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Graft Polymerization of Methyl Methacrylate onto Chemically Modified Wools Using $Na_2S_2O_3$-H_2O_2 Redox System as Initiator

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ABSTRACT

Graft polymerization of methyl methacrylate onto natural and modified wools was performed using the $Na_2S_2O_3$-H_2O_2 redox system as initiator. High graft yields were rapidly obtained with natural, reduced, oxidized wools and, to a less extent, with S-carboxymethylated fibers. S-Aminoethylated, deamined, and some acetylated wools were less easily grafted, and practically no grafting was observed with dinitrophenylated wools. The IR and NMR analysis of isolated polymethacrylic chains did not reveal any stereoregulating effect on methyl methacrylate polymerization due to crystalline components of wool structure. The percentages of graft-on and the molecular weights of the separated poly(methyl methacrylates) were found to be dependent on chemical groups in wool and also on the extent of oxidative processes and of competitive homopolymerization. There is some reason to believe that a part of short polymer chains was not truly grafted but only entwisted in the wool structure.

INTRODUCTION

Hydrogen peroxide is frequently used as a component of redox systems for initiating graft polymerizations of vinyl monomers onto

natural macromolecules. Fe^{2+}-H_2O_2 [1, 2], thiourea-H_2O_2 [3], or $Na_2S_2O_3$-H_2O_2 [4, 5] systems have been successfully tested in grafting onto wool fibers. With the last redox pair, Geczy and Abdel-Fattah [4, 5] easily grafted large quantities of very homogeneous polymethacrylic chains onto wool in spite of the contrarious effect of an unwished homopolymerization. From results obtained in grafting onto reduced, esterified, and deamined wools, the authors have concluded that amino groups in wool act as the main sites of grafting. They also thought that such other chemical functions as thiol or phenol –OH groups could have an active part in the initiation process.

The present paper attempts to specify the effect of various wool modifications on the extent of grafting and on the dimensions of the grafted chains. The role of potential active sites, oxidative degradation, and parallel homopolymerization are also discussed.

EXPERIMENTAL

Materials

Merino wool fibers were scoured, then washed with distilled water, and dried.

Methyl methacrylate was washed with a 5% NaOH solution and distilled under N_2 reduced pressure after being washed with distilled water and dried over anhydrous Na_2SO_4.

All other materials were commercial grade and used without further purification.

Wool Modifications

Reduction. The wool fibers were reduced by the method of Sweetman and MacLaren [6] using tri-n-butylphosphine. Five grams of natural wool was treated with 1.25 mL tri-n-butylphosphine dispersed in 500 mL aqueous n-propanol (20% w/w) flushed with a N_2 stream. The reaction mixture was shaken gently for 48 h at 20°C. The reduced wool was then washed with 2 × 250 mL of a 50% ethanol solution and immersed for 24 h in a mixture of 250 mL pH 8 buffer (0.4 M borate) and 250 mL n-propanol saturated with N_2. The reduced fibers were washed with distilled water and dried.

S-Carboxymethylation. Five grams of reduced wool was immersed for 6 h at 25°C in 500 mL of a 0.1 M iodoacetate and 0.3 M Na_2HPO_4 solution. The S-carboxymethylated fibers were then washed with distilled water and dried.

S-Aminoethylation. The S-aminoethylation of reduced fibers was carried out by the method of MacLaren and Sweetman [7]. Five grams of wool fibers was treated with 50 μmol of 2-bromoethylamine and 6.25 mL of tri-n-butylphosphine in a mixture of 250

mL of n-propanol and 250 mL of pH 8 buffer (0.4 M borate). After flushing the reaction mixture with N_2, the S-aminoethylation was pursued for 72 h at 20°C. The modified wool was then washed with distilled water and again immersed in a pH 8 buffer for 24 h. The S-aminoethylated fibers were washed with water and dried.

Dinitrophenylation. Six grams of natural wool was immersed in a mixture of 6 g of $NaHCO_3$ in 150 mL of H_2O and 10.5 g of 1-fluoro-2,4-dinitrobenzene in 300 mL of acetone. The bath was heated at 40°C and gently shaken for 24 h. Again, the wool fibers were treated with a new solution for 24 h at 40°C. The yellow dinitrophenylated wool was then washed with distilled water and Soxhlet extracted with acetone before drying.

Acetylation. The natural wool was acetylated in two ways: (1) 5 g of wool fibers was treated with 250 mL of acetic anhydride for 30 min at 138°C. The wool fibers were then washed with distilled water and dried. (2) Five grams of wool fibers was immersed in 250 mL of a 0.2 M acetic anhydride solution in dimethyl formamide for 6 h at 60°C. The wool fibers were then washed with distilled water and dried.

Deamination. One and one-half grams of natural wool was treated for 12 d at 22°C with 165 mL of a solution containing 42 g of $NaNO_2$ and 35.3 g of anhydrous acetic acid. The wool fibers were then filtered, washed with distilled water, and dried.

Oxidation. Five grams of natural wool was oxidized with 500 mL of a 3% H_2O_2 solution in H_2O-dioxane (80/20 w/w) mixture for 3 h at 70°C.

Thiol and (α + ϵ) Amino Contents

The thiol content was obtained by the colorimetric method of Meichelbeck et al. [8] using 5,5'-dithiobis-2-nitrobenzoic acid.

The (α + ϵ) amino content was determined by the ninhydrin method [9].

Polymerization Conditions

The polymerizations were carried out under experimental conditions defined by Geczy and Abdel-Fattah [4, 5]. Three to 7 mL of methyl methacrylate, 10 mL of a 30% H_2O_2 solution, and 20 mL of dioxane were added to 20 mL of a 0.4 M sodium thiosulfate solution. The contents were diluted with distilled water to 100 mL and heated at 70°C. One gram of wool was added and the mixture was shaken for different time periods at 70°C. At the end of the reaction time, the wool fibers were removed, washed with distilled water, and Soxhlet extracted with benzene for 24 h. They were again washed with distilled water and dried.

Isolation of Grafted Polymethacrylic Chains

The separation of polymethacrylic chains from the natural part of the grafted wools was performed by the two-step HCl digestion method [10]. The grafted fibers (0.5 g of the natural part) were digested with 35 mL of a 6 N HCl solution for 30 min at 100°C. The residue was filtered and washed with HCl solution. The digestion was repeated for 24 h in sealed tubes at 100°C. The residue was then washed with boiling water and dried. The purification was carried out by successive precipitations with methanol from benzene (1 time) and acetone (3 times) solutions.

IR and NMR Spectra

The IR spectra of the isolated residues were determined from KBr pellets (6 mg residue/500 mg KBr) using a Perkin-Elmer model 21 spectrophotometer.

The NMR spectra of the purified poly(methyl methacrylate) were measured at 120°C on a 100 MHz Varian NMR spectrophotometer from a 10% solutions in o-dichlorobenzene. The area of the peaks in the α-methyl group resonance with τ values of 8.67, 8.81, and 8.92 were used for the calculation of the percentages of isotactic, heterotactic, and syndiotactic triads.

Average Molecular Weights and Polydispersity

The molecular weight distribution, average molecular weights, and polydispersities were obtained by gel permeation chromatography using a chromatograph Waters model 200 equipped with standard Styragel columns.

Dinitrophenylation of the Separated Poly(methyl Methacrylates)

Whalley's method [11] was used for the dinitrophenylation of the amino acid residue still linked to the end of the isolated poly(methyl methacrylate). Fluorodinitrobenzene (0.3 g) and a few drops of triethylamine were added to 6 mL of a 5% poly(methyl methacrylate) solution in benzene. The solution was kept at 30°C for 24 h. The polymer was then precipitated with diethyl ether and carefully washed. The polymer was dissolved in ethyl acetate and again precipitated with methanol. This last procedure was repeated at least 3 times.

RESULTS AND DISCUSSION

The choice of chemical modifications in wool fibers was largely determined by the results previously reported by Geczy and Abdel-Fattah [4, 5]. These authors attributed the grafting to an initiating effect of $Na_2S_2O_3$-H_2O_2 system on amino, thiol, and eventually tyrosine residues in wool. Therefore, we have attempted to change the amino and thiol contents of wool fibers by various ways including deamination, acetylation, dinitrophenylation, reduction, S-aminoethylation, S-carboxymethylation, and oxidation. Deamination by nitrous acid is an old method for removing basic groups, but an important oxidation of disulfide and thiol groups and a removal of tyrosine residues also occurs. The acetylation affects amino and hydroxyl functions and also thiol groups in the most severe experimental conditions. The treatment with fluorodinitrobenzene leads to the arylation of amino, sulfhydryl, phenol, –OH, and imidazole groups. Cystine, cysteine, and other groups are involved in oxidation. The reduction of disulfide bonds by tri-n-butylphosphine and the alkylation of thiols by iodoacetic acid or 2-bromoethylamine appear as the most specific modifications. The last reaction is of particular interest for it constitutes a very convenient method for increasing the amino content of wool fibers.

The grafting of natural and modified wools was performed in the way described in experimental section. The extent of graft-on was calculated after various reaction times as the weight percent increase based on the dry weight of the original wool. The resulting values can be seen in Table 1 and Fig. 1.

It is important to note that parallel to the grafting process an unwished homopolymerization always takes place in the reaction mixture. The homopolymer contaminates the grafted wool and must be removed by an extraction with benzene. Several authors [12] have found, however, that the extraction is sometimes partly uneffective when the homopolymer is intimately entwisted in the wool structure.

As shown in Fig. 1, the course of graft polymerization appears to be very different from one wool to another. For a natural wool, a very high graft yield is obtained after half an hour and nearly no further grafting is observed for longer reaction times. A similar behavior is found for oxidized and acetylated wools; the extent of grafting is, however, considerably lowered when the acetylation is performed at 138°C. Constant graft yields observed after half an hour are probably related to the important decrease of monomer concentration and also to the isolation of initiating sites by the polymer deposition.

We also note in Fig. 1 that the graft yields found for S-carboxymethylated fibers tend to reach the values obtained for the natural wool only after a long reaction time. The curves observed for reduced and S-aminoethylated wools present a maximum near 2 h; lower values obtained later may reveal that an oxidative degradation

TABLE 1. Experimental Results

	Wool	$[-SH]_0$ (μmol/g wool)	$[-(\alpha+\epsilon)NH_2]_0$	Graft time (min)	Graft yield (%)	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
A[a]	Natural	33	217	15	245	1.28	3.90
				30	345	1.34	3.80
				60	343	1.34	3.90
				120	340	1.32	3.90
				180	340	1.30	3.80
	Acetylated (60° C-DMF)	27	73	15	172	0.97	2.25
				30	269	0.93	2.10
				60	342	0.915	2.65
				120	351	0.88	2.65
				180	343	0.765	2.50
	(138° C)		55	15	69	1.41	2.10
				30	133	1.23	2.10
				60	221	0.90	2.65
				120	220	0.945	2.75
				180	220	1.11	3.60
B[a]	Natural	33	217	15	108	1.30	3.60
				30	175	1.35	3.60
				60	183	1.34	3.70
				120	182	1.32	3.60
				180	180	1.32	3.60
	Dinitrophenylated			30	5		
				60	5		
				120	5		
				180	3		
	Deamined			30	5		
				60	11		
				120	23		
				180	26		

(continued)

TABLE 1 (continued)

	Wool	$[-SH]_0$ (μmol/g wool)	$[-(\alpha + \epsilon)NH_2]_0$	Graft time (min)	Graft yield (%)	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
	Reduced	630	217	30	137	0.895	3.70
				60	183	0.755	3.30
				120	208	0.755	4.20
				180	176	0.805	3.60
C[a]	Natural	33	217	15	81		
				30	128	1.42	2.80
				60	130	1.41	2.80
				120	128	1.40	2.90
				180	126	1.37	3.00
	Oxidized	7		30	127	1.78	2.60
				60	123	1.68	2.25
				120	121	1.68	2.35
				180	126	1.78	2.35
	S-Carboxy-methylated	13	217	15	77	1.34	3.30
				30	95	1.44	3.20
				60	110	1.54	3.50
				120	127	1.57	3.15
				180	129	1.40	4.00
	S-Amino-ethylated	46	450	15	22	0.553	2.50
				30	36	0.372	2.25
				60	53	0.434	2.20
				120	59	0.448	2.00
				180	40	0.517	2.50

[a]Initial weight percent of methyl methacrylate: 6 (A), 5 (B) and 3 (C) %.

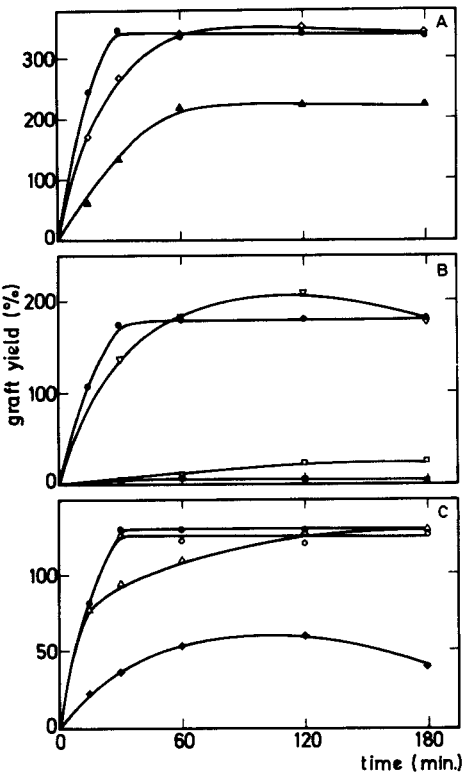

FIG. 1. Plots of graft yields against reaction times for natural (●), acetylated [138°C (▲), 60 C-DMF (◇)], dinitrophenylated (■), deamined (□), reduced (▽) oxidized (○), S-carboxymethylated (△), and S-aminoethylated (◆) wools grafted in experimental conditions A (6% MMA), B (5% MMA), and C (3% MMA).

of wool components favored by the open structure takes place at least for long polymerization times. If the percentages of grafting observed for reduced wool are not very far from those found for natural wool, the grafting seems to be largely hindered for S-aminoethylated wools. It is seen that very low graft yields are obtained for deamined wools and that dinitrophenylated fibers are practically not grafted even after reaction times as long as 3 h.

The percentages of grafting found for reduced and oxidized wools suggest that thiol groups do not take a prominent part in grafting. Moreover, no evident effects of carboxylic and cysteic acid groups introduced by S-carboxymethylation and oxidation are observed from curves in Fig. 1. The absence of significative grafting with dinitrophenylated wool can be the result of the blocking of potential active

sites as thiol, amino or phenol –OH. The low graft yields obtained for deamined and some acetylated fibers support the idea that amino groups could act as sites of grafting. However, this assumption is not confirmed by the behavior of S-aminoethylated wool which is grafted with difficulty in spite of its high amino content.

These conclusions must be considered with reserve. The steric hindrance of bulky dinitrophenylated groups, which tends to restrict the diffusion of reagents in wool fibers, could also explain the low graft yields found after dinitrophenylation. It is also very likely that oxidative reactions affect a large fraction of thiol groups and can justify that values found for reduced wool are not very different from those observed with natural fibers. Furthermore, it is clear that the interfering effect of homopolymerization competes with graft polymerization and therefore modifies considerably the conditions of grafting. This point will be examined later.

The hydrolysis of the natural part of the grafted wools was performed by the two-step digestion method proposed by Arai et al. [10]. After purification, the residue was analyzed by IR spectroscopy in order to control the progress of the degradation. The IR spectra correspond exactly to that found for an atactic poly(methyl methacrylate), which means that the hydrolysis is practically complete. The NMR spectra of poly(methyl methacrylates) so obtained entirely confirm the atactic character of the polymer chains; the percentages of isotactic, heterotactic, and syndiotactic triads are respectively in the range of 5-10, 25-30, and 60-65% and are quite similar to those found for a classical homopolymer.

Average molecular weights of separated poly(methyl methacrylates) and the corresponding polydispersities were determined from analyses of gel permeation chromatograms. The values of number-average molecular weights and the polydispersity index ($\overline{M}_w/\overline{M}_n$) are collected in Table 1. It is interesting to note that the $\overline{M}_n$ values are between 3×10^4 and 2×10^5, very much lower than those reported by Geczy and Abdel-Fattah [5] ($> 10^6$). Furthermore, the polydispersity index lie in the range of 2-4, far from values near 1.0 calculated by the previous authors from molecular weight distributions obtained by turbidimetric titrations. Therefore the great homogeneity of chain lengths postulated by Geczy and Abdel-Fattah is not confirmed by the present results.

We have plotted in Fig. 2 the number-average molecular weights as a function of polymerization time. We observe immediately that $\overline{M}_n$ evolves in various ways for the different wools. This is not surprising in view of the behaviors already observed for the extent of grafting. Figure 2 shows that number-average molecular weights obtained in grafting onto natural wool are practically constant for reaction times greater than 0.5 h; this behavior is entirely consistent with the fact that graft yields do not vary for these times. Compared with natural fibers, reduced and oxidized or S-carboxymethylated

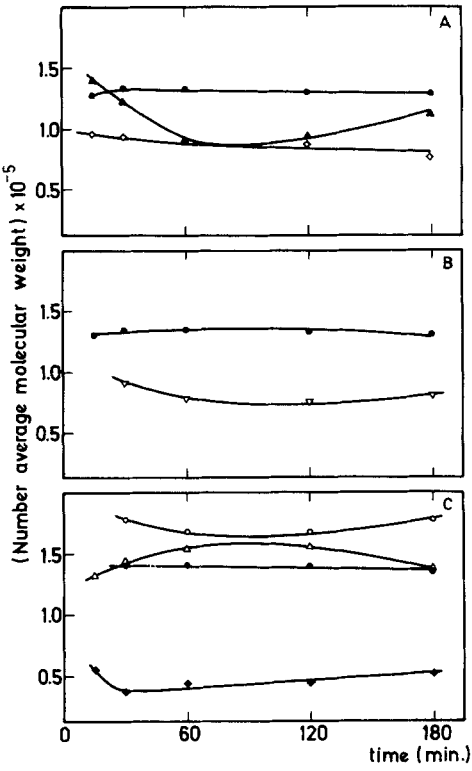

FIG. 2. Plots of number-average molecular weights against reaction times for natural (●), acetylated [138°C (▲), 60°C-DMF (◇)], reduced (▽), oxidized (○), S-carboxymethylated (△), and S-aminoethylated (◆) wools grafted in experimental conditions A (6% MMA), B (5% MMA) and C (3% MMA).

wools are characterized by lower and higher molecular weights, respectively. This implies that thiol groups play a part in the initiation process but, as previously reported, this assumption is not entirely confirmed by the corresponding graft yields. On account of the large divergences observed in the grafting of natural, S-aminoethylated, deamined, and acetylated wools, we can expect an important effect of amino groups on the molecular weights of grafted chains. As shown in Fig. 2, it is clear that low graft yields previously found for the S-aminoethylated wool are essentially due to the presence of very short polymer chains. If we assume with Geczy and Abdel-Fattah [4] that amino groups act as sites of grafting, we must also consider that the increase of initiation rate resulting from the high amino content is completely counterbalanced by an important effect leading to very

short polymer chains and then to low graft yields. Low percentages of grafting and high molecular weights obtained with fibers acetylated at 138° C for polymerization times lower than 0.25 h can be due to a decrease of initiation rate in accord with the low amino content. This is not true for higher reaction times and also for wool acetylated at 60° C in dimethylformamide where molecular weights are found to be very much lower.

As for the extent of grafting, the results in Fig. 2 clearly reveal the influence of wool modifications on the conditions of grafting. However, they do not give absolute evidence of the participation of thiol and amino groups in the initiation process.

Some of the preceding behaviors are characterized by the presence of short polymer chains which cannot be explained by a simple initiating effect of amino, thiol, or other groups. The eventuality that these short chains should not be formed in grafting cannot be neglected. We have therefore attempted to determine quantitatively the number of truly grafted polymethacrylic chains. For this purpose we have used the DNP method proposed by Arai et al. [10] which consists of a quantitative measurement of the number of amino acid residues still linked to the end of polymethacrylic chains after hydrolysis: the separated polymer chains were treated with fluorodinitrobenzene and the resulting dinitrophenylated poly(methyl methacrylate) was analyzed by UV spectroscopy in ethyl acetate. The number of DNP end groups per polymer chain was then calculated from

$$Z\ (\text{DNP end groups}) = \frac{A_{10}\overline{M}_n(\text{DNP-PMMA})}{10\epsilon d}$$

where A_{10} is the optical density of a 1% (w/v) DNP-PMMA solution at 340 nm in ethyl acetate, $\epsilon (= 1.0 \times 10^4$ mol/L.cm) is the molar extinction coefficient, $\overline{M}_n$ (DNP-PMMA) is the number-average molecular weight of the DNP-PMMA, and d is the thickness of the solution.

The number of DNP end groups per polymer chain so obtained is found in the range of 0.6-0.7 for natural, oxidized, and reduced wools; it lies near 0.55 for S-aminoethylated wool and near 0.4 and 0.25 for fibers acetylated at 60 and 138° C, respectively. All these lower than unity values seem to indicate that an important part of the synthetic polymer is not truly grafted but only entwisted in the wool structure. It is evidently also possible that some of the amino acid residues linked to the end of polymethacrylic chains are completely removed during hydrolysis. At the present time, we have no evidence of such an effect although the hydrolysis is relatively easy in this case.

The possibilities of characterizing an unextracted homopolymer were carefully examined. Two fractions of the same isolated poly(methyl methacrylate) were separated by gel permeation chromatography; the fraction with high molecular weights shows a Z value much higher ($Z \simeq 1.5$) than that found for the other fraction having low

molecular weights ($Z < 0.5$). This can be interpreted as the presence of an homopolymer with short chains. In this hypothesis, low molecular weights observed for S-aminoethylated and also for acetylated wools should be related to large amounts of short ungrafted chains as shown by the corresponding Z values. If so, we do not believe that chain transfer reactions, as in the case of initiations with 2,2'-azobisisobutyronitrile [13] and benzoyl peroxide [14], are responsible for these results. We think that the adsorption phenomena in wool could play a prominent part in the preceding behaviors, and that amino groups could be particularly concerned, especially through interactions with hydrogen peroxide [15].

In conclusion, evidence is given for the contribution of various factors to the polymerization of methyl methacrylate onto wool in the presence of the $Na_2S_2O_3$-H_2O_2 redox system. Grafting is dependent on chemical groups in wool but also on oxidative degradation and competitive homopolymerization. It is probable that a part of the deposed polymer chains is not truly grafted in the wool structure and that adsorption phenomena have an important effect on the experimental conditions. We believe that it is important that this point be clarified in the near future.

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