig. 3) that increasing the cupric sulfate concentration is accompanied by an outstanding increase in the graft yield until a concentration of 0.01*M* cupric sulfate is reached. Beyond this the graft yield decreases sharply as the cupric sulfate concentration increases. This is observed with methods I and II; however, method I proves to be better than method II in producing higher grafting. With Fe<sup>3+</sup>, on the other hand, the graft yield increases with increasing ferric sulfate concentration from 0.001 to 0.01*M*. Further increase in the ferric sulfate concentration has practically no effect on the graft yield regardless of the method used.

It is also obvious (Fig. 3) that though maximum grafting occurred at ferric sulfate and cupric sulfate concentrations of 0.01*M*, the maximum graft yield obtained with cupric sulfate was significantly greater than that of ferric sulfate. That is, while the presence of 0.01*M* cupric sulfate causes about an eightfold increase in the graft yield, the presence of ferric sulfate at the same concentration brings about a sixfold increase.

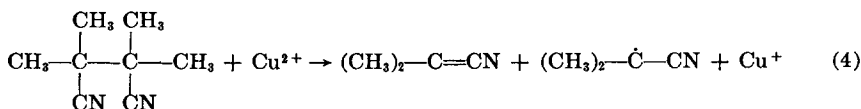
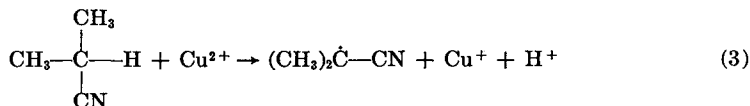
The outstanding increase in the graft yield upon including cupric sulfate in the polymerization system may possibly be explained by the following:

1. Monomer reactivity is enhanced through participation of Cu<sup>2+</sup> ions in complexes formed between nylon amides, water, and monomer.<sup>10</sup> The complexation of an acceptor monomer such as MMA involves interaction with its carbonyl group, enhancing its electron capability and promoting the formation of a donor-acceptor complex as stated above. Enhanced monomer reactivity is also apparently due to association of complexed monomer into an organized array since nylon acts as a matrix for such alignment.

2. The decomposition of AIBN may simply be described by eqs. (1) and (2).<sup>11</sup>



Obviously, of the AIBN decomposition products, only the cyanoisopropyl radical (I) can initiate polymerization. The presence of Cu<sup>2+</sup> ions seems to increase the free-radical species in the polymerization system perhaps through one-electron oxidation of tetramethyl succinodinitrile (II), isobutyronitrile (III), and/or tricyano-2,3,5-trimethylhexane (IV). This is exemplified by eqs. (3) and (4).



The  $\text{Cu}^+$  ion so formed would be oxidized back to the cupric salt, that is, the  $\text{Cu}^{2+}$  ion, by atmospheric oxygen and this conversion presumably involves a radical intermediate.<sup>12</sup>



It is very likely that the  $\text{HO}_2$  radical is involved in the initiation of polymerization or most probably undergoes reactions to yield ultimately  $\text{H}_2\text{O}_2$  as well as  $\cdot\text{OH}$  radicals. In addition, the formation of both the  $\cdot\text{OH}$  and  $\text{HO}_2$  radicals<sup>13,14</sup> in the decomposition of hydrogen peroxide by metallic ions is well established. Hence radicals such as  $\text{HO}_2$  or  $\text{HO}\cdot$  increase the growing homopolymer chains, which in turn increase the possibility of creation of active sites on nylon backbone via a chain transfer process. It is very possible that the  $\text{HO}\cdot$  and/or  $\text{HO}_2$  radicals attack nylon directly to form nylon macroradicals that are capable of initiating grafting.

The sharp drop in the graft yield with higher concentrations of cupric sulfate could be attributed to a variety of reasons. First is termination of free radicals in solution, on homopolymer, and/or an nylon; the  $\text{Cu}^{2+}$  ions seem to act as a radical trap. Second is termination of the graft by  $\text{Cu}^+$  ions leading to lower molecular weight;  $\text{Cu}^+$  ions are presumably formed in excessive amounts upon using high concentration of cupric sulfate. Third there seems to be a certain  $\text{Cu}^{2+}$  concentration that favors complexation of the monomer with nylon. Beyond this concentration the  $\text{Cu}^{2+}$  ions perturb such complexation.

The higher graft yield obtained with method I compared to method II (Fig. 3) is expected. In method I, first the  $\text{Cu}^{2+}$  ions were allowed to be adsorbed onto nylon fibers. The presence of the  $\text{Cu}^{2+}$  ions in the vicinity of nylon certainly favors grafting since the involvement of  $\text{Cu}^{2+}$  in a monomer-nylon complex would be easier. Furthermore, the creation of free-radical species under the influence of  $\text{Cu}^{2+}$  ions would be in the proximity of nylon thus assisting formation of nylon macroradicals.

Similar to the  $\text{Cu}^{2+}$  ions,  $\text{Fe}^{3+}$  ions seem to increase the free-radical species in the polymerization system. As a result, higher grafting may be achieved in the presence of  $\text{Fe}^{3+}$  ions than in their absence.

The greater efficiency of  $\text{Cu}^{2+}$  ions in producing higher graft yields than  $\text{Fe}^{3+}$  ions (Fig. 3) suggests that  $\text{Fe}^{3+}$  ions do not promote complexation of the monomer with nylon to enhance monomer reactivity to any considerable extent. Furthermore, attachment of  $\text{Cu}^{2+}$  ions to nylon seems to involve an ionic bond which can be easily broken to allow the  $\text{Cu}^{2+}$  ions to participate in the reactions already indicated. With  $\text{Fe}^{3+}$  ions, on the other hand, the attachment seems to entail ionic bonding as well as chelate bonding. The strong association of  $\text{Fe}^{3+}$  ions with nylon via chelate bonding would partly inhibit the contribution of  $\text{Fe}^{3+}$  ions in the grafting reaction. This is indeed substantiated by the fact that no decrease in grafting was observed at higher ferric sulfate concentration, unlike at higher concentration of cupric sulfate. At higher concentration of ferric sulfate, the combination of  $\text{Fe}^{3+}$  ions with nylon seems to be mainly through chelate bonding. It is of interest to point out, in this connection, that previous reports on the adsorption reaction of several metallic ions with silk, wool, cellulose, and

poly(vinyl chloride) have disclosed ionic and chelate bond formation, depending upon the kind of the metallic ion used.<sup>14-17</sup>

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