Grafting of Nylon 66 with Methyl Methacrylate Using Dimethylaniline–Benzyl Chloride–Acetic Acid Initiating System

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Synopsis

Grafting of nylon 66 with methyl methacrylate (MMA) under the initiating influence of dimethylaniline (DMA)–benzyl chloride (BC)–acetic acid (AC) mixture was studied to discover optimal conditions for grafting. Results of this investigation showed that a mixture of water/ethanol at a ratio of 90:10 constitutes the most favorable medium for the grafting reaction. Optimal grafting occurred when a concentration of 0.16 mole/l. DMA plus 0.17 mole/l. BC plus 0.2 mole/l. AC was used. Using lower or higher concentrations of this initiator led to lower grafting. On the other hand, increasing MMA concentration brings about a significant increase in the graft yield. The same holds true for reaction time and temperature, though an induction period was observed at a lower temperature (65°C) and when lower monomer concentration (2%) was used.

INTRODUCTION

Dimethylaniline–benzyl chloride–acetic acid mixture has been used as initiator for vinyl polymerization.[1] Its use as initiator for grafting of methyl methacrylate (MMA) onto wool[2] and partially carboxymethylated cotton[3] has recently been reported by us. Detailed equations suggested for the mechanism involved in the graft polymerization reaction have been cited elsewhere.[2,3]

The present paper shows the ability of this system to induce graft polymerization of MMA onto nylon 66.

EXPERIMENTAL

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

Methyl methacrylate (MMA) was purified in a manner similar to that previously described.[4] Dimethylaniline, Merck, free from monoethylaniline, was distilled under vacuum in nitrogen atmosphere. The colorless product was preserved under nitrogen in a dark bottle. Benzyl chloride, Merck, was freshly distilled under reduced pressure. Ethanol, *n*-propanol, isopropanol, *n*-butanol, *tert*-butanol, dimethylformamide (DMF), and acetic acid (AC) were pure grade chemicals.

Unless otherwise stated, the graft polymerization reaction was carried out as

follows: The nylon sample (1 g) was introduced in a 70-ml glass-stoppered Erlenmayer flask containing 50 ml of a solution consisting of water, solvent, DMA, BC, AC, and MMA, at a specific temperature. Details of the polymerization conditions are given elsewhere in the text. The flasks were immediately stoppered and kept in a thermostat for different periods from 30 to 240 min. The entire operation was conducted in atmospheric oxygen. During the reaction, the nylon was kept immersed in the solution. The fibers were then removed, thoroughly washed, repeatedly Soxhleted with acetone, and dried to constant weight. The graft yield (increase in weight) was based on the dry weight of the nylon backbone.

RESULTS AND DISCUSSION

Reaction Medium

Table I shows the graft yield obtained with nylon 66 when polymerization of MMA was initiated by the DMA/BC/AC system in presence of nylon 66 using a water/ethanol mixture at various ratios. It is clear that the graft yield depends on the constitution of the reaction medium. Pure ethanol is not suitable as a medium for grafting since the latter is quite low regardless of the duration of polymerization, whereas in pure aqueous medium substantial grafting is possible, particularly at longer polymerization time. On the other hand, the use of a water/ethanol mixture is more advantageous in producing higher grafting as compared with aqueous and nonaqueous media.

Replacement of ethanol with other solvents, viz., n-propanol, isopropanol,

TABLE I
Effect of Ethanol/Water Ratio on Graft Copolymerization[a]

Reaction time, hr	Graft yield, %, at indicated ethanol/water ratio						
	0:100	5:95	10:90	25:75	50:50	75:25	100:0
½	4	8	12	9	6	2	2
1	8	20	30	28	16	6	4
2	30	50	80	32	28	12	6
3	70	86	150	48	40	16	6

[a] [DMA]:[BC]:[AC], 0.16:0.175:0.2 mole/l.; MMA, 8%; temperature, 70°C; reaction time, 3 hr; M/L ratio, 1:50.

TABLE II
Effect of Solvent/Water Ratio on Graft Copolymerization[a]

Solvent	Graft yield, %, at indicated solvent/water ratio					
	0:100	10:90	25:75	50:50	75:25	100:0
Ethanol	70	150	48	40	16	6
N-Propanol	70	80	20	16	12	8
Isopropanol	70	76	16	12	8	8
n-Butanol	70	72	16	12	10	8
tert-Butanol	70	66	14	12	10	8
DMF	70	80	24	14	14	10

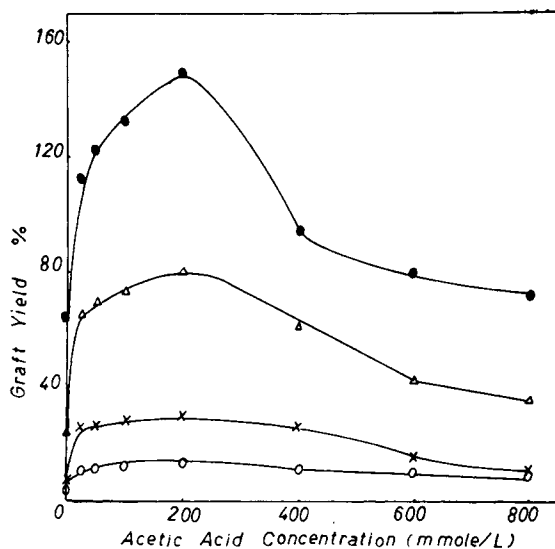[a] [DMF]:[BC]:[AC], 0.16:0.175:0.2 mole/l.; MMA, 8%; temperature, 70°C; reaction time, 3 hr; M/L ratio, 1:50.

Fig. 1. Effect of acetic acid concentration on graft yield per cent: (O) ½ hr; (×) 1 hr; (△) 2 hr; (●) 3 hr; [DMA]: [BC], 0.16:0.175 mole/l.; ethanol:water, 10:90; MMA, 8%; temperature, 70°C; M/L ratio, 1:50.

n-butanol, *tert*-butanol and dimethyl formamide, leads to the same situation (Table II). That is, a significant enhancement in the graft yield is achieved when water is included in the nonaqueous grafting system. Also, grafting increases considerably as the ratio of water in the solvent/water mixture increases. Within the range studied and regardless of the solvent used, a solvent/water mixture of 10:90 constitutes the most favorable reaction medium for grafting nylon 66 with MMA by using the DMA/BC/AC initiating system.

The enhancement of grafting by incorporation of water in the polymerization system could be associated with higher nylon swellability. The effect of this is to improve diffusion of both monomer and initiator within nylon. Furthermore, hydrogen and/or hydroxyl radicals may be formed under the influence of the primary radical species of the initiating system on water. Abstraction of hydrogen atoms from nylon by these hydrogen or hydroxyl radicals results in nylon macroradicals which are capable of initiating grafting.

Here, too, one should recognize that the nature of the solvent has a considerable effect on the extent of grafting (Table II), since it would be reflected on (a) capability of the solvent to swell nylon, (b) miscibility of the solvent with monomer, (c) formation of solvent radical from the primary radical species of the initiating system, (d) contribution of the solvent radical in activation of nylon, and (e) termination of the graft chain radical and nylon macroradical via chain transfer. Obviously, the first four factors favor grafting by simplifying access and diffusion of monomer, whereas the last factor decreases grafting by lowering the molecular size of the graft.

Acetic Acid Concentration

Figure 1 shows the effect of acetic acid concentration on the graft yield. As can be seen, increasing the acetic acid concentration to 0.2 mole/l. causes a significant enhancement in grafting. Beyond this value, the opposite situation is
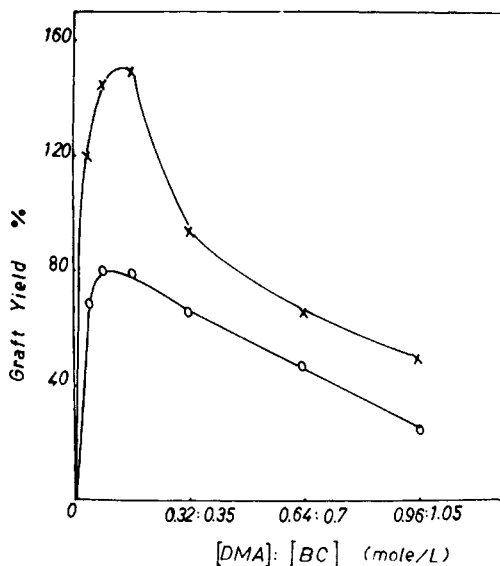
Fig. 2. Influence of initiator system concentration on graft yield per cent: (O) 2 hr; (X) 3 hr; [AC], 0.2 mole/l.; ethanol:water, 10:90; MMA, 8%; temperature, 70°C; M/L ratio, 1:50.

encountered. The increase in grafting at low acid concentration could presumably be ascribed to complex formation between DMA and the acid, which favors the auto-oxidation of DMA.[1-3] On the other hand, the lower grafting obtained upon using higher acid concentration suggests formation of aniline salt derivatives with lower initiating activity.[5] Besides, there is an increase in hydrogen ion concentration when larger amounts of the acid are used. Such ions would act as terminators for free radicals formed in the reaction medium.[6] This, in turn, would be reflected in the initiation of grafting.

Concentration of DMA/BC Mixture

Figure 2 shows graft yield versus concentration of DMA/BC mixture in nearly equimolecular quantities. As is evident, increasing the initiator DMA:BC concentration to ca. 0.16:0.17 mole/l. brings about an outstanding enhancement in the graft yield. Thereafter, increasing the initiator concentration lowers grafting. That is, maximum grafting occurs when a concentration of 0.16 mole/l. DMA together with 0.17 mole/l. BC is used.

The decrease in grafting upon using higher concentration of the initiator mixture can be ascribed to increased termination possibilities with increase in the abundance of free-radical species in the medium and/or possible formation of quaternary ammonium salt via reaction of DMA with BC. This quaternary ammonium salt does not affect polymerization.[1]

Monomer Concentration

The dependence of the rate of grafting on MMA concentration can be seen in Figure 3. The rate of grafting is higher the higher the concentration of MMA in the polymerization system. Within the range studied, maximum grafting of ca. 55% was achieved by using a monomer concentration of 2%. This contrasts with a graft yield of ca. 160% when a 12% monomer concentration was used.
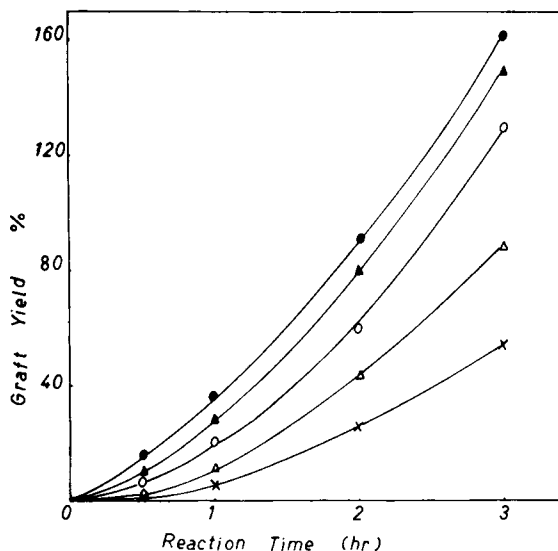
Fig. 3. Influence of MMA concentration on rate of grafting: (×) 2% MMA; (△) 4% MMA; (○) 6% MMA; (▲) 8% MMA; (●) 12% MMA; [DMA]:[BC]:[AC], 0.16:0.175:0.2 mole/l.; ethanol:water, 10:90; temperature, 70°C; M/L ratio, 1:50.

The enhancement in grafting by increasing monomer concentration can be interpreted in terms of gel effect caused by solubility of poly(methyl methacrylate) in its own monomer.[7-9] The ultimate function of this are (a) promotion of grafting through hindrance of growing polymer chain radicals by coupling and (b) increasing nylon swellability, thereby assisting and facilitating diffusion of monomer to active sites on the nylon backbone.

It is rather likely that, at higher MMA concentration, complexation of nylon with MMA occurs.[10,11] This complexation increases MMA reactivity through 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.[12] Hence, it may probably be correct to say that a possible gel effect together with possible complexation of MMA with nylon are responsible for the higher rate of grafting at higher monomer concentration, since there is little reason to believe that one of the two possibilities is operating to the exclusion of the other.

Reaction Temperature

Figure 4 illustrates the effect of the polymerization temperature on the rate of grafting. It is clear that the grafting rate is significantly higher at 75°C than at 65°C; the rate follows the order 75° > 70° > 65°C. Within the range studied, this suggests that as the temperature rises, factors that operate in favor of grafting seem to be accentuated. Among these factors are (a) creation of active species, i.e., free radicals, in the reaction medium; (b) swelling properties of nylon; (c) monomer solubility; (d) diffusion of monomer from the reaction medium to the nylon fiber; and (e) initiation and propagation of the graft. The effect of these factors taken together certainly is increased grafting.
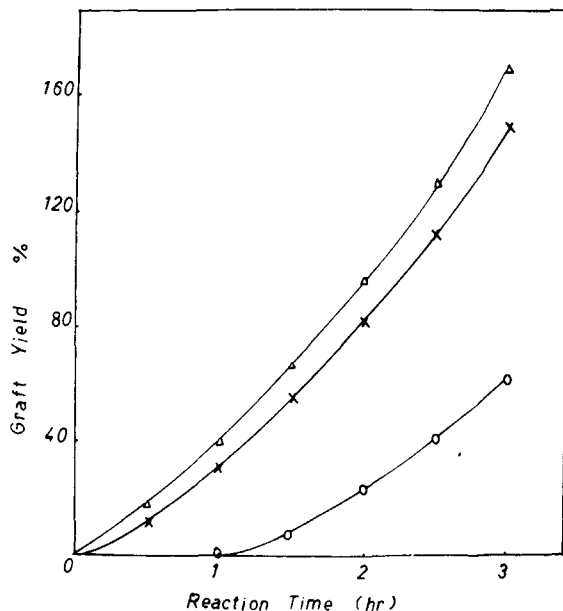
Fig. 4. Effect of temperature on grafting MMA onto nylon: (O) 65°C; (X) 70°C; (△) 75°C; [DMA]:[BC]:[AC], 0.16:0.175:0.2 mole/l.; ethanol:water, 10:90; MMA, 8%; M/L ratio, 1:50.

Reaction Time

Table I and Figures 3 and 4 show that increasing reaction time is accompanied by a significant increase in the percentage graft yield. Within the range studied, the graft yield increases as the reaction time increases, and no leveling off of the grafting occurs. However, there is an induction period when lower monomer concentration is used (Fig. 3) or when the grafting is performed at a lower temperature (Fig. 4).

References

1. L. Horner and K. H. Knapp, *Makromol. Chem.*, **93**, 69 (1966).

2. A. Bendak, M. I. Khalil, M. H. El-Rafie, and A. Hebeish, *J. Appl. Polym. Sci.*, **19**, 335 (1975).

3. A. Hebeish, M. H. El-Rafie, M. I. Khalil, and A. Bendak, *J. Appl. Polym. Sci.*, **21**, 1901 (1977).

4. A. Hebeish, M. I. Khalil, and M. H. El-Rafie, *Angew. Makromol. Chem.*, **37**, 149 (1974).

5. T. Fueno, H. Okamoto, T. Tsuruta, and J. Furukawa, *J. Polym. Sci.*, **36**, 407 (1959).

6. T. Sato and T. Oster, *Makromol. Chem.*, **125**, 1 (1969).

7. A. Bendak and A. Hebeish, *J. Appl. Polym. Sci.*, **17**, 1953 (1973).

8. A. Hebeish, A. Kantouch, M. I. Khalil, and M. H. El-Rafie, *J. Appl. Polym. Sci.*, **17**, 2547 (1973).

9. A. Hebeish, S. H. Abdel-Fattah, and A. Bendak, *Angew. Makromol. Chem.*, **37**, 11 (1974).

10. M. H. El-Rafie, M. I. Khalil, and A. Hebeish, *J. Appl. Polym. Sci.*, **19**, 1677 (1975).

11. M. H. El-Rafie and A. Hebeish, *J. Appl. Polym. Sci.*, **19**, 1815 (1975).

12. N. Gaylord, *J. Polym. Sci. C*, **37**, 153 (1972).