

Graft Copolymerization of Vinyl Monomers in Wool Fibers

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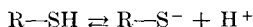
Synopsis

Graft copolymerization of vinyl monomers, mainly methyl methacrylate, in reduced, successively alkylated, or KCN-treated wool fibers was performed in the redox LiBr-persulfate system without homopolymer. The reduction gives a striking effect in promoting the graft copolymerization. Methylation or ethylene recrosslinking of the reduced wool, especially the former, decreases the graft-on remarkably. By the KCN treatment in which the conversion of disulfide to lanthionine bonds occurs, the grafting is decreased in the bromide-persulfate system but promoted in the system with persulfate alone. Methylation or KCN treatment of wool as well as reduction brings about a great increase in the absorption of persulfate. The grafting of the lanthionine-containing wool in the redox system accompanied by the liberation of bromine might be retarded by the pronounced bromination of monomers over the inhibiting of homopolymerization, because the lanthionine bonds are more stable to bromine than the disulfide bonds. In general, disulfide bonds and the other easily oxidized components of wool may perhaps play an important role in regulating the bromination of monomers and in the graft copolymerization without homopolymer. The molecular weight of graft polymer is decreased distinctly with increasing extent of reduction of wool. From these results, the thiol groups on wool are considered to give predominantly graft centers by the radicalotropy from SO_4^- , $\text{OH}\cdot$, and/or $\text{Br}\cdot$.

INTRODUCTION

The graft copolymerization of vinyl monomers by the action of peroxide of persulfate is known to take place more readily in reduced wool than in untreated wool.¹⁻⁴ This fact has been explained not only by the increased swelling or accessibility of wool fibers, but also by such actions of the thiol groups as the ability to promote the decomposition of oxidizing agents and their participation in radical formation from the catalyst radicals and chain transfer from the growing homopolymer radicals ($\text{P}\cdot$).⁵⁻⁸

Ionization:



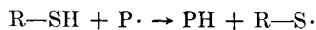
Decomposition:



Radicalotropy:



Chain transfer



In a previous study, we found that the aqueous redox system containing bromide and persulfate ions was utilized effectively for the graft copolymerization of various acrylates in wool fibers at a relatively low temperature and without homopolymerization.⁹ This specific grafting procedure is also more effective for reduced wool than natural wool. We therefore attempted to elucidate the reaction mechanism for this graft copolymerization by using reduced, successively alkylated, and cyanide-treated wool fibers.

EXPERIMENTAL

Materials

The tops of Merino wool fibers were extracted with acetone in a Soxhlet apparatus for about 24 hr., washed with cold water, and then air-dried.

Thioglycollic acid (TGA), sodium sulfide, and potassium cyanide were of highest laboratory reagent quality and used without further purification, as were methyl iodide, ethylene dibromide, diethylene glycol monobutyl ether (BC), lithium bromide, and potassium persulfate. The monomers for grafting, methyl acrylate (MA), ethyl acrylate (EA), *n*-butyl acrylate (*n*-BA), methyl methacrylate (MMA), and acrylonitrile (AN), were distilled and purified as in the usual way.

Preparation of Modified Wool

The reduction of wool (0.5–1.0 g.) was generally carried out with an aqueous solution of thioglycollic acid adjusted to about pH 5 with sodium hydroxide at 30°C. with varying time of reaction. The reduced wool was washed well with water (0.5–1 liters), ethanol, or 0.01*N* hydrochloric acid, again with water, and then subjected to the grafting or alkylation as soon as possible after being pressed dry with filter paper. The concentration of thioglycollic acid solution was determined by titration with 0.1*N* iodine solution. In the present study, no quantitative measurement of thiol groups in the reduced wool fibers was done.

The alkylation of reduced wool was carried out with methyl iodide or ethylene dibromide according to the procedure of Crewther,¹⁰ the treated wool being washed with water, ethanol, and again with water, then air-dried.

Reduction with sodium sulfide and the formation of lanthionine cross-linkage with potassium cyanide were also carried out according to the procedure of Wolfram and Speakman.⁴

The graft copolymerization was performed mostly in the lithium bromide–ammonium or potassium persulfate redox system and occasionally,

for comparison, in the conventional aqueous persulfate system without bromide. The preparation of the lithium bromide redox system was carried out as follows. First, a weighed amount of BC as monomer-solubilizer, vinyl monomers, then a 50% lithium bromide aqueous solution were successively mixed sufficiently slowly in a highly concentrated solution of persulfate to avoid arise in temperature. This reaction mixture was maintained at a constant temperature (10 or 30°C.) and the dried wool samples were immersed to graft for the specified time, with occasional shaking to remove the air bubbles. After the reaction period, the wool fibers were washed with water alone in the case of the lithium bromide redox system unless otherwise specified. The reason was that the reaction system in which the grafting proceeds with almost no homopolymer formation was chosen following the previous report. Since the persulfate system without bromide allows a large amount of homopolymer to form, the grafted wool fibers were Soxhlet-extracted with acetone for 24 hr. and then washed with water. The extent of grafting was expressed as the weight per cent increase based on the original dry weight of wool fibers. For the reduced wool only, the dry weight of untreated wool before reduction was taken as the original weight. Also, in the graft experiments performed in parallel with the persulfate absorption experiments, the extent of grafting was calculated from the weight increase based on the conditioned weight at 65% R.H.

Measurement of Absorption of Persulfate

The rates of absorption of persulfate by untreated and modified wool fibers were determined by the following procedure. The wool fibers (0.5 g.) conditioned at 65% R.H. were immersed in 50 ml. of 7.78×10^{-3} mole/l. aqueous solution of potassium persulfate at 30°C. for varying times. The amounts of persulfate absorbed in wool fibers were calculated from the determination of the change in concentration of the solution according to the procedure of Kolthoff and Carr.¹¹

Separation and Molecular Weight Determination of Graft Polymers

To separate the graft polymers from the wool, the decomposition of wool with 72% sulfuric acid was used.¹² Though the direct decomposition of wool was observed to be incomplete, especially for the grafted product from untreated wool, the pretreatment of grafted product with thioglycollic acid was found to be quite effective in decomposing the wool component almost completely. Therefore, before the acid decomposition, all the grafted samples were first treated with 0.5*N* thioglycollic acid (pH 5.0) for 30 hr. at 55°C. at a liquor ratio of 100:1 and then washed with water. The acid decomposition was subsequently carried out, the samples being at first treated with 72% sulfuric acid for 120 min. at 40°C. at a liquor ratio of 40:1, diluted with eight times as much water, and then heated in a boiling water bath until complete decomposition was achieved (about 120 min.). The insoluble residues were filtered off, washed well with water until the

filtrate became neutral, and purified by solution in acetone, filtering, and then precipitation with water, this being repeated three times. For a dilute acetone solution of the purified graft polymers, the viscosity measurements were carried out at 25°C. The intrinsic viscosity was calculated by using the single-point method for poly(methyl methacrylate) of Valles et al.:¹³

$$[\eta] = 2(\eta_{sp}/c)/(\eta_{sp} + 2)$$

where c is the concentration of the polymer (in grams per 100 ml.). The molecular weight was obtained from the equation:¹⁴

$$[\eta] = 9.6 \times 10^{-5} M^{0.69}$$

RESULTS AND DISCUSSION

Grafting in Wool Reduced with Thioglycolic Acid

The wool fibers reduced with thioglycolic acid were grafted with methyl or ethyl acrylate, methyl methacrylate, and acrylonitrile in the lithium bromide-potassium persulfate system. These results are shown in Table I. From these results, it is evident that the reduction of wool strongly promotes the graft copolymerization of various vinyl monomers.

TABLE I
Graft-on of Various Monomers for Wool Fibers Reduced with TGA

Pretreatment ^a	Monomer	Graft-on, % ^b
Untreated	MMA	95.6
Reduced	"	215
Untreated	MA	4.8
Reduced	"	110
Untreated	EA	1.3
Reduced	"	62.7
Untreated	AN	7.8
Reduced	"	66.9

^a Reduction: 0.12–0.15*N* TGA; 26 hr.; 30°C.; liquor ratio 100:1.

^b Grafting: LiBr 27.5%; K₂S₂O₈ 0.2%, BC 15%; H₂O 52.3%; monomers 5% (by weight); 3 hr.; 30°C.; liquor ratio 100:1.

To determine the effect of the extent of reduction on the grafting, methyl methacrylate was grafted on the wool fibers reduced at varying concentrations of thioglycolic acid. The grafting was carried out in both the lithium bromide-potassium persulfate and persulfate systems, both procedures being followed by acetone extraction of grafted wool. The results are given in Table II. It can be seen that the graft-on of methyl methacrylate increases with increasing extent of reduction of the wool fibers in both grafting systems.

Furthermore, the rate of *n*-butyl acrylate grafting in the untreated and reduced wool fibers was measured at about 10°C. with ammonium per-

TABLE II
Effect of Extent of Reduction at Varying Concentration of TGA on Graft-on of MMA

Concentration of TGA, N^a	Graft-on, %	
	LiBr-K ₂ S ₂ O ₈ ^b	K ₂ S ₂ O ₈ ^c
0	90.2	78.4
0.001	89.1	—
0.010	99.0	—
0.025	136	—
0.05	106	—
0.10	155	138
0.20	166	182
0.50	228	243

^a 24 hr.; 30°C.; liquor ratio 100:1.

^b LiBr 20.0%; K₂S₂O₈ 0.2%, BC 22.5%; H₂O 52.3%, MMA 5.0% (by weight); 5 hr.; 30°C.; liquor ratio 100:1.

^c K₂S₂O₈ 0.2%, BC 22.5%, H₂O 72.3%, MMA 5.0% (by weight); 24 hr.; 30°C.; liquor ratio 100:1.

sulfate as catalyst. These results are shown in Figure 1. It is quite evident that the reduction of disulfide bonds to thiol groups strongly promotes graft copolymerization of wool fibers.

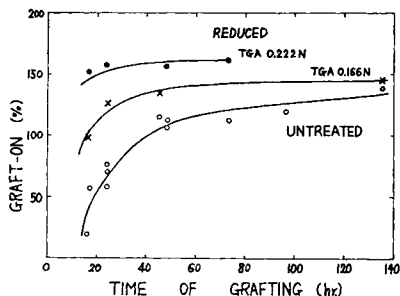


Fig. 1. Rate of *n*-butyl acrylate grafting in untreated and reduced wool fibers. Reduction: 40 hr.; 30°C.; liquor ratio 100:1. Grafting: LiBr 16%, (NH₄)₂S₂O₈ 1.0%, BC 40.0%, H₂O 38.0%, *n*-BA 5.0% (by weight); 9–12°C.; liquor ratio 100:1.

Grafting in Alkylated Wool

In order to clarify the role of thiol groups in the graft copolymerization, alkylation of reduced wool and subsequent grafting with methyl methacrylate in the lithium bromide-persulfate system were performed. The wool (0.15 g.) reduced under the same conditions as mentioned in Table II was alkylated gently by shaking with 30 ml. of 0.1M Na₂HPO₄ containing 1 ml. of methyl iodide as blocking agent or ethylene dibromide as recrosslinking agent for 48 hr. at 30°C. The conditions of grafting were the same as in Table II. These results are shown in Figure 2. On alkylation of thiol groups, the graft-on decreases rapidly, especially in methylated wool, with increasing extent of reduction.

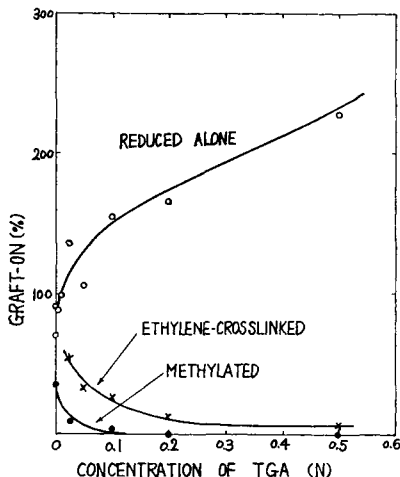


Fig. 2. MMA graft-on of reduced and alkylated wool at varying concentration of TGA.

In this case, since the swelling of wool fibers should be greater in methylated wool than in recrosslinked wool, the grafting can not be considered to be dominated by the swelling of fibers. Here, it is noteworthy that the grafting behavior seems to correspond qualitatively to the results of Crewther,¹⁰ according to which the amount of disulfide groups or the total amount of thiol and disulfide groups remaining after reduction and successive alkylation is always less in methylated wool than in ethylene-recrosslinked wool.

Furthermore, since the graft-on of unreduced wool with a small content of thiol groups ($2 \text{ mole}/10^5 \text{ g.}$) is decreased remarkably by the methylation treatment in which the thiol contents are reported to be decreased by half,¹⁰ the thiol groups might be presumed to play a predominant role in graft copolymerization. On the other hand, in the reduced and subsequently alkylated wool fibers the content of disulfide bonds is decreased markedly, while the thiol content is as great or rather more than that of the untreated wool. Therefore, even if the thiol groups become the main centers of grafting, the role of disulfide bonds must be taken into consideration.

Thiol radicals may also be formed from the disulfide bonds to some extent. However the oxidation of disulfide bonds to cysteic acid residues by the action of the liberated bromine seems to be more important.¹⁵ Also, the bromination of monomers should occur simultaneously in the graft copolymerization without homopolymerization if the liberation of bromine is adequate. When the content of disulfide bonds is relatively low, the bromination of monomers will be more pronounced and consequently the graft copolymerization retarded. This may be a reason for the marked decrease in graft-on of the reduced and methylated wool fibers. Similar phenomena are also seen in the lanthionine-containing wool as described below.

Absorption of Persulfate by Modified Wool

Wolfram and Speakman⁴ have pointed out that the absorption affinity of wool fibers for persulfate plays an essential role in promoting internal polymerization. However, no data are reported for reduced or alkylated wool. Therefore, it is of interest to measure the persulfate affinity of these modified wool fibers from aqueous solution. The experimental results obtained are shown in Table III.

TABLE III
Absorption of Persulfate by Untreated, Reduced, Methylated, and KCN-Treated Wool Fibers from 7.78×10^{-3} mole/l. $K_2S_2O_8$ Solution at 30°C.

Treatment	Amount of persulfate absorbed after various times, $\times 10^4$ equiv./g.						
	15 min.	30 min.	60 min.	120 min.	180 min.	240 min.	300 min.
Untreated	—	0.173	0.234	0.640	0.965	1.27	2.08
Reduced with TGA ^a	2.26	4.31	8.27	11.20	12.85	—	—
Reduced with Na_2S ^b	2.36	2.89	7.23	10.10	11.20	—	—
Methylated after TGA reduction ^c	5.00	—	7.12	8.89	10.05	—	—
KCN-treated ^d	4.95	7.42	10.71	11.65	12.03	—	—

^a 0.5*N* TGA; 24 hr.; 30°C.; liquor ratio 100:1.

^b 0.042*M* Na_2S ; 20 min.; 25°C.; liquor ratio 50:1.

^c Reduction: 0.5*N* TGA; 48 hr.; 30°C.; liquor ratio 100:1. Methylation: 0.1*M* Na_2HPO_4 , 30 ml. containing 1 g. CH_3I ; 24 hr.; 30°C.; liquor ratio 30:1. Reduction-methylation: two cycles.

^d 0.65% KCN; boiled for 30 min.; liquor ratio 40:1.

TABLE IV
Comparison of MMA Graft-on for Untreated, Reduced, Methylated, and KCN-treated Wool Fibers in LiBr- $K_2S_2O_8$ or $K_2S_2O_8$ System

Treatment	Graft-on, %	
	LiBr- $K_2S_2O_8$ ^a	$K_2S_2O_8$ ^b
Untreated	96.8	78.4
Methylated ^c	54.3	54.3
Reduced with TGA ^d	133	183
Reduced with Na_2S ^d	203	316
Methylated with TGA reduction ^d	~0	~0
KCN treated ^d	23.8	300

^a LiBr 27.5%, $K_2S_2O_8$ 0.2%, BC 22.5%, H_2O 44.8%, MMA 5.0% (by weight) 3 hr.; 30°C.; liquor ratio 100:1.

^b Same conditions as mentioned in Table II.

^c 0.1*M* Na_2HPO_4 , 60 ml. containing 1 g. CH_3I ; 48 hr.; 30°C.; liquor ratio 60:1.

^d Same conditions as mentioned in Table III.

It can be seen that the persulfate absorption affinity of wool fibers is increased markedly even after subsequent methylation for a given degree of reduction. This fact indicates that the great decrease of graft-on in the methylated wool after reduction is not attributable to the change of the absorption affinity for catalyst or the change of the fiber swelling, but to the decrease of the amounts of thiol and/or disulfide groups.

The grafting of the methylated wool is hindered in the system with persulfate alone as well as in the bromide-persulfate system (Table IV).

Reduction with sodium sulfide also affects the grafting qualitatively in the same way as treatment with thioglycolic acid (Tables III and IV).

Grafting in KCN-Treated Wool

It has been reported that the disulfide bonds in wool are almost quantitatively converted to lanthionine bonds by treatment with an aqueous solution of potassium cyanide, this being accompanied by some increase in the thiol content.^{4,16} Therefore, we attempted to graft potassium cyanide-treated wool fibers in order to obtain more details to the reaction mechanism of graft copolymerization. First, measurement of the affinity for persulfate yielded the result that the cyanide treatment brings about rather greater affinity compared with the reduction treatment, as shown in Table III. In spite of this result, the grafting of methyl methacrylate in the cyanide-treated wool is retarded in the bromide-persulfate system but promoted markedly in the system with persulfate alone, as shown in Table IV. The rates of methyl methacrylate grafting in the persulfate system for untreated, reduced, and cyanide-treated wool fibers are compared in Table V.

TABLE V
Rate of MMA Grafting for Untreated, Reduced, and KCN-Treated Wool Fibers in $K_2S_2O_8$ System

Treatment	Time of grafting, min.	Graft-on, %
Untreated	120	0
	180	13.8
	300	20.0
	1440	78.4
Reduced with TGA ^a	20	17.2
	45	57.6
	80	62.9
	120	91.0
	240	163
	1440	183
KCN-Treated ^a	60	15.6
	95	51.1
	180	124
	300	226
	1440	300

^a Same conditions as mentioned in Table III.

The bromine liberated in the bromide–persulfate system reacts widely and in a complicated way with various amino acid residues in wool fibers, as described before. In addition to oxidation of thiol and disulfide groups to cysteic acid groups, bromination of tyrosine residues is also probable.¹⁷ The consumption of bromine by these reactions affects graft copolymerization without homopolymerization regulating the bromination of monomers.

Since the lanthionine crosslinkage formed by the cyanide treatment is known to be more stable than the disulfide linkage to such oxidizing agents as bromine,¹⁸ the greater part of bromine is considered to be consumed in the bromination of monomers, which decreases the grafting. On the contrary, in the persulfate system in the absence of bromine, some increases of thiol content accompanying the cyanide treatment may promote graft copolymerization much more than in the untreated wool.

The effect of the bromination of tyrosine residues on the grafting will be reported in a later paper.¹⁹

Effect of Reduction on Molecular Weight of Graft Polymers

From the results obtained above, the thiol groups are thought to provide the main centers of grafting. If this is the case, the molecular weight of the graft polymers must decrease with increasing extent of reduction of wool fibers. Some experiments were carried out to verify this, in which wool fibers were reduced to various extents by varying the concentration of thioglycollic acid and then grafted with methyl methacrylate in the bromide–persulfate system, the time of reaction being regulated to give approximately the same extent of graft-on (20–30%). The graft polymers were isolated from the wool by digestion of the wool with 72% sulfuric acid. The molecular weight of the purified graft polymers as determined from the viscosity is shown in Table VI.

As expected the molecular weight of graft polymers decreased distinctly with increasing extent of reduction of wool. This result seems to indicate that the centers of grafting are mostly thiol groups.

TABLE VI
Effect of Reduction of Wool on Molecular Weight of MMA Graft Polymers

Concentration of TGA, <i>N</i> ^a	Time of grafting, min. ^b	Graft-on, %	Molecular weight of graft polymer (MMA) × 10 ⁻⁴
Untreated	45	27.1	32.4
0.048	35	33.6	11.5
0.096	25	23.9	7.56
0.192	20	24.5	4.57
0.477	15	21.0	4.57

^a Reduction: 24 hr.; 30°C.; liquor ratio 50:1.

^b Grafting: LiBr 27.5%; K₂S₂O₈ 0.2%; BC 22.5%; H₂O 44.8%; MMA 5.0% (by weight); 15–45 min.; 30°C.; liquor ratio 100:1.

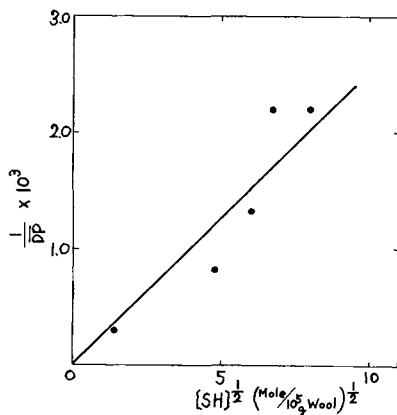
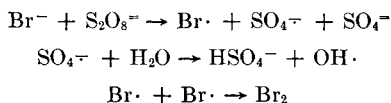


Fig. 3. Reciprocal of degree of polymerization of MMA graft polymers vs. square root of thiol contents.

The initiation of graft copolymerization in the bromide–persulfate redox system is presumed to be followed from the formation of free radicals by the reactions



Thus, the radicalotropy to thiol groups on wool from the sulfate ion, hydroxyl, and/or bromine radicals might occur.

When the reciprocal of the degree of polymerization of graft polymers is plotted against the square root of the thiol contents (estimated from the experimental data of Patterson et al.,²⁰ as their conditions of reduction were almost the same as ours), an approximately linear relation passing through the origin is obtained, as shown in Figure 3. This is also considered to indicate that the grafting has occurred mainly on the thiol groups on wool. This point is now being investigated in detail.

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Résumé

La copolymérisation greffée de monomères vinyliques, principalement de méthacrylate de méthyle sur des fibres de laine réduite, successivement alcoylée ou triatée dans le cyanure de potasse a été réalisée en utilisant un système oxydo-réducteur LiBr-persulfate sans formation de homopolymère. La réduction améliore considérablement la copolymérisation greffée. La méthylation où le pontage à l'éthylène de la laine réduite et principalement la méthylation diminue fortement le greffage. Par traitement au cyanure de potassium suite auquel il y a transformation en lanthionine des liens disulfures, le greffage est défavorisé dans le système bromure-persulfate tandis qu'il est favorisé par le système persulfate seul. La méthylation ou le traitement au cyanure de potassium de la laine aussi bien que la réduction augmente considérablement l'absorption pour le persulfate. Le greffage de la laine contenant de la lanthionine dans le système oxydo-réducteur s'accompagne de la libération de brome et peut être défavorisée par une bromuration prononcée des monomères par rapport à l'inhibition de l'homopolymérisation parce que les liens lanthionines ne sont plus stables à l'égard du brome que les liens disulfures. En général les liens disulfures et les autres composants aisément oxydés avec de la laine peuvent jouer un rôle important dans la régulation de la bromuration des polymères et dans le processus de copolymérisation greffée sans homopolymères. Le poids moléculaire du polymère greffé décroît nettement avec une augmentation du taux de réduction de la laine. Au départ de ces résultats, on considère que les groupes thiols sur la laine constituent les sites principaux du greffage par la radicalotropie des radicaux $\text{SO}_4\cdot\text{OH}\cdot$ et/ou $\text{Br}\cdot$.

Zusammenfassung

Die Propfcopolymerisation von Vinylmonomeren, hauptsächlich Methylmethacrylat auf reduzierte, sukzessive alkylierte oder mit KCN behandelte Wollfasern wurde im LiBr-Persulfat-Redoxsystem ohne Bildung von Homopolymerem durchgeführt. Die Reduktion ist von erstaunlicher Wirksamkeit für die Propfcopolymerisation. Methylierung oder Äthylen-Wiedervernetzung der reduzierten Wolle, besonders ersteres, setzt die Aufpfropfung in bemerkenswerter Weise herab. Durch die KCN-Behandlung, bei welcher eine Umwandlung von Disulfidbindungen in Lanthionin auftritt, wird die Aufpfropfung im Bromid-Persulfatsystem beeinträchtigt, im System mit Persulfat allein dagegen verstärkt. Methylierung oder KCN-Behandlung von Wolle sowie Reduktion bewirkt die grosse Zunahme der Persulfatabsorption. Die mit einer Freisetzung von Brom begleitete Aufpfropfung auf die lanthioninhaltige Wolle im Redoxsystem kann durch die bevorzugte Bromierung der Monomeren gegenüber der Inhibierung der Homopolymerisation beeinträchtigt werden, da die Lanthioninbindungen gegen Brom beständiger sind als die Disulfidbindungen. Im allgemeinen könnten die Disulfidbindungen und andere leicht oxydable Wollkomponenten eine wichtige Rolle bei der Regulierung der Monomerenbromierung und dem Ablauf der Propfcopolymerisation ohne Homopolymer-

bildung spielen. Das Molekulargewicht des Pfropfpolymeren wird mit steigendem Reduktionsgrad der Wolle deutlich herabgesetzt. Auf Grund der Ergebnisse werden die Thiolgruppen der Wolle als vorwiegende Quellen für die Aufpfropfungszentren durch radikalbildende Reaktion mit SO_4^- , OH^\cdot oder Br^\cdot betrachtet.

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