

Interfacial Polycondensation.

I. The Formation of Surface Graft Polymers on Wool

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Synopsis

By means of interfacial polycondensation, ultrathin coatings of polyamides, polyurethanes, polyureas, polyesters, polycarbonates, and various copolymers can be formed on the surface of a substrate. If the substrate contains reactive groups (such as $-\text{NH}_2$, $-\text{OH}$, $-\text{NCO}$, $-\text{COCl}$, etc.), graft polymer is formed. The graft polymer is not removed by extensive extraction with good solvents for the polymer. In contrast, if wool is used as a substrate and is acetylated prior to the polymerization (to block the grafting sites), the thin coating of polymer is readily extracted. Digestion of the treated wool with enzymes that react with the wool, but not with the grafted coating, permits a characterization of the grafted polymer; amino acid analysis of the residue from the enzyme digestion provides evidence that the grafting sites on the wool are probably the free amino and hydroxyl groups located in the *N*-terminal amino acids or internal amino acids containing these groups in their side chain.

I. INTRODUCTION

The formation of condensation polymers by interfacial polymerization has been known for several years.¹ This polymerization occurs at the interface between two immiscible solvents, each containing a very reactive difunctional intermediate.

In a simple demonstration of the principle of interfacial polycondensation, a thin film of polymer forms almost instantaneously at the boundary between the two immiscible solvents when they are brought into contact. With many polymers the film formed is sufficiently coherent to be removed continuously as a small solvent-swollen thread (rope). Alternatively, the polymerization may be carried out in a high speed mixer, one solution being poured into the other with vigorous stirring. Polymerization occurs, in this instance, at the liquid-liquid interface of the small droplets formed by the vigorous stirring.¹

If instead of placing the two immiscible solutions in direct contact, they are brought into contact indirectly by first applying one solution to a substrate to provide an extremely thin layer of the solution on the surface of the substrate, and subsequently dipping the substrate into the second solution, an ultrathin film of the polymer is formed on the surface of the sub-

strate. If the substrate contains reactive groups similar to those of the reactive intermediates, graft polymer formation ensues; the film is chemically anchored to the substrate. The formation of a variety of graft polymers on the surface of wool by interfacial polycondensation, to impart interesting fiber and fabric modification, has been reported.²⁻⁵ The present paper contains evidence that graft polymers are, indeed, formed by this method and suggests that interfacial polycondensation may be a general procedure for the formation of surface graft polymers on suitable substrates.

II. SYNTHESIS OF SURFACE GRAFT POLYMERS OF WOOL BY INTERFACIAL POLYMERIZATION

Interfacial polycondensation is suitable for the formation of thin layers of polymers, grafted or ungrafted, on a substrate surface. With substrates which do not contain reactive groups, ungrafted polymer is formed. For those with only a few reactive functional groups (of the type $-\text{NH}_2$, OH , $-\text{O}^-$, $-\text{SH}$, $-\text{S}^-$, $-\text{COCl}$, $-\text{NCO}$, $-\text{OCOC}$), limited grafting is possible; with substrates containing a large number of reactive groups, extensive grafting results. In a sense, the substrate with reactive functional groups acts as a comonomer in the interfacial polycondensation.

There are several requirements for surface graft polymer formation by this method. First, the substrate must contain groups with reactivity comparable to that of the reactive intermediates; second, the groups must be accessible for reaction; third, the substrate must be capable of being wetted by one of the solutions (which would be applied first); and, fourth, the substrate must be free of interfering contaminants. Wool meets all these requirements. It contains $-\text{OH}$ and $-\text{NH}_2$ groups, which are of comparable reactivity to that of the intermediates used in interfacial polymerization. These groups are present throughout the cross section of the fiber, including the surface. Wool is readily wetted by either an aqueous solution (containing wetting agent to facilitate the wetting) or by organic solvents. The surface of the wool is freed from contaminants by thorough scouring.

By interfacial polymerization, polyamides,^{2,3} polyurethanes,⁴ polyureas, polyesters, polycarbonates,⁵ and a variety of copolymers⁶ have been formed on the surface of wool. In most cases, it is believed that graft polymers are formed.

From one to two per cent polymer has been grafted, with amounts in excess of this being present as ungrafted homopolymer. The reagents employed for the formation of the surface graft polymers of different species are given in Table I.

Interfacial polymerization has many attractive features, when compared with alternative methods of polymerization. The reaction occurs almost instantaneously at room temperature; purity of reagents is less critical than in melt polymerization; the ratio of reagents is not critical; the reaction

TABLE I

Graft polymer	Treating solutions	
	1 Aqueous	2 Water-immiscible organic
Polyamide	Diamine	Diacid chloride
Polyurethane	Diamine	Bischloroformate
Polyurea	Diamine	Diisocyanate or phosgene
Polyester	Diol	Diacid chloride
Polycarbonate	Diol	Bischloroformate
Copolymer	Diol/diamine	Diacid chloride/bis chloroformate/diisocyanate

can be carried out in presence of air under ordinary atmospheric conditions; it is suitable for preparation of most types of polycondensation graft polymers; it can be employed with heat sensitive substrates or heat sensitive intermediates.

The results obtained are influenced, however, by several reaction variables. These include the nature of the polymer, time of exposure of the

TABLE II
Surface Graft Polymers of Wool by Interfacial Polymerization. Polyamides

Reagents used ^a			Time, sec. ^b	Resin on fabric, %	Area shrinkage, % ^c
Step 1	Step 2	Organic solvent			
4 HMDA	2 SC	CCl ₄	5	4.4	4.0
4 HMDA	2 SC	CCl ₄	15	4.6	4.0
2 SC	4 HMDA	CCl ₄	15	1.3	3.0
4 HMDA	2 SC	Skellysolve B	15	4.3	15.4
2 SC	4 HMDA	Skellysolve B	15	2.2	3.0
2 SC	4 HMDA	Toluene	15	1.5	5.9
4 HMDA	3 AzC	CCl ₄	15	1.5	2.0
3 AzC	4 HMDA	CCl ₄	15	1.0	6.9
4 HMDA	3 PC	CCl ₄	15	2.0	2.0
3 PC	4 HMDA	CCl ₄	60	1.0	1.0
4 HMDA	1 AC	CCl ₄	15	2.4	10.7
8 HMDA	2 AC	Toluene	15	5.5	3.0
4 MXDA	4 SC	Benzene	20	5.7	5.0
2 EDA	3 AC	Aliphatic HC	10	2.0	7.0
2 CHMBA	3 SC	Aliphatic HC	10	2.0	15.4
2 IBPA	3 SC	Aliphatic HC	10	2.0	13.9

^a Numbers refer to weight per cent of ingredient in the solution. All amines were in aqueous solutions containing twice as much sodium carbonate as amine, and 0.15 wt.-% nonionic detergent. HMDA, hexamethylenediamine; EDA, ethylenediamine; MXDA, *m*-xylylenediamine; IBPA, iminobispropylamine; CHMBA, 1,4-di(aminomethyl)-cyclohexane; SC, sebacyl chloride; AzC, azelaoyl chloride; AC, adipoyl chloride; PC, pimeloyl chloride.

^b Time of immersion in each treating solution, steps 1 and 2.

^c With 2 min. wash in Accelerotor.

TABLE III
Surface Graft Polymers of Wool by Interfacial Polymerization: Polyurethanes

Reagents used ^a		Organic solvent	Time, sec. ^b	Resin on fabric, %	Area shrinkage, % ^c
Step 1	Step 2				
4 HMDA	3 EGBC	CCl ₄	30	2.5	11.6
2 HMDA	2 EGBC	Benzene	30	0.6	11.1
2 MXDA	3 EGBC	Benzene	30	1.7	10.7
4 HMDA	3 DGBC	CCl ₄	30	4.1	3.0
2 HMDA	3 DGBC	Benzene	30	1.8	10.3
4 HMDA	3 HDBC	Benzene	30	2.4	0
4 HMDA	3 HDBC	CCl ₄	30	4.6	1.0
4 MXDA	3 HDBC	CCl ₄	30	5.6	4.0
3 EDA	3 HDBC	Aromatic	30	2.8	10.1
3 PIP	3 HDBC	Aromatic	30	2.3	15.0

^a Numbers refer to weight per cent of ingredient in the solution. The amines were used in aqueous solution containing twice as much sodium carbonate as amine, and 0.15 wt.-% nonionic wetting agent; the bischloroformates, in the specified organic solvent. EDA, ethylenediamine; HMDA, hexamethylenediamine; MXDA, *m*-xylylenediamine; PIP, piperazine; EGBC, ethyleneglycol bischloroformate; DGBC, diethylene glycol bischloroformate; HDBC, 1,6-hexanediol bischloroformate.

^b Immersion time in each solution, steps 1 and 2.

^c With 2 min. wash in Accelerotor.

TABLE IV
Surface Graft Polymers of Wool by Interfacial Polymerization:
Polyureas, Polyesters, and Polycarbonates

Reagents used ^a		Organic solvent	Time, sec. ^b	Resin on fabric, %	Area shrinkage, % ^c
Step 1	Step 2				
4 HMDA	3 MBPI	Benzene	30	1.4	9.8
4 HMDA	3 MBPI	CCl ₄	60	1.7	8.8
4 MXDA	3 TDI	Benzene	30	6.0	7.9
3 TDI	4 MXDA	Benzene	60	3.9	20.0
4 MXDA	3 TDI	CCl ₄	60	5.2	20.0
4 BPA	3 TPC	CH ₂ Cl ₂	30	0.9	23.5
4 BPA	3 SC	Benzene	60	1.4	24.4
4 BPA	3 TPC	CCl ₄	60	1.0	24.4
4 BPA	5 HDBC	Benzene	60	4.2	20.0
4 BPC	5 PDBC	Benzene	60	3.6	23.5

^a Diamines and diols used in aqueous solutions; the diisocyanates and diacid chlorides, in the specified organic solvent. Numbers refer to weight per cent of the ingredient in the solution. HMDA, hexamethylenediamine; MXDA, *m*-xylylenediamine; BPA, 2,2-bis(*p*-hydroxyphenyl)propane; BPC, 2,2-bis(3-methyl-4-hydroxyphenyl)-propane; MBPI, methylenebis(*p*-phenyl isocyanate), TDI, toluene diisocyanate; SC, sebacyl chloride; TPC, terephthaloyl chloride; HDBC, 1,6-hexanediol bischloroformate; PDBC, 2,2-dimethyl-1,3-propanediol bischloroformate.

^b Immersion time in each solution, steps 1 and 2.

^c With 2 min. wash in Accelerotor.

substrate to the treating solutions, type of organic solvent used, concentrations of the treating solutions, the ratio of reagents used, and others.³

Typical syntheses for several types of surface graft polymers on wool are summarized in Tables II–V. Results for grafted polyamides are given in Table II; for polyurethanes, in Table III; for polyureas, polyesters, and polycarbonates in Table IV; and for copolymers in Table V. In all instances the experimental procedure consisted of serial application of the two treating solutions to the wool fabric by a dip-pad procedure. The fabric was immersed in the first solution for the specified time (1 min. or less) and then passed through squeeze rolls to give a wet pick up of 50–60%. The fabric was then immersed in the second treating solution for the specified time (1 min. or less) and finally passed through squeeze rolls again to remove excess solution. The interfacial formation of the graft polymer occurs during the second step of this procedure. The treated fabric was washed thoroughly in water and dried at constant temperature and humidity. The amount of polymer formed on the fabric was estimated by gain in weight.

Data on resistance of the treated fabrics to felting shrinkage are included, since extensive study has indicated that grafting of the polymer is necessary (in these quantities) to impart good shrink-resistance to the fabric. In

TABLE V
Surface Graft Polymers of Wool by Interfacial Polymerization: Copolymers

Copolymer	Reagents used ^a		Organic solvent	Time, sec. ^b	Resin on fabric, %	Area shrinkage, % ^c
	Step 1	Step 2				
Amide-urea	3 HMDA	1.5 SC 1.5 MBPI	Benzene	30	3.3	5.9
Amide-urethane	3 HMDA	1.5 DGBC 1.5 SC	Benzene	30	4.0	2.0
Amide-ester	1.5 HMDA 2.5 BPC	3 SC	Benzene	60	4.7	2.0
Amide-amide	3 HMDA	1.5 SC 1.5 AC	Toluene	30	2.0	12.6
Urea-urethane	3 HMDA	1.5 TDI 1.5 HDBC	Benzene	30	3.5	5.0
Urethane-urethane	1.5 HMDA 1.5 MXDA	3 HDBC	Toluene	30	3.7	2.0
Urethane-urethane	3 HMDA	1.5 HDBC 1.5 PDBC	Toluene	30	2.5	2.0

^a Numbers refer to weight per cent of ingredient in the solution. The diamines and diols were used in aqueous solution; the diacid chlorides, diisocyanates, and bischloroformates, in the specified organic solvent. HMDA, hexamethylenediamine; MXDA, *m*-xylylenediamine; MBPI, methylene-bis(*p*-phenyl isocyanate); TDI, toluene diisocyanate; SC, sebacyl chloride; AC, adipoyl chloride; DGBC, diethylene glycol bischloroformate; HDBC, 1,6-hexanediol bischloroformate; PDBC, 2,2-dimethyl-1,3-propanediol bischloroformate; BPC, 2,2-bis(3-methyl-4-hydroxyphenyl)propane.

^b Immersion time in each solution, steps 1 and 2.

^c With 2 min. wash in Accelerotor.

other words, the shrinkage protection provides fairly good indirect evidence for grafting in these systems. Data reported were obtained in an accelerated wash test with the use of the Accelerotor.² More direct evidence for graft polymer formation is given in the following section.

III. CHARACTERIZATION OF POLYMER FORMED

Wool modified by polyhexamethylene sebacamide (nylon 610) has been the most thoroughly characterized of the surface graft polymers. The characterization work on wool modified by this polyamide is described here.

A. Electron Microscopy

A sample of wool fabric modified by interfacial formation of 2% polyamide 610 was examined by electron microscopy. By means of a surface replication technique, using single fibers (taken from the treated cloth), the polymer was found to be present as an ultrathin film covering the fiber surface. This film was estimated to have a thickness of 200–300 Å.⁷ The average thickness of a dried film formed in the absence of a substrate under otherwise similar conditions (in a beaker) has been reported¹ to be about 30,000 Å. (150 times thicker than that formed on the wool). The thinness of the film formed on the wool fiber is due, of course, to the limited quantity of reagent available from the first step for reaction in the second step.

B. Solvent Extraction

Solvent extraction was carried out to ascertain whether the ultrathin film could be dissolved from the fiber. Grafted polymer should not be removable by extraction; ungrafted polymer should be. Extensive extraction of a treated sample (containing 2% polyamide 610) with formic acid or benzyl alcohol did not remove the polymer; the treated sample lost no weight during the extraction. In addition, the extracted sample was as resistant to felting shrinkage as the unextracted sample (Table VI).

When a wool modified by a polyurethane was extracted with chloroform and chloroform–methyl alcohol mixtures, the polyurethane was partially extracted (Table VII), but there was little or no loss in shrinkage protection.

TABLE VI
Solvent Extraction of Wool Shirting Modified by Polyamide 610

Solvent	Resin on fabric, %		Area shrinkage, % ^a	
	Before extraction	After extraction	Before extraction	After extraction
Benzyl alcohol	2.0	2.0	0	0
Benzyl alcohol	None	None	32.9	28.8
Formic acid	2.0	2.0	0	12.6
Formic acid	None	None	32.9	42.2

^a With 2 min. wash in Accelerotor.

These results suggest that graft polymer is formed, and that the grafted polymer is responsible for the shrinkage protection. The removal of a small amount of a surface deposit of ungrafted polymer has no appreciable effect upon the shrink-resistance of the treated fabric.

TABLE VII
Solvent Extraction of Wool Modified by Polyurethane Derived from
Hexamethylenediamine and Ethylene Glycol Bischloroformate^a

Amount of polyurethane on wool, %		Area shrinkage, % ^b	
Before extraction	After extraction	Before extraction	After extraction
0	0	48	48
2.5	1.3	1	3
4.4	1.9	0	0
4.6	2.8	0	3

^a Solvent: chloroform; chloroform-methyl alcohol.

^b With 2 min. wash in Accelerotor.

Further verification was obtained by treating wool fabric with preformed polymer. In this experiment, the polyamide 610 was prepared by interfacial polymerization in the absence of wool. The polymer was isolated, purified, dissolved in formic acid or benzyl alcohol, the polymer applied to the wool, and the solvent evaporated. Samples so prepared were subjected to solvent extraction and to shrinkage tests. In Table VIII the results of these tests are summarized.

TABLE VIII
Solvent Extraction and Shrinkage Data for Wool Treated with Preformed Polyamide 610

Polymer on fabric, %		Area shrinkage, % ^b	
Before extraction	After extraction ^a	Before extraction	After extraction
None	None	48	48
2.2 ^c	None	45	47
1.0 ^d	None	44	47

^a Extracted with formic acid. Weight loss measured.

^b With 2 min. wash in Accelerotor.

^c Applied from formic acid solution.

^d Applied from benzyl alcohol solution.

The polymer preformed and applied to the wool is readily extracted; 2%, by weight, thus applied, imparts no shrinkage resistance to the wool, although less than 2% of the same polymer, polymerized *in situ*, provides complete shrinkage protection. It is believed that the preformed polymer, applied from solvent, was displaced from the wool by the detergent during the laundering. There is, of course, no reason to expect it to have been chemically grafted to the fiber.

C. Blocking of Grafting Sites

The most likely grafting sites on the wool are the free amino and hydroxyl groups. If grafting during interfacial polymerization results from participation of these groups, it should be possible to block such participation by reacting the groups (blocking them) prior to the polymerization reaction. This was done by acetylating the wool with acetic anhydride prior to interfacial polymerization. Extraction and shrinkage data from acetylated wool subsequently modified by interfacial formation of polyamide 610 are given in Table IX.

TABLE IX
Interfacial Polymerization on the Surface of Acetylated Wool (Polyamide 610)^a

Acetyl on fabric, %	Polymer on fabric, %		Area shrinkage, % ^b	
	Before extraction	After extraction	Before extraction	After extraction
None	None	None	48.0	48.0
None	1.1	1.1	13.6	16.4
6.0	None	None	32.0	34.0
6.0	1.1	None	27.0	34.4

^a Formic acid extraction.

^b With 2 min. wash in Accelerotor.

These results demonstrate again that formation of polyamide 610 on ordinary wool imparts shrinkage protection, and the polymer is not extracted by a good solvent for the polymer. In contrast, polyamide 610 formed interfacially on acetylated wool confers no shrinkage protection, and the polymer is readily extracted with formic acid. This evidence strongly suggests that graft polymer is formed on ordinary wool. If the failure of the polymer to be extracted from ordinary wool were due to entrapment of the *in situ* formed polymer, rather than to grafting, the polymer formed *in situ* on the acetylated wool should also have resisted extraction.

D. Enzyme Digestion of Treated Wool; Determination of the Grafting Sites on the Wool

Wool is readily digested by various enzymes which have no effect on polyamide 610. By subjecting a sample of wool modified with 2% polyamide 610, formed *in situ* by interfacial polymerization, to digestion by papain in an aqueous solution containing urea and mercaptoethanol, essentially all the wool was solubilized. The residue (which was 2% of original weight of treated wool) consisted of hollow tubes whose surface structure was reminiscent of the surface structure of the wool fiber. It was readily soluble in formic acid. By ultracentrifugation, the soluble material was found to have a molecular weight in excess of 10,000. Analysis of the total residue for amino acids is given in Table X. The amino acids accounted for

TABLE X
Amino Acids in Residue from Papain Digest of Wool Modified with 2%
Poly(hexamethylene Sebacamide)*

Amino acid	Amt. amino acid, μ mole	Groups per 100 groups	
		In residue from digest	In wool
Lysine	0.030	2.8	2.3
Histidine	0.016	1.5	0.7
Arginine	0.050	4.7	6.9
Aspartic acid	0.045	4.2	6.2
Threonine	0.136	12.8	6.1
Serine	0.101	9.5	11.1
Glutamic acid	0.097	9.1	12.0
Proline	0.060	5.6	7.3
Glycine	0.157	14.7	8.7
Alanine	0.052	4.9	4.9
Valine	0.083	7.8	5.0
Methionine	0.024	2.3	0.5
Isoleucine	0.033	3.1	2.9
Leucine	0.067	6.3	7.2
Tyrosine	0.078	7.3	4.2
Phenylalanine	0.036	3.4	2.8
Half cystine	0	—	11.2

* Analyses by Beckman automatic amino acid analyzer.

3% of the total weight of the residue. As will be noted in Table XI, all amino acids occurring as endgroups in wool protein or containing —OH or —NH₂ in side chain groups are found in the residue from enzyme diges-

TABLE XI
Amino Acids Probably Involved as Grafting Sites in Treated Wool

Endgroups in wool		Reactive main chain amino acids	Groups per 100 groups	
Amino acid	Relative abundance*		In enzyme digest residue	In wool
Glycine	5.2	—	14.7	8.7
Threonine	4.8	Threonine	12.8	6.1
Valine	2.4	—	7.8	5.0
Serine	1.3	Serine	9.5	11.1
Glutamic acid	1.3	—	9.1	12.0
Alanine	1.3	—	4.9	4.9
Aspartic acid	0.6	—	4.2	6.0
		Tyrosine	7.3	4.2
		Lysine	2.8	2.3
		Histidine	1.5	0.7

* Data of Middlebrook.⁸

tion, and in an abundance in accord with their relative abundance as endgroups rather than their relative abundance in wool as a whole. Several amino acids not present as end groups in wool protein and containing no

TABLE XII
Amino Acids Not Occurring in Endgroups in Wool or Occurring in Main Chain of Wool
but Possessing No Reactive Side Chains

Amino acid	Groups per 100 groups	
	In enzyme digest residue	In wool
Leucine	6.3	7.2
Proline	5.6	7.3
Phenylalanine	3.4	2.8
Isoleucine	3.1	2.9
Methionine	2.3	0.5

reactive groups in their side chain were also found in the residue; data for these acids are given in Table XII.

The method of enzyme digestion and of detailed analysis of the residue, therefore, gives promise of being suitable for separating the grafted polymer from the wool substrate and for providing evidence for the particular amino acids involved in the grafting sites. Further work of this nature is in progress.

The evidence points to the formation of graft polymer on the surface of wool through reaction with NH_2 , and possibly OH , groups in the protein. It illustrates the general principle of forming graft copolymers on the surface of substrates which contain suitably reactive groups.

The authors thank Helen M. Kivela for the amino acid analyses; Marian Allis, Margery Andrews, Lura Humble, and Iva Montgomery for shrinkage measurements; J. B. Bartulovich for the ultracentrifuge results.

Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

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Résumé

Par polycondensation interfaciale on peut former des couches ultrafines de polyamides, polyuréthanes, polyurées, polyesters, polycarbonates et de copolymères divers sur la surface d'un substrat. Si le substrat contient des groupes réactionnels ($-\text{NH}_2$, $-\text{OH}$, $-\text{NCO}$, $-\text{COCl}$, etc.) on forme du polymère greffé. Le polymère greffé ne peut être enlevé par un lavage intensif avec de bons solvants pour le polymère. Au contraire, si on emploie comme substrat de la laine qui a été acétylée avant la polymérisation (pour bloquer les sites de greffage) on peut finalement extraire la fine couche de polymère.

La digestion de la laine ainsi traitée, avec des enzymes qui réagissent avec la laine, mais pas avec la couche greffée, permet d'identifier le polymère greffé. Par analyse des acides aminés du résidu de la réaction enzymatique on peut montrer que les sites de greffage sur la laine sont sans doute les groupes aminés et hydroxyles libres situés sur les acides aminés terminaux ou sur les acides aminés internes qui possèdent un tel groupe sur une chaîne latérale.

Zusammenfassung

Durch Grenzflächenpolykondensation können ultradünne Schichten von Polyamiden, Polyurethanen, Polyharnstoffen, Polyestern, Polycarbonaten und verschiedenen Copolymeren auf die Oberfläche eines Substrates aufgebracht werden. Wenn das Substrat reaktionsfähige Gruppen (wie $-\text{NH}_2$, $-\text{OH}$, $-\text{NCO}$, $-\text{COCl}$, etc.) enthält, entsteht ein Pfropfpolymeres. Das Pfropfpolymeres wird durch lang dauernde Extraktion mit guten Lösungsmitteln für das Polymeres nicht entfernt. Dagegen wird die dünne Polymerschicht leicht extrahiert, wenn Wolle als Substrat verwendet und vor der Polymerisation zur Blockierung der Pfropfstellen acetyliert wird. Nach enzymatischem Abbau der behandelten Wolle, der die aufgepfropfte Schicht nicht angreift, kann das gepfropfte Polymeres charakterisiert werden. Aus einer Aminosäureanalyse der nach dem enzymatischen Abbau zurückbleibenden Reste geht hervor, dass als Pfropfstellen auf der Wolle wahrscheinlich die freien Amino- und Hydroxylgruppen wirksam sind, die sich in *N*-endständigen Aminosäuren oder in Aminosäuren mit diesen Seitengruppen innerhalb der Kette befinden.

Received August 8, 1963