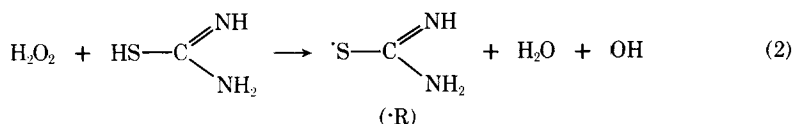
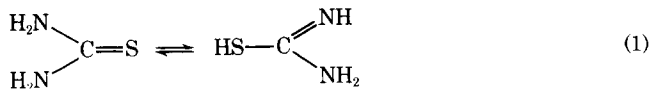


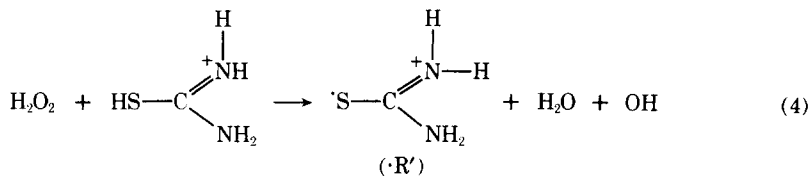
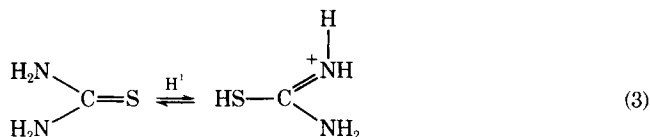
Thiourea-Induced Graft Polymerization of Methyl Methacrylate onto Wool in Aqueous Acidic Medium

Thiourea in combination with hydrogen peroxide,¹ tertiary butyl peroxide,² or ferric salts³ has been disclosed to be an efficient initiator for grafting wool with methyl methacrylate (MMA). The mechanism suggested for generation of radicals in the polymerization system in the absence and presence of acid may be suggested as follows:

In the absence of acid:



In the presence of acid:



Radicals ·R and/or ·R' abstract hydrogen from thiol, aminohydroxyl groups and other reactive groups in wool (WH) to yield wool radical (W·):



This is followed by addition of vinyl monomer to wool radical in a chain process.

A similar mechanism could possibly be suggested for systems with ferric salts or other oxidizing agents in conjunction with thiourea.

In the present work, we have found that thiourea alone is able to initiate graft polymerization onto wool. Merino wool fibers were purified by extraction with acetone in a Soxhlet apparatus for 24 hr, followed by washing with distilled water and drying at ambient conditions. MMA was purified before use.³ The graft polymerization reaction was carried out as follows: A 25-ml portion of acidified thiourea solution together with MMA was taken in a 100-ml glass-stoppered Erlenmeyer flask. To this, wool was added and the content of the flask was shaken well. Details of the polymerization conditions are given along with the results. After the desired grafting time, the sample was removed, washed thoroughly with water, and repeatedly Soxhlet extracted with benzene to constant weight.

The per cent grafting was based on bone-dry weight of wool. The per cent conversion of monomer to homopolymer during grafting was based on the weight of monomer used.

The dependence of grafting on the thiourea concentration is shown in Figure 1. As is evident, the graft yield increases significantly by increasing thiourea concentration within the range studied. The same situation is encountered with respect to reaction time (Fig. 2) though an induction period

TABLE I
Effect of Kind of Acids

Acid concentration, mmole/l.	Graft yield, %			
	HCl	H ₂ SO ₄	Oxalic acid	Acetic acid
10	272	272	—	211
30	285	254	168	220
50	283	258	228	237
70	287	251	231	268
100	288	258	246	268

of 5 min is observed. The kind and amount of acid also affect the magnitude of grafting (Table I), similar to previous work using different initiating systems.⁴⁻⁶

Thiourea alone is incapable of initiating either polymerization of vinyl monomers⁷ or their grafting onto nylon 6.⁸ On the other hand, thiourea acts as a transfer agent in vinyl polymerization⁹ and forms efficient initiating redox systems with different oxidants for vinyl polymerization⁷ and grafting.⁸

Results of the current work are rather interesting. Thiourea alone initiates grafting of MMA onto wool, and the efficiency of grafting is very high since little homopolymer is formed (Fig. 1). It appears that thiourea behaves as an accelerator in an aqueous system containing wool, MMA, and acid. It reduces wool to bring about modified fibers containing groups with weak bonds, e.g., S—H. Abstraction of hydrogen from such groups, for example, by oxidation with occluded oxygen, is relatively easier and leads to wool radicals capable of initiating grafting. It also seems that fibers modified

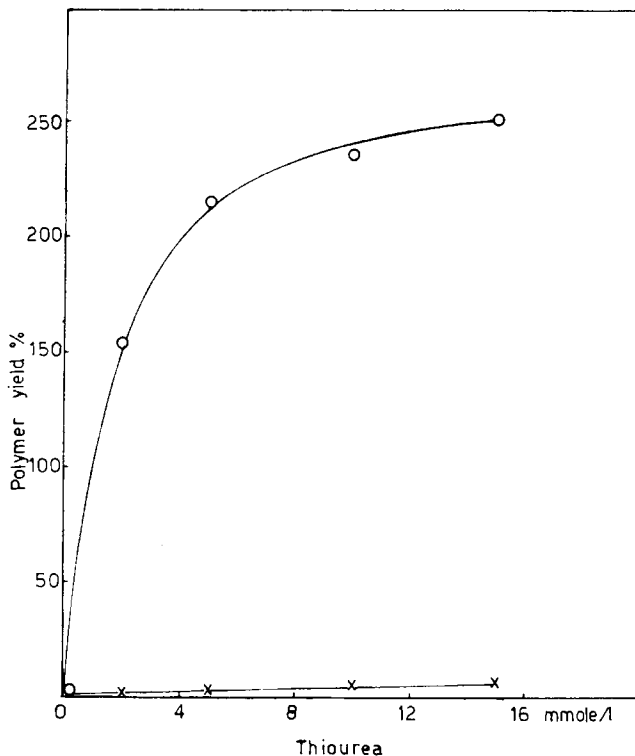


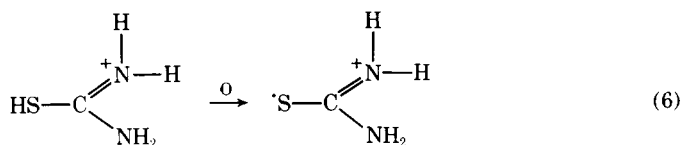
Fig. 1. Effect of thiourea concentration on polymer yield: (O) graft yield per cent; (X) homopolymer per cent; MMA, 8%; H₂SO₄, 30 mmole/l.; time, 2 hr; temperature, 70°C; M/L ratio, 1:50.

under the influence of thiourea have great ability to form complex with MMA. Such complexation has been reported to enhance monomer reactivity¹ and gives rise to higher grafting.

It is rather possible that anisotropic swelling of wool accounts for radical formation involving thiourea. Polymerization initiated by anisotropic swelling and eventual scission of chemical bonds in the wool would be expected to proceed quite fast, particularly at the temperature used, i.e., 70°C. The properties of thiourea as swelling agent might enhance this effect. The induction period noted (cf. Fig. 2) could be due to the time required for complete diffusion of aqueous thiourea and monomer into the wool fibers before initiation occurs. Strong acid should also favor swelling of wool.

Obviously, there is little reason to believe that one of the aforementioned possibilities is operating to the exclusion of the other. Hence, it may probably be correct to say that the high graft yield obtained with thiourea-wool-acid-MMA-water systems could be associated with (a) the presence of —S—H groups in the wool molecule which facilitate radical formation via hydrogen abstraction; (b) increased monomer reactivity via easier complex formation with thiourea-reduced wool; and (c) a combination of anisotropic swelling and thiourea-unique redox properties.

It may be argued that grafting is initiated by free radicals generated as a result of oxidation of isothiurea with occluded oxygen!



However, this is rather improbable since the argument is in full contrast with previous reports.^{7,8} Furthermore, inclusion of oxidant such as potassium bromate in the polymerization system, instead of enhancing grafting, causes an outstanding reduction in the graft yield, depending upon the oxidant concentration (cf. Fig. 3). A tremendous amount of homopolymer was also observed. Here, thiourea

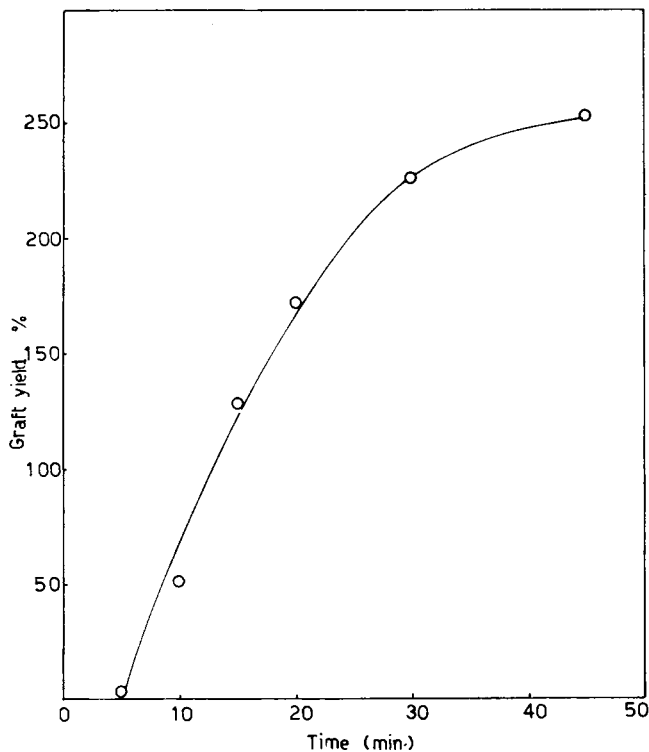


Fig. 2. Effect of reaction time on graft yield: MMA, 8%; H₂SO₄, 30 mmol/l.; temperature, 70°C; M/L ratio, 1:50.

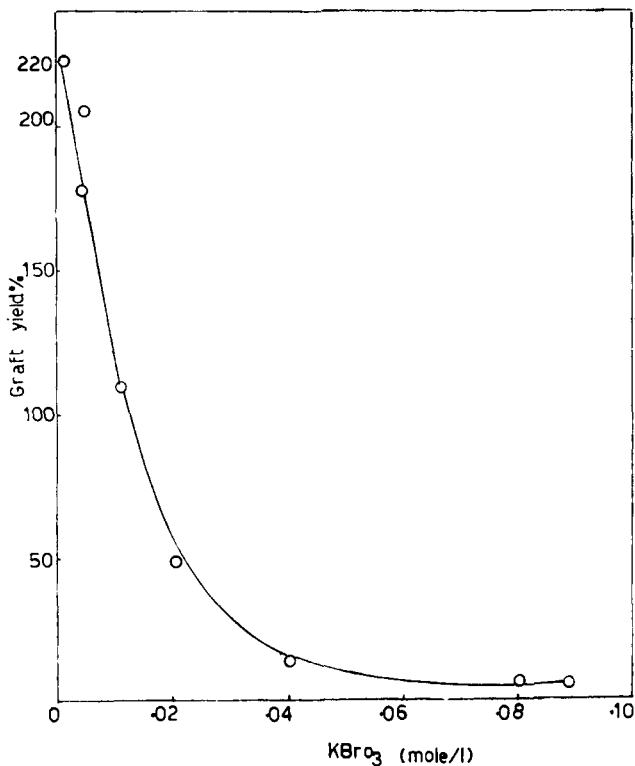


Fig. 3. Graft yield as a function of potassium bromate concentration: MMA, 8%; H₂SO₄, 30 mmole/l.; time, 2 hr; temperature, 70°C; M/L ratio, 1:50.

is involved with the oxidant BrO₃⁻ in a redox system; thus, its reducing action on wool is presumably negligible. That is, in the presence of the oxidant, a radical similar to that shown in eq. (6) is generated and is essentially responsible for initiation of grafting and homopolymerization.

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Received March 18, 1976
Revised April 28, 1976