

Graft Copolymerization of Nylon 6 with Methyl Methacrylate Using Dimethylaniline/Cu²⁺ Ion System*

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Synopsis

The ability of dimethylaniline (DMA)/Cu²⁺ ion initiator to induce grafting of methyl methacrylate (MMA) onto nylon 6 was investigated under a variety of conditions. It was found that the graft yield is dependent on the concentration of the Cu²⁺ ion, of DMA, and of MMA. While the graft yield increases as the monomer concentration increases, there are optimal concentrations of DMA and Cu²⁺ ion. Below or above these concentrations, lower grafting occurred. The type of cupric salt also affects grafting to varying degrees. While the presence of CuSO₄ and Cu(NO₃)₂ accelerates grafting, the presence of CuCl₂ offsets the reaction. Increasing the reaction temperature and reaction time favorably influences grafting. Addition of acetic acid enhances grafting, whereas formic acid decreases grafting. Preswelling of nylon with formic acid leaves the susceptibility of nylon toward grafting practically unaltered. Studies of the copolymerization reaction was not confined to the graft yield but was extended to homopolymer formation and total conversion.

INTRODUCTION

Chemical modification of polyamide fibers such as nylon 6 via grafting with vinyl monomers has been the subject of a number of publications.¹⁻⁸ This is indeed a very fascinating field for research with unlimited future possibilities for improving the properties of the product.

The use of dimethylaniline (DMA) as a cocatalyst with cupric nitrate,⁹ benzoyl peroxide,¹⁰ or benzoyl chloride (BC)¹¹ for polymerization of vinyl monomers has been reported. The ability of dimethylaniline N-oxide (DMAO) together with benzoic anhydride¹² or cobaltous salts¹³ to induce the vinyl polymerization has also been studied. In both cases, i.e., upon using DMA or DMAO, the polymerization has been shown to proceed through a radical mechanism.

In a very recent work, we have disclosed that DMA/BC mixture is a very effective initiator for inducing grafting of MMA onto wool,¹⁴ modified celluloses,¹⁵ and nylon 6.⁸ As has been reported,¹⁴ the mechanism involved in grafting proceeds via free-radical species in the reaction medium. These free radicals attack the polymer to be grafted, which in turn is converted to a macroradical capable of initiating grafting.

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In this paper, we present the results of graft copolymerization of MMA onto nylon 6 using the DMA/Cu²⁺ ion system as initiator. The copolymerization reaction was studied with respect to percentages of graft yield, homopolymer, total conversion, and graft efficiency.

EXPERIMENTAL

Nylon 6 fibers were kindly supplied by Hungarian Viscose Factory. The fibers were used without further purification.

Cupric sulfate, cupric nitrate, and cupric chloride were B.D.H. reagent grade.

Methyl methacrylate, dimethylaniline, and solvents were purified before use according to methods described elsewhere.¹⁴

Unless otherwise stated, the graft copolymerization reaction was carried out in a 50-ml stoppered Erlenmeyer flask. The required amounts of DMA, cupric salt, solvent, and monomer were added to distilled water so as to give a total volume of 25 ml. Nylon fiber (0.5 g) was then immediately introduced into the flask. The latter was stoppered, kept in a thermostat, and the contents stirred occasionally during polymerization. After the desired reaction time, the contents were filtered on a sintered glass crucible, washed with water, dried in an oven at 105°C for 5 hr, cooled to room temperature, and weighed. The sample was then Soxhlet extracted with either benzene or acetone, dried as described above, and weighed.

The percentages of graft yield, homopolymer, total conversion, and graft efficiency were calculated as follows:

$$\% \text{ graft yield} = \frac{\text{dry wt. of grafted sample} - \text{dry wt. of original sample}}{\text{dry wt. of original sample}} \times 100$$

$$\% \text{ homopolymer} = \frac{\text{dry wt. of homopolymer}}{\text{wt. of monomer used}} \times 100$$

$$\% \text{ graft efficiency} = \frac{\text{wt. of grafted polymer}}{\text{wt. of grafted polymer} + \text{wt. of homopolymer}} \times 100$$

$$\% \text{ total conversion} = \frac{\text{wt. of grafted polymer} + \text{wt. of homopolymer}}{\text{wt. of monomer used}} \times 100$$

The term polymer yield, which is shown in some of the figures, is used in this paper to refer to either the graft yield, homopolymer, or total % conversion.

RESULTS AND DISCUSSION

Since the aim of this work is to discover the optimal conditions for grafting of nylon 6 with MMA using DNA/Cu²⁺ ion system, the grafting reaction was carried out under various reaction conditions. The reaction was found to be influenced by the following parameters: (1) cupric ion concentration, (2) type of cupric salt, (3) DMA concentration, (4) MMA concentration, (5) addition of acids, (6) reaction temperature, (7) reaction time, (8) reaction medium, and (9) preswelling of nylon.

Presented below are the results of these studies along with their discussion.

Cupric Ion Concentration

The effect of Cu²⁺ ion concentration on the graft yield obtained upon grafting MMA onto nylon 6 is shown in Figure 1. At first glance, it is clear that sub-

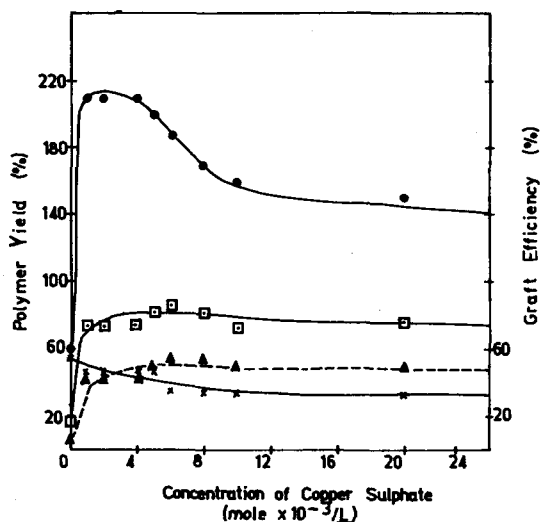
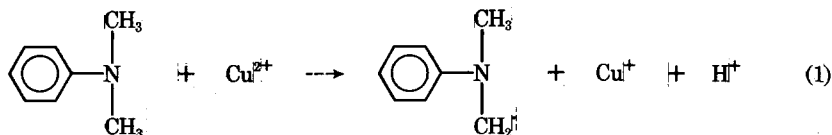


Fig. 1. Copper sulfate concentration vs. % polymer yield and % graft efficiency: (O) graft yield; (Δ) % homopolymer; (□) % total conversion; (X) % graft efficiency. Temp., 70°C; 12% MMA; 40 mmole/l. DMA; water/isopropyl alcohol, 80:20; time, 4 hr; *M/L* ratio, 1:50.

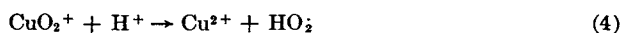
stantial graft formation occurred even in the absence of Cu^{2+} ion, indicating the auto-oxidation of DMA via free radical intermediate. Radical species so generated by auto-oxidation of DMA seem to attack nylon and result in nylon macroradical capable of initiating grafting. A significant increase in the graft yield could be achieved when Cu^{2+} ion was included in the system. For instance, a graft yield of 210% was obtained in the presence of CuSO_4 (0.8 mmole/l.). This contrasts with a graft yield of 60% in the absence of Cu^{2+} ion.

Variation of the graft yield with concentration of Cu^{2+} ion in the polymerization system is rather interesting. A concentration range of 0.8–4 mmole/l. brings about comparable, if not identical, graft yields. Using concentrations more than 4 mmole/l. lowers grafting to a considerable degree. Nevertheless, the graft yields obtained even in the presence of high concentrations of Cu^{2+} ion are still much greater than in their absence. Indication of this is that Cu^{2+} ion does play a significant role in effecting grafting.

The enhancement of grafting by the presence of Cu^{2+} ion could be associated with either of the following two possibilities: (1) A one-electron oxidation of DMA, leading to methylanilinomethyl radical, as suggested by eq. (1):



(2) The cuprous ion formed in reaction (1) would be oxidized back to the cupric state by atmospheric oxygen, and this conversion must presumably involve radical intermediates, as suggested¹⁶ by eqs. (2)–(4):



The radical HO_2 may be involved presumably in the initiation of grafting or can undergo reactions leading to the formation of hydrogen peroxide as well as hydroxyl radical. Furthermore, the formation of both the $\text{HO}\cdot$ and HO_2 radicals^{17,18} in the decomposition of hydrogen peroxide by metallic ions is well established. There is, however, little reason to believe that one of the two possibilities is operating to the exclusion of the other.

The decrease in the magnitude of grafting upon increasing the Cu^{2+} ion concentration could be interpreted in terms of termination by the Cu^{2+} ion. Indeed, the results of the current work (Fig. 1) imply that the Cu^{2+} ion may participate in (a) the termination process with the growing polymer chain of the graft, (b) the initiation step with DMA, and (c) the termination process with the nylon macroradicals. The combined effect of (a) and (c) seems to prevail over (b) at higher Cu^{2+} ion concentrations, thereby lowering the graft yield.

Similar to the graft yield, the homopolymer increases significantly in the presence of Cu^{2+} ion (Fig. 1). However, the values of per cent homopolymer are not seriously reduced when high concentrations of Cu^{2+} ion are used. Moreover, the increase in the homopolymer by increasing Cu^{2+} ion concentration responds to a wider range of Cu^{2+} ion concentration as compared to the graft yield. Differences in the ability of Cu^{2+} ion in initiating and terminating the graft and homopolymer would account for this.

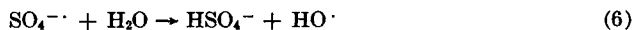
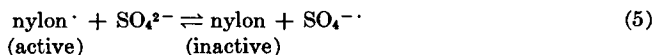
The total conversion of MMA monomer to poly(methyl methacrylate) (PMMA) in presence and absence of Cu^{2+} ion is given in Figure 1. Here, too, the total conversion is much greater in presence of Cu^{2+} ion than in its absence. It shows a trend which is similar to that of the homopolymer. An interesting feature is that in the range of Cu^{2+} ion concentration wherein the graft yield decreases and the homopolymer increases, the total conversion showed a constant value. This is in agreement with the point that during grafting of vinyl monomers to preexisting polymer, there are two competitive reactions, namely, grafting and homopolymerization.¹⁹ Increment in the magnitude of any of these reactions would be at the expense of the other.

Figure 1 also shows the efficiency of grafting. Apparently, the efficiency is slightly higher in the absence of Cu^{2+} ion than in its presence. This is expected since the homopolymer/graft ratio in the presence of Cu^{2+} ion is much greater than the corresponding ratio in absence of Cu^{2+} ion.

Type of Cupric Salt

The anion of the cupric salt has a significant influence on the initiation and termination steps during polymerization. This is clearly shown in Figures 2 and 3. While the CuSO_4 and $\text{Cu}(\text{NO}_3)_2$ work extremely well as a cocatalyst with DMA, CuCl_2 prevents grafting. The homopolymer formed in presence of CuCl_2 is also quite poor.

The data (Figs. 2 and 3) suggest that the anion of the cupric salt participates in the polymerization process. The advantages of using CuSO_4 may be accounted for by the mechanism suggested by eqs. (5) and (6):



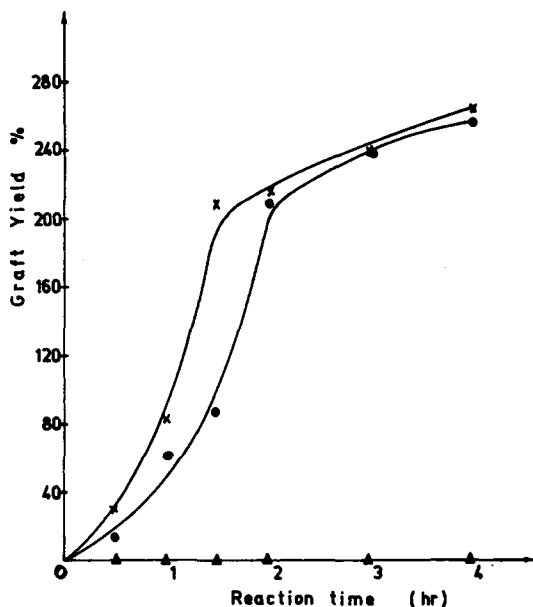
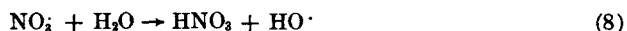
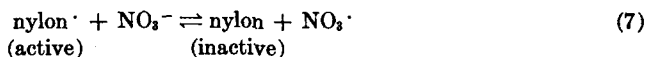


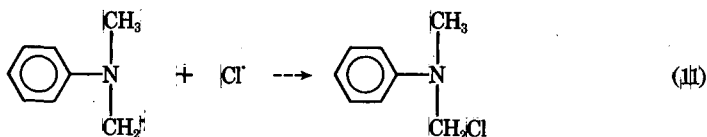
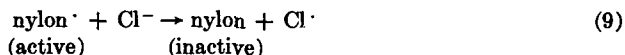
Fig. 2. Rates of grafting of nylon 6 using different types of cupric salts: (○) CuSO₄; (×) Cu(NO₃)₂; (Δ) CuCl₂; 20 mmole/l. cupric salt concentration; 40 mmole/l. DMA; 12% MMA; temp., 70°C; *M/L* ratio, 1:50.

Similar to other substrates,²⁰⁻²² nylon macroradicals may be formed under the influence of SO₄⁻ and/or HO·. The same mechanism can also be applied for Cu(NO₃)₂, as suggested by eqs. (7) and (8):



where the NO₃ and/or HO· may also participate in polymerization.^{23,24}

In the presence of CuCl₂, on the other hand, the Cl⁻ anion seems to terminate the nylon macroradical and/or the methylanilinomethyl radical, presumably according to eqs. (9)–(11):



The strong ability of Cl· to combine with itself and/or with methylanilinomethyl radical would account for the irreversibility of reaction (9), unlike reactions (5) and (7) for the CuSO₄ and Cu(NO₃)₂, respectively. That is why CuCl₂ fails to act as a cocatalyst with DMA. It is of interest to point out that previous reports disclosed the strong ability of Cl· to combine²³ and the slight initiation activity of the hydrochloride of the aniline derivative.^{13,14}

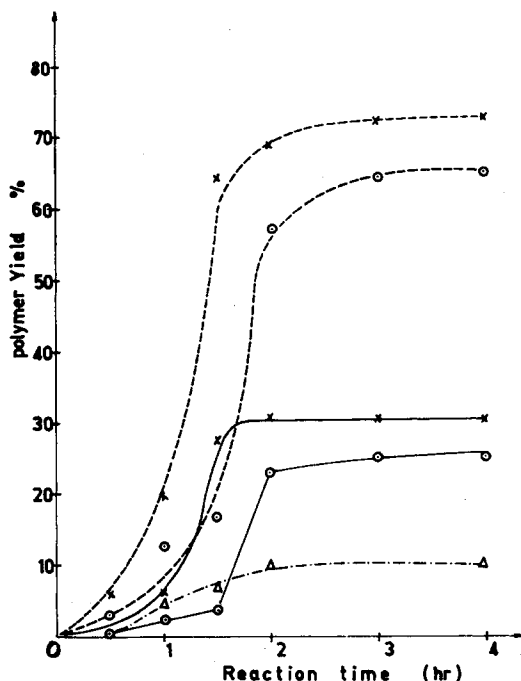
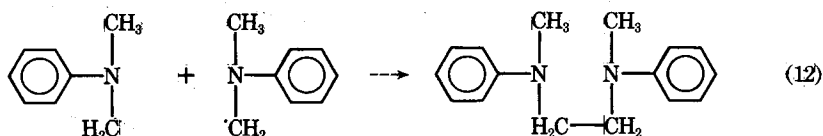


Fig. 3. Effect of different types of cupric salts on the rates of homopolymerization and total conversion: (○) CuSO_4 ; (×) $\text{Cu}(\text{NO}_3)_2$; (Δ) CuCl_2 ; (—) % homopolymer; (---) % total conversion; (-·-·-) % homopolymer and % total conversion.

DMA Concentration

Figure 4 shows the effect of DMA concentration on percentages of graft yield, homopolymer, total conversion, and graft efficiency. It is obvious that the graft yield increases tremendously as the DMA concentration increases. This is observed up to a concentration range of 20–40 mmole/l. Further increase in DMA concentration lowers grafting significantly.

The higher graft yield obtained upon increasing the DMA concentration is direct evidence that the methylanilinomethyl radical does participate in the initiation of the graft, whereas the fall in the graft yield upon using higher DMA concentrations provides evidence that the methylanilinomethyl radical is involved in termination of the graft. It is rather possible that the lower graft yield obtained upon using higher concentration of DMA is due to termination by coupling of the methylanilinomethyl radical, as shown in eq. (12):



Variation of the total conversion with the DMA concentration (Fig. 4) parallels expectation. This has already been discussed under cupric ion concentration. The explanation given there would work here also.

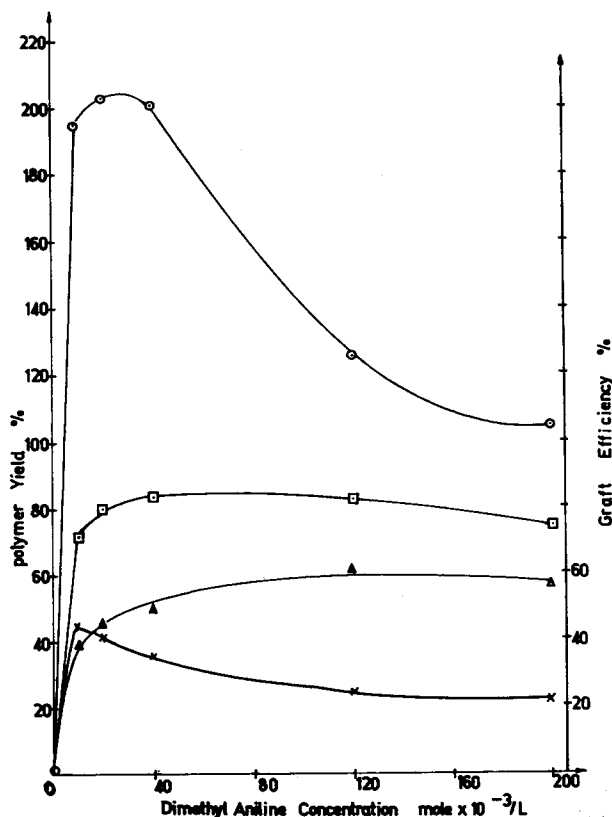


Fig. 4. Dimethylaniline concentration vs. % polymer yield and % graft efficiency: (O) % graft yield; (Δ) % homopolymer; (\square) % total conversion; (\times) % graft efficiency. Temp., 70°C; 12% MMA; 5 mmole/l. CuSO_4 ; water/isopropyl alcohol, 80:20; time, 4 hr; M/L ratio, 1:50.

Monomer Concentration

The effect of MMA concentration on the copolymerization reaction was evaluated in a series of polymerizations in which three monomer concentrations, viz., 4%, 8%, and 12%, were used. Figure 5 shows the graft yield obtained at these concentrations. It is evident that increasing the monomer concentration causes an outstanding enhancement in the graft yield, particularly when the grafting reaction is allowed to proceed for longer periods.

The enhancement of grafting at higher monomer concentrations could be interpreted in terms of the gel effect.²⁵ The latter is brought about as a result of the solubility of PMMA in its own monomer. Hence, besides hindering the termination of the growing polymer chain radicals by coupling, the gel effect causes perhaps swelling of nylon, thus assists diffusion of monomer to the growing grafted chains and active sites on the nylon backbone, thereby enhancing grafting.

It is rather possible to assume that complex formation between nylon and MMA occurs, and this complex is more favorable at higher MMA concentrations. Complexation of nylon with the monomer activates the latter through formation

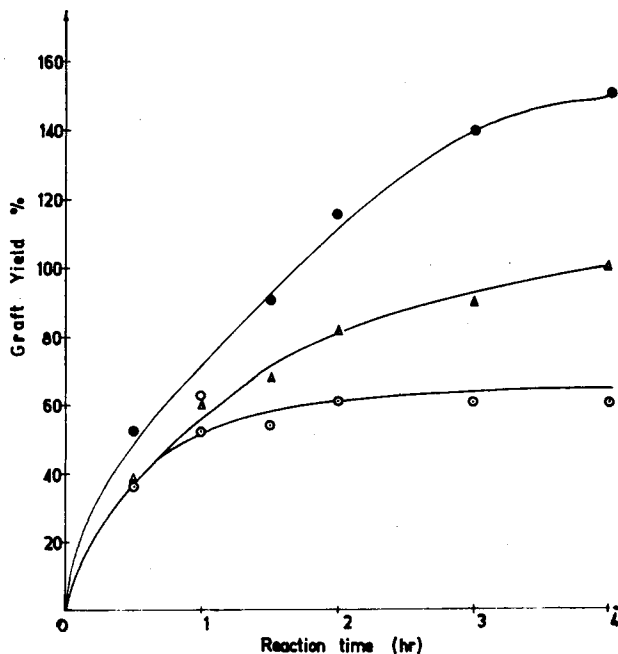


Fig. 5. Influence of methyl methacrylate concentration on the rate of grafting: (O) 4% MMA; (Δ) 8% MMA; (\bullet) 12% MMA. Temp., 70°C; 20 mmole/l. CuSO_4 ; 40 mmole/l. DMA; water/isopropyl alcohol, 80:20, M/L ratio 1:50.

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 has been converted to a strong acceptor. Enhanced monomer reactivity is also apparently due to association of complexed monomer into organized array, since nylon acts as a matrix for such alignment. Of course, the effect of the enhanced monomer reactivity is increased grafting. A similar assumption has been reported for grafting cellulose^{23,26,27} and wool^{28,29} with MMA.

Figure 6 shows data for the homopolymer formed during grafting at the three concentrations studied. Unlike grafting, the magnitude of polymerization does not change significantly by increasing the monomer concentration. This, indeed, substantiates the fact that grafting is favored at higher monomer concentration and would validate the above assumption.

Figure 7 shows the data for the total conversion. As is obvious, the total conversion is higher the lower the monomer concentration. Since the total conversion is the sum of the amount of monomer converted to grafted polymer plus the amount of monomer converted to homopolymer, and since grafting is less at low monomer concentration (see Fig. 5), grafting should be favored at higher monomer concentration. This again supports the assumption outlined above.

Addition of Acids

The grafting reaction has been reported^{23,24} to be accentuated by including acids in the reaction medium, the extent of accentuation being dependent on the kind and amount of acid used. In Figure 8 are shown the graft yields obtained in

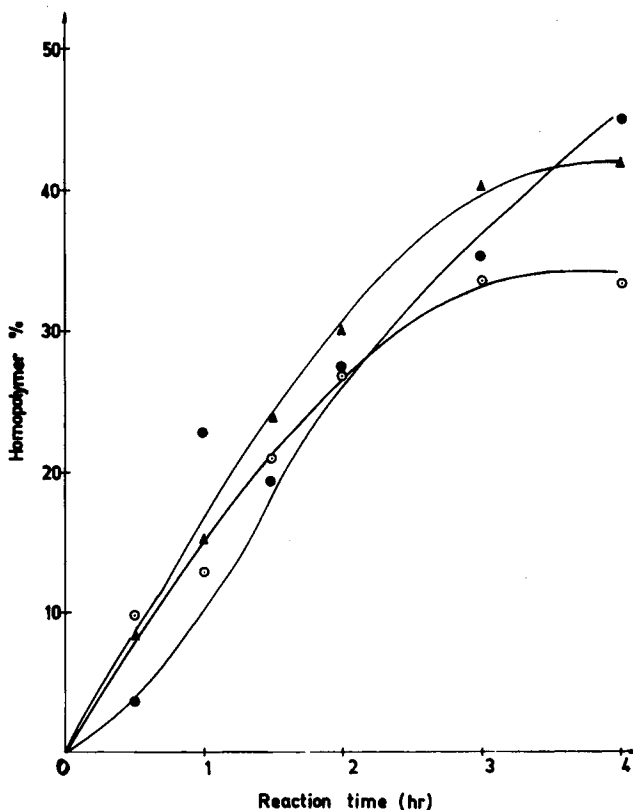


Fig. 6. Influence of methyl methacrylate concentration on the rate of homopolymerization: (○) 4% MMA; (Δ) 8% MMA; (●) 12% MMA. Temp., 70°C; 20 mmole/l. CuSO₄; 40 mmole/l. DMA; water/isopropyl alcohol, 80:20; *M/L* ratio, 1:50.

the presence and absence of either acetic or formic acid. While incorporation of acetic acid in the reaction medium speeds up the rate of grafting, addition of formic acid to the reaction medium causes the reverse, particularly in the later stages of the reaction.

The increased grafting in the presence of acetic acid could be anticipated to the ability of this acid to accelerate the auto-oxidation of DMA, via hydrogen-bonded complex formation, to yield aminohydroperoxides which function as chain carriers in the auto-oxidation,¹¹ whereas in the presence of formic acid, it is very likely that this acid provides hydrogen ions which act as a terminator for the free radicals formed in the reaction medium. Once it occurred, it would reflect on the initiation of grafting.^{13,14}

Reaction Temperature

The effect of raising the polymerization temperature is to bring about a significant acceleration in the rate of grafting. This is clearly shown in Figure 9, where the rate of grafting at 80°C is much greater than at 60°C; the rate follows the order 80°C > 70°C > 60°C.

The favorable effect of temperature on grafting could be attributed to the following factors taken together: (a) creation of more active species, i.e., free

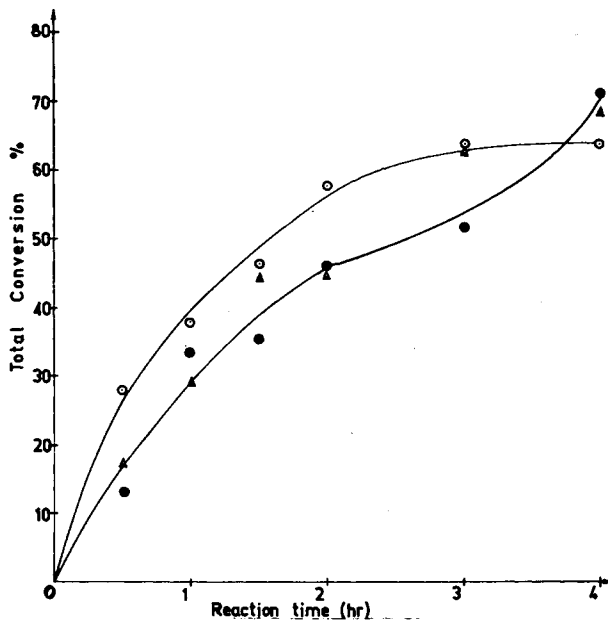


Fig. 7. Effect of methyl methacrylate concentration on total conversion: (○) 4% MMA; (Δ) 8% MMA; (●) 12% MMA. Temp., 70°C; 20 mmole/l. CuSO₄; 40 mmole/l. DMA; water/isopropyl alcohol, 80:20; *M/L* ratio, 1:50.

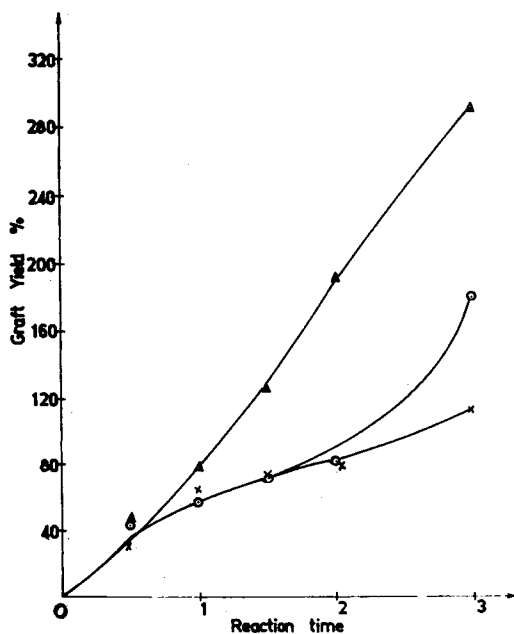


Fig. 8. Effect of addition of acids on the rate of grafting of nylon 6: (Δ) 12 ml/l. acetic acid; (×) 12 ml/l. formic acid; (○) no acid. Temp., 70°C; 20 mmole/l. CuSO₄; 40 mmole/l. DMA; 12% MMA; *M/L* ratio, 1:50.

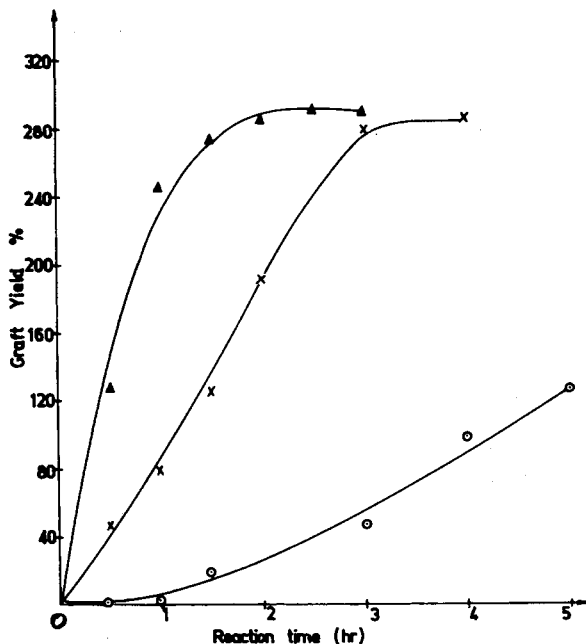


Fig. 9. Effect of temperature on rate of grafting: (○) 60°C; (×) 70°C; (Δ) 80°C; 20 mmole/l. CuSO_4 ; 40 mmole/l. DMA; 12% MMA; 12 ml/l. acetic acid; M/L ratio, 1:50.

radicals, in the reaction medium; (b) enhancement of the swellability of nylon fibers; (c) increased solubility of the monomer; (d) higher rate of monomer diffusion from the reaction medium to the nylon fiber; and (e) enhancement in the rate of initiation and propagation of the graft. It is to be expected that the net effect of all these factors leads to higher grafting.

Reaction Time

Figures 2, 3, and 5-7 show that increasing the reaction time causes a significant increment in the percentages of graft yield, homopolymer, and total conversion. It can also be seen that the polymerization reaction is characterized by an initial fast rate followed by a slower one, and in most cases the per cent polymer yield tends to level off. Leveling off of the per cent polymer yield could be ascribed to depletion in monomer and initiator concentration as well as reduction in the available active centers on the nylon backbone in case of the graft yield.

Preswelling

Nylon 6 was preswollen in solutions containing different concentrations of formic acid (15%, 30%, 45%, and 60%) for 30 min at 25°C. The nylon fibers were then washed with dilute ammonia, thoroughly washed with water, and air dried. Following this, the nylon fibers were grafted with MMA under the conditions indicated in Table I. Results of the graft yields, homopolymer, and total conversion are also listed in the same table. The data clearly reveal that preswelling of nylon 6 with formic acid under the conditions studied has practically no favorable effect on the copolymerization reaction.

TABLE I
Effect of Preswelling of Nylon 6 with Formic Acid^a

Reaction time, hr	Graft yield, %	Homopolymer, %	Total conversion, %
Untreated Nylon			
2	143.3	58.6	65.9
3	178.8	69.2	82.3
4	178.8	69.2	82.3
Nylon Treated with 15% Formic Acid			
2	174	57.7	70
3	177.6	63.6	76.5
4	177.4	66.1	69
Nylon Treated with 30% Formic Acid			
2	144	52.5	60
3	179	65.2	61.8
4	218.6	61.8	81.2
Nylon Treated with 45% Formic Acid			
2	120	45.6	49
3	180	61.2	74
4	185.9	64.4	78.6
Nylon Treated with 60% Formic Acid			
2	52.4	30.7	22.7
3	104	46.5	47.2
4	124.5	67	71.2

^a 20 mmole/l. CuSO₄; 40 mmole/l. DMA; 12% MMA; temperature, 70°C; water/ethanol, 80:20; M/L ratio 1:50.

Reaction Medium

Table II contains data for the per cent graft yield obtained when the grafting reaction was carried out in different media. It is clear that in some of the pure organic solvents examined, the graft yields are quite poor while with the others, no grafting occurred at all. The opposite holds true for purely aqueous medium, where considerable grafting takes place. A combination of aqueous and non-aqueous solutions provides the best media for grafting. Of these, a mixture of water/ethanol at a ratio of 90:10 constitutes the most favorable medium for grafting MMA onto nylon 6 by using the DMA/Cu²⁺ ion initiating system of those studied.

TABLE II
Effect of Solvents on Per Cent Graft Yield^a

Solvent	Graft yield, %							
	0% ^b	2.5%	5%	10%	15%	20%	40%	100%
Ethanol	187	236	237	244	237	212	53	5
<i>n</i> -Propanol	187	211	228	202	192	192	52	8
Isopropanol	187	244	235	197	182	175	52	9
Ethyl acetate	187	207	207	226	204	172	50	0
Dimethylformamide	187	187	197	207	208	188	70	0

^a 1 mmole/l. CuSO₄; 20 mmole/l. DMA; 12% MMA; time, 4 hr; temperature, 70°C.

^b Solvent ratio.

Variation of grafting upon using different solvents either alone or in admixture with water could be associated with differences in (a) capability of swelling nylon; (b) miscibility with monomer; (c) formation of solvent radical and/or hydrogen and hydroxyl radicals from water under the influence of the primary radical species of the initiating system; (d) contribution of these solvents, hydrogen and/or hydroxyl radicals in activation of nylon; and (e) termination of the graft chain radical and nylon macroradical via chain transfer. While the first four factors favor grafting by simplifying access and diffusion of monomer, the last factor adversely affects grafting by lowering the molecular size of the graft.

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