

Graft Copolymerization of Methacrylates onto Wool Fibers

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SYNOPSIS

Grafting of butyl (BuMA), decyl (DeMA), and octadecyl methacrylate (ODeMA) onto reduced wool was carried out by using $K_2S_2O_8$ or $K_2S_2O_8$ -LiBr redox system as initiator. The influence of the monomer and monomer concentration, temperature, and duration of the reaction on the percentage of grafting was studied. Evidence of grafting was provided by scanning electron microscopy, size exclusion chromatography, and infrared spectroscopy.

INTRODUCTION

In recent years many attempts have been made to modify wool fibers in order to improve some of their properties, e.g., shrinkage, hygroscopicity, thermal stability, dye uptake, etc.

One method of modification is grafting of vinyl monomers onto wool by a free radical mechanism. In this case the produced activated sites, along the peptide chains, initiate the polymerization of the vinyl monomers.

Free radicals may be produced on the polypeptide backbone by high-energy irradiation,¹⁻³ low-energy irradiation in presence or absence of sensitizers,⁴⁻⁶ and by powerful oxidizing agents such as periodate,⁷ ceric,⁸⁻¹³ and permanganate¹⁴ ions.

Free radicals on the wool macromolecules can also be produced by benzoyl peroxide^{15,16} or by the action of redox systems such as hydrogen peroxide-thiourea,¹⁷ peroxydiphosphate-thiourea,¹⁸ potassium persulfate-ferrous ammonium sulfate,¹⁹ potassium persulfate-thiomalic acid,²⁰ Fe^{2+} -hydrogen peroxide (Fenton's reagent),²¹ hydrogen peroxide-sodium thiosulfate,^{22,23} and potassium peroxydiphosphate-2-amino ethanethiol.²⁴

One of the most successful initiators studied for grafting vinyl monomers onto wool is potassium persulfate. Valentine and co-workers first investigated the graft copolymerization of acrylonitrile with

ammonium and potassium persulfate.²⁵ Arai, Komine, and Negishi²⁶ reported that the small amount of cysteine present in wool was responsible for the grafting of methyl methacrylate with $K_2S_2O_8$ as initiator and that the internally deposited polymers were truly grafted and crosslinked between wool chains. Arai, Negishi, and co-workers^{2,26-35} have also extensively studied the grafting of the methyl methacrylate onto wool with lithium bromide-potassium persulfate redox system as initiator, and they obtained significant percentages of grafted polymer practically without homopolymerization.

In the present study graft copolymerization of butyl, decyl, and octadecyl methacrylate onto reduced wool was carried by using $K_2S_2O_8$ and $K_2S_2O_8$ -LiBr redox system as initiators. These particular methacrylates have been chosen because the corresponding homopolymers have low glass transition temperature, and therefore they will not be expected to alter the flexibility of the wool fibers. The percentage of grafting has been determined as a function of monomer and monomer concentration, temperature, and duration of the reaction.

Evidence of the grafting was obtained by size exclusion chromatography (SEC), scanning electron microscopy (SEM), and infrared spectroscopy (IR).

EXPERIMENTAL

Materials

Australian 64's Merino wool was extracted for 24 h with acetone and 24 h with petroleum ether in a

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Table I SEC Results for Polymers Obtained after Hydrolysis and by Extraction of Grafted Wool

Monomer	Concentration of Monomer (mol/L)	Initiator	Duration of Polymeriz. (h)	Temperature of Polymeriz. (°C)	Polymer Obtained after Hydrolysis of Grafted Wool		Polymer Obtained by Extraction of Grafted Wool			
					$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	I^a	I^a
BuMA	0.282	K ₂ S ₂ O ₈	27	30	108.1	12.4	126.0	12.3	8.7	10.3
BuMA	0.282	K ₂ S ₂ O ₈ -LiBr	4	30	167.2	12.0	217.5	15.1	13.9	14.4
DeMA	0.088	K ₂ S ₂ O ₈	47	50	109.4	11.6	158.7	17.3	9.5	9.2
DeMA	0.099	K ₂ S ₂ O ₈ -LiBr	5	40	149.5	16.3	208.7	24.8	9.2	8.4
ODeMA	0.198	K ₂ S ₂ O ₈	27	30	233.6	20.3	330.0	26.9	11.5	12.3
ODeMA	0.133	K ₂ S ₂ O ₈ -LiBr	5	30	357.7	40.6	486.7	53.2	8.8	9.2

^a Based on polystyrene calibration. $I = \bar{M}_w/\bar{M}_n$.

Soxhlet apparatus, then washed in running water for 48 h, and dried in air at room temperature.

Butyl methacrylate (BuMA) and decyl methacrylate (DeMA) were washed with 5% sodium hydroxide solution, then dried with anhydrous sodium sulfate and distilled under reduced pressure. Octadecyl methacrylate (ODeMA) was purified by repeated crystallizations from methanol to constant melting point. The monomer was then vacuum dried. Gas chromatography, ¹H-NMR, and IR were used to check monomers purity. The results indicated that all monomers were virtually free of impurities.

First or special reagent-grade lithium bromide, potassium persulfate, thioglycolic acid (TGA), and diethylene glycol monobutyl ether (DEGMB) were used without further purification.

Apparatus

The size exclusion chromatograms were obtained using a Waters 150C instrument with a six-column μ -Styragel set (porosities ranging from 10² to 10⁶ Å) operating in THF at 30°C.

The scanning electron micrographs were obtained with a JEOL JSM 3CC scanning electron microscope operating at an accelerating voltage of 20 kV by using a polaroid Type 6 11 positive film. [The samples were mounted on Al stubs with double-sided tape, sputter coated with Au/Pd (30 nm).]

The infrared spectra were obtained with a JASCO PS-701 G Diffraction Grating Infrared Spectrophotometer.

Reduction of Wool Fibers

Woolen samples (1 g) were treated for 24 h at 30°C with a 0.2N solution of TGA adjusted to pH 4.7 (100 mL), washed with water, ethanol, and again with water (200 mL each), pressed out with filter paper, and then subjected to grafting.

Graft Copolymerization

The graft copolymerization was carried out by using two procedures as reported by Negishi, Arai, and co-workers.²⁶⁻²⁸

1. A 1-g portion of reduced wool was treated with 100 g of solution containing 0.2% K₂S₂O₈, 22.5% DEGMB, *a* percent monomer, and 77.3-*a* percent H₂O (by weight).
2. A 1-g portion of reduced wool was treated with 100 g of solution containing 0.2% K₂S₂O₈, 27.5% LiBr, 22.5% DEGMB, *a* per-

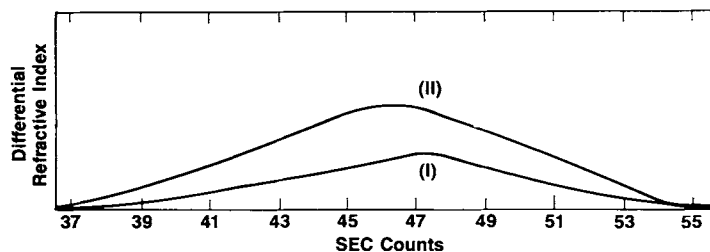


Figure 1 SEC chromatograms of grafted PBuMA onto wool after hydrolysis (I) and of PBuMA obtained by extraction (II) of grafted wool.

cent monomer and 49.8-a percent H₂O (by weight).

The concentration of monomer, the duration, and the temperature of the reaction were varied.

After the copolymerization the grafted samples were extracted with benzene, a solvent for the poly(methacrylate esters) used in this study, in a Soxhlet apparatus for 48 h in order to completely remove the homopolymer. Finally the samples were dried at 50°C in a vacuum oven to constant weight.

The percentage of grafting was determined by using the following relationship:

$$\% \text{ grafting} = (w_2 - w_1) \frac{100}{w_1}$$

where w_1 and w_2 are the weight of the wool and of the grafted wool, after solvent extraction of the homopolymer, respectively.

Evidence of Grafting

Some selected samples of grafted wool, after extraction with benzene, were hydrolyzed with 6*N* HCl at 115°C for 24 h. All the wool went into solution, leaving behind resinous masses, which were washed free of acid, dried, dissolved in benzene, and purified by two precipitations.

The infrared spectra of these resinous masses have the characteristic bands of PBuMA, PDeMA, and PODEMA f.e. the carbonyl stretch band lies between 1700 and 1725 cm⁻¹ and the carbon-hydrogen stretch band between 2915 and 2960 cm⁻¹.

The apparent weight-average molecular weight \bar{M}_w , apparent number-average molecular weight \bar{M}_n , and the polydispersity coefficient $I = \bar{M}_w/\bar{M}_n$ of the polymethacrylates isolated after hydrolysis of the grafted wool and of the corresponding polymers precipitated with methanol from the extract of grafted wool were determined by SEC, using polystyrene standards for calibration. The results are given in

Table I and an example is shown in Figure 1. It seems that the \bar{M}_w and \bar{M}_n values of the grafted polymethacrylates are lower than the corresponding homopolymers. This is probably due to the fact that the copolymerization taking place at the fiber surface is more sterically hindered than the homopolymerization taking place in the solution. This may be also due to the fact that on the fiber surface the rate of termination (mainly disproportionation for these monomers) would be expected to be higher than it would be in solution, since radicals are in close proximity at the fibers. The high values of the polydispersity coefficient indicate that initiation sites of substantially different reactivity are being created and that side reactions are taking place during the polymerization of methacrylates in this heterogeneous system.

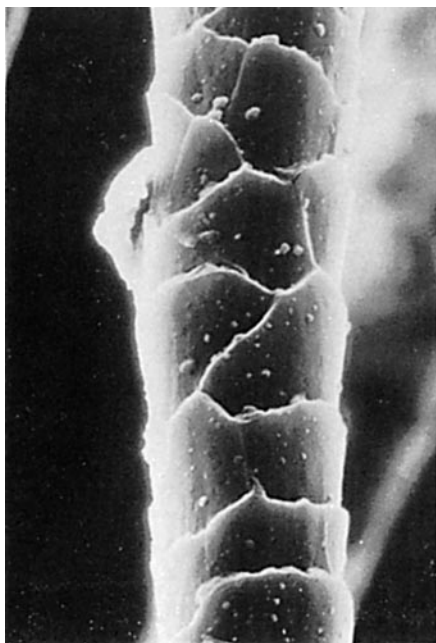
Physical mixtures of PBuMA, PDeMA, or PODEMA and wool were prepared by dispersing wool in benzene solution of PBuMA, PDeMA, or PODEMA. The dispersion was stirred for 24 h and filtered. The residue was extracted with benzene for 48 h in a Soxhlet. After extraction the residue was hydrolyzed with 6*N* HCl at 115°C for 24 h. No residue of PBuMA, PDeMA, and PODEMA was obtained, indicating that the benzene removes completely the homopolymer from the physical mixtures.

Comparison of scanning electron micrographs of untreated wool fiber and grafted wool fiber indicated that considerable polymer was deposited onto the wool fibers and the surface structure of the fibers was altered (Fig. 2).

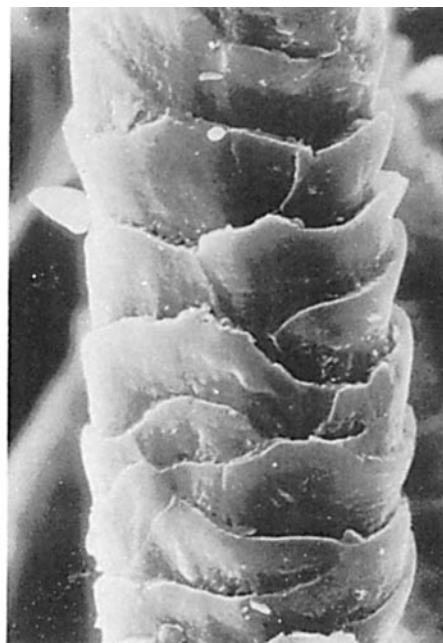
RESULTS AND DISCUSSION

Effect of Monomer on Grafting

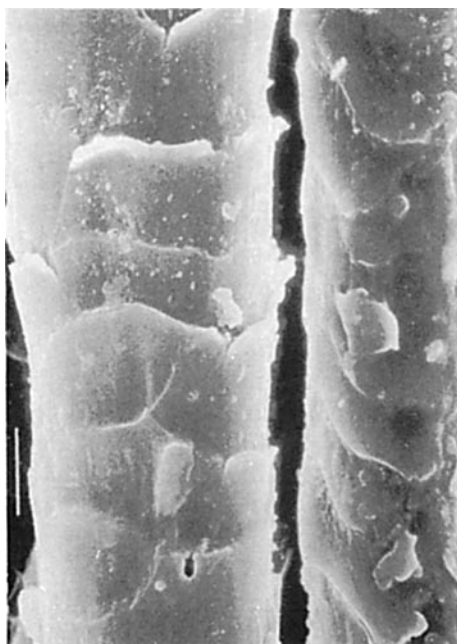
The results presented in Figures 3 and 4 indicate that the percentage of grafting decreases with increasing the bulkiness of the side group. This means



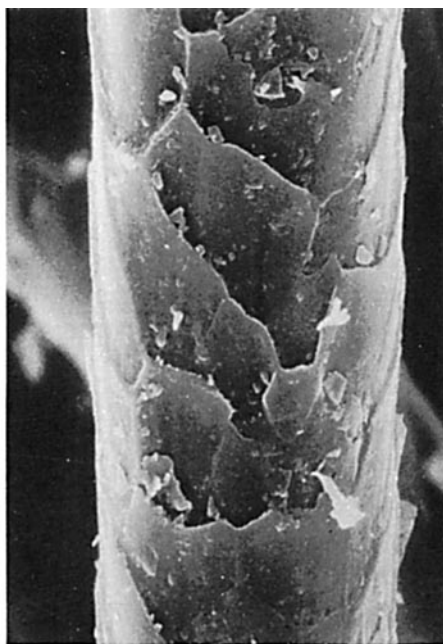
Unreacted Wool



Wool-g-Poly BuMA



Wool-g-Poly DeMA



Wool-g-Poly O DeMA

Figure 2 Scanning electron micrographs of unreacted wool, wool-g-polyBuMA, wool-g-polyDeMA, and wool-g-polyODeMA (magnification 1300 times).

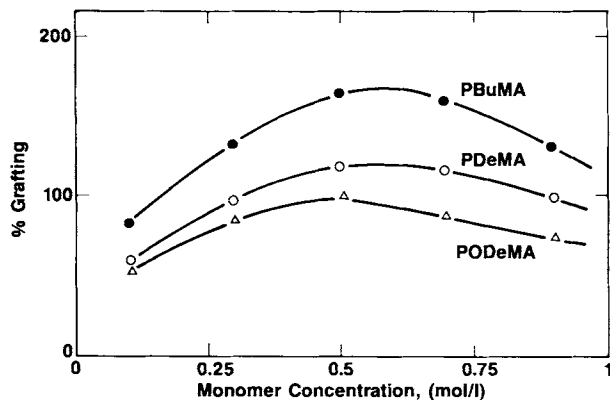


Figure 3 Percent grafting vs. monomer concentration for reduced Merino 64's wool (initiator: $K_2S_2O_8$, temp.: $30^\circ C$, duration: 24h).

that as the size of the side group increases, diffusion of monomers to all available active sites is not possible. These results are also confirmed by SEM.

Effect of Monomer Concentration

The effect of monomer concentration on grafting was studied in the range of 0.1–1 mol/L by keeping all other conditions constant. The results are given in Figures 3 and 4. The percentage of grafting initially increases with increasing monomer, reaches a maximum, and then decreases. The maximum, in all cases, decreases with increasing the size of the side group of the monomer and is at higher concentrations for the system $K_2S_2O_8$ -LiBr than for $K_2S_2O_8$. In the beginning with increasing the concentration of the monomer, more monomer reaches

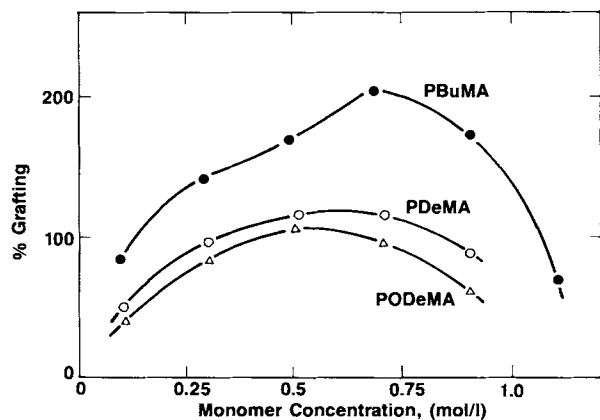


Figure 4 Percent grafting vs. monomer concentration for reduced Merino 64's wool (initiator: $K_2S_2O_8$ -LiBr, temp.: $30^\circ C$, duration: 2h).

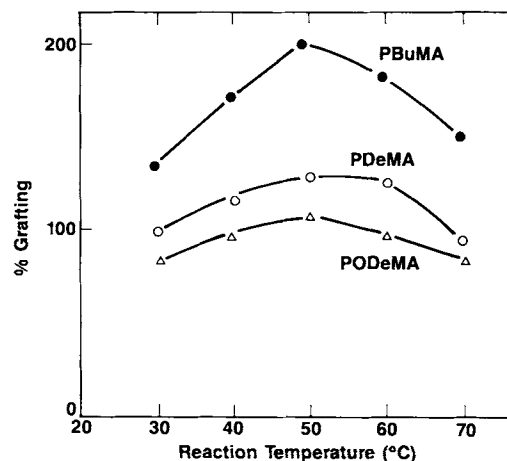


Figure 5 Percent grafting vs. reaction temperature for reduced Merino 64's wool (initiator: $K_2S_2O_8$, duration: 24h, $c = 0.3$ mol/L).

the wool active sites and copolymerizes onto the wool. After a certain concentration (0.5–0.6 mol/L for $K_2S_2O_8$ and 0.55–0.7 for $K_2S_2O_8$ -LiBr system) it seems that the diffusion rate of monomer onto the wool is affected by the polymer deposition, which is increased greatly with increasing concentration. The higher maxima of the methacrylates with the smallest size group may be due to their higher diffusibility through wool fibers. The higher maxima in the case of $K_2S_2O_8$ -LiBr system can be attributed in the presence of LiBr, which on one hand activates more wool sites for copolymerization and on the other hand enhances the swellability of wool.

Effect of Temperature

The graft copolymerization of the monomers was studied at five different temperatures from 30– $70^\circ C$ keeping all other conditions constant. The results are given in Figures 5 and 6.

The percentage of grafting initially increases as the temperature rises, reaches a maximum ($50^\circ C$ for $K_2S_2O_8$ and $40^\circ C$ for $K_2S_2O_8$ -LiBr system) and finally decreases. The initial increase is mainly due to the increase in the diffusion rate of monomer onto the wool because on the one hand of the increased mobility of monomers and on the other hand of the enhanced swellability of wool. At higher temperatures it seems that the homopolymerization in solution is faster than the copolymerization onto the wool fibers. The lower maximum of $K_2S_2O_8$ -LiBr system shows the higher initiation efficiency of this system.

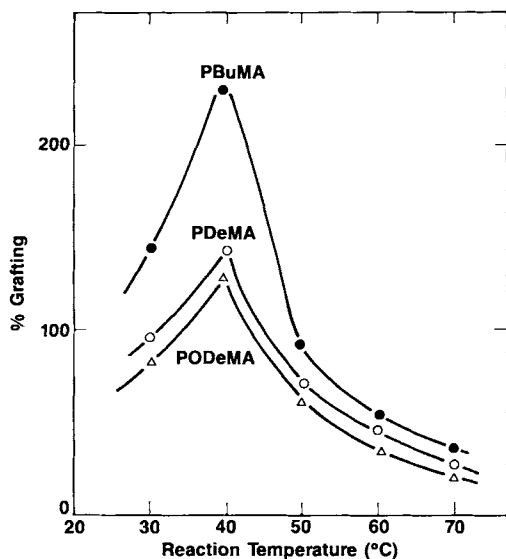


Figure 6 Percent grafting vs. reaction temperature for reduced Merino 64's wool (initiator: $K_2S_2O_8$ -LiBr, duration: 2 h, $c = 0.3$ mol/L).

Effect of Reaction Duration

The graft copolymerization of BuMA, DeMA, and ODeMA onto wool was studied at duration times ranging from 24–144 h ($K_2S_2O_8$) and from 1–7 h ($K_2S_2O_8$ -LiBr) keeping all other conditions constant. The results are given in Figures 7 and 8.

In the beginning the percentage grafting increases, reaches a maximum (96 h for $K_2S_2O_8$ and 5 h for $K_2S_2O_8$ -LiBr), and then decreases.

The fall in percentage of grafting may be attributed to the formation of polymer deposits that affects the accessibility of monomer to the active sites,

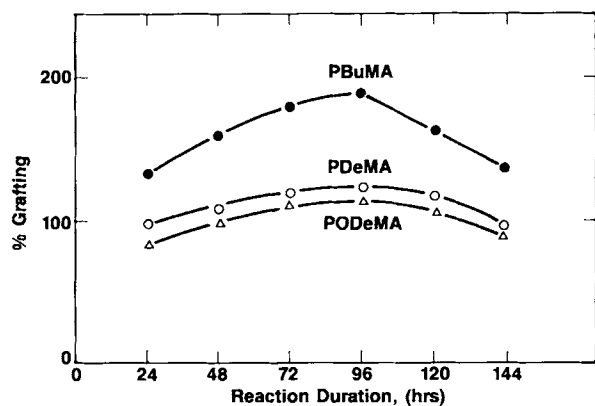


Figure 7 Percent grafting vs. reaction time for reduced Merino 64's wool (initiator: $K_2S_2O_8$, temp.: $30^\circ C$, $c = 0.3$ mol/L).

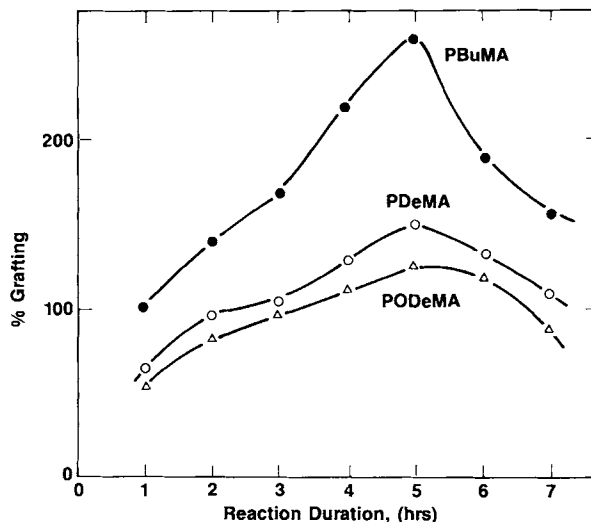


Figure 8 Percent grafting vs. reaction time for Merino 64's wool (initiator: $K_2S_2O_8$ -LiBr, temp.: $30^\circ C$, $c = 0.3$ mol/L).

thus reducing the grafting. However, other factors might also influence the fall in percentage of grafting, and further studies are required to elucidate this matter. It should be noted here that in almost 20 times, less duration the $K_2S_2O_8$ -LiBr gives more grafting than the $K_2S_2O_8$ system.

In conclusion the $K_2S_2O_8$ -LiBr system for BuMA, DeMA, and ODeMA is much more efficient for grafting the wool than potassium persulfate alone. The grafting can be controlled by varying the concentration and the side group of the monomer, the temperature, and the duration of the reaction. In a coming paper the properties (shrinkage, hygroscopicity, dye uptake, mechanical, etc.) of grafted wool with these methacrylates will be discussed.

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