Modification of Woolen Fabrics through Grafting with Methacrylic Esters

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ABSTRACT: Grafting of methyl, *n*-butyl, *n*-decyl, and *n*-octadecyl methacrylate onto reduced woolen fabrics was carried out by using $K_2S_2O_8$ and $K_2S_2O_8$-LiBr redox system as initiators. The success of the grafting was proven by scanning electron microscopy, size exclusion chromatography, and infrared spectroscopy. The felting shrinkage and water-repellency tests were applied on the modified fabrics. Dyeing with an α-bromoacrylamido and an aminoxanthene dye was carried out and the color-fastness tests were applied on the modified dyed fabrics. The influence of the grafted polymethacrylates on the shrinkproofing, water-repellency, and dyeing properties of the woolen fabrics was discussed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2399–2407, 1997

Key words: woolen fabrics; grafting; methacrylic esters; shrinkage; color fasteness; water repellency

INTRODUCTION

The most important disadvantage of woolen fabrics is the felting shrinkage, due to the presence of overlapping scales on the fiber surface. During washing or friction, scales of adjacent fibers interlock and a "walking" or "ratchet" effect occurs, allowing the fibers to migrate until they are completely entangled and thus producing a permanent setting.[1,2] The elimination of felting shrinkage by coating fiber surfaces with polymers has been studied extensively.[3–16]

In a previous article[17] the grafting of *n*-butyl (BuMA), *n*-decyl (DeMA), and *n*-octadecyl methacrylate (ODeMA) onto reduced wool fibers by using $K_2S_2O_8$ and $K_2S_2O_8$-LiBr as initiators was studied. The evidence of grafting was provided by scanning electron microscopy of the modified fibers and by size exclusion chromatography, as well as by IR spectroscopy of the polymethacrylates obtained after hydrolysis of the wool with 6 *N* HCl.

In this article the same technique was used for grafting the above monomers and methyl methacrylate (MMA).

The felting shrinkage tests were carried out on the modified fabrics to study the shrinkproofing ability of the polymethacrylates.

The dyeing of the modified woolen fabric with two kinds of dyes suitable for dyeing of wool, an α-bromoacrylamido reactive dye[18–24] and an aminoxanthene (rosamine) acid dye[22] and the color-fastness properties of these dyed woolen samples were also studied.

Finally, the role of the grafted onto wool methacrylates on the water repellency[25–28] was investigated.

EXPERIMENTAL

Materials

A 225 g/m^2 undyed woolen fabric containing 23 ends and 19 picks/cm was used. The fabric was extracted for 24 h with acetone and 24 h with petroleum ether in a Soxhlet apparatus, then washed in running water for 48 h and dried in air at room temperature.

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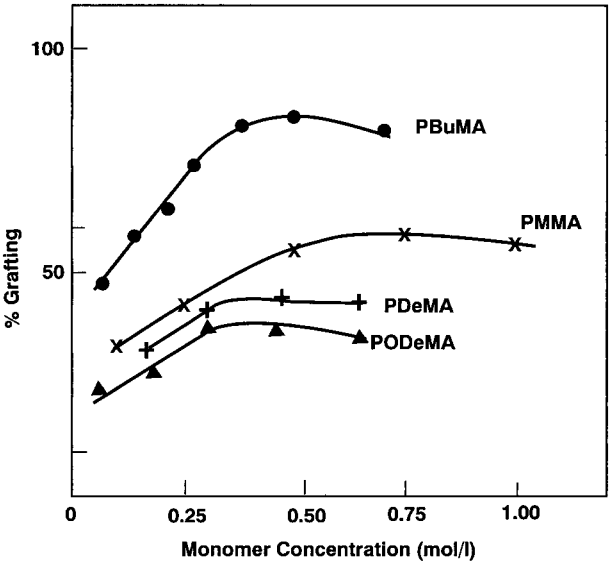

Figure 1 Percent grafting vs. monomer concentration for reduced woolen fabric (initiator $K_2S_2O_8$, temperature 30°C, duration 72 h).

MMA was purified by distillation under reduced pressure (24°C/24 mmHg). The purity checked by GC was better than 99.5%. The purification of BuMA, DeMA, and ODeMA was described in the previous article.[17]

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

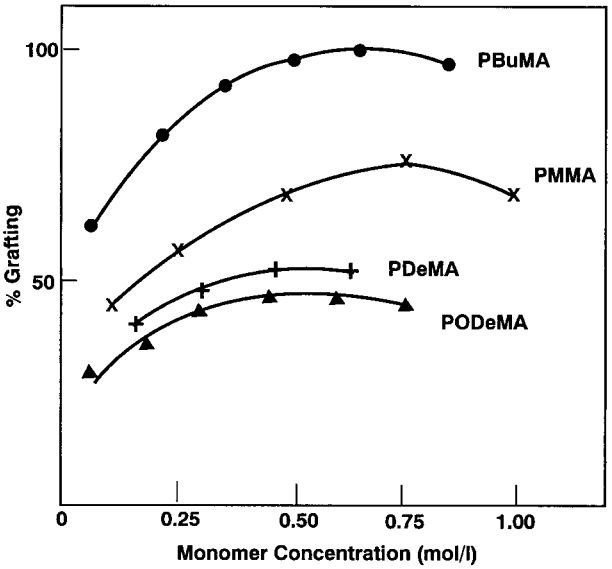

Figure 2 Percent grafting vs. monomer concentration for reduced woolen fabric (initiator $K_2S_2O_8$-LiBr, temperature 30°C, duration 4 h).

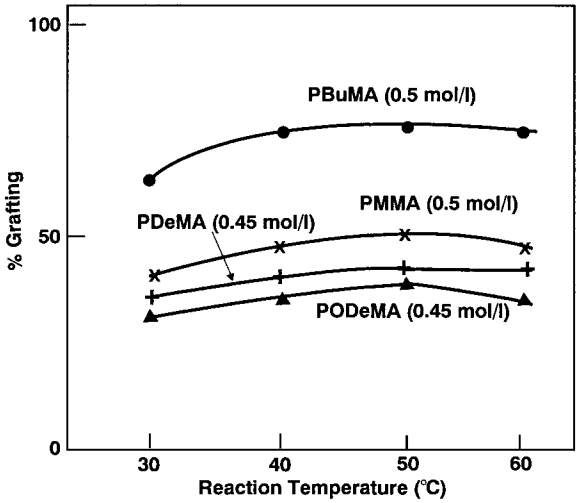

Figure 3 Percent grafting vs. reaction temperature for reduced woolen fabric (initiator $K_2S_2O_8$, duration 24 h).

The dyes Lanasol Rouge 2G (C.G.Y.) (C.I. Reactive Red 116) and Acid Red XB (C.G.Y.) (C.I. Acid Red 52 and C.I. 45100) and the auxiliary product Albegal B (an amphoteric levelling agent) were generously supplied by Ciba–Geigy. Sodium sulfate, ammonium sulfate, acetic acid, and sulfuric acid, which were used as dyeing assistants, were first reagent grade.

Apparatus

The characteristics of the scanning electron microscope, IR spectrometer, and size exclusion

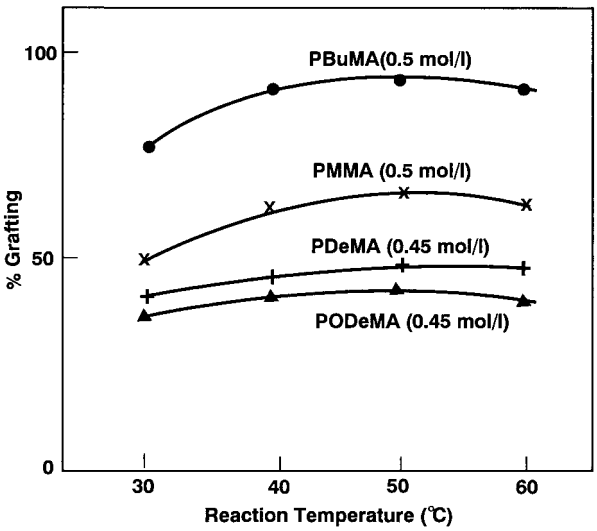

Figure 4 Percent grafting vs, reaction temperature for reduced woolen fabric (initiator $K_2S_2O_8$-LiBr, duration 2 h).

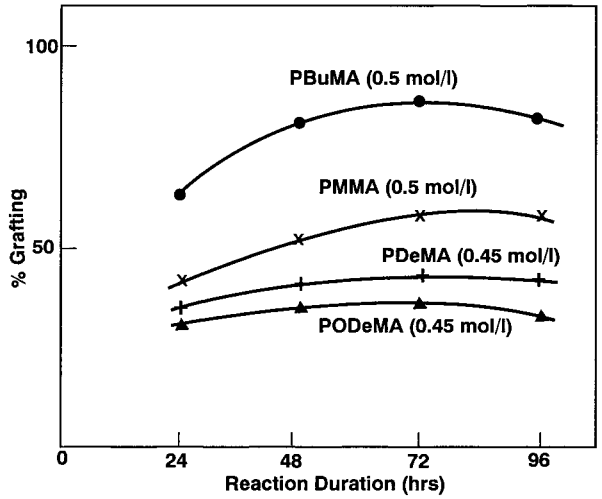

Figure 5 Percent grafting vs. reaction time for reduced woolen fabric (initiator $K_2S_2O_8$, temperature 30°C).

chromatography were given in the previous article.[17] The T_g of the polymehacrylates was determined with TA Instruments DSC 2910 Modulated DSC.

The area shrinkage was determined with the Cubex International Shrinkage Testing Apparatus according to International Wool Secretariat (IWS) Test Method No. 185.

The dyeing of the grafted woolen fabric was performed in a Linitest Bath. An Electrophotometer ELKO III was used to determine the optical densities of the solutions at the wavelength of maximum absorption (λ = 550 nm with filter

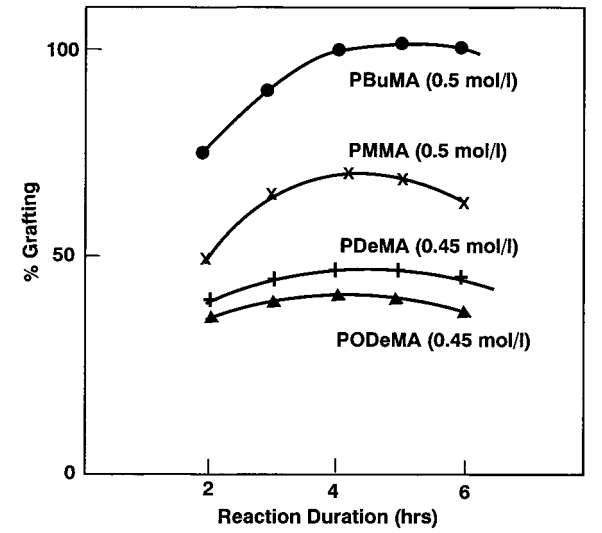

Figure 6 Percent grafting vs. reaction time for reduced woolen fabric (initiator $K_2S_2O_8$-LiBr, temperature 30°C).

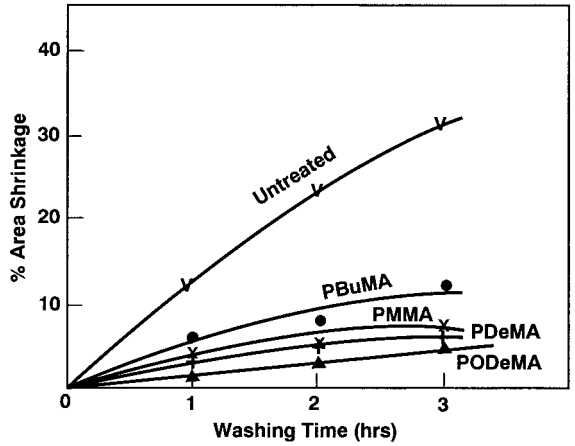

Figure 7 Percent area shrinkage vs. washing time for reduced woolen fabric (initiator $K_2S_2O_8$, c = 0.5 mol/L).

S55E for the reactive dye and λ = 587 nm with filter S59E for the acid dye).

The water repellency of woolen fabric was determined by the Spray Test Apparatus according to the ASTM D583-63 Method.

Reduction of Woolen Fabrics and Graft Copolymerization

Reduction of the disulfide groups of the wool macromolecular chains to mercaptan groups gives radicals that initiate the polymerization of the monomers was performed with TGA according to the protocole given in the previous article for wool.[17]

The reduced fabrics were grafted with the monomers in aqueous solution of DEGMB and of the initiator ($K_2S_2O_8$ and K_2S_2O8-LiBr), at differ-

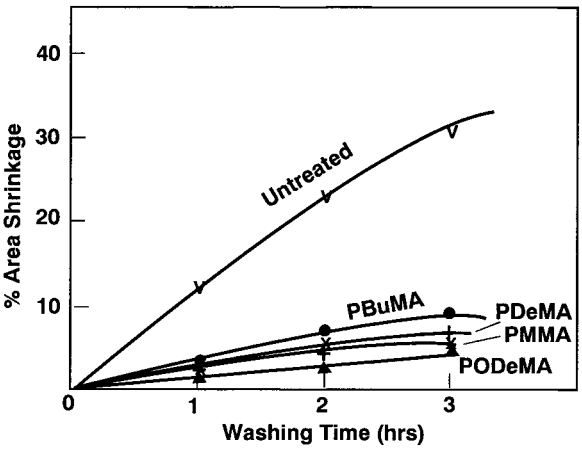

Figure 8 Percent area shrinkage vs. washing time for reduced woolen fabric (initiator $K_2S_2O_8$-LiBr, c = 0.5 mol/L).

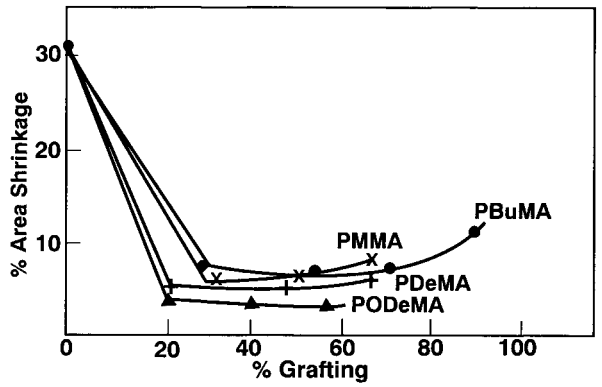

Figure 9 Percent area shrinkage after 3 h vs. percent grafting for reduced woolen fabric (initiator $K_2S_2O_8$).

ent monomer concentration, temperature, and reaction time. The evidence of the chemically attached polymethacrylate onto the wool macromolecules was provided either by SEM of the fabrics or by SEC and IR spectroscopy of the homopolymers obtained after hydrolysis of the wool by HCl 6 *N*. Details are given in our previous article.[17]

The yield of the grafting was expressed as:

$$\% \text{ Grafting} = (W2 - W1)/W1 \times 100$$

where W_1 is the weight of the initial fabric and W_2 the weight of the grafted fabric after the elimination of the absorbed homopolymer by extraction.

Felting Shrinkage Test

Test specimens (12.5 × 12.5 cm) were prepared by sewing the edges with a dimensionally stable thread and marking with small knots of cotton thread. The marks allow three separate length measurements in both warp and fill directions.

Washing was carried out at 40°C for 3 h in a phosphate buffer solution, of pH = 7. This solution consisted of 4.5 g NaH_2PO_4 and 8.0 g Na_2HPO_4 in 1 L water.

The distance between the reference points was measured by spreading the specimens under a glass plate, after rinsing and sqeezing lightly.

The area felting shrinkage was calculated from the width and length felting shrinkage:

$$\text{Area Felting Shrinkage } (\%) = \text{W.S.} + \text{L.S.} - (\text{W.S.} \times \text{L.S.}/100)$$

where W.S. is the width felting shrinkage (%) and L.S. is the length felting shrinkage (%).

The time dependence of the area of felting shrinkage was determined by measuring periodically of the area of shrinkage of the samples during washing.

To study the effect of surface coverage on the area of felting shrinkage, specimens of woolen fabric were grafted with different monomer concentrations. They were then washed according to the International Wool Secretariat (IWS) Test Method and their area of shrinkage was measured.

Dyeing Properties

Samples of untreated and grafted woolen fabric were dyed by the following procedures.

Dyeing with Reactive Dye

Samples (1.0 g) were placed in stainless dye vessels containing 50 mL of aqueous solutions consisting of 1.5% (w/w) of the reactive dye Lanasol Rouge 2G, 4% (w/w) ammonium sulfate, 1% (w/w) sulfuric acid, 5% (w/w) sodium sulfate, and 1% (w/w) of the auxiliary product Albegal B, which is an amphoteric levelling surfactant agent (percentages are based on the weight of sample to be dyed); the pH of the dyebath was 5.6–6. Then vessel caps were screwed on to prevent the escape of dyebath and the closed dye vessels were immersed in a Linitest bath (dyeing machine) and agitated throughout the dyeing period. In the beginning the temperature of the dyebath was

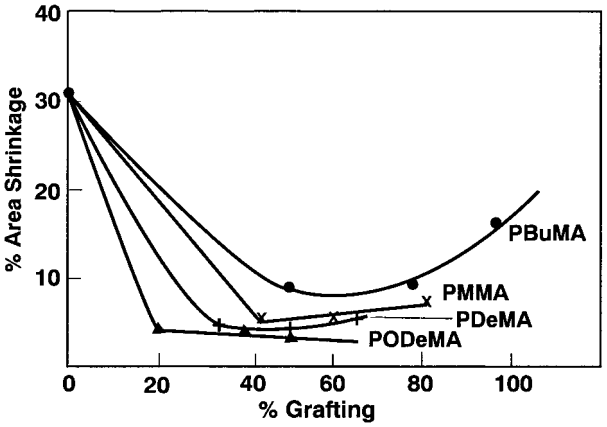

Figure 10 Percent area shrinkage after 3 h vs. percent grafting for reduced woolen fabric (initiator $K_2S_2O_8$-LiBr).

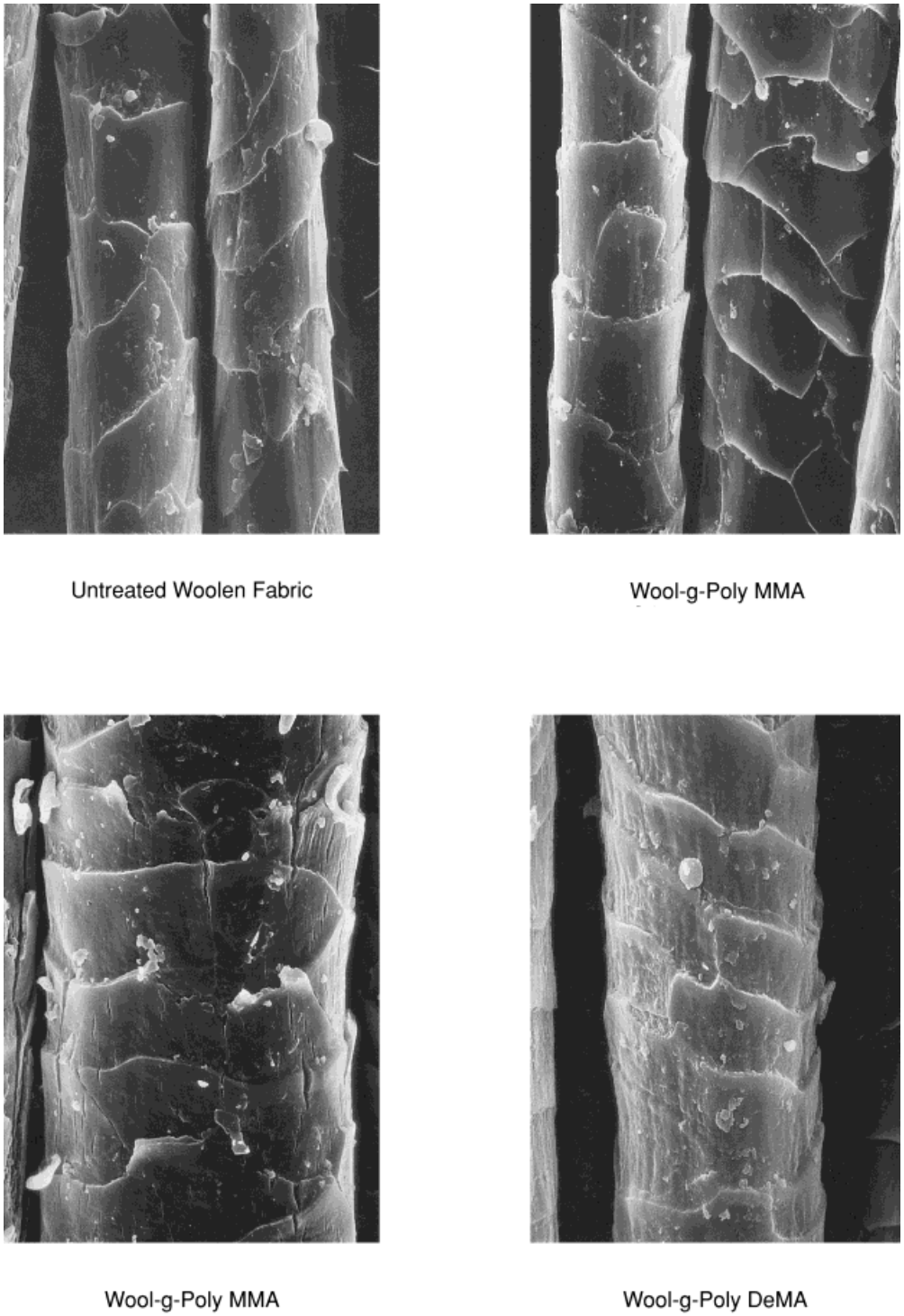

Figure 11 Scanning electron micrographs of unreacted woolen fabric, wool-*g*-polyMMA (initiator $K_2S_2O_8$), wool-*g*-polyMMA (initiator $K_2S_2O_8$-LiBr), and wool-*g*-polyDeMA (initiator $K_2S_2O_8$-LiBr) (magnification 1300 times).

50°C for 15 min, then the temperature was raised to 100°C at the rate of 1°C/min and maintained at 100°C for 70 min.

Small aliquots were removed from the dyebath periodically and analyzed for the dye remaining in solution by measurement of the λmax of the dye at 550 nm (filter S55E) using an ELKO III Electrophotometer.

Dyeing with Acid Dye

Samples (1.0 g) were placed in stainless dye vessels containing 50 mL of aqueous solutions consisting of 1.5% (w/w) of the acid dye Acid Red XB, 4% (w/w) sulfuric acid, and 5% (w/w) sodium sulfate (percentages based on the weight of wool to be dyed); the pH of the dyebath is 2.3–3.5. Then the vessel caps were screwed on and the closed dye vessels were immersed in a Linitest dyeing machine, and agitated throughout the dyeing period. In the beginning, the temperature of the dyebath was 50°C for 15 min, then the temperature was raised to 100°C at the rate of 1°C/min and maintained at 100°C for 60 min.

Also, small aliquots were removed from the dyebath periodically and analyzed for the dye remaining in solution by measurement of the λmax of the dye at 587 nm (filter S59E) using the ELKO III Electrophotometer.

The Exhaustion values were calculated by using the follow relation:

$$\% \text{ Exhaustion} = (OD_o - OD_t)/OD_o \times 100$$

where OD_o is the optical density of the dyebath at time $t = 0$
and OD_t is the optical density of the dyebath at time t.

Color Fastness Test of the Dyed-Grafted Woolen Fabric

After dyeing, the woolen samples were washed thoroughly with water and air dried for 48 h.

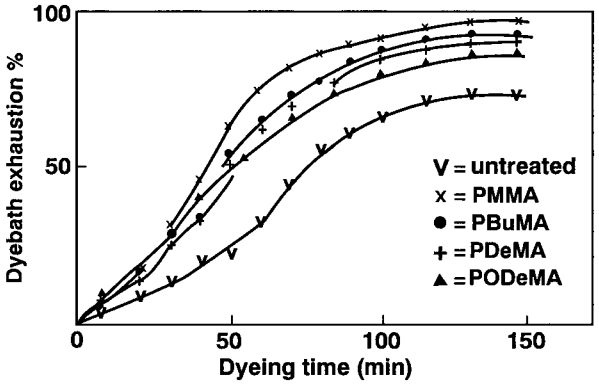

Figure 12 Percent dyebath exhaustion vs. dyeing time for reduced woolen fabric (initiator $K_2S_2O_8$, temperature 30°C, duration 24 h, c = 0.5 mol/L).

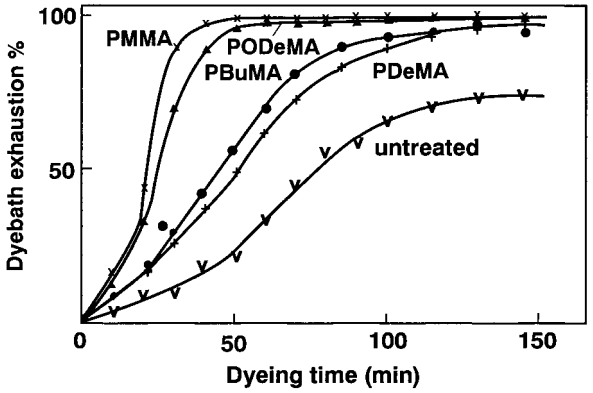

Figure 13 Percent dyebath exhaustion vs. dyeing time for reduced woolen fabric (initiator $K_2S_2O_8$-LiBr, temperature 30°C, duration 2 h, c = 0.5 mol/L).

Then, color-fastness tests were carried out to these samples using the procedures described as Standard Methods of Society Dyers and Colourists (S.D.C.) (1978). Color Fastness to light (B 01), to water (E 01), to sea water (E 02), to hot water (E 08), to perspiration (E 04), to washing (C 03), to dry cleaning (D 01), to bleaching (hypochlorite) (N 01), and to rubbing (dry and wet) (X 12).

Water Repellency Test

The water repellency of the grafted woolen samples was determined by the Spray Test Method (ASTM D 583-63). This method is intended for determining the effectiveness of water-repellent finishes on the fabric surface.

In this test, three specimens for each test (17.5

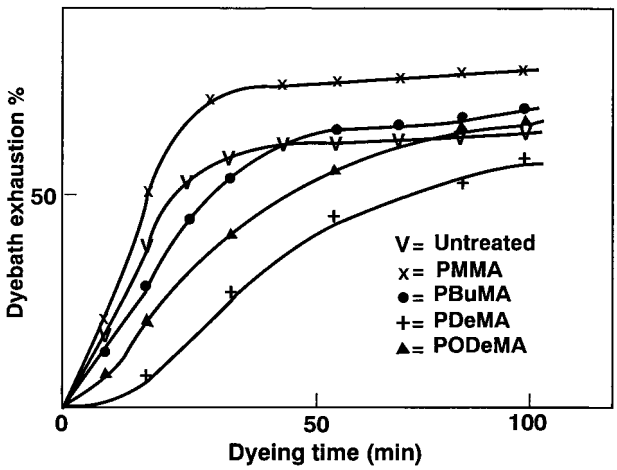

Figure 14 Percent dyebath exhaustion vs. dyeing time for reduced woolen fabric (initiator $K_2S_2O_8$, temperature 30°C, duration 24 h, c = 0.5 mol/L).

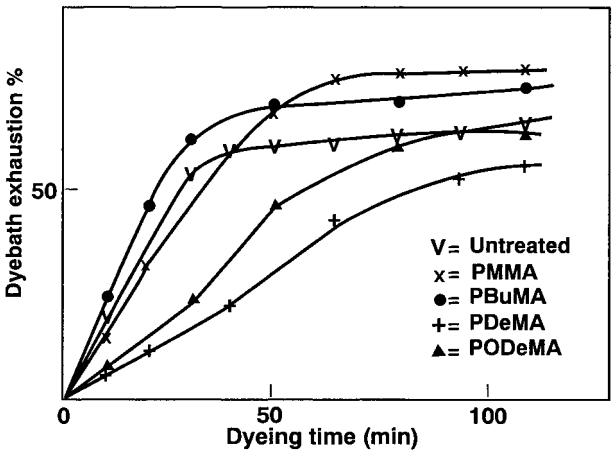

Figure 15 Percent dyebath exhaustion vs. dyeing time for reduced woolen fabric (initiator $K_2S_2O_8$-LiBr, temperature 30°C, duration 2 h, c = 0.5 mol/L).

× 17.5 cm) were sprayed with water by the Spray test Apparatus, the appearance of the specimens after spraying was compared with a set of standard photographs, and the water repellent effect was assessed subjectively. An approximate guide to water-based stain repellency was obtained: the higher the spray rating, the better the strain resistance. A scale from 0 (no water repellency) to 100 (excellent water repellency) was employed. A minimum spray rating of 80–90 is generally essential for strain-repellent finishes.

RESULTS AND DISCUSSION

Graft Copolymerization

The result of the percent grafting for the different monomers at different monomer concentration, temperature, and duration of the grafting for the two initiator systems are presented in Figures 1 to 6.

In all graphs the degree of grafting decreases with increasing bulkiness of the side group. This is due to the fact that as the side group increases, the diffusion of the monomer to all active sites available along the wool macromolecule is sterically hindered. Only PMMA does not obey this trend; despite the fact that it has a smaller side group than PBuMA, it achieves a lower degree of grafting. Therefore, it seems that the extent of grafting does not only depend on the bulkiness of the side group of the monomeric unit involved, but also on the glass transition temperature (T_g) of the corresponding polymer.

The T_g of the grafted homopolymers PMMA, PBuMA, PDeMA, and PODeMA are, respectively, 105, 20, −70, and −100°C, as measured by Differential Scanning Calorimetry. All the grafting temperatures experienced here are higher than the T_g of the corresponding polymers, with the exception of PMMA. Consequently, the addition of MMA to the free radicals is diffusion delayed due to the presence of glassy PMMA.

The extent of grafting is therefore facilitated by the smallness of the side group and the thermal mobility of the grafted polymer. This explains why the grafting of BuMA is more extensive than that of MMA (the T_g factor overbalances the bulkiness of the side group) and the grafting of MMA is higher than that of DeMA or ODeMA (the bulkiness overwhelms the T_g factor).

Comparison of grafting on fibers[17] and on tissue, when all other conditions are kept the same, clearly demonstrates that the denser the texture of the fabric the less grafting occurs.

Felting Shrinkage

As noted in the Introduction, felting shrinkage is due to the cuticular scales of wool that overlap

Table I Graft Copolymerization of Methacrylates onto Woolen Fabrics

Sample	Monomer	Monomer (mol/L)	Initiator	Duration/Temper. (h/°C)	Grafting (%)
1	Unmodified	—	—	—	—
2	MMA	0.3	$K_2S_2O_8$	26/30	37
3	MMA	0.4	$K_2S_2O_8$-LiBr	5/30	64
4	BuMA	0.3	$K_2S_2O_8$	27/30	98
5	BuMA	0.3	$K_2S_2O_8$-LiBr	4/30	140
6	DeMA	0.1	$K_2S_2O_8$	47/50	40
7	DeMA	0.1	$K_2S_2O_8$-LiBr	5/40	50
8	ODeMA	0.2	$K_2S_2O_8$	27/30	19
9	ODeMA	0.15	$K_2S_2O_8$-LiBr	5/30	48

Table II Color Fastness of Grafted Woolen Fabric Dyed with Reactive Dye Lanasol Rouge 2G

Color Fastness to	1	2	3	4	5	6	7	8	9
Light	5	7	6	6	5	6	6	6	6
Water	4–5	5	5	5	5	5	5	5	5
Sea water	4–5	5	4–5	5	5	5	5	4–5	4–5
Hot water	5	5	5	4–5	5	5	5	5	5
Perspiration	4–5	4–5	5	4–5	5	5	4–5	5	5
Washing	4–5	5	5	5	5	5	5	5	5
Dry cleaning	5	5	5	5	5	5	5	5	5
Bleaching	4	4–5	4–5	4	4	4	4	4	4
Rubbing wet	4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
Rubbing dry	4–5	5	5	5	5	5	5	5	5

during friction or washing. Grafting of wool with polymers leads to the coverage of these scales (Figs. 7 and 8) and, thus, to the reduction of the phenomenon of shrinkage.

From the results presented in Figures 9 and 10 it is clear that the best antifelting properties are obtained with low or medium percentage of grafting, while at high degrees of grafting, felting shrinkage begins to increase again.

This may be attributed to the fact that with the large extent of grafting the polymer is amassed uniformly on the cuticular scales, so the scales project again and are mutually entangled. This is also verified by observing the scanning electron micrographs (Fig. 11).

Dyeing Properties

The results presented in Figures 12 and 13 indicate that the grafted woolen samples were dyed more rapidly and absorbed more of the reactive dye Lanasol Rouge 2D than the untreated sample. This may be attributed to the chemical treatment that causes (a) the partial or complete destruction of the epicuticle, and consequentely, an increase in the swellability of the cortex, which is now more accessible to the dye molecules; and (b) the production of additional thiol groups, which promotes dyeability because of their higher activity than the corresponding disulfide bonds.

The experimental data presented in Figures 14 and 15 indicate that in the case of the dye Acid Red XB, the presence of the grafted polymethacrylates does not practically alter the dyeing properties of the wool fabric.

A general observation is that the higher the amount of grafted polymethacrylate, the lower the amount of dye absorbed. This is on the one hand due to the stereochemical hindrance, and the other hand due to the binding of the most of the thiol groups to the polymer.

Color Fastness

The samples used in this study are listed in Table I.

Color Fastness properties are given in Table II for the samples dyed with the reactive dye

Table III Color Fastness of Grafted Woolen Fabric Dyed with Acid Dye Acid Red XB

	1	2	3	4	5	6	7	8	9
Light	3	4	4	4	4–5	4	4–5	4–5	4–5
Water	4–5	5	5	4	5	4	5	4	4
Sea water	4–5	5	5	5	5	5	5	4	4–5
Hot water	2	2–3	2	2–3	2	3	3	2	2
Perspiration	4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5
Washing	1	2	2–3	1–2	2	2	1–2	2	2
Dry cleaning	5	5	5	5	5	5	5	5	5
Bleaching	2	3	3–4	3–4	3–4	2	2	2	2
Rubbing wet	3	3	3–4	3	3	3	3–4	3	3–4
Rubbing dry	3	3–4	4	3–4	3–4	3–4	4	3–4	3–4

Table IV Water-Repellent Properties of Woolen Fabric Grafted with Polymethacrylates

Samples	Water Repellency (Spray) Rating
1	0
2	80–90
3	70–80
4	80
5	90
6	80
7	80
8	100
9	90

and in Table III for the samples dyed with the acid dye.

From these results it is clear that the grafted woolen samples present better light fastness for both dyes (reactive and acid) than untreated samples. This may be attributed to the grafted polymer, which covers the surface of the fiber and protects the absorbed dye from the light and especially from the ultraviolet radiation; it is reminded here that polymethacrylate esters absorb close to the ultraviolet, which has sufficient energy to destroy the chromophor groups of the dyes.

The grafted samples present also somewhat better color wetfastness for both dyes when compared with untreated samples (to water, to seawater, to hot water, and to washing). This may be attributed to the water repellency of the grafted woolen fabric so that the penetration of water into the fiber becomes difficult.

The test color-fastness properties are almost the same for either grafted or untreated woolen samples.

Water Repellency

The samples that were used in this study are given in Table I.

The results of the Spray Test presented in Table IV indicate that the saturation of the untreated woolen fabric is general, while the grafted samples with a spray rating from 70 to 100 become almost or completely water repellent. This is due to the covering of the surface of the woolen fabric with polymethacrylates, which have water repellent properties.

CONCLUSIONS

The extent of grafting on woolen fabrics depends on both the bulkiness of the side group of the monomer and the glass transition temperature of the corresponding polymethacrylate. Furthermore, the denser the texture of the fabric, the less grafting occurs.

Low and medium percentages of grafting provide the best results for felting shrinkage, dyeability, and color fastness.

Finally, grafted samples are completely water repellent.

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