Graft Polymerization of Methacrylate Onto Wool Using Dimethylaniline–Benzyl Chloride Mixture as Initiator

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Synopsis

Graft polymerization of wool with methyl methacrylate (MMA) initiated by a dimethylaniline–benzyl chloride (DMA/BC) mixture was extensively studied. The grafting and homopolymerization reactions are influenced by the nature of the solvent used; ethanol proved to be the best. Using water as a cosolvent enhances significantly both graft formation and homopolymerization. A mixture of water/ethanol at a ratio of 90:10 constitutes the optimal medium for the grafting reaction. Addition of acetic acid or formic acid in low concentration (0.2 mole/l.) favors grafting. The opposite holds true for sulfuric and hydrochloric acid. Kinetic investigations showed that the rates of total conversion (R_p) and grafting (R_p') are dependent of the concentrations of DMA, BC, acetic acid (Ac) and amount of wool (W), as well as temperature. They can be expressed by the following equations:

$$R_p = K \, [DMA]^{0.92} \, [BC]^{0.80} \, [MMA]^{0.84} \, [W]^{1.50} \, [Ac]^{-0.2}$$

$$R_p' = K \, [DMA]^{0.92} \, [BC]^{0.80} \, [MMA]^{0.72} \, [W]^{2.60} \, [Ac]^{-0.30}$$

The overall activation energies for the total conversion and grafting reactions amount to 8.5 and 9.0 kcal/mole, respectively; whereas the corresponding energies for initiations E_d and E_d' are 7.0 and 8.0 kcal/mole, respectively. The changes in the physical and/or chemical structure of wool via reduction, acetylation, and dinitrophenylation are reflected on the susceptibility of wool toward grafting. While reduced wool showed higher grafting, the graft yields obtained with acetylated and dinitrophenylated wools were quite poor. The alkali solubility of wool graft copolymer was determined and its tendency to felt was examined. Evidences for grafting were provided and a tentative mechanism for grafting initiation was suggested.

INTRODUCTION

Previous studies in this laboratory and others have shown that grafting of vinyl monomers onto wool can be achieved via either physical or chemical activation of wool.[1-3] Irradiation of wool by high-energy radiation[3-6] or low-energy radiation in the presence and absence of sensitizers[6-12] results in wool macroradicals which are capable of initiating grafting. Similar wool radicals can be brought about under the action of redox system,[13-16] ceric ions,[17,18] periodate ions.[19] (acetonly acetonato)–copper(II)–trichloro-acetic acid complexes,[20-23] potassium permanganate,[24,25] and benzoyl

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peroxide.[26]   Formation of wool macroradicals through chain transfer has also been reported.[27]

The use of DMA/BC mixture as initiator for polymerization of MMA and other vinyl monomers has been reported to proceed by free-radical species formed upon the auto-oxidation of DMA.[28-30]   Presence of acetic acid, azobisisobutyronitrile, cobalt compounds, benzyl chloride, or acetic anhydride during polymerization enhances markedly the polymerization yield owing to the accelerating effect of these compounds on the auto-oxidation of DMA.[28]   However, to the authors' knowledge, no one has reported yet on the possible use of this initiator to graft wool or other fibers with vinyl monomers.

It is the aim of one of the research programs of this laboratory to implement DMA/BC mixture for initiating grafting of MMA on different fibers, viz., wool, cotton, modified celluloses, and nylon.   Presented here are the results of graft polymerization of wool with MMA using the said initiator.

EXPERIMENTAL

Merino wool fibers were Soxhlet extracted with acetone for about 24 hr, washed with cold, distilled water, dried at room temperature, and conditioned.   Reduced wool was prepared by thioglycollic acid (TGA) treatment of wool (0.2N TGA, 25°C, 16 hr, liquor ratio 1:100).   Acetylated wool was prepared using a mixture of acetic anhydride/acetic acid and sulfuric acid as a catalyst.[31]   Dinitrophenylated wool (DNP-wool) was prepared by its treatment with 1-fluoro-2,4-dinitrobenzene in ethanolic solution for several days at room temperature.[32]   MMA was washed successively with 5% NaOH and water, then dried with anhydrous sodium sulfate, and distilled under reduced pressure in nitrogen before use.   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.   Solvents, ethanol, n-propanol, isopropanol, n-butanol, $tert$-butanol, dimethylsulfoxide (DMS), dimethylformamide (DMF), dioxane, and acetic, formic, sulfuric, and hydrochloric acids are pure-grade chemicals.

The graft polymerization reaction was carried out as follows: A conditioned wool 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, acid, 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 varied from 30 to 240 min.   The entire opertion was conducted in atmospheric oxygen.   During the reaction, the wool was kept well immersed in the solution.   The fibers were then removed, thoroughly washed, repeatedly Soxhleted with acetone, and dried to constant weight.

The percentage graft yield and percentage total conversion were calculated from the following equations:

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

% total conversion

$$= \frac{\text{weight of grafted polymer} + \text{weight of homopolymer}}{\text{weight of monomer used}} \times 100.$$

The alkali solubility of wool was carried out in $0.1N$ NaOH solution for 1 hr at 65°C according to Leaveau's techniques.[33]

The felting of wool and the wool–graft copolymers was carried out according to the method reported by Blankenburg and Zahn.[34] Details of the procedure adopted were described elsewhere.[20]

RESULTS AND DISCUSSION

To start with, the graft polymerization reaction was performed in different organic solvents; the grafting system consisted of MMA, wool, DMA, BC, Ac, and solvent. The solvents used were ethanol, n-propanol, isopropanol, n-butanol, $tert$-butanol, DMF, DMS, and dioxane. Table I (last column) shows clearly that regardless of the nature of solvent employed, considerable grafting has occurred. However, the nature of solvent did affect the extent of grafting. Of the solvents used, ethanol proved to be the best solvent for grafting.

Variation of grafting upon using different solvents could be associated with differences in their (a) capability of swelling wool,[35] (b) miscibility 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 wool, and (e) termination of the graft chain radical and wool

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

Solvent type	Graft yield, %				
	10:90[b]	25:75	50:50	75:25	100:0
Ethanol	122	108	76	62	52
n-Propanol	104	80	65	55	48
Isopropanol	94	73	57	48	42
n-Butanol	88	67	51	45	40
$tert$-Butanol	82	62	48	40	36
Dimethylformamide	100	92	77	60	48
Dimethylsulfoxide	88	68	56	47	40
Dioxane	95	86	68	56	45

[a] [DMA]:[BC], 0.16:0.175 mole/l.; MMA, 8%; 4 hr; temperature, 70°C; wool:-liquor ratio, 1:50.

[b] Solvent:water ratio.

TABLE II
Effect of DMA in Admixture with BC, Ac, or Both on Total Conversion[a]

		Total conversion, %, after			
Initiating mixture, mole/l.		30 min	60 min	120 min	180 min
DMA:BC	(0.16:0.175)	2.0	4.0	8.0	19.5
DMA:Ac	(0.16:0.20)	3.5	9.0	23.0	41.0
DMA:BC:Ac	(0.16:0.175:0.2)	10.0	21.5	40.0	62.0

[a] MMA, 8%; ethanol:water, 10:90; temperature, 70°C; wool:liquor ratio, 1:50.

macroradical via chain transfer. While the first four factors favor grafting by simplifying access and diffusion of monomer, the last factor adversely affect grafting by lowering the molecular size of the graft.[27,36]

Incorporation of water in the grafting medium is interesting from both the academic and practical points of view. Presence of water has been reported to increase grafting by swelling and improving the diffusion of monomer within the substrate to be grafted.[6,27,38-44] 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 wool by these hydrogen or hydroxyl radicals results in wool macroradicals which are capable of initiating grafting.[6]

Results of this work (Table I) make it evident that with all the solvents used, 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 MMA on wool by using DMA/BC/Ac initiating system. This reflects the influence of water on grafting and could be explained on lines similar to those pointed out above.

Here, too, one should recognize that the use of a DMA/BC/Ac mixture as initiator was based on its higher initiation efficiency in polymerizing MMA as compared with DMA/BC and DMA/Ac mixtures. This may be realized from Table II.

Effect of Acids

Horner et al.[28] have disclosed that addition of acetic acid to the DMA/BC initiating system accelerates the rate of vinyl polymerization. We have also shown[25,45] that the copolymerization reactions are significantly influenced by the presence of acid; the influence is dependent upon the kind and concentration of the acid used. It appears, therefore, of interest to examine the effect of different acids on grafting wool with MMA by using an DMA/BC mixture as initiator.

Table III contains data for grafting in acetic acid, formic acid, sulfuric acid, and hydrochloric acid at various concentrations. Obviously, higher grafting is attained at low concentrations of acetic acid and formic acid.

TABLE III
Grafting of MMA Onto Wool by DMA/BC Initiator System Using Different Acids[a]

	Graft yield, %				
Acid used	Zero[b]	0.20 mole/l.	0.40 mole/l.	0.60 mole/l.	0.80 mole/l.
Acetic	110	160	104	98	90
Formic	110	130	90	83	80
Sulfuric	110	50	30	20	17
Hydrochloric	110	40	22	16	15

[a] [DMA]/[BC] 0.16:0.175 mole/l.; ethanol:water, 10:90; MMA, 8%; temperature, 70°C; 4 hr; wool:liquor ratio, 1:50.
[b] Concentration of acid.
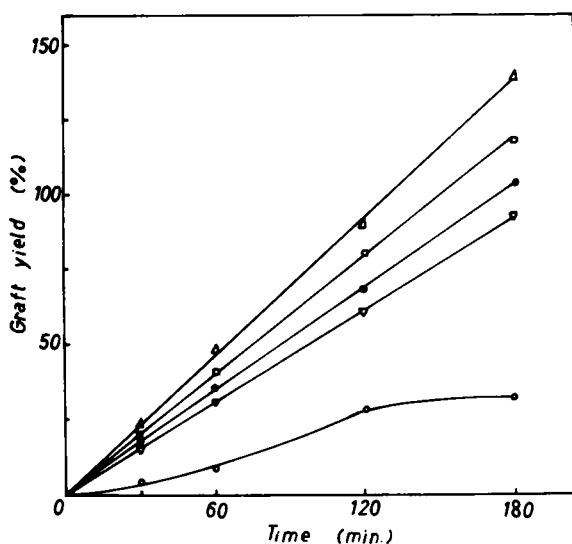
Fig. 1. Rate of grafting of MMA onto wool at different concentrations of acetic acid. Acetic acid concentration, mole/l.: (O) zero; (△) 0.2; (□) 0.4; (●) 0.6; (▽) 0.8. [DMA]/[BC], 0.16:0.175 mole/l.; ethanol/water, 10:90; MMA, 8%; temperature, 70°C; wool:liquor ratio, 1:50.

The opposite holds true for grafting at higher concentrations of these two acids. Presence of sulfuric and hydrochloric acids, on the other hand, reduces grafting to a marked degree whatever concentration is employed. The fall in the graft yields upon using mineral acids or organic acid at high concentrations could be interpreted in terms of formation of aniline derivative salts which have slight initiation activity.[30] Formation of such salts would be expected to rely on the concentration and dissociation of the acid.

Thus, the higher graft yields obtained with organic acids, compared to mineral acids, are presumably due to their smaller dissociation constants. Furthermore, the outstanding increase in grafting at low concentration of organic acids suggests a complex formation between DMA and the acid

possibly via hydrogen bonding. Such a complex favors the auto-oxidation of DMA (see below), whereas at higher concentrations of the acid (even if it is organic), there is a possibility for salts of aniline derivatives to be formed which, as already stated, do not possess high initiating activity. The latter seems to differ markedly with the kind of salts formed. Apparently the hydrochlorides acquire very low initiating activity since grafting falls markedly in the presence of hydrochloric acid.

However, it should be noted that, besides formation of aniline salts, there is an increase in hydrogen ion concentration when higher acid concentrations are used. Such ions would act as terminators for free radicals formed in the reaction medium.[30] This, in turn, would be reflected in the initiation of grafting.

Figure 1 shows the rate of grafting obtained at different concentrations of acetic acid. Here, too, within the range studied, a higher rate of grafting is achieved with lower acid concentrations. It was also found that the rate (mole/l.-sec) of total conversion (R_p) and rate of grafting (R_p') are inversely proportional to the 0.20 and 0.30 power of acetic acid concentration [Ac], respectively.

Effect of Benzyl Chloride Concentration [BC]

Figure 2 shows the rates of grafting obtained with different [BC] at constant concentration of [DMA] and [Ac]. It is clear that the grafting rate is appreciably influenced by changing the molar ratio of [DMA] to [BC]. The equimolecular quantities of both components constitutes the
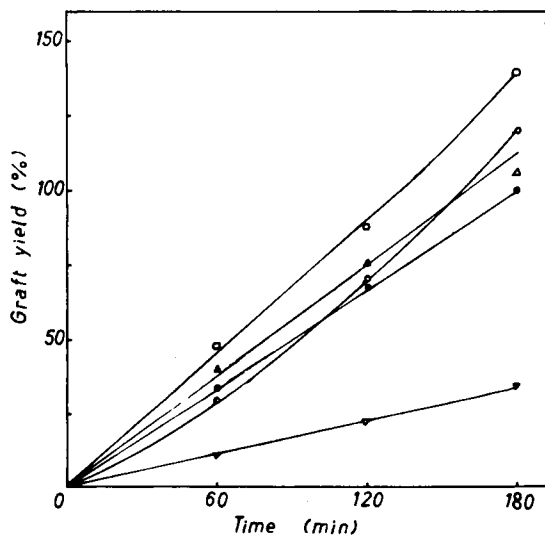

Fig. 2. Rate of grafting of MMA onto wool at different concentrations of benzyl chloride. [BC], mole/l.: (O) zero; (△) 0.087; (□) 0.175; (●) 0.35; (▽) 0.70. [DMA], mole/l.: 0.16; [Ac], mole/l.: 0.2; ethanol/water, 10:90; MMA, 8%; temperature, 70°C; wool:liquor ratio, 1:50.
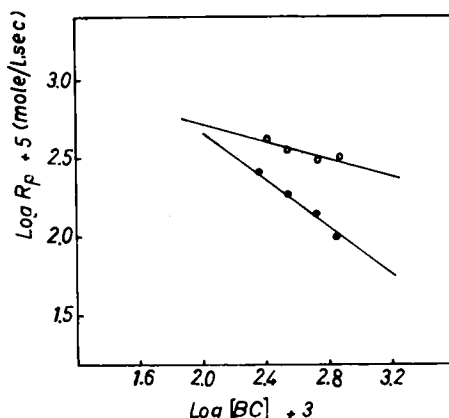
Fig. 3. Rates of grafting and total conversion of MMA reactions vs. [BC]: (—O—) R_p rate of total conversion of MMA reaction; (—●—) R_p' rate of graft copolymerization reaction; [DMA], 0.16 mole/l.; [Ac], 0.2 mole/l.; ethanol/water, 10:90; MMA, 8%; temperature, 70°C; wool:liquor ratio, 1:50.

best mixture for inducing graft polymerization. This, indeed, is in agreement with previous reports.[28-30]

Kinetic investigation (Fig. 3) of the effect of [BC] on rate of total conversion (R_p) and rate of grafting (R_p') at constant [DMA] and [Ac] revealed that they are inversely proportional to the 0.20 and 0.77 power of [BC], respectively.

Effect of Concentration of DMA/BC Mixture

Figure 4 shows the influence of the concentration of the DMA/BC mixture in nearly equimolecular quantities on grafting and total conversion. Increasing the initiator DMA:BC concentration up to ca. 0.32:0.35 mole/l. is accompanied by a significant increment in both total conversion and grafting, whereas further increase in initiator concentration causes a decrement in the amount of graft formation as well as total conversion. In other words, maximum grafting and total conversion occur when a concentration of 0.32 mole/l. DMA plus 0.35 mole/l. BC is used. The decrease in total conversion and grafting upon using higher concentration of the initiator mixture could be attributed to increased termination possibilities with increase in abundance of free-radical species in the medium. However, possible formation of quaternary ammonium salt, by reaction of DMA with BC, which does not effect polymerization,[28] cannot be ruled out.

From the kinetic point of view (Fig. 5), it was found that the rate of total conversion (R_p) and rate of grafting (R_p') are proportional to the 0.92 power of [DMA] and to the 0.80 power of [BC].

Effect of Monomer Concentration

Figure 6 illustrates the effect of MMA concentration on the extent of grafting. As is evident that the higher the graft yield, the higher the
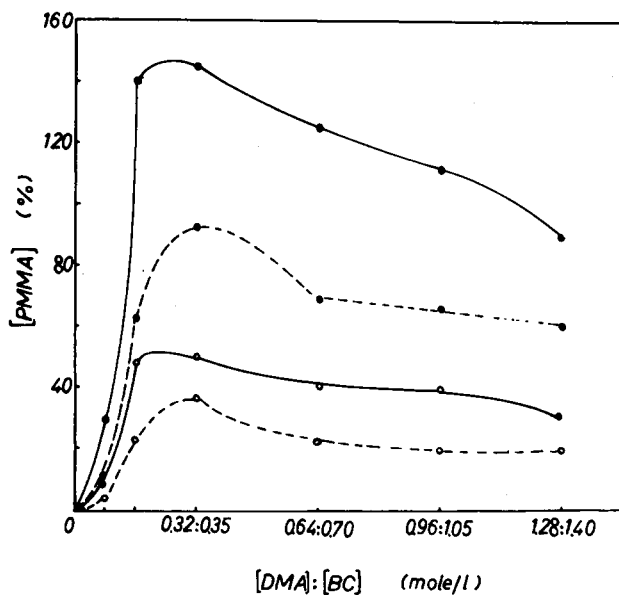
Fig. 4. Influence of initiator system concentration on graft yield and total conversion of MMA to PMMA: (———), % graft yield; (- - -) % conversion; (○) 1 hr; (●) 3 hr; [Ac], 0.2 mole/l.; ethanol/water, 10:90; MMA, 8%; temperature, 70°C; material:-liquor ratio, 1:50.
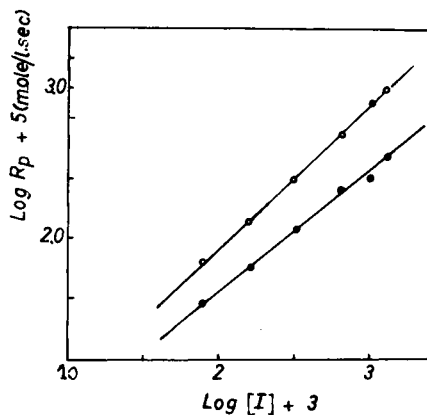

Fig. 5. Rates of grafting reaction, R_p' and total conversion of MMA reaction, R_p vs. initiator system concentration: (—○—) R_p; (—●—) R_p'; [Ac], 0.2 mole/l.; ethanol/water, 10:90; MMA, 8%; temperature, 70°C; wool:liquor ratio, 1:50.

concentration of MMA. The same holds true for total conversion. This is in agreement with previous studies[27,45,46] which ascribed this to gel effect brought about as a result of the solubility of PMMA in its own monomer. Besides this, probable complex formation between wool and MMA is more favorable at higher MMA concentrations. Complex formation of
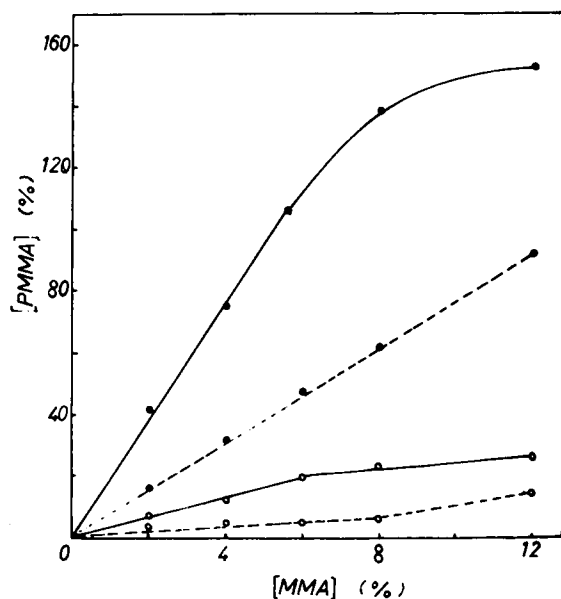
Fig. 6. Influence of MMA concentration on the rates of conversion and grafting reactions: (——) % graft yield; (- - -) % conversion; (—O—) 1 hr; (—●—), 3 hr; [DMA]/[BC]/[Ac], 0.16:0.175:0.2 mole/l.; ethanol/water, 10:90; temperature, 70°C; wool:liquor ratio, 1:50.
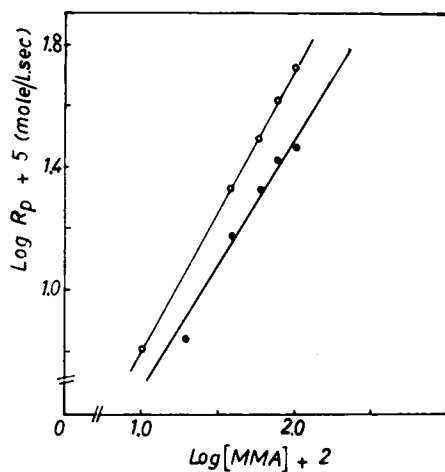

Fig. 7. Rates of grafting and total conversion reactions of MMA versus MMA concentration: (O) R_p; (●) R_p'; [DMA]/[BC]/[Ac], 0.16:0.175:0.2 mole/l.; ethanol/water, 10:90; temperature, 70°C; wool:liquor ratio, 1:50.

wool with the monomer activate the latter through formation of donor–acceptor complex thereby giving rise to higher grafting.[47]

Kinetic investigation (Fig. 7) showed that the rate of total conversion (R_p) and rate of grafting (R_p') are proportional to the 0.84 and 0.72 power of [MMA], respectively.

Effect of Temperature

Figure 8 shows that increasing the temperature from 65°C to 75°C enhances the rate of grafting considerably. This could be attributed to the favorable influence of temperature on wool swellability, monomer solubility, and its diffusion, auto-oxidation of the initiator, and initiation and propagation of the graft. It should be emphasized, in this connection, that working at lower temperatures than those indicated in Figure 8 gave poor grafting after very long induction periods (more than 3 hr at 50°C).

From the Arrhenius plot of $\log R_p$ versus $1/T$ (Fig. 9), the overall activation energy was found to be 8.5 kcal/mole and 9.0 kcal/mole for total conversion and grafting reactions, respectively. These rather small values are, however, approximate to those obtained in other polymerization systems in the presence of a macromolecule.[48] Using the value of $E_p - \frac{1}{2} E_t = 4 \sim 5$ kcal/mole, given by Tobolsky et al.,[49] where E_p and E_t are energies of propagation and termination, respectively, the activation energies of initiation E_d, E_d' were calculated from these values as follows:

$$E_d = 2E_a - (2E_p - E_t)$$

where E_a is the overall activation energy; $E_d = 7$ kcal/mole for total conversion reaction of MMA to PMMA, and $E_d' = 8$ kcal/mole for graft
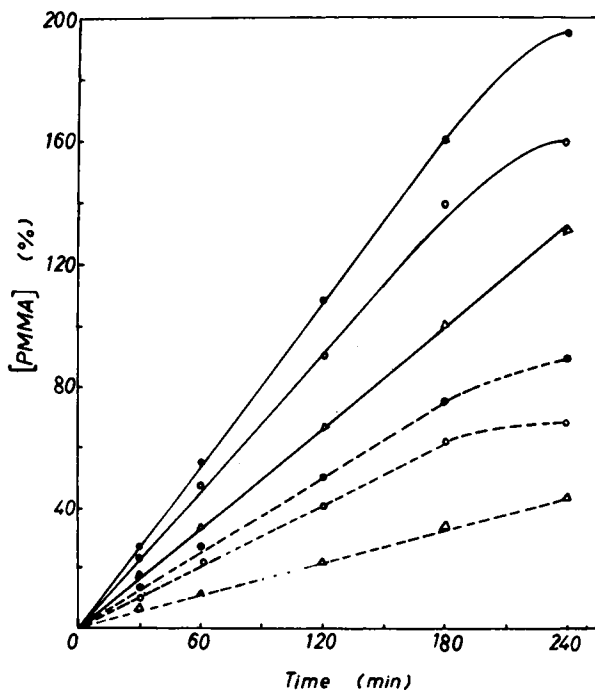

Fig. 8. Rates of grafting of MMA on wool at various temperatures: (———) % graft yield: (- - -) % conversion; (△) 65°C; (○) 70°C; (●) 75°C; [DMA]/[BC]/[Ac], 0.16:0.175:0.2 mole/l.; ethanol/water, 10:90; MMA, 8%; wool:liquor ratio, 1:50.
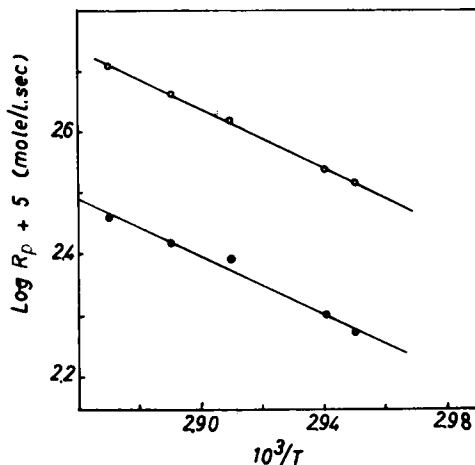
Fig. 9. Arrhenius plots for polymerization of MMA in the presence of wool: [DMA]/[BC]/[Ac], 0.16:0.175:0.2 mole/l.; ethanol/water, 10:90; MMA, 8%; wool:liquor ratio, 1:50, (O) R_p, rate of total conversion of MMA reaction; (●) R_p', rate of graft copolymer reaction.

polymerization reaction. These calculated values were about one third to one tenth of those obtained in usual radical polymerization and were even very small compared with those seen in the usual redox system polymerization.[48]

Effect of Amount of Wool

Figure 10 shows the rates of total conversion (R_p) and grafting (R_p') obtained upon polymerization of MMA in the presence of varying amounts of wool. The data (Fig. 10) indicate that the rate of total conversion (R_p) and the rate of the grafting reaction (R_p') are proportional to the amount of wool present during polymerization.
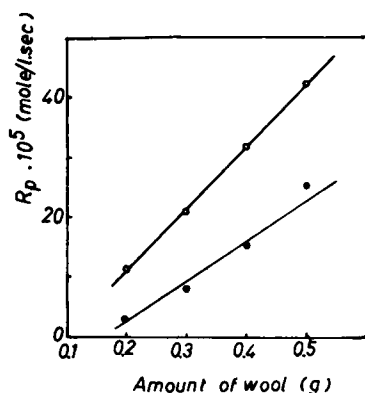

Fig. 10. Amounts of wool vs. rates of total conversion of MMA (R_p) and graft polymerization reactions (R_p'): (—O—) R_p; (—●—) R_p'; [DMA]/[BC]/[Ac]: 0.16:-0.175:0.2 mole/l.; ethanol/water, 10:90; MMA, 8%; temperature, 70°C.
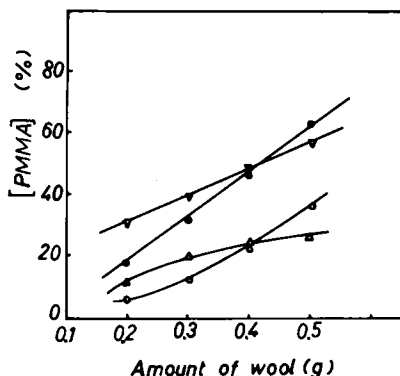
Fig. 11. Amounts of wool vs. conversion, graft yield, homopolymer, and graft efficiency percentages: (—O—) graft yield % (based on monomer weight); (△) homopolymer %; (—●—) conversion %; (▽) graft efficiency %; [DMA]/[BC]/[Ac], 0.16:-0.175:0.2 mole/l.; ethanol/water, 10:90; MMA, 8%; 3 hr; temperature, 70°C.

The relationship between the amount of wool and percentages of grafting efficiency, total conversion, homopolymer, and graft yield (based on monomer weight) are shown in Figure 11. Of interest is that the grafting efficiency increases as the amount of wool in the polymerizing medium increases. This suggests that polymerization of MMA induced by DMA/BC/Ac in the presence of wool takes place preferentially in the wool matrix with the abundance of wool in the medium, hence the integrated surface area of the fibers affects greatly the diffusion of the monomer and free-radical species as well as increases the possibility of free-radical formation on the wool backbone. Kinetic trials showed that the rates R_p and R_p' are proportional to the 1.5 and 2.6 powers of wool concentration [W], respectively.

With respect to the variables studied, kinetic measurements of R_p and R_p' can now be formulated as follows:

$$R_p = K \frac{[DMA]^{0.92}[BC]^{0.80}[MMA]^{0.84}[W]^{1.5}}{[Ac]^{0.20}}$$

$$R_p' = K \frac{[DMA]^{0.92}[BC]^{0.80}[MMA]^{0.72}[W]^{2.6}}{[Ac]^{0.30}}.$$

Nature of Wool

The behavior of modified wools obtained by reduction, acetylation, or dinitrophenylation of wool toward grafting may be realized from Table IV. It is clear that reduced wool shows higher grafting than the unmodified wool. The opposite is the case with acetylated and dinitrophenylated wools.

Reduction of wool with TGA is well known to increase considerably its thiol content. The higher grafting obtained with reduced wool could, therefore, be associated with the easy abstraction of hydrogen atom via a

TABLE IV
Influence of Modification of Wool on Graft Yield[a]

| | Graft yield, % | | | |
Substrate	1 hr[b]	2 hr	3 hr	4 hr
Untreated wool	48	90	140	160
TGA-reduced wool	120	148	178	206
Acetylated wool	4	6	20	36
Dinitrophenylated wool	—	—	4	7

[a] [DMA]:[BC]:[Ac], 0.16:0.175:0.20 mole/l.; ethanol:water, 10:90; MMA, 8%; temperature, 70°C; material:liquor ratio, 1:50.
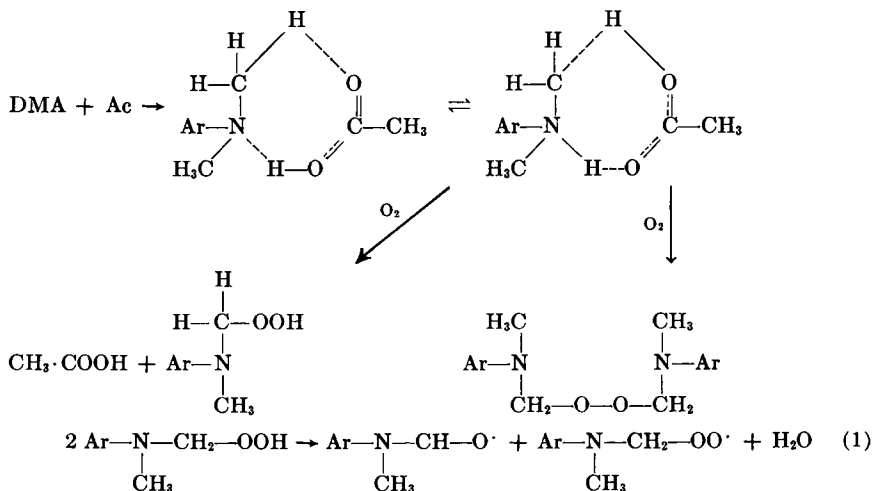
[b] Reaction time.

chain transfer process.[17,27,46] Nevertheless, increased accessibility of wool toward grafting by reduction cannot be neglected.
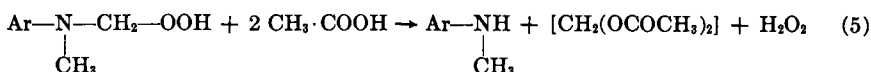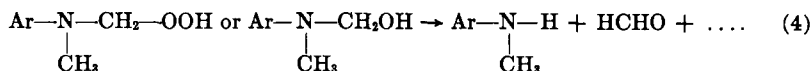
Acetylation and dinitrophenylation of wool reduces significantly its susceptibility toward grafting. This is, again, in accordance with previous reports[17,18] which ascribed this to the presence of acetyl or dinitrophenyl groups in the wool molecule. These groups were assumed to cause (a) lowering of the swellability of wool fibers, (b) blocking of some of the hydroxyl and amino groups (possible sites for grafting), and (c) hindrance of adsorption of MMA owing to low fiber swellability and repulsion of MMA molecule by the negatively charged substituted nitro groups in the case of DNP-wool. The net effect of all these functions is decreased grafting.

Tentative Mechanism for Initiation of Grafting

According to previous studies,[28-30,50] creation of free-radical species in a system containing DMA, BC, and Ac follows several paths:

1. Ac accelerates the auto-oxidation of DMA, via hydrogen-bonded complex formation, to yield aminohydroperoxides which function as chain carrier in the following auto-oxidation:

$$2 \ Ar\text{—}N\text{—}CH_2\text{—}OOH \rightarrow Ar\text{—}N\text{—}CH\text{—}O^{\cdot} + Ar\text{—}N\text{—}CH_2\text{—}OO^{\cdot} + H_2O \quad (1)$$

$$Ar-\underset{\underset{CH_3}{|}}{N}-CH_2-OO\cdot \ +\ Ar-\underset{\underset{CH_3}{|}}{N}-CH_3 \rightarrow Ar-\underset{\underset{CH_3}{|}}{N}-CH_2-O-OH \ +\ Ar-\underset{\underset{CH_3}{|}}{N}-CH_2\cdot \quad (2)$$

$$Ar-\underset{\underset{CH_3}{|}}{N}-CH_2-OOH \ +\ 2\ Ar-\underset{\underset{CH_3}{|}}{N}-CH_3$$

$$\rightarrow Ar-\underset{\underset{CH_3}{|}}{N}-CH_2-OH \ +\ H_2O \ +\ 2\ Ar-\underset{\underset{CH_3}{|}}{N}-CH_2\cdot \quad (3)$$

$$Ar-\underset{\underset{CH_3}{|}}{N}-CH_2-OOH \ or\ Ar-\underset{\underset{CH_3}{|}}{N}-CH_2OH \rightarrow Ar-\underset{\underset{CH_3}{|}}{N}-H \ +\ HCHO \ +\ \ldots. \quad (4)$$

$$Ar-\underset{\underset{CH_3}{|}}{N}-CH_2-OOH \ +\ 2\ CH_3\cdot COOH \rightarrow Ar-\underset{\underset{CH_3}{|}}{NH} \ +\ [CH_2(OCOCH_3)_2] \ +\ H_2O_2 \quad (5)$$

$$H_2O_2 \rightarrow 2\ HO\cdot \quad (6)$$
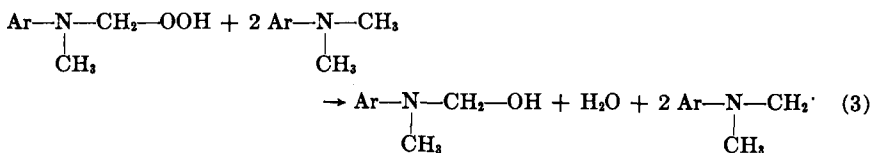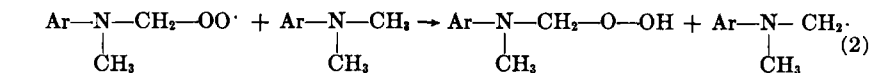
2. The nucleophilic attack of the dimethylamino nitrogen of DMA on the methylene carbon in the BC gives rise to generation of free radicals as suggested by eq. (7):

$$Ar-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N^{\delta+}}}\ldots\ldots\underset{\underset{Ar}{|}}{CH_2}-Cl^{\delta-} \rightarrow \unders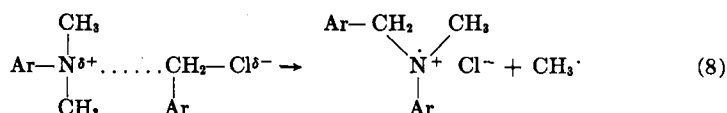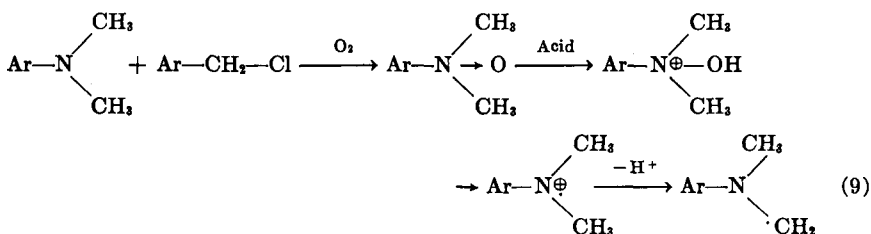et{\underset{Ar}{|}}{\overset{\overset{H_3C}{\diagdown}\ \overset{CH_3}{\diagup}}{N^+}\ Cl^-}\ CH_2 \ +\ Ar\cdot \quad (7)$$
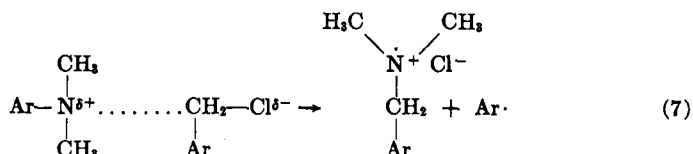
3. Alkyl exchange of the anilines occurred upon reacting DMA with BC and creation of methyl radicals as suggested by eq. (8):

$$Ar-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N^{\delta+}}}\ldots\ldots\underset{\underset{Ar}{|}}{CH_2}-Cl^{\delta-} \rightarrow \underset{\underset{Ar}{|}}{\overset{\overset{Ar-CH_2\diagdown\ \diagup CH_3}{}}{N^+}\ Cl^-} \ +\ CH_3\cdot \quad (8)$$

4. Formation of dimethylaniline N-oxide is possible in the presence of atmospheric oxygen and benzyl chloride. This oxide can undergo further fission, thereby producing free radicals as suggested by eq. (9):

$$Ar-\overset{\diagup CH_3}{\underset{\diagdown CH_3}{N}} \ +\ Ar-CH_2-Cl \overset{O_2}{\longrightarrow} Ar-\overset{\diagup CH_3}{\underset{\diagdown CH_3}{N}}\rightarrow O \overset{Acid}{\longrightarrow} Ar-\overset{\diagup CH_3}{\underset{\diagdown CH_3}{N^\oplus}}-OH$$

$$\rightarrow Ar-\overset{\diagup CH_3}{\underset{\diagdown CH_3}{N^\oplus}} \overset{-H^+}{\longrightarrow} Ar-\overset{\diagup CH_3}{\underset{\diagdown \cdot CH_2}{N}} \quad (9)$$

If $R\cdot$ represents the free radicals suggested by eqs. (1)–(3) and (6)–(9), grafting onto wool would occur according to the reactions suggested by eqs, (10) and (11):

$$R\cdot \ +\ WH \rightarrow RH \ +\ W\cdot \quad (10)$$

$$W\cdot \ +\ M \rightarrow WM\cdot \overset{M}{\longrightarrow} grafting \quad (11)$$
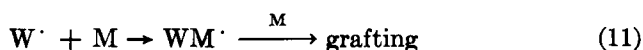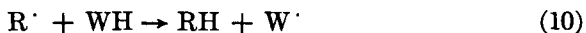
where WH and M represent wool and monomer, respectively. Wool radicals (W·) would also be created by solvent radical or hydrogen or hydroxyl radicals of water should such radicals be formed under the influence of the primary radical species on solvent and water.

That grafting has occurred is evidenced by the following:

(a) Extraction of the grafted products with acetone decreases the add-on till a stage is reached beyond which repeated extraction has practically no effect on the increase in weight (graft yield) of wool.

(b) Prior chemical modification of wool by acetylation and dinitrophenylation (cf Table IV) lowers the susceptibility of wool toward grafting because such modified wools lack most of the active sites (amino and hydroxyl groups) required for grafting. The reverse situation was encountered with reduced wool where more grafting sites (thiol groups) are additionally created sites on the wool molecules.[17,18,24,25]

(c) A comparison of the alkali solubility of the grafted product with that of a physical mixture of wool/PMMA and untreated wool reveals that the grafted product showed much lower solubility than the physical mixture and untreated wool (see below).

Alkali Solubility

The rates of alkali solubility of grafted wool, native wool, and a physical mixture of wool and PMMA are shown in Table V. The solubility test was performed for various time intervals following a standard procedure.[33] It is clear that the rate of alkali solubility of the untreated wool and the physical mixture are comparable, whereas that of the grafted wool is significantly lower. The reduction in alkali solubility after polymerization suggests that the synthetic polymer chains act as diffusion barriers toward alkali penetration into the wool fibers. In this way, the polypeptide chains, salt linkages, and disulfide linkages in wool are protected and remained practically unimpaired. Similar findings have been previously reported[27,44,46] and considered the fall in alkali solubility of wool after polymerization as a good indication that true grafting has occurred.

TABLE V
Rate of Alkali Solubility of Grafted Wool

Alkali solubility treatment, min	Native wool	Physical mixture of wool and PMMA (70:30)	Grafted wool (30% graft yield)[a]
10	5	3.5	—
20	9	8.0	—
30	11	10.0	—
45	13	13.0	2.0
60	16	15.5	5.0

[a] [DMA]/[BC]/[Ac]: 0.16:0.175:0.20 mole/l.; ethanol/water, 10:90; MMA, 8%; temperature, 70°C; material liquor ratio, 1:50.

TABLE VI
Felt Properties of Wool–Graft Copolymers[a]

Substrate	Graft, %	Felting improvement (% decrease in felting)
Untreated wool	—	zero
Wool–poly(methyl methacrylate) graft copolymer	4	37
	10	61
	40	no ball
	80	no ball
	100	no ball

[a] Felting of untreated wool is 0.13 g/cm^3.

Felting Properties

Previous reports[18,20,44] have shown that grafting of MMA and other vinyl monomers onto wool causes a considerable reduction in the tendency of wool to felt. Table VI shows the felting properties of wool after being grafted to different levels with MMA. Clearly, a significant improvement in the antifelt properties of wool is achieved at low graft yields, while higher grafting levels eliminates felting completely. The grafted polymer chains seem to impart greater dimensional stability as well as increase the internal viscosity of wool thereby making the latter resistant to deformation during the felting operation.

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