

Grafting of Wool with Vinyl Monomers by Using Trichloroacetic Acid-Bis(Acetylacetonato)-Copper(II) Cocatalyst

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Synopsis

Graft copolymerization of wool with methyl methacrylate (MMA) and acrylonitrile (AN) was effected under the catalytic influence of trichloroacetic acid (TCA) together with bis(acetylacetonato)copper(II). Investigation of the action of the cocatalyst on wool in the absence of monomer revealed that the treated wool is completely soluble in dilute alkali. The effect of storage on the catalyzed wool was also studied. Increasing the period of storage, before adding the monomer, causes a significant decrease in the graft yields, indicating vitiation of some of the free radicals on the wool backbone. Based on these studies, a mechanism for the grafting reaction was proposed. Moreover, grafting of wool modified through its disulfide bonds and amino and hydroxyl groups suggests that the thiol, hydroxyl, and amino groups participate in the grafting reaction as sites for graft attachment. Wool-graft copolymers show excellent antifelt properties, particularly at higher levels of grafting.

INTRODUCTION

Grafting of wool with vinyl monomers via a free-radical mechanism has been studied using a variety of methods, e.g., high-energy radiation,¹ low-energy radiation in the presence and absence of sensitizer,^{2,3} and redox systems^{4,5} to initiate free-radical formation. Recently, initiation of free radicals by powerful oxidizing agents such as Ce(IV) ions which attack the wool directly has been reported.^{6,7} Moreover, production of free radicals on the wool backbone has been possible by a complex formed between trichloroacetic acid or its ammonium salt and bis(acetylacetonato)-copper(II).⁸ This system has the advantage that no homopolymer occurs during grafting, particularly when trichloroacetic acid is used. It also gives high grafting yields compared to other means of chemical initiation. However, not much work has been published on the parameters which decide the efficiency of grafting when trichloroacetic acid together with bis(acetylacetonato)copper(II) was employed as initiator for grafting.

In this work, we are trying to fill this gap. The storage stability of the free-radical activity produced by treatment of wool with trichloroacetic acid along with bis(acetylacetonato)copper(II) was also examined.

Further, sites of graft attachment on wool were attempted. Here too, improvement in the antifelt properties of wool brought about by grafting was reported.

EXPERIMENTAL

Merino wool fibers were Soxhlet extracted with acetone for about 24 hr, followed by washing with cold distilled water, air dried, and conditioned.

KCN-treated wool was brought about by treating purified wool with a solution of KCN (0.65%) for various periods (15, 30, and 60 min) at boiling. A material to liquor ratio of 1:40 was used,⁹ whereas dinitrophenylated wool was prepared by reacting the purified wool with dinitrofluorobenzene in ethanolic solution for several days at room temperature.¹⁰ Acetylation of wool was carried out using a mixture of acetic anhydride and acetic acid using sulfuric acid as catalyst.¹¹

Acrylonitrile monomer (AN) was freshly distilled before use. Methyl methacrylate (MMA) was washed successively with 5% NaOH and water, then dried with anhydrous sodium sulfate, and distilled under reduced pressure in nitrogen before use.

Trichloroacetic acid (TCA) was reagent grade and was used without further purification. Bis(acetonylacetonato)copper(II) [Cu(acac)₂] was prepared by refluxing acetyl acetone in the presence of copper hydroxide. The product was extracted with chloroform and crystallized twice from benzene.⁸

A conditioned wool sample (1 g) was immersed in a solution containing a known concentration of TCA together with 0.5% Cu(acac)₂. Unless otherwise stated, the container was stoppered and left at room temperature for 16 hr. At this point, the sample was squeezed so as to give a wet pickup of ca. 100%. The catalyzed woollen material was then introduced in an Erlenmeyer flask containing the requisite amount of monomer in 50 ml distilled water which was kept at a specific temperature in a thermostatted water bath. The flask was immediately stoppered and the contents were stirred occasionally during grafting. After the desired grafting time, the sample was removed and washed well with water. Removal of any formed homopolymer was carried out by thorough soaping and washing in the case of AN and by Soxhlet extraction with acetone to constant weight in the case of MMA. Calculation of the percentage grafting was based on dry weight.

Felting Measurements

The felting of wool and wool-graft copolymers was carried out according to the method reported by Blankenburg and Zahn.¹² Wool sample (1 g) was introduced into a stoppered bottle with 50 ml phosphate buffer at pH 6 and shaken in a three-dimensional shaker of 150 rpm for 1 hr. The resulting wool ball was dried at room temperature and its average diameter was calculated. The density of the ball was calculated and taken as index of felting.

Alkali Solubility

The alkali solubility was carried out by treating wool sample (1 g) with 100 ml 0.1*N* NaOH solution for 1 hr at 65°C, with occasional shaking.

RESULTS AND DISCUSSION

Conditions Affecting Grafting

Grafting of wool fibers with MMA and AN using TCA together with Cu(acac)₂ as a cocatalyst was studied under a variety of conditions. Variables studied include time and temperature of the reaction, and concentrations of monomer and catalyst. It was observed that with

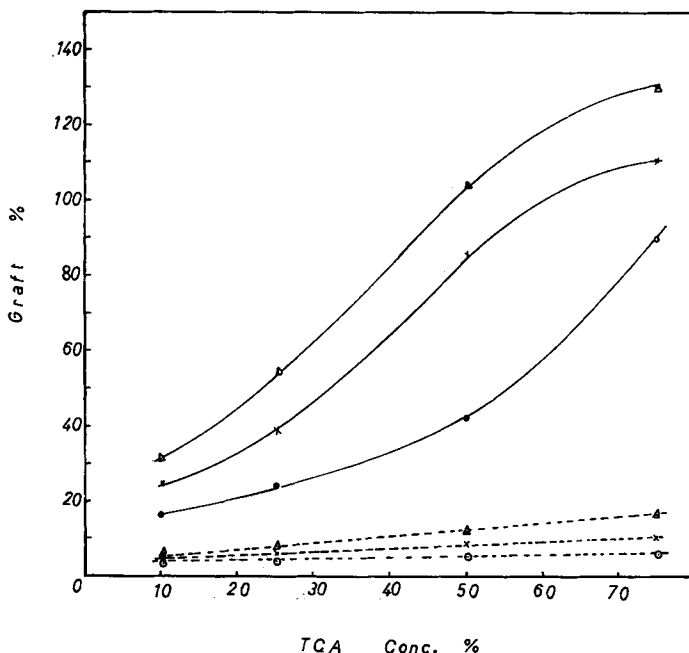


Fig. 1. Per cent graft yield vs. trichloroacetic acid (TCA) concentration: (—) 4% MMA; (----) 4% AN. Catalyst, TCA, 0.5% Cu(acac)₂; impregnation in the catalyst for 16 hr at room temp.; pickup 100%; grafting temp., 60°C. Grafting time: (○) 1 hr; (×) 3 hr; (Δ) 6 hr. Material/liquor ratio, 1:50.

both monomers, the extent of grafting is greatly enhanced by increasing the magnitude of these variables, in particular the TCA concentration (cf. Fig. 1). However, the graft yields obtained with MMA are much greater than those obtained with AN, perhaps due to the low response of AN to the free radical initiated on the wool backbone compared to that of MMA. Similar observations were reported by us when grafting was induced by ceric ions.⁷

An interesting feature is that no homopolymer was formed under any of the conditions studied, an observation which agrees with previous reports.⁸ This may be due to the absorbance of the cocatalyst on wool fibers and/or the ability of the cocatalyst to induce grafting faster than polymerization of the monomer in solution.

The conditions of the impregnation of wool in the cocatalyst influence also its reactivity toward graft polymerization. By increasing the temperature of the catalyst solution, it was possible to greatly reduce the time of impregnation. For example, 3 hr of contact at 60°C resulted in 42% graft yield on using 25% TCA, and 110% yield on applying 75% TCA, both in the presence of 0.5% Cu(acac)₂. These values are compared with 56% and 130% graft yields on activating wool for 16 hr at room temperature under the same conditions.

This indicates that, though the impregnation time was shortened to a considerable degree, appreciable graft yields could be obtained. Unfortunately, however, this was accompanied by discoloration and damage of the fibers. A partial dissociation of TCA-Cu(acac)₂ complex seems to occur during impregnation at higher temperatures. As a result, free radicals, ·CCl₃, are produced and may attack the wool keratine, thereby causing discoloration and degradation of the woollen material.

Action of the Cocatalyst on Wool

It has been pointed out above that damage of wool fibers was noticeable particularly when the wool was treated with TCA-Cu(acac)₂ complex at relatively high temperatures, i.e., 60°C, prior to grafting. In order to obtain more information on the nature of the reaction of wool with the said complex, treatment of wool was performed under conditions identical to those of grafting but without addition of the monomer. Wool was impregnated with 75% TCA plus 0.5% Cu(acac)₂ at room temperature for 16 hr, followed by squeezing to 100% pickup. The wool sample (1 g) was then treated for 6 hr at 60°C in 50 ml distilled water. It was found that this treatment gave a degraded woollen product the alkali solubility of which reached 100%. Treating wool with TCA alone under the same conditions gave a woollen material having a solubility of 28%, compared with a solubility of 16% for untreated wool.

Knowing that the TCA-Cu(acac)₂ complex dissociates to produce CCl₃ radicals,¹³ the complete alkali solubility of wool treated with the cocatalyst, compared to that of wool treated with TCA or the untreated wool, may be taken as indication that the reaction of wool with the complex in question is oxidative in nature and the oxidation takes place via a free-radical intermediate.

Activity of Catalyzed Wool

It has been reported that the complex formed by TCA with Cu(acac)₂ is a catalyst, whereas each component alone is not. This was explained by assuming that the presence of Cu(II) in the vicinity of the CCl₃ group

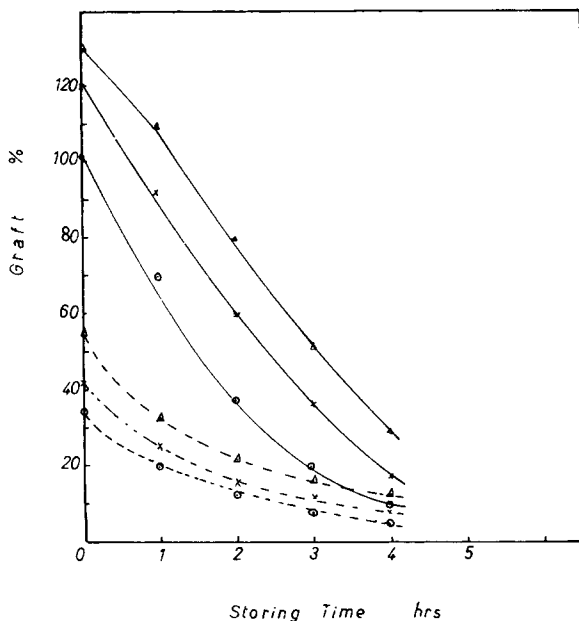


Fig. 2. Effect of storage on the free-radical activity of catalyzed wool: (—) 75% TCA, 0.5% $\text{Cu}(\text{acac})_2$; (----) 25% TCA, 0.5% $\text{Cu}(\text{acac})_2$. Impregnation in the catalyst for 16 hr at room temp.; pickup, 100%; monomer 4% MMA; grafting temp., 60°C. Grafting time: (○) 2 hr; (×) 4 hr; (△) 6 hr; material/liquor ratio, 1:50.

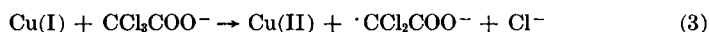
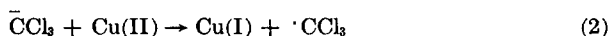
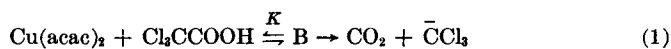
facilitates the electron shifts.¹³ Thus, oxidation of wool with the said complex would involve a free-radical intermediate, i.e., woollen radical. In order to study the activity of this intermediate, reaction of the latter with a vinyl monomer would constitute a useful tool in this respect.

Wool catalyzed with TCA-Cu(acac)₂ complex was stored for various periods of time before addition of the monomer. The extents of reaction, expressed as graft yields, after different storing times are taken as a measure of wool activity, i.e., the activity of the woollen radical. Figure 2 shows the extents of poly(methyl methacrylate) grafted to wool after storing the catalyzed wool for different periods of time. It is apparent that the extent of grafting decreases as the storing time increases. This is the case when higher and lower concentrations of TCA, at constant Cu(acac)₂, were employed. However, though higher grafting was achieved with highly catalyzed wool, the reduction in the rate of wool activity, as shown by the decrease in the graft yields, is much faster than that of wool catalyzed with low concentrations of TCA. This may be explained as follows: It is well known that the life of an individual free radical is extremely short.¹⁴ Thus, the fact that wool treated with TCA-Cu(acac)₂ cocatalyst can initiate grafting even after storage of 4 hr cannot be due to individual free radicals surviving for such long periods. During storage, the termination of a particular free radical may be accompanied by creation of another

free radical, probably via a charge transfer. Thus, data on decay of free-radical activity shown here essentially represent the difference between the rates of termination and creation of free radicals under the experimental conditions used. It is likely that at high catalyst concentration, where initiation of free radicals on the wool backbone is great, the rate of termination is more pronounced than the rate of formation of new radicals, thereby reducing the activity of wool to grafting.

Tentative Mechanism

It has been disclosed that decomposition of TCA-Cu(acac)₂ leads to $\cdot\text{CCl}_3$ radicals.¹³ We have shown that this catalyst attacks wool and causes its deterioration. This is evidenced by the complete alkali solubility of wool treated with the said complex. Further, the catalyzed wool can initiate polymerization of a vinyl monomer even after 6 hr of storing. This means that wool does participate in a reaction system containing water, wool, cocatalyst, and monomer. Thus, initiation, propagation, and termination of the grafting reaction of a vinyl monomer with wool in the presence of TCA-Cu(acac)₂ complex as a cocatalyst may generally be represented as follows:



where B is the complex of TCA with Cu(acac)₂, WH is wool, and M is the vinyl monomer.

Equations (1) and (2) show the formation of the complex and its further decomposition to yield free radical via an electron transfer which is facilitated by the presence of Cu(II) in the vicinity of the CCl₃ group. The free radical, i.e., $\cdot\text{CCl}_3$, attacks wool molecule thereby giving rise to active site, i.e., free radical, on the latter, eq. (4). Initiation of a graft chain on wool occurs by addition of the wool free radical to the double bond of the first monomer molecule, eq. (5). Subsequent addition of monomer molecules to the initiated chain constitutes the propagation step, eq. (6). Termination may occur by combination where two growing chains terminate each other, eq. (7). Obviously, increasing the concentration of TCA at constant Cu(acac)₂ would favor eqs. (1) and (2). Moreover, another molecule of the complex may be formed via excess TCA and

$\text{Cu}(\text{acac})_2$ which is released in the reaction medium through the oxidation of $\text{Cu}(\text{I})$ to $\text{Cu}(\text{II})$, eq. (3). This would account for the significant increment in the grafting yield by increasing TCA concentration (cf. Fig. 1). This mechanism concurs with the kinetic studies on homopolymerization of MMA using the same catalyst.¹³

Grafting of Modified Wools

In the foregoing section, we have shown that grafting of wool with a vinyl monomer in the presence of TCA together with $\text{Cu}(\text{acac})_2$ proceeds via a free-radical mechanism. However, the sites of grafting were not actually elucidated. It is well known that wool contains various functional groups such as hydroxyl, amino, carboxyl, imino, and disulfide. These groups may react with $\cdot\text{CCl}_3$, thereby giving rise to free radicals which are capable of initiating grafting on the wool backbone. Thus, in an attempt to ascertain the role of each of the functional groups in grafting wool with a vinyl monomer using the said system, experiments were performed with modified samples of wool under the conditions of grafting described earlier.

Modification of the Disulfide Group. The effect of treatment of wool with KCN was found to bring about conversion of wool disulfide linkages to lanthionine. The treatment is also accompanied by some increase in the thiol content.^{15,16} Results of the graft yields obtained with wool treated with KCN for varying lengths of time (Table I) reveal that the time of KCN treatment does play a prominent role in the susceptibility of wool towards grafting. For instance, treating wool with KCN for 15 min produces a substrate which shows higher graft yields than untreated wool. Further increase in yield was achieved by prolonging the time of KCN treatment to 30 min, whereas treatment of wool for 60 min results in a modi-

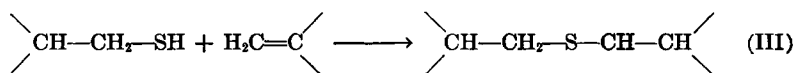
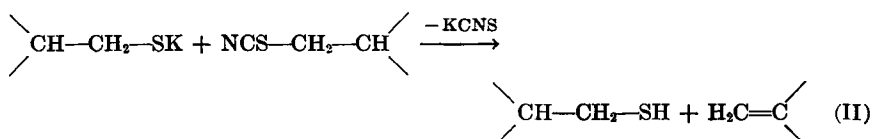
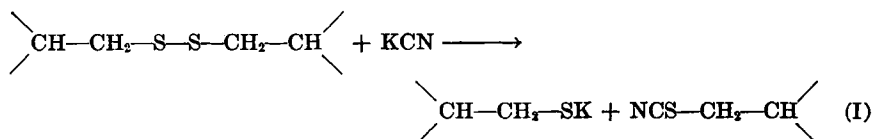
TABLE I
Grafting of MMA on Wool and Modified Wools*

Substrate	2 hr	Graft, % 4 hr	6 hr
Untreated wool	34.2	42.0	56.5
KCN-treated wool (for 15 min)	65.9	100.6	108.3
KCN-treated wool (for 30 min)	86.4	110.4	119.4
KCN-treated wool (for 60 min)	56.5	82.8	96.7
Reduced wool	126.5	140.7	147.4
Dinitrophenylated wool	1.5	2.0	2.8
Acetylated wool	5.0	7.0	8.0

* Catalyst, 25% TCA + 0.5% $\text{Cu}(\text{acac})_2$; impregnation time in the catalyst, 16 hr; temp. of impregnation, room temp.; pickup, 100%; monomer, 4% MMA; grafting temp., 60°C; material to liquor ratio, 1:50.

fied woollen material with lower response to grafting as compared to the other KCN-treated substrates. However, the graft yields obtained with the former are still higher than those of the untreated wool.

This observation suggests that treatment of wool with KCN may proceed as follows:



Thus, it is likely that eq. (2) is prevailing over (3) upon short treatment with KCN. As a result, a greater amount of graft is formed owing to the ease with which a hydrogen atom of the —SH group is abstracted by $\cdot\text{CCl}_3$. At longer treatment with KCN, on the other hand, (3) would predominate, thereby decreasing the graft yield due to absence of reactive sites. At any event, there is an increase in the thiol content of the modified wool over unmodified wool. Since the graft yield obtained with the former is much higher than that of the latter, the thiol groups might be presumed to play a predominant role in graft copolymerization. Indeed, wool treated with thioglycolic acid⁹ containing plenty of thiol groups shows graft yields which are significantly higher than those of the untreated wool.

Modification of Amino and Hydroxyl Groups. Dinitrophenylation and acetylation of wool are known to cause blocking of hydroxyl as well as amino groups of wool molecule. Thus, dinitrophenylated wool would be expected to give lower grafting than the untreated wool if either or both groups participate in the grafting reaction as sites for initiation. Indeed, the graft yields obtained with dinitrophenylated wool are so small that they can be neglected (Table I). This clearly implies that amino and hydroxyl groups in the wool molecules act as the main sites for grafting.

Effect of Grafting on the Felting Properties of Wool

One of the most outstanding drawbacks of wool is its tendency to felt. By grafting a synthetic polymer to wool molecules it may be possible to eliminate or at least to reduce this handicap. Table II shows the felting properties of wool after being grafted with MMA and AN to different levels. Obviously, there is a significant improvement in the antifelt properties at low levels of grafting, whereas at high levels the tendency of wool to felt is completely eliminated. At the same level of grafting,

TABLE II
Felt Properties of Wool Graft Copolymers*

Substrate	Graft, %	Felting improvement (% decrease in felting)
Untreated wool	—	zero
Wool-poly(methyl methacrylate) graft copolymer	5	35
	12	59
	25	70
	40	no ball
	60	no ball
	100	no ball
	150	no ball
Wool-polyacrylonitrile graft copolymer	4	30
	8	42
	10	50

* Felting of untreated wool is 0.13 g/cm².

AN produces the same improvement as MMA. The reduction in the tendency of wool to felt is due to the attached synthetic polymer, which perhaps leads to greater dimensional stability to wool. The fact that the antifelt properties increase by increasing the grafted polymer would support this, in agreement with previous reports.⁷

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