Graft Polymerization of Methyl Methacrylate onto Chemically Modified Wools Using LiBr–$K_2S_2O_8$ Redox System as Initiator

J. NIEZETTE, R. GEURTS, and R. ERILLI, *Laboratoire de Chimie Physique, Université de Liège, Sart Tilman, B 4000 Liege, Belgium*

Synopsis

Graft polymerizations of methyl methacrylate onto natural, reduced, S-carboxymethylated, S-aminoethylated, sulfated, acetylated, and oxidized wools were performed at 30°C using a LiBr–$K_2S_2O_8$ redox system as initiator. The extent of grafting was found to be dependent on the thiol and amino contents of wool fibers; carboxylic, sulfated groups, and oxidation intermediates had no significative influence on graft yields. The polymethacrylic chains obtained after hydrolysis of the natural part of the copolymer and analyzed by infrared and NMR spectroscopies were characterized by an atactic structure quite comparable to that found for a corresponding homopolymer. There was no stereoregulating effect on methyl methacrylate polymerization due to the crystalline components of the wool structure. A quantitative determination of the number of amino acid residues linked to the end of polymethacrylic chains after hydrolysis indicated that chain termination occurs both by disproportionation and recombination of macroradicals for natural, sulfated, S-carboxymethylated, and S-aminoethylated wools; for reduced and oxidized wools, only a recombination by disproportionation was observed in accordance with the open structure of these wool fibers. The chain lengths of the isolated poly(methyl methacrylates) were also found to be consistent with the participation of thiol and amino groups in grafting. It seems, however, that amino groups do not themselves act as initiating sites.

INTRODUCTION

Vinyl and related monomers were successfully grafted onto wool using redox systems as initiators.[1] Negishi and Arai[2–5] and Arai and co-workers[6–14] have extensively studied the grafting of natural, reduced, and some alkylated wools in the presence of a LiBr–$K_2S_2O_8$ redox system. They obtained significant percentages of grafted polymer at a moderate temperature without homopolymerization. From their results, the authors concluded that the sulfhydryl groups of cysteine residues act as the only sites of grafting.

The aim of the present work is to investigate the behavior of various modified wools grafted with methyl methacrylate in the conditions described by Arai et al. The extent of grafting and the characteristics of grafted chains are particularly examined and discussed in this article.

EXPERIMENTAL

Materials

Merino wool fibers were scoured and then washed with distilled water before drying.

Methyl methacrylate was washed with a 5% NaOH solution, then with distilled

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water, dried over anhydrous Na_2SO_4, and distilled under N_2 reduced pressure just before use.

All other materials were commercial grade and used without further purification.

Wool Modifications

Reduction

Wool keratin was reduced with tri-*n*-butylphosphine using the method of Sweetman and Mac Laren[15]: 5 g of natural wool was immersed in 500 ml of aqueous *n*-propanol (20% w/w). The reaction mixture was flushed with N_2; 1.25 ml of tri-*n*-butylphosphine was added, and the components were shaken gently at 20°C for 48 hr under N_2 pressure. The reduced wool was filtered, washed with 2 × 250 ml of a 50% ethanol solution, and immersed for 24 hr in a mixture of 250 ml of pH 8 buffer (0.4*M* borate) and 250 ml of *n*-propanol saturated with N_2. The fibers were filtered, washed with distilled water, and dried.

S-Carboxymethylation

The S-carboxymethylation of wool fibers was carried out by reaction of reduced wool with sodium iodoacetate: 5 g of reduced wool obtained in the way just described was treated with 500 ml of a 0.1*M* iodoacetate and 0.3*M* Na_2HPO_4 solution. The reaction was pursued for 6 hr at 25°C. The S-carboxymethylated wool fibers were washed with distilled water and dried at 45°C.

S-Aminoethylation

Wool keratin was S-aminoethylated with 2-bromoethylamine in the way described by Mac Laren and Sweetman[16]: 5 g of wool was immersed in a mixture of 250 ml of *n*-propanol, 250 ml of pH 8 buffer (0.4*M* borate), 50 mmol of bromoethylamine, and 6.25 ml of tri-*n*-butylphosphine; the reaction mixture was flushed with N_2 and shaken gently at 20°C for 3 days. The wool was then filtered, washed with distilled water, and again immersed in a pH 8 buffer at 20°C for 1 day. The S-aminoethylated wool was then washed with distilled water and dried.

Sulfation

The sulfation of wool fibers was carried out by the method of MacLaren and Kilpatrick[17]: 5 g of wool keratin was treated at 20°C with 85 ml of H_2SO_4(36)*N* containing 0.05% of cetyl trimethyl ammonium bromide. After 2 min, the wool fibers were rapidly immersed in 2 liter of cold water and washed with a vigorous water stream for 30 min. Then, the wool was equilibrated for 2 hr at 20°C with a pH 7 buffer (0.1*M* KH_2PO_4 and 1*M* KCl). The wool fibers were then washed for 2 hr in different baths of cold water and dried at 45°C.

Acetylation

The acetylation of natural wool was carried out in two ways: (a) Five grams of wool fibers were treated with 250 ml of acetic anhydride for 30 min at 138°C. The acetylated wool was washed with distilled water and dried. (b) Five grams of wool fibers were immersed in 250 ml of a 0.2*M* acetic anhydride solution in dimethylformamide. The mixture was heated at 60°C for 6 hr. The acetylated wool was washed with distilled water and dried.

Oxidation

Five grams of wool fibers were oxidized by 500 ml of a 3% H_2O_2 solution in H_2O–dioxane (80/20 w/w) for 3 hr at 70°C. The wool was washed with distilled water and dried.

Thiol and ($\alpha + \epsilon$) Amino Content

The thiol content of untreated and modified wools was determined by the colorimetric method of Meichelbeck, Hack, and Sentler[18] using 55′-dithiobis-2-nitrobenzoic acid. This method is not suitable for sulfated wool fibers.

The ($\alpha + \epsilon$) amino content was obtained by the ninhydrin method.[19]

Polymerization Conditions

The polymerizations were carried out using the procedure reported by Negishi and Arai[2,3]: a reaction mixture containing wool fibers (1%), methyl methacrylate (5%), LiBr (27.5%), $K_2S_2O_8$ (0.2%), diethylene glycol monobutyl ether (22.5%), and water (43.8%) was maintained at 30°C for time periods of 0.25 to 5 hr. At the end of the reaction time, the grafted fibers were removed, washed with water, and dried. For reduced wools, some polymerizations were made under N_2 pressure to prevent the oxidation of thiol groups by atmospheric O_2. The absence of homopolymerization was confirmed by Soxhlet extraction of grafted wool with acetone.

Isolation of Grafted Polymethacrylic Chains

The two-step HCl digestion method proposed by Negishi, Arai, and Okada[4] was used for the separation of the grafted polymethacrylic chains from the original wool. The grafted wool (0.5 g of the wool portion) was digested with 35 ml of a 6*N* HCl solution for 30 min at 100°C. The residue was filtered and washed with the HCl solution. The digestion was again allowed to proceed for 24 hr at 100°C in sealed tubes. Then, the residue was washed with boiling water and dried. The separated polymer was purified by successive precipitations with methanol from benzene (one time) and acetone (three times) solutions.

Infrared and Nuclear Magnetic Resonance Spectra

The infrared spectra of the separated residues were measured with a Perkin–Elmer model 21 infrared spectrophotometer using KBr pellets (500 mg) containing 6 mg of powdered residue.

The NMR spectra of isolated polymethacrylic chains were determined at 120°C on a 100 MHz Varian NMR spectrophotometer from a 10% solution in *o*-dichlorobenzene. The microtacticity of polymethacrylates was calculated from the area of the peaks in the α methyl group resonance with τ values 8.67, 8.81, and 8.92, corresponding to the percentages of isotactic, heterotactic, and syndiotactic triads, respectively.

Average Molecular Weights

The molecular weight distribution and the different average molecular weights were obtained by gel permeation chromatography using a Waters model 200 chromatograph equipped with standard Styragel columns.

Dinitrophenylation of Separated Polymethacrylic Chains

The dinitrophenylation of the amino acid residues linked to the end of separated polymethacrylic chains was performed by the Whalley's method[20]: 6 ml of a 5% poly(methyl methacrylate) solution in benzene were treated with 0.3 g of fluorodinitrobenzene and a few drops of triethylamine for 24 hr at 30°C. The polymer was precipitated by an excess volume of diethyl ether, carefully washed, and dried. It was again dissolved in ethyl acetate and precipitated with methanol. The purification with ethyl acetate–methanol pair was repeated three times at least.

RESULTS AND DISCUSSION

As mentioned before, the initiating effect of the LiBr–$K_2S_2O_8$ redox system was largely discussed by Arai et al., who concluded that the grafting is closely related to the presence of thiol groups in wool fibers. Therefore, we have chosen to modify the natural wool in such a way that cysteine residues are concerned. So, thiol concentration was raised by reduction of cystine bonds and decreased by sulfation and oxidation. In the last two processes, the modification is evidently not limited to thiol groups alone: serine, threonine, and tyrosine residues are affected by sulfation; cystine and other groups are also oxidized; sulfated functions, cysteic acid, intermediate oxides, and acids are introduced during sulfation and oxidation. Moreover, the thiol groups obtained after reduction were blocked by carboxymethylation and aminoethylation. These reactions are much more specific than sulfation and oxidation. They lead also to the incorporation of new acid and basic functions in wool. Finally, in order to specify the results obtained with S-aminoethylated wools, we have decreased the amino content of wool by acetylation with acetic anhydride: N-acetyl groups and also O-acetyl groups are thus fixed on lysine, arginine, histidine, serine, threonine, and tyrosine residues. In the most severe experimental conditions (acetic anhydride at 138°C), a part of the cysteine residues is also blocked by this reagent.

Extent of Grafting

Natural and modified wools were subjected to grafting in the way described in the Experimental Section. The percentages of graft-on so obtained for reaction times as long as 5 hr are given in Figure 1. They were expressed as the weight percent increase based on the original dry weight of the wool. Some of these results can be directly compared with those obtained by Arai, et al.,[4,10] especially in the case of natural, reduced, and S-carboxymethylated wools.

Figure 1 reveals typical behavior already described by many authors: the grafting yields increase with time but the polymerization rate tends to decrease as the reaction proceeds. The decrease of grafting rates can be explained by the lowering of monomer concentration and of the number of initiating sites, as well as by a more difficult penetration of monomer inside the wool fibers.

It is important to note that, in all cases, any homopolymerization does not take place in reaction mixtures as previously found by Negishi and Arai.[2] One can also observe that a saturation effect seems to be manifest for reduced wool fibers. This effect is also probable for other wools but it must be dependent on the swelling degree of the fiber structure.

An induction period can be seen in the first stages of the reaction for natural wool, but this effect is not so evident for modified wools. Indeed, the inhibition period tends to shorten or disappear for many modified wool fibers. Similar results were observed by Negishi, Arai, and Okada[4]. These authors have noticed that, during the inhibition period, a part of the cysteine residues is oxidized into cystine by the action of redox initiating system and also by the free oxygen present in the reaction mixture. The inhibition period could correspond to the consumption of dissolved oxygen in processes which should be all the more rapid as the thiol content is high and as the wool structure is open.

The most interesting feature in Figure 1 is the large differences in graft yields observed in respect of the nature of wool fibers: so, acetylated wools exhibit a very poor tendency to grafting; S-carboxymethylated, sulfated, and oxidized

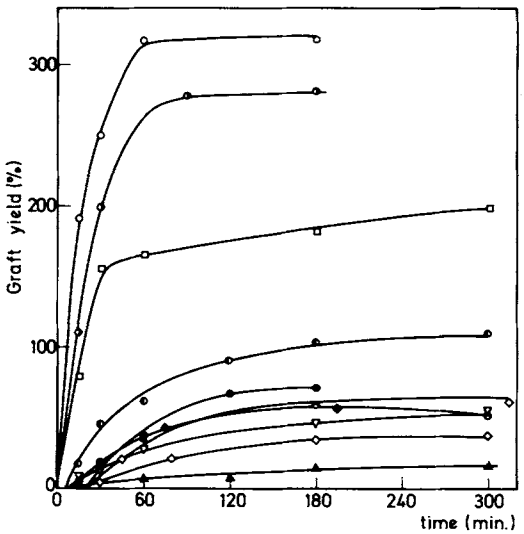

Fig. 1. Graft yield % as function of reaction time for natural (●), reduced ($[-SH]_o$ = 83 (◐), 360 (◑), and 630 (○) μmol/g wool), S-carboxymethylated (⊖), S-aminoethylated (□), sulfated (♦), acetylated [138°C (▲), 60°C-DMF (◇)], oxidized (▽) wools.

wools show degrees of grafting slightly lower than those found for natural wools. In contrast, S-aminoethylated and reduced wools are much more easily grafted than natural wool.

In order to compare these observations with the assumption of a preponderant participation of thiol groups in grafting, we have determined the initial rates of graft-on which are collected in Table I. These values are plotted against the square root of thiol content as shown in Figure 2. It is easy to derive a linear relationship between the two parameters by considering a classical kinetic scheme for radical polymerization with an initiation step only dependent on thiol content.[4] This linear relationship can be observed for natural, reduced, oxidized, and S-carboxymethylated wools; the extrapolation of the concentration axis corresponds to 3.2 μmol/g of unreactive thiol groups, a value close to that found by Negishi, Arai, and Okada.[4]

However, large divergences must be noted for S-aminoethylated and acetylated

TABLE I
Initial Rates of Grafting for Natural and Modified Wools

Wool	$[-SH]_o$ μmol/g wool	$[-(\alpha + \epsilon)NH_2]_o$ μmol/g wool	$(dG/dt)_o$ %/hr
Natural	23	217	85
Reduced	83		155
	360	217	420
	630		600
S-carboxymethylated	13	217	55
S-aminoethylated	46	450	295
Sulfated	<23	—	60
Acetylated			
(138°C)	—	55	8
(60°C, DMF)	23	73	25
Oxidized	7	—	40

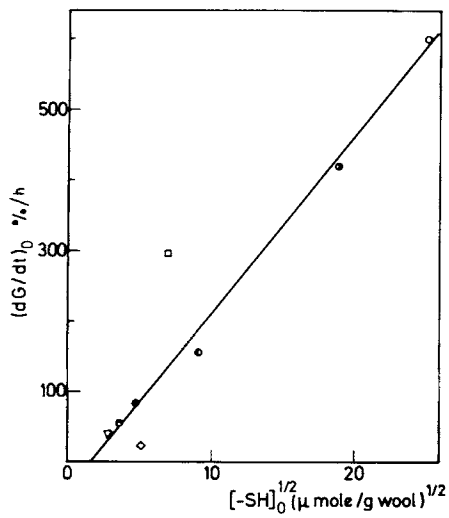

Fig. 2. Initial rates of grafting as function of $[-SH]_o^{1/2}$ for natural (●), reduced (◐), (◑), (○), S-carboxymethylated (◓), S-aminoethylated (□), acetylated [60°C-DMF (◇)], oxidized (▽) wools.

wools. A high content in amino groups is characterized by a high rate of grafting while a low content tends to largely reduce the graft yields.

We can deduce from Figures 1 and 2 that thiol groups undoubtedly play a prominent part in grafting compared to carboxylic, sulfated groups and oxidation intermediates. The increase in swelling and accessibility of wool fibers due to the scissions of cystine bonds during oxidation or reduction seems of little importance. On the contrary, evidence is given for the important contribution of amino groups in grafting. All these effects will be specified later.

Structure of Grafted Poly(methyl Methacrylate)

The grafted wool fibers were hydrolyzed by the two-step digestion method described in the Experimental Section until the major part of the natural structure was destroyed. A residue of short white fibers was then obtained which was easily dissolved in benzene. After several purifications, the residue was analyzed by infrared and NMR spectroscopies.

The infrared spectra exhibit all the bands of an atactic poly(methyl methacrylate) without any other characteristic absorption. The peaks corresponding to the keratin structure are missing which is a confirmation of the important degradation of the natural part of the graft copolymer. The infrared spectra do not reveal the presence of isotactic sequences as postulated in some cases by Negishi et al.[5] This result is verified by the analysis of NMR spectra which give better information about the presence of stereoregular sequences in poly(methyl methacrylate), the resonance of the proton of the methyl group being currently used for the quantitative determination of short stereoregular configurations. So, the percentages of isotactic, heterotactic, and syndiotactic triads determined for several polymethylacrylic chains separated from natural and reduced grafted wools are, respectively, 6–10% (iso), 27–32% (hetero), and 59–62% (syndio). These values are homogeneous and independent of the nature of the wool fibers and of the extent of grafting. They are also very close to those found for a standard homopolymer (8–30–62%). This behavior indicates that, at least under our experimental conditions, there is no stereoregulating effect on methyl methacrylate polymerization due to the crystalline components of the wool structure.

Chain Dimensions of Grafted Poly(methyl Methacrylate)

The polymethacrylic chains resulting from the hydrolysis of the graft copolymer were characterized by their average molecular weights determined by gel permeation chromatography.

The discussion of these values as a function of the nature of wool fibers and of the extent of grafting has also required an investigation into the mechanism of chain termination which was done by the DNP method using the procedure of Arai, Komine, and Negishi.[6] This method consists of an end group analysis of [DNP–poly(methyl methacrylates)] obtained by the action of fluorodinitrobenzene onto the polymethacrylic chains separated from the grafted wool. The number of dinitrophenylated end groups Z is then calculated from the UV absorption spectra of yellow DNP–PMMA solutions in ethyl acetate using the following expression:

$$Z = \frac{A_{10} \cdot \overline{M}_{n(\text{DNP-PMMA})}}{10 \cdot \epsilon \cdot d}$$

where A_{10} is the optical density at 340 nm for a 1% w/v DNP–PMMA solution, $\epsilon = 1.0 \times 10^4$ mol/liter/cm is the molar extinction coefficient, $\overline{M}_{n(\text{DNP-PMMA})}$ is the number average molecular weight of dinitrophenylated poly(methyl methacrylate), and d is the thickness of the solution.

For ease in the discussion, the results of the end group analysis are reported first. They are collected in Table II.

The number of DNP end groups per polymer chain found for natural, sulfated, S-carboxymethylated, and S-aminoethylated wools are between 1.4 and 1.8; this implies that the termination of these wools occurs both by recombination and disproportionation of macroradicals since Arai et al.[6] have demonstrated that any more than one DNP end group cannot be linked to each end of a polymer chain in the case of LiBr–$K_2S_2O_8$ initiation. Some Z values in Table II are close to unity and are then characteristic of a termination by disproportionation; they are those found for polymer chains resulting from grafting onto reduced and oxidized wools. These low values confirm the assumption of Arai et al.[6] that an open wool structure is favorable to termination by disproportionation.

As previously reported, the average molecular weights were determined by gel permeation chromatography. All the observed chromatograms are characterized by unimodal distributions. The polydispersities are in the range of 2–4 ($\overline{M}_w/\overline{M}_n$) and vary very slowly with polymerization time. The lowest values are found for oxidized and highly reduced wools, and may be due to the open structure of these fibers leading to more homogeneous polymerization conditions.

Figure 3 shows plots of the number average molecular weight against reaction time for polymethacrylic chains separated from grafted wools. We can see that the polymer resulting from grafting onto natural, oxidized, S-carboxymethylated, and sulfated wools has a $\overline{M}_n$ value located near 2×10^5. A higher molecular weight is found for S-aminoethylated wool, and lower values are observed for reduced and acetylated wools. The low molecular weight corresponding to reduced wools is evidently consistent with the hypothesis of a participation of thiol groups in the initiation process: a high extent of grafting but also a low chain length are expected in this case. For the other wools, it is difficult to discuss the $\overline{M}_n$ values without considering the mechanism of termination. In a classical reaction

TABLE II

Number of DNP End Groups Z/Polymer Chain, Extrapolated Number Average Molecular Weights $(\overline{M}_n)_o$[a], Initial Rates of Site Formation for Natural and Modified Wools

Wool	Z	$(\overline{M}_n)_o \times 10^{-5}$	$(ds/dt)_o$ μmol wool^{-1} hr^{-1}
Natural	1.65	1.82	5.7
Reduced[b]			
(83)	0.97	0.90	18.5
(360)	0.99	0.46	100
(630)	1.00	0.37	176
S-carboxymethylated	1.43	1.98	3.5
S-aminoethylated	1.71	2.72	25
Sulfated	1.40	1.70	—
Oxidized	0.98	1.90	1.8

[a] Value extrapolated for $G = 0$.

[b] Thiol content.

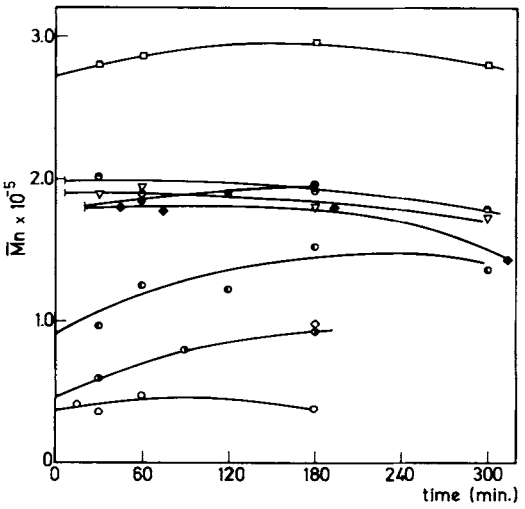

Fig. 3. Number average molecular weights against reaction times for natural (●), reduced ($[-SH]_o$ = 83 (◐), 360 (◑), 630 (○) μmol/g wool), S-carboxymethylated (◓), S-aminoethylated (□), sulfated (♦), acetylated [60°C-DMF (◇)], oxidized (▽) wools.

scheme with an initiation step only dependent on thiol content, the kinetic chain length $\overline{DP}/Z$ can be expressed by

$$\overline{DP}/Z = (dG/dt)/k_i[-SH]$$

where $\overline{DP}$ is the average degree of polymerization.

The preceding expression is illustrated in Figure 4. All the values are found in the initial stage of the reaction. The interpretation of this figure is hazardous on account of the scatter of experimental plots. The most important divergence with the previous expression is, however, observed for the S-aminoethylated wool (>50%), which might again indicate that the initiation is not exclusively controlled by the thiol content but also by the amino concentration.

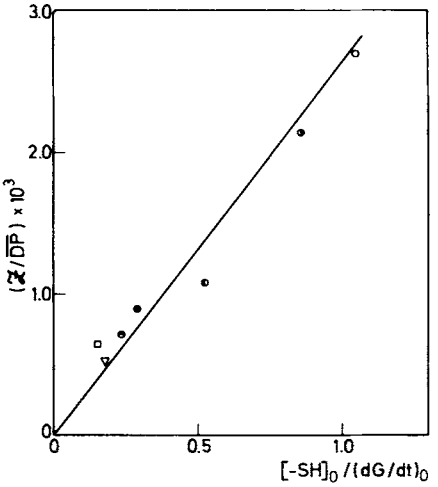

Fig. 4. Reciprocal of chain length $(Z/\overline{DP})_o$ against $[-SH]_o/(dG/dt)_o$ for natural (●), reduced (◐), (◑), (○), S-carboxymethylated (◓), S-aminoethylated (□), oxidized (▽) wools.

Number of Grafting Sites

The number of grafting sites s per gram of wool fibers was calculated from the graft yield G, the number average molecular weight $\overline{M}n$ of isolated poly(methyl methacrylate), and the number of DNP end-groups Z using the expression

$$s = \frac{Z \cdot G \cdot 10^4}{\overline{M}_n} \text{ (}\mu\text{mol/g wool)}$$

The evolution of the number of grafting sites with time is reported in Figure 5. To some extent, the curves exhibit a shape comparable to those found for graft yields on account of the slight variation of molecular weight with time. For all wool fibers, the rate of sites formation tends to be reduced as the reaction proceeds and, in some cases, a maximum value is reached after 2 or 3 hr.

The number of grafting sites is always much lower than the potential reactive centers, –SH or others, present in the ungrafted wools. It is evident that a great part of the active groups disappears in oxidative processes; furthermore, some of them can be considered as unreactive because they are naturally inaccessible or they are isolated by the polymer deposition. It is also important to note that Arai et al.[12,13] have assumed that the grafting centers are not found in all the components of the wool structure but they originate mainly from the crystalline microfibrils.

Most of the values obtained for the number of grafting sites support the idea of the participation of thiol groups in the initiation process. This is clearly indicated in Figure 6, where the initial rates of sites formation are plotted against thiol contents. Except for S-aminoethylated wools, experimental data fit well with a linear relationship. The behavior of S-aminoethylated wools is also a new confirmation for the contribution of amino groups to the chain initiation, but we can suppose that amino groups do not act themselves as initiating sites because an extrapolated value close to zero is obtained with other wools in spite of their high amino content.

In conclusion, the results obtained for the extent of grafting and for the chain length of the separated poly(methyl methacrylate) evidently show that thiol groups of cysteine residues are the effective sites of grafting, as postulated earlier

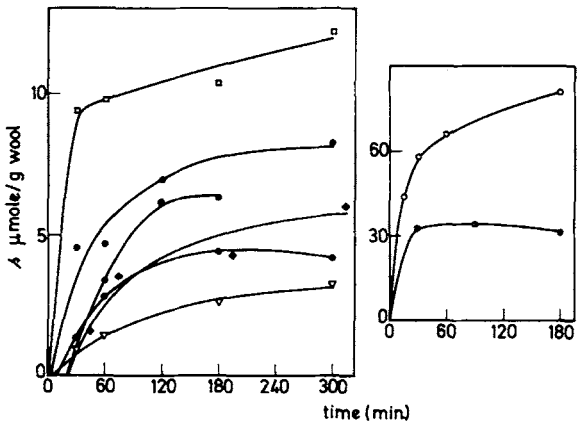

Fig. 5. Number of initiating sites as function of reaction time for natural (●), reduced ([–SH]$_o$ = 83 (◐), 360 (◑), 630 (○) μmol/g wool), S-carboxymethylated (⊖), S-aminoethylated (□), sulfated (◆), oxidized (▽) wools.

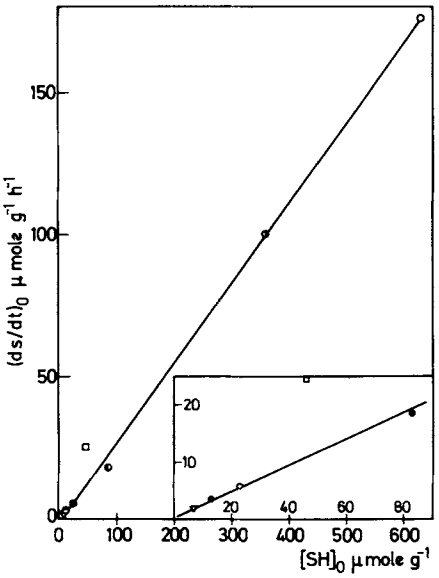

Fig. 6. Initial rates of sites formation as function of thiol content for natural (●), reduced (◐), (◑), (○), S-carboxymethylated (◓), S-aminoethylated (□), oxidized (▽) wools.

by Arai et al. Moreover, it appears that amino groups play a part in the polymerization process and more especially in the initiation step. It does not seem, however, that amino groups are also centers of grafting. We think that they could interfere with anions or acids formed in redox reactions during initiation and thereby regulate the concentration of reactive species inside the wool fibers.

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