Radiation-Induced Graft Copolymerization of Methyl Methacrylate onto Natural and Modified Wool. I. Grafting and Characterization

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Synopsis

The radiation-induced graft copolymerization of methyl methacrylate onto wool fibers and chemically modified (oxidized, methylated, reduced, and crosslinked) wool fibers was investigated in dimethylformamide at room temperature. The homopolymer was separated from the graft copolymer by Soxhlet extraction. The grafting increased with increase in radiation dosage from 0.5 to 1.5 Mrads. The % graft-on depended on the nature of the wool fibers and decreased in the following order: methylated wool, reduced wool, oxidized wool, natural wool, and crosslinked wool. The molecular weights of the grafted copolymer (after separation from the wool fibers) and homopolymers were determined viscometrically. An increase in the radiation dosage reduced the molecular weights of the polymers.

INTRODUCTION

Graft copolymerization of wool with vinyl monomers using chemical initiators has been extensively investigated by several workers.[1-3] Comparatively little attention has been paid to radiation grafting of wool fibers. Burke et al.[4] have used the trapped-radical irradiated wool to graft acrylonitrile and have estimated the free radicals by ESR. A mutual method of radiation-induced graft copolymerization has been used to graft styrene, methyl methacrylate, acrylonitrile,[5] and other vinyl and allyl monomers[6,7] onto wool. Armstrong and Rutherford[8] have reported radiation grafting using vapor-phase technique. The importance of swelling of the wool fibers in inducing adequate grafting has been pointed out by Puig.[9]

In the present work, graft copolymerization of methyl methacrylate onto wool was carried out by the mutual irradiation technique. The chemical modification of wool may influence the grafting, and such studies may indicate the grafting sites in the wool fibers. The wool fibers were therefore modified by oxidation, reduction, methylation, and crosslinking. Recently, Arai et al.[3] have reported the grafting of methyl methacrylate and styrene onto wool and reduced and S-carboxylated wool fibers using an LiBr–$K_2S_2O_8$ system for grafting.

EXPERIMENTAL

Materials

Indian Malpura wool fibers were purified by Soxhlet extraction with petroleum ether for 24 hr followed by repeated washing with distilled water and then drying in air.

Methyl methacrylate of BDH grade was washed with 5% sodium hydroxide solution to remove the inhibitor and then distilled.

Dimethylformamide was distilled before use. All other chemicals used for chemical modification were of chemically pure grade.

Modification

Oxidation of wool fibers was carried out with 3% (10 vol) hydrogen peroxide at 50°C for 3 hr with a material-to-liquor ratio of 1:100 at pH 4. After treatment, these were washed repeatedly with cold distilled water and then dried in air. This procedure is similar to that reported by Smith and Harris.[10]

The reduction of wool fibers was done by sodium bisulfite.[11] The samples were repeatedly washed with distilled water and dried in air.

For methylation,[12] the wool fibers were treated with dimethyl sulfate (0.2 ml/g) and sodium acetate (0.35 g/g) in 15 ml water. An identical solution was added twice after an interval of 90 min. The wool samples were washed with distilled water and dried in air.

In crosslinking[13] of wool fibers, samples were treated for 48 hr at 50°C with 6% solution of formaldehyde adjusted to pH 6.5 at a material-to-liquor ratio of 1:100 and then washed with distilled water and dried in air.

Elemental analysis of C, N, and H was done for wool and chemically modified samples. Cystine was estimated colorimetrically by using chromotropic acid according to the method of Roff.[14]

Grafting Method

Grafting experiments were carried out in Pyrex tubes 16 mm in diameter and about 15 cm in length. The wool samples, 0.5 g, were placed in the tube and 5.0 ml of the dimethylformamide solvent was added and the tubes kept for 24 hr. Methyl methacrylate, 5.0 ml, was added immediately before irradiation. The mixtures were irradiated at room temperature for different time intervals in a ^{60}Co source at a constant dose rate of 80 rad/sec. The grafted fibers were freed from the homopolymer by Soxhlet extraction with benzene to constant weight. The graft-on was calculated as the percent increase in weight over the original weight of the sample. Initial experiments with acetone, dioxane, ethyl alcohol, methyl alcohol, and benzene revealed that grafting was maximal in dimethyl-formamide and in a monomer-to-solvent ratio of 1:1.

TABLE I
Element Analysis and Cystine and Formaldehyde Contents for Natural and Chemically Modified Wool Samples

Wool	C, %	H, %	N, %	Cystine, %
Natural wool	44.5	6.82	13.74	8.82
Reported for				
Merino wool	50	7	16–17	10.4–13.0
Oxidized wool	44.25	6.85	15.36	8.40
Reduced wool	43.8	7.15	13.94	9.60
Methylated wool	45.6	7.05	13.72	not done
Crosslinked wool	44.15	7.08	14.10	not done

The method of Negishi et al.[15] was used for determination of the molecular weights of the grafts. The wool component of the grafted samples was removed by decomposing the samples with 72% sulfuric acid for 2 hr at 40°C at a liquor to material ratio of 40:1, then diluting with eight times as much water and heating in a boiling water bath until complete decomposition occurred. The insoluble residue was filtered off and washed well until the filtrate was neutral. The polymer was then dissolved in acetone and reprecipitated by adding methanol as nonsolvent. The homopolymers were also precipitated in a similar way. The molecular weights of the graft copolymers and homopolymers were determined by viscosity measurement. A dilute polymer solution (0.1–0.5 g/dl) in acetone was used, and the measurements were carried out in an Ubbelohde suspension viscometer at 30°C. The K and α values were taken from the literature[16]:

$$[\eta] = 7.7 \times 10^{-5}[M]^{0.7}$$

RESULTS AND DISCUSSION

The results of elemental analysis and of cystine and CH_2O contents for the various chemically modified wool samples are given in Table I. Reported values for Merino wool are also given in Table I.[17] The percentage cystine content reported in the literature varies between 10% and 13%. But we are getting a slightly lower value. During the analysis of some of the samples, Ward et al.[18] obtained a cystine value of 8.33 to 8.75. The variation in the amino acid content of different varieties of wools is not unexpected and may arise for various reasons. It has been reported that high alkalinity of suint (pH 8.5–10.5) causes damage to wool fiber.[19] Indian Magra wool is reported to have two thirds the cystine content of Merino wool.[20] The alkaline suint is responsible for the formation of lanthionine in these samples. Thus, canary stained wools have lower cystine and higher lanthionine contents.[21]

As a result of oxidation, the cystine content is reduced slightly, whereas the carbon and hydrogen contents are practically unaltered. However, the surprising fact is an increase in the nitrogen content.

Reduction of wool causes an increase in cystine content, and the carbon and hydrogen percentage decreases. The more accessible cystine S is reduced to —SH by sodium bisulfite.[22]
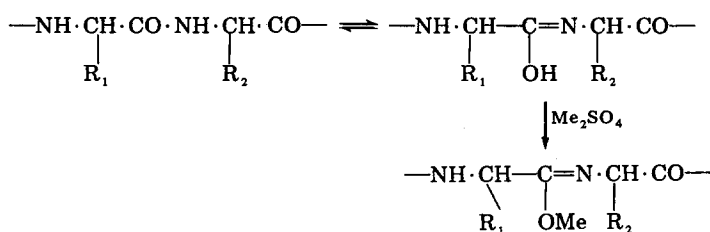
As expected, the carbon and hydrogen contents increase in methylated wool due to the introduction of methoxyl groups. An increase of 1.1% of C and 0.23% of H over natural wool has been observed, which amounts to ≈1.26% introduction of —CH_3 groups. Repeated methylation with $(CH_3)_2SO_4$ has been reported to give a limiting value of 1.9–2.0% CH_3 groups.[12] Since we have carried out the methylation reaction only three times, the relatively unreactive groups may not be methylated.

In Table II, the changes in the percent graft-on in wool and modified wool by increasing the radiation dosage are given. In all the cases there is a sharp increase in % graft-on up to 1.5 Mrad; after that, % graft-on becomes more or less constant. Percent graft-on is maximum in methylated wool and minimum in crosslinked wool. The order is methylated wool > reduced wool > oxidized wool > natural wool > crosslinked wool. Methylation with dimethyl sulfate esterifies about 25% of the free carboxyl groups; some of the methyl sulfate reacts with the amino group, and the remainder is believed to methylate the polypeptide chain which

TABLE II
Percent Conversion of Monomer to Homopolymer and Copolymer with Radiation Dose

Dose, Mrad	Wool	Natural wool	Oxidized wool	Reduced wool	Methylated wool	Crosslinked wool
0.5	Homopolymer, %	22.5	18.5	17.7	16.3	21.8
	Graft, %	1.9	3.8	5.1	7.9	2.3
	Total conversion, %	24.4	22.3	22.8	24.2	24.1
	Grafting efficiency	0.08	0.17	0.22	0.32	0.095
1.0	Homopolymer, %	33.8	39.1	35.8	31.8	46.7
	Graft, %	4.4	5.7	6.2	10.1	4.6
	Total conversion, %	38.2	44.8	42.0	41.9	51.3
	Grafting efficiency	0.116	0.127	0.148	0.24	0.09
1.5	Homopolymer, %	45.3	48.2	49.9	48.7	60.7
	Graft, %	6.8	9.3	9.8	13.9	5.7
	Total conversion, %	52.1	57.5	59.7	62.6	66.4
	Grafting efficiency	0.13	0.16	0.16	0.22	0.09

is capable of enolizing:

$$—NH \cdot \underset{R_1}{CH} \cdot CO \cdot NH \cdot \underset{R_2}{CH} \cdot CO— \quad \rightleftharpoons \quad —NH \cdot \underset{R_1}{CH}—C\underset{OH}{=}N \cdot \underset{R_2}{CH} \cdot CO—$$

$$\Big\downarrow Me_2SO_4$$

$$—NH \cdot \underset{R_1}{CH}—C\underset{OMe}{=}N \cdot \underset{R_2}{CH} \cdot CO—$$

where Me_2SO_4 = dimethyl sulfate.

During the keto–enol tautomerism, there may be a possibility of formation of an active site which increases the grafting. In methylation of the enol form, a large part of the methyl groups introduced may be very labile and removed by irradiation to give the maximum percent graft-on in case of methylated wool. Crosslinking with formaldehyde can occur between guanidino group. The probability of formation of active sites upon irradiation becomes less, and hence the lowest percent graft-on is obtained.

The homopolymer was estimated quantitatively. The % conversion of monomer to homopolymer and graft copolymer was calculated as follows:

$$\% \text{ conversion to homopolymer} = \frac{\text{wt of homopolymer}}{\text{wt of monomer}} \times 100$$

$$\% \text{ conversion to graft-copolymer} = \frac{\text{wt of grafted monomer}}{\text{wt of monomer}} \times 100$$

total % conversion = % conversion to homopolymer

+ % conversion to graft copolymer

$$\text{grafting efficiency} = \frac{\text{grafted monomer}}{\text{total \% conversion}}$$

It was found that both homopolymer and graft copolymer increased on increasing the dosage (Table II). This can be attributed to the creation of more active sites in the presence of higher dosage. In the initial stages, the grafting

takes place in the amorphous regions of the fiber; but as the irradiation dosage increases, grafting in the semicrystalline regions of the fibers may also take place. The grafting efficiency (Table II) was greatest for methylated wool. However, there was variation in the grafting efficiency at different dosages.

Table III summarizes the molecular weights of the homopolymer and the grafted copolymer during the radiation of wool and chemically modified fibers in the presence of methyl methacrylate. The molecular weight of the homopolymer decreases as the dosage increases from 0.5 Mrad to 1.0 Mrad and then becomes almost constant. The molecular weight of the grafted copolymer also decreases with increase in dosage. The molecular weight of grafted chains is higher than that of the corresponding homopolymer. This may be due to reduced chances of bimolecular termination in the wool fibers. An increase in the radiation dose increases the % graft-on as well as the homopolymer yield. This implies that the viscosity of the system increases, and the "gel effect" should help to increase the molecular weight. The decrease in average molecular weight, $\overline{M}_v$, can only be explained by chain scission reactions. PMMA is a degrading type of polymer; in the presence of solvents such as CCl_4 and benzene, a considerable decrease in molecular weight has been obtained at radiation dosages of 0.5 Mrad and above.[23-25] In the present work, grafting was carried out in the presence of DMF as a solvent. The observed decrease in $\overline{M}_v$ of grafted polymer may be due to solvent-catalyzed degradation in the presence of gamma rays.

TABLE III
Molecular Weight of Poly(methyl Methacrylate) and Grafted Poly(methyl Methacrylate) (After Separation from Wool) Obtained by Radiation-Induced Grafting onto Wool and Chemically Modified Wool

Wool	Graft-on, %	Mol. wt of graft copolymer $M \times 10^{-5}$	Mol. wt of homopolymer $M \times 10^{-5}$
Natural	17.6	6.428	4.607
wool	41.1	4.310	2.401
	63.3	3.394	3.612
	73.2	2.266	2.300
	77.5	1.128	2.158
	35.8	7.031	4.221
Oxidized	53.4	6.138	2.269
wool	87.1	5.258	2.496
	88.0	3.241	2.332
	81.0	3.293	2.295
	47.5	3.794	3.374
	58.1	3.090	2.382
Reduced	91.3	2.031	2.133
wool	95.0	2.245	2.110
	99.8	2.439	2.257
	74.3	5.467	3.063
	94.7	4.071	2.257
Methylated	129.7	2.784	2.214
wool	100.1	2.509	2.288
	93.8	2.716	2.183
	21.9	7.703	3.20
	42.8	5.005	2.444
Crosslinked	53.1	3.338	2.226
wool	44.2	1.420	2.183
	44.2	0.512	2.275

However, to ascertain this, further work on the effect of radiation on the molecular weight of PMMA in the presence of DMF is in progress.

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