Studies of the Chemical Modifications of Wool and Their Effects on the Wool–Water Relationship. Part I. Chemical Modification of Wool

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Synopsis

Wool has been modified to render it more hydrophobic by two methods. The first method involved treating the wool with benzoyl, lauroyl, stearoyl, and dodecenyl chlorides and with trifluoroacetic anhydride. Substantial degrees of reaction with the wool were achieved when the correct solvent media and reaction conditions were used. These varied with the particular reagent employed. Pyridine was particularly effective with the acid chlorides, whereas dimethyl sulfoxide was best with trifluoroacetic anhydride. Pyridine is believed to function both as a swelling agent and as an acid acceptor in these treatments. The second method of treatment was the grafting of vinyl and allyl monomers to wool by the use of high energy radiation. Both ^{60}Co γ-rays at 0.3 Mrad/hr. and Van de Graaff β-radiation at 3 Mrad/min. were found to be highly effective. The presence of a swelling agent in the monomer solution was found to be essential even in the case of acrylonitrile in dimethyl formamide. Water and methanol in small amounts were found to be highly efficient swelling agents. Substantial quantities of monomer could be grafted in most cases without difficulty when the correct conditions were used.

This paper describes the modification of wool by reacting with acid chlorides and one acid anhydride, and by the radiation grafting of various vinyl monomers. The wool–water relationships of the modified wools were then studied, including the loss of free water, i.e., the drainage of water from fabric, the water vapor isotherms, and to a lesser extent the diffusivity of water in the modified and unmodified wool fibers. In this first part the two methods of modification will be described and discussed.

DIRECT CHEMICAL MODIFICATION

The direct chemical modification was based upon the known chemical reactivity of the wool. It is well established that wool is made up essentially of proteins, and the amino acids of which the protein is composed have been identified.[1] It is also known that there are a number of reactive functional groups attached to the protein chain including amine, hydroxyl, and phenolic. When such groups are brought into contact with

an organic reagent such as an acid chloride they should undergo normal reactions to form amides or esters.   If the acid chloride were to contain a hydrophobic organic structure, then it should be possible to render the wool more hydrophobic.

Thus, absorption and diffusion of moisture in wool should be reduced by reaction of the wool with acid halides.   This would be due to the conversion of polar amine and hydroxyl groups to the less polar amides and esters and also to the deposition of hydrophobic groups on the polypeptide chain.   Both of these effects should contribute to reducing the ease of moisture transport.   There is ample precedent in the literature[2-6] to predict that the expected reactions should be feasible.   A description of the specific acid halides chosen for study and the conditions for their reactions will now be presented in detail.

Materials

The wool used was undyed fabric (J. P. Stevens Style No. 13200-1) with an average fiber diameter of 22 μ.   This was extracted in a Soxhlet extractor at least 8 hr. with ether followed by 8 hr. with ethanol.[3]   The fabric was stored in a desiccator over calcium sulfate before use.

The reactants chosen for this investigation were benzoyl chloride, stearoyl chloride, lauroyl chloride, dodecenyl chloride and trifluoroacetic anhydride.   Dodecenyl chloride was obtained from the Rohm and Haas Company; the others were obtained from the Eastman Organic Chemicals Company.   All were used without further purification.

The reaction media were pyridine, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), all from Matheson, Coleman and Bell.   The highest quality obtainable was reagent grade for DMSO and spectra quality for the others.   These were also used without further purification.

Procedure

Weighed strips of the wool fabric, $1/2 \times 2$ in., were placed in a glass tube approximately 100 mm. long and 17 mm. in diameter which had a ground glass joint on the open end.   The reaction medium was added and remained in contact with the wool for approximately 20 hr. at room temperature.   The acid halide was then added to the mixture, the tube attached to a head assembly containing a drying tube on the opening and a water-cooled cold finger condenser, and the tube was then immersed in a preset heating bath.   Teflon sleeves were used on the ground joints to avoid contamination from stopcock grease.

In several instances, the solutions warmed rapidly when the acid halide was added.   In these cases the halide was added slowly and the solution was cooled in an ice bath.

After reaction the wool samples were washed in order with benzene, alcohol, water, alcohol, and benzene.   They were then dried to constant weight in a vacuum desiccator over calcium sulfate, and the per cent weight gain calculated from the difference between initial and final weights divided
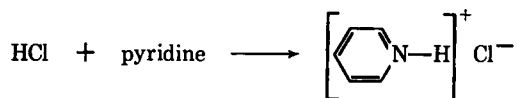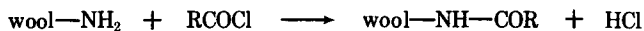
by the initial weight. Calcium sulfate was considered to be a suitable and convenient drying agent for the comparative weighings needed in this research. The actual weight gains or losses duplicated well when repeated early in the program and only single experiments were therefore conducted for the major part of the work. Control experiments were made in which the cleaned and extracted wool was treated with the various solvents used under the same experimental conditions as the chemical treatment. No changes in weight occurred.

Results and Discussion

The direct chemical modification of wool depended upon the reactivity of the functional groups attached to the polypeptide backbone. Known examples of these groups include amino, hydroxyl, phenolic, and sulfhydryl, all of which should react with an acid halide or anhydride. The reaction should result in the attachment of the acid group to the wool by primary chemical bonds. This concept has been recognized and considerable work has been done, for example, with acid chlorides[2] and isocyanates[3,5] and anhydrides.[5] These investigations have shown that reactions with wool were influenced by reaction temperature and medium, and that the extent of reaction was not the same for all acid halides. The action of the medium has not been entirely elucidated, but the primary effect is believed to be the penetration and swelling of the wool,[4,5] thus providing improved access to the reactive sites by the acid halides. This information was the experimental basis for the preparation of chemically modified wool.

The acid halides selected were benzoyl chloride, stearoyl or lauroyl chloride, and trifluoroacetic anhydride, which would serve as examples of aromatic, aliphatic, and hydrophobic strong acid groups. The term "acid halide" as used here includes the acid chlorides and also the trifluoroacetic anhydride.

The solvents or swelling agents which were chosen for their known activity were pyridine, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Along with the solvent and swelling action, these might also behave as Lewis bases, which could favor the reaction by removing byproduct acid:

$$\text{wool—NH}_2 \ + \ \text{RCOCl} \ \longrightarrow \ \text{wool—NH—COR} \ + \ \text{HCl}$$

$$\text{HCl} \ + \ \text{pyridine} \ \longrightarrow \ \left[\begin{array}{c} \bigcirc\!\!-\!\!\text{N—H} \end{array} \right]^+ \text{Cl}^-$$

A preliminary series of reactions was run with benzene as a (presumably) inert diluent so that the refluxing reaction mixture could be maintained at a constant temperature near 80°C. Each of the swelling agents (40% by volume) was used with each of the acid halides for a total of nine reactions.

The detailed conditions and observations of all the reactions have been listed in Table I. A summary of the preliminary reaction results, however,

TABLE I
Summary of All Acid Halide–Wool Reactions

Expt. no.	Swelling agent	Acid halide[a]	Time, hr.	Temp., °C.	Weight gain of wool, %[b]
1	Pyridine, 9 ml.	Benzoyl chloride	24	25	3.0
2	"	"	4	70	18.9
3	"	"	2	76	28.6
4	"	"	1	105	30.5
5	Pyridine, 4 ml. + benzene, 6 ml.	Stearoyl chloride	2	Bath = 90	2.5
6	Pyridine, 4 ml. + benzene, 6 ml.	Lauroyl chloride	2	"	4.2
7	Pyridine, 9 ml.	Lauroyl chloride	24	25	-14.6
8	"	"	4	70	3.9
9	"	"	2	76	19.3
10	"	"	1	105	26.3
11	"	Trifluoroacetic anhydride	24	25	-8.5
12	Pyridine, 4 ml. + benzene, 6 ml.	Trifluoroacetic anhydride	2	Bath = 90	-14.7
13	Dimethylformamide, 9 ml.	Benzoyl chloride	24	25	-15.4
14	"	"	4	70	-11.1
15	"	"	1	105	5.6
16	DMF, 3.8 ml. + benzene, 6 ml.	"	2	Bath = 90	1.1
17	DMF, 3.8 ml. + benzene, 6 ml.	Stearoyl chloride	2	"	9.3
18	DMF, 9 ml.	Lauroyl chloride	24	25	-6.5
19	"	"	4	70	10.0
20	"	"	2	76	20.0
21	"	"	1	105	24.3
22	DMF, 3.8 ml. + benzene, 6 ml.	Trifluoroacetic anhydride	2	Bath = 90	Dissolved
23	Dimethyl sulfoxide	Benzoyl chloride	24	25	-3.5
24	"	"	4	70	13.1
25	"	"	2	76	17.1
26	DMSO, 3.5 ml. + benzene, 6 ml.	"	2	Bath = 90	1.0

				Bath	
27	DMSO, 3.5 ml. + benzene, 6 ml.	Stearoyl chloride	2	Bath = 90	9.5
28	DMSO	Lauroyl chloride	24	25	−8.1
29	"	"	4	70	−14.0
30		Trifluoroacetic anhydride	24	25	14.6
31	DMSO, 3.5 ml. + benzene, 6 ml.	Trifluoroacetic anhydride	2	Bath = 90	1.9
32	Acetone	Benzoyl chloride	24	25	3.5
33	"	Lauroyl chloride	24	25	3.3
34	Methylene chloride	Benzoyl chloride	24	25	3.6
35	"	Lauroyl chloride	24	25	3.7
36	Triethylamine	Benzoyl chloride	4	70	−10.3
37	"	Lauroyl chloride	4	70	4.3
38	Dimethylformamide, 3.8 ml.	Dodecenyl chloride	24	25	6.8
39	"	"	4	70	7.6
40	"	"	2	70	5.8
41	"	"	1	105	11.4
42	Dimethyl sulfoxide, 3.5 ml.	"	24	25	14.5
43	"	"	4	70	12.5
44	"	"	2	70	13.9
45	Pyridine, 4 ml.	"	24	25	5.3
46	"	"	4	70	25.4
47	Pyridine	"	2	70	18.3
48	"	"	1	105	123.2
49	Tetrahydrofuran, 3.5 ml.	"	24	25	−3.1
50	"	"	2	70	0.4

a Weight of benzoyl chloride = 3.45 g., stearoyl chloride = 7.42 g., lauroyl chloride = 5.36 g., trifluoroacetic anhydride = 5.14 g., dodecenyl chloride = 5.00 g. All = 0.025 moles in 9 ml. unless otherwise stated.

b Original weight of wool = approximately 0.15–0.20 g. Other swelling agents screened were tetrahydrofuran, dimethyl ether of diethylene glycol, butanone, dioxane, dibenzyl ether, and cyclohexanone. All gave weight loss rather than gain.

TABLE II
Acid Halide–Wool Reactions in Benzene–Swelling Agent Mixtures[a]

| | Weight gain of wool, % | | |
Acid halide	Pyridine	DMF	DMSO
Benzoyl chloride	2.5	1.1	1.0
Stearoyl chloride	4.2	9.3	9.5
Trifluoroacetic anhydride	−14.7	Dissolved	1.9

[a] These reactions were run for 2 hr. in a bath maintained at 90°C.

may be found in Table II. The maximum addition of acid groups based upon the original weight of the wool was a gain of 2.5% for the benzoyl chloride and 9.5% for the stearoyl chloride. With trifluoroacetic anhydride and DMSO the gain was 1.9%, but the other anhydride solutions dissolved the wool.

In order to increase the amount of acid deposition on the wool, subsequent reactions used pure swelling agents without any inert diluent and higher temperature as well. Higher temperature could not be used, however, with trifluoroacetic anhydride or DMSO. The tendency of trifluoroacetic anhydride solutions to dissolve the wool suggested that lower temperature might be beneficial in this case. The DMSO could not be used at higher temperature because of thermal instability.

These changes in reaction conditions had the desired effect. Using undiluted swelling agents as the reaction media increased the deposition of acid groups, and raising the temperature improved the weight gain still further. The maximum deposition was a weight gain of 30% with benzoyl chloride and 26% with lauroyl chloride, both in pyridine at 105°C. On the other hand, a lower temperature was preferred with trifluoroacetic anhydride in DMSO, which yielded about 15% weight gain after 24 hr. at room temperature. Complete data are shown in Table I, and results are summarized in Table III.

As can be seen from Tables II and III, there was a definite influence of the solvent on the extent of reaction. Furthermore, the reactions seemed to be influenced by the particular acid halide–swelling agent combination. That is, benzoyl chloride apparently added to a greater extent with pyri-

TABLE III
Acid Halide–Wool Reactions in Undiluted Swelling Agents

| | Time, hr. | Temp., °C. | Weight gain of wool, % | | |
Acid halide			Pyridine	DMF	DMSO
Benzoyl chloride	4	70	18.9	−11.1	13.1
	1	105	30.5	5.6	—
Lauroyl chloride	4	70	3.9	10.0	−14.0
	1	105	26.3	24.3	—
Trifluoroacetic anhydride	24	25	−8.5	—	14.6

dine than with DMF, whereas lauroyl chloride added slightly more with DMF than with pyridine. Trifluoroacetic anhydride gave reasonable addition only in DMSO. These results suggest that the swelling agent not only swells the wool but also affects the reactivity of the acid halide.
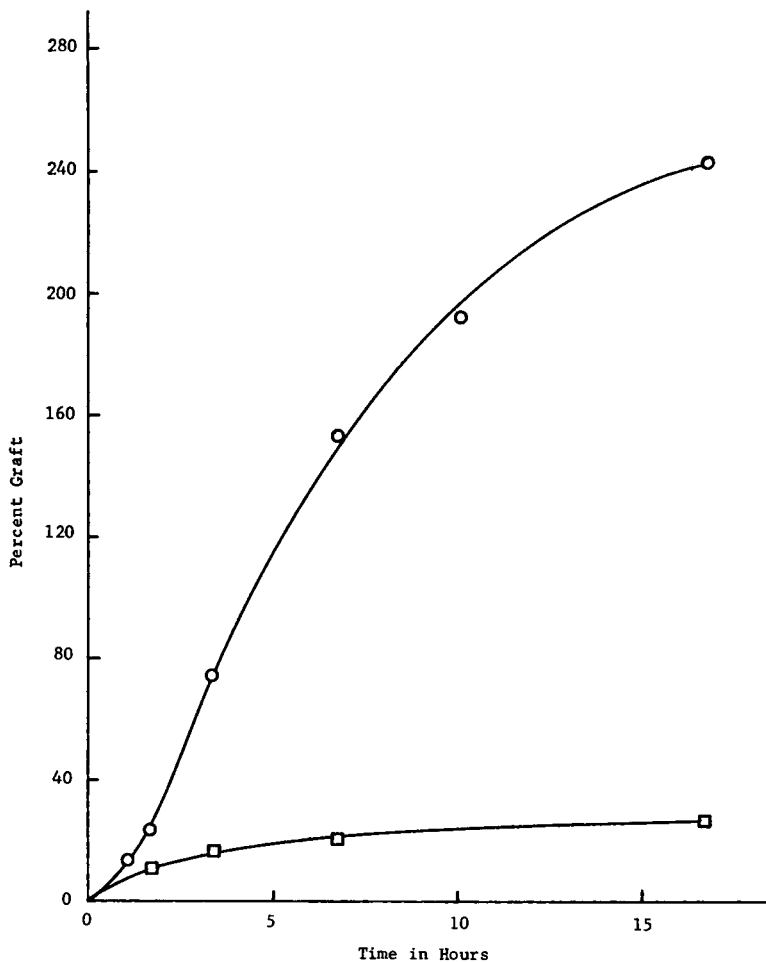

Fig. 1. Mutual radiation grafting of styrene to wool, 3.06M styrene in dioxane: (O) 7.5% water added; (□) 1.6% water added. Dose rate, 0.3 Mrad/hr.

One characteristic of these swelling agents was a relatively high Hildebrand solubility parameter;[7] 10.7 for pyridine and 12.0 for DMF. In hopes of finding still more effective swelling agents, a number of ether and ketone solvents, also of rather high solubility parameters, were run with benzoyl and lauroyl chlorides at 25 and 70°C. The maximum weight gain of the wool was only 4%, however, so none of these solvents were as effective as pyridine, DMF, or DMSO. A complete list is included in Table I.

The reaction product of the acid halides with wool presumably yielded mostly amide functions.   A somewhat different direct chemical modification seemed possible, however, if an allyl chloride derivative could be used in place of the acid halide for reaction with the amine groups on the wool:

$$\text{wool—NH}_2 + \text{ClCH}_2\text{CH=CHR} \longrightarrow \text{wool—N(CH}_2\text{CH=CHR)}_2 + \text{HCl}$$

In order to add hydrophobic character, the allyl chloride should contain a long hydrocarbon chain.

An available example of such a reactant was dodecenyl chloride, actually 1-chloro-5,5,7,7-tetramethyl-2-octene.   This was used with the same experimental methods as with the acid halides.   The swelling agents were pyridine, DMF, DMSO and tetrahydrofuran, and these were used at 25, 70 and (except DMSO and tetrahydrofuran) 105°C. as shown in Table IV.

TABLE IV
Dodecenyl Chloride–Wool Reactions in Undiluted Swelling Agents

Swelling agent	Time, hr.	Temp., °C.	Weight gain of wool, %
Dimethylformamide	24	25	6.8
	4	70	7.6
	1	105	11.4
Dimethyl sulfoxide	24	25	14.5
	4	70	12.5
Pyridine	24	25	5.3
	4	70	25.4
	1	105	123.2

Once again, one of the swelling agents was more effective than the others, in this case, pyridine.   At 70°C. a weight gain of 25% was observed, in contrast with a maximum of about 15% for the other swelling agents.   At 105°C., however, the gain was 123%.   This surprisingly high weight gain suggests that the reaction proceeded beyond simple substitution, and perhaps to a quaternary ammonium salt:

$$\text{wool—N(CH}_2\text{CH=CHR)}_2 + \text{Cl—CH}_2\text{—CH=CHR} \longrightarrow$$
$$\text{wool—N(CH}_2\text{CH=CHR)}_3{}^+\text{Cl}^-$$
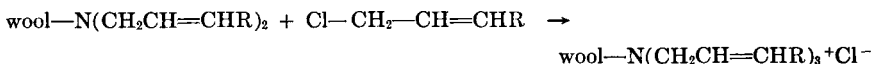
The unusual extent of the reaction also suggests that the dodecenyl chloride reacted with sites which were not available to the acid halides, perhaps due to a deeper penetration of the fiber structure by the former. Unfortunately, despite the extensive deposition, this modification did not confer beneficial drying properties on the wool.

The purpose of this work was mainly to prepare chemically modified wool samples to test their drying behavior in comparison with polymer-grafted samples.   Therefore, a detailed study of the chemistry of the reactions was beyond the scope of this effort.   A few observations may be pertinent, however.

As would be expected from their heterogeneous nature, the reactions of the wool were generally not smooth or straightforward. In many cases there was an immediate precipitate when the acid halide was introduced into the reaction mixture, and the wool samples were almost all discolored. Furthermore, the weight loss observed in some of the experiments suggests that addition of the acid groups was proceeding simultaneously with dissolution of the wool substrate. This phenomenon, which has been observed by other workers,[6] might account for the higher weight gain in 2 hr. at 76°C. than in 4 hr. at 70°C. observed with several of the combinations listed in Table I. Thus, the final weight gain or loss of the wool may have to be viewed from a kinetic rather than an equilibrium standpoint. Despite these complications, significant amounts of additive were obviously attached to the wool, and the level of addition was in substantial agreement with that of other workers.[2,6]

RADIATION GRAFTING

The same wool fabric, treated in a similar way to that used for the chemical modifications, was used for all the graft polymerizations reported in this paper. The grafting experiments were carried out in Pyrex tubes, 16 mm. in diameter and about 15 cm. in length. A weighed strip of wool fabric $1/2 \times 2$ in. (about 0.17 g.), was placed in the tube before constricting, and 8.0 cc. of a monomer–solvent–water mixture was added by hypodermic syringe under a dry nitrogen atmosphere. The styrene content was maintained at $3.06M$ in dioxane; the water or methanol content was varied as shown in the actual data. The tubes were attached to a high vacuum line, degassed by five freeze-thaw cycles at below 10^{-4} mm. Hg pressure, and sealed under vacuum. It was found that essentially similar results were obtained when the wool was degassed separately and degassed monomer added under high vacuum. The samples were irradiated in a 4000-curie ^{60}Co gamma cell (by kind cooperation of the N. C. State University School of Textiles) at 25°C. and a dose rate of about 0.3 Mrad/hr. The tubes were then opened and the homopolymer in the solution was isolated by precipitation in methanol, filtering, and drying. The wool samples were washed to constant weight with benzene and reweighed. The increase in weight divided by the original weight $\times$ 100 was recorded as the per cent of grafting. Typical grafting–time curves at two degrees of swelling are presented in Figure 1. It can be seen that the amount of grafting per given dose depends greatly on the water content of the monomer solution. This is believed to be due to the swelling action of the water enabling the more rapid diffusion of monomer to the active centers created in the fibers by the radiation. The general shape of the grafting–dose curves has been discussed in detail previously[8] and has been satisfactorily explained by a kinetic scheme developed in detail elsewhere.[9] It appears logical that grafting conducted at low degrees of swelling would have the graft mainly located near the surfaces of the fibers, whereas at high degrees of swelling grafting should occur throughout the fiber structure.

A few grafting experiments were also made by using a 3 M.e.v. Van de Graaff electron accelerator at the High Voltage Engineering Corporation, Burlington, Mass., at a dose rate of about 3 Mrad/min. Graftings up to 60% were obtained.

In the case of acrylonitrile, dimethylformamide was chosen as the solvent in order to keep the polyacrylonitrile in solution. The addition of small amounts of water or methanol to the solution was found to be necessary for appreciable grafting at the dose rate used, presumably due to their swelling action. A few grafting experiments were also conducted with acrylonitrile by the vapor phase method developed by Armstrong and Rutherford.[10] In this method, wool cloth strips were suspended on a rack inside a one-liter stainless steel sample container. The sample container was flushed for 2 hr. with prepurified nitrogen (1000 cm.^{3}/min.) saturated at 75°F. and atmospheric pressure with the two-phase acrylonitrile–water system. This flushing was used to purge the system of oxygen and to allow the acrylonitrile and water time to diffuse into the wool fiber. The samples were placed in the irradiation position for various time intervals (2, 3, and 4 hr.) with the flushing continuing. After irradiation the samples were removed and the polymer addition determined by the weight gain of the sample. Graftings up to 50% were readily obtained by both techniques.

Attempts were also made to graft a number of monomers which would lead to hydrophobic polymers. These included 2-ethylhexyl acrylate and stearyl methacrylate and a number of fluorinated monomers and some allyl esters.

The 2-ethylhexyl acrylate grafts were prepared by simply padding the monomer on to the wool surface from a 15% and a 30% solution in methanol and irradiating to 0.3 Mrad. Increases in weight of 15% and 37% were obtained after washing.

Stearyl methacrylate was grafted in pure monomer containing a few per cent of added methanol. At 0.5 Mrad, 6.6% grafted; beyond this a crosslinked mass resulted. In addition to these, 1,1-dihydroperfluoro-n-undecyl acrylate was studied, but crosslinked polymer resulted in each case. The acrylates and methacrylates polymerize rapidly by radiation and are not suitable for grafting by the direct method. Stearyl methacrylate was grafted also by adding the monomer containing 6% methanol under vacuum to preirradiated wool.

The allyl monomers grafted successfully in dioxane solution with a small amount of added water. The per cent grafting was quite small and reached a maximum at about 1 Mrad. α-Methylstyrene was investigated since it was thought it might lead to crosslinking of the fibers. One polystyrene-treated wool was prepared by soaking the wool in 1% polystyrene solution in wet dioxane, centrifuging, and drying.

The exact details of the grafting experiments are included in Tables II and III of Part II of this series.[11] It is believed that increasing the amount of swelling agents such as water or methanol in the grafting solution leads

to grafting deeper into the fiber and that the location of the grafted polymer can be varied from the surfaces throughout the fiber. Work is currently in progress to investigate the changes in location with variations in the grafting conditions. The wool was hydrolyzed away and the grafted side chains separated and examined. Untreated wool will dissolve completely in warm 10% aqueous sodium hydroxide in about 4 hr. The styrene-grafted wools, on the other hand, did not dissolve or disintegrate even after one week of alkaline hydrolysis. However, it was found that a mixture of equal volumes of benzene and 5% potassium hydroxide, to which sufficient water had been added to form two layers, was quite effective. The wools were refluxed in this mixture for about 12 hr. Untreated wool disappeared to give two yellowish but clear layers, whereas grafted wools formed opaque emulsions. A sample of wool grafted in 18% methanol solution in dioxane to 140% was treated in this way. The emulsion was acidified with hydrochloric acid and poured into excess methanol and the insoluble precipitate collected. It was found that the residue could be divided into roughly equal parts by benzene. The benzene-insoluble portion was, however, soluble in dimethylformamide. The infrared spectrum of both polystyrene fractions showed bands normally associated with carbonyl and amide groupings. The benzene-insoluble portion showed much stronger bands than the soluble portion. Ninhydrin reagent also gave the characteristic blue color normally associated with the presence of proteins. The experiments described above leave little doubt that actual grafting takes place and that alkaline hydrolysis leaves behind polystyrene containing attached amino acid residues. Even prolonged acid hydrolysis failed to render the insoluble fraction soluble in benzene. A full discussion of the grafting experiments themselves may be found elsewhere.[8,9]

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Résumé

La laine a été modifiée par deux méthodes en vue d'augmenter ses propriétés hydrophobes. La première méthode comporte un traitement de la laine par des chlorures de benzoyle, lauroyle, stéaroyle et dodécényle et anhydrides trifluoroacétiques. Des degrés de conversion importants avec la laine ont été atteints lorsque des solvants et des conditions de réaction adéquats ont été utilisés. Celle-ci ont été variées suivant le réactif particulier utilisé. La pyridine était particulièrement effective pour les chlorures acides, tandis que le diméthylsulfoxyde était le meilleur en présence d'anhydride trifluoroacétique. La pyridine agit à la fois comme agent gonflant et comme accepteur d'acide au cours de ces traitements. La seconde méthode de traitement consiste dans le greffage de monomères vinyliques ou allyliques à la laine en utilisant des radiations à haute énergie. Aussi bien le cobalt 60 à 0.3 MRads/h que la radiation β de Van de Graaff à 3 MRads/min. ont été trouvées être des sources particulièrement effectives. La présence d'agent gonflants dans la solution de monomère est essentielle même dans le cas du polyacrylonitrile dans le diméthylformamide. L'eau et le méthanol en faible quantité substantielles de monoméres peuvent être greffées dans la plupart des cas sans difficultés, lorsque des conditions adéquates ont été utilisées.

Zusammenfassung

Schafwolle wurde nach zwei Methoden modifiziert, um sie stärker hydrophob zu machen. Die erste Methode besteht in einer Behandlung der Wolle mit Benzoyl-, Lauroyl-, Stearoyl- und Dodecenylchlorid und mit Trifluoressigsäureanhydrid. Ein wesentliches Ausmass der Reaktion mit der Wolle wurde bei Verwendung der richtigen Lösungsmittel und Reaktionsbedingungen erreicht. Diese waren vom besonderen verwendeten Reagens abhängig. Pyridin war mit den Säurechloriden besonders wirksam, während Dimethylsulfoxyd für Trifluoressigsäureanhydrid am besten geeignet war. Es wird angenommen, dass Pyridin bei dieser Behandlung sowohl als Quellungsmittel als auch als Säureakzeptor fungiert. Die zweite Behandlungsmethode bestand in der Aupfropfung von Vinyl- und Allylmonomeren auf die Wolle durch Anwendung hochenergetischer Strahlung. Als hochgradig wirksame Quellen erwiesen sich Co⁶⁰-Gamma- bei 0,3 Mrad/h und Van-de-Graaff-Betastrahlen bei 3 Mrad/min. Die Anwesenheit eines Quellungsmittels in der Monomerlösung war sogar im Falle von Acrylonitrile in Dimethylformamid wesentlich. Wasser und Methanol erwiesen sich in kleinen Mengen als hockwirksame quellungsmittel. Bei Anwendung der richtigen Bedingungen konnten in den meisten Fällen ohne Schwierigkeit wesentliche Monomermengen aufgepfropft werden.