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$KBrO_3$-INITIATED GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE ONTO WOOL FIBER

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ABSTRACT

Since the graft copolymerization of vinyl monomers onto a wool backbone improves the properties of wool fibers, the present study reports the graft copolymerization of methyl methacrylate (MMA) onto a wool backbone using potassium bromate in aqueous sulfuric acid at 50°C. It is known that metal ions have the power to change the environment of a protein molecule, so the effect of Fe^{2+} and Co^{2+} ions on the graft copolymerization of MMA was also studied. The effects of monomer, $KBrO_3$, pH, wool, and temperature on graft copolymerization were also studied. Evidence for grafting and site of grafting are also discussed.

INTRODUCTION

Graft copolymerization of vinyl monomers onto a wool backbone is recognized as a promising method to improve the properties of keratin fibers and to impart some new characteristics to the natural product. Various initiation techniques have been tried with varying degrees of success, including initiation by chemical and radiation methods [1]. Among chemical methods, redox-initiated grafting is advantageous because, in the presence of redox systems, grafting can be carried out under mild conditions, and side reactions are at a minimum. Although redox couples involving potassium bromate have been shown to be very promising as polymerization initiators [2, 3], they have not often been used in graft copolymerization reactions [1, 4, 5]. This paper presents a study of graft copolymerization of methyl methacrylate (MMA) onto a wool backbone by using potassium bromate in aqueous sulfuric acid at 50°C.

Proteins have been found to be closely associated with metal cations in biological systems, and the natures of the metal-protein complexes vary with the nature of the metal. The presence of many reactive side chains in the protein molecules helps in binding most metals very firmly. This metal binding is known to affect the physical and biological properties of the proteins. In the case of wool, the sites involved in metal binding may be the —OH, $—NH_2$, —COOH, or —SH groups. It was reported [6] that ferrous sulfate gives bonds with wool fiber which are very stable to the refluxing action of boiling N/10 HCl and the treatment of H_2S-H_2O solution for a longer period. Since metal ions have the power of changing the environment of a protein molecule, the effect of Fe^{2+} and Co^{2+} ions on the graft copolymerization of MMA onto wool fiber using $KBrO_3$ was also studied, and the results are reported here.

EXPERIMENTAL

Preparation, purification, and characterization of graft copolymer samples were described in an earlier paper [1].

RESULTS AND DISCUSSION

Systems Studied

1. $KBrO_3$-MMA-wool
2. $KBrO_3$-Fe^{2+}-MMA-wool
3. $KBrO_3$-Co^{2+}-MMA-wool

Effect of Reaction Time

An increase in the reaction time increased the amount of graft formed during the initial period, tending toward constancy around 240 minutes. The levelling-off may be attributed to the fact that at higher conversions the concentrations of the reactants (monomer, initiator) and the number of available reactive sites on the wool backbone will be reduced. Therefore, the grafting time was fixed at 240 minutes for the three systems studied (Fig. 1).

Rate of Homopolymerization, R_h

Under the experimental conditions employed in this study, the rate of homopolymerization was always found to be much less than that of graft copolymerization, R_g. The R_h value was less than 10% of R_g for the grafting system involving $KBrO_3$ alone. The presence of metal ions reduced this value further. In the case of Systems 2 and 3, the R_h values were 4.8% and 1%, respectively. Further, the kinetic chain-lengths were also too low for the homopolymers (e.g., $\overline{X}_n = 413$ in System 3).

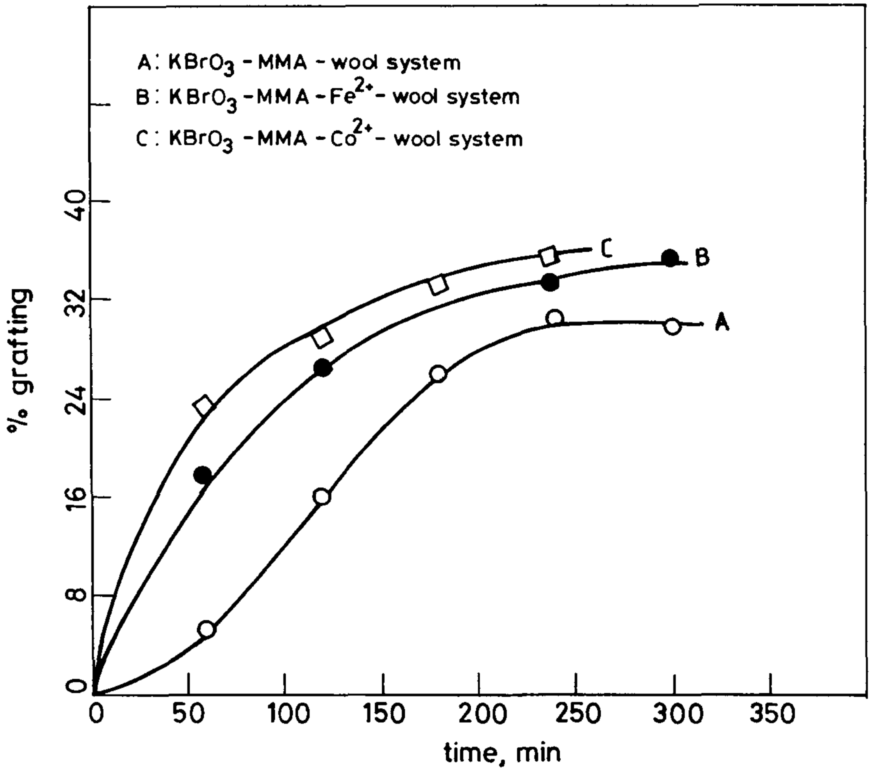

FIG. 1. Percentage grafting vs time.

Rate of Graft Copolymerization, R_g

Effect of Monomer

As expected, the grafting rate increased with an increase in the monomer concentration. The order with monomer on R_g was 1.5 for System 1 and 1 for both Systems 2 and 3 (Fig. 2). The higher monomer exponent in System 1 may be due to the complex nature of the initiation reactions involving monomer molecules as participating reactants used to generate initiating free-radicals [7]. Further evidence for this came from chain-length measurements. The order of MMA on chain length was 0.5 in System 1 and 1 in the other two systems (Fig. 3). The pattern of the plots of grafting efficiency vs [MMA] showed that System 1 behaved differently from the other two systems. The increase in efficiency with an increase in [MMA] in System 1 suggested the additional involvement of monomer apart from $KBrO_3$ and wool in the initiation reaction (Fig. 4).

The Effect of $KBrO_3$

In all three systems an increase in the concentration of $KBrO_3$ increased the rate. This is understandable because the radical center formed on the wool fiber is enhanced when the concentration of the oxidant is enhanced, and hence the reaction

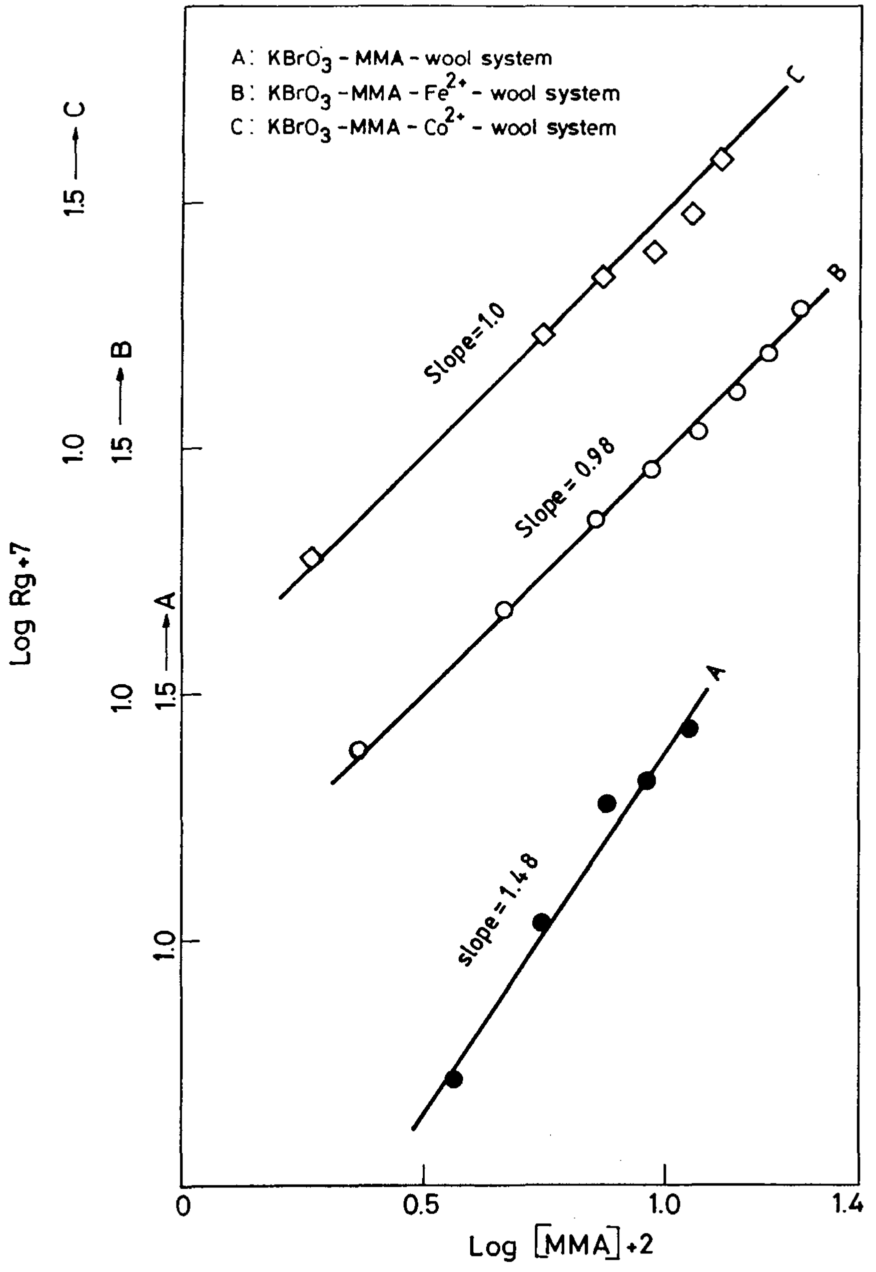

FIG. 2. Monomer variation. Log R_g vs log [MMA].

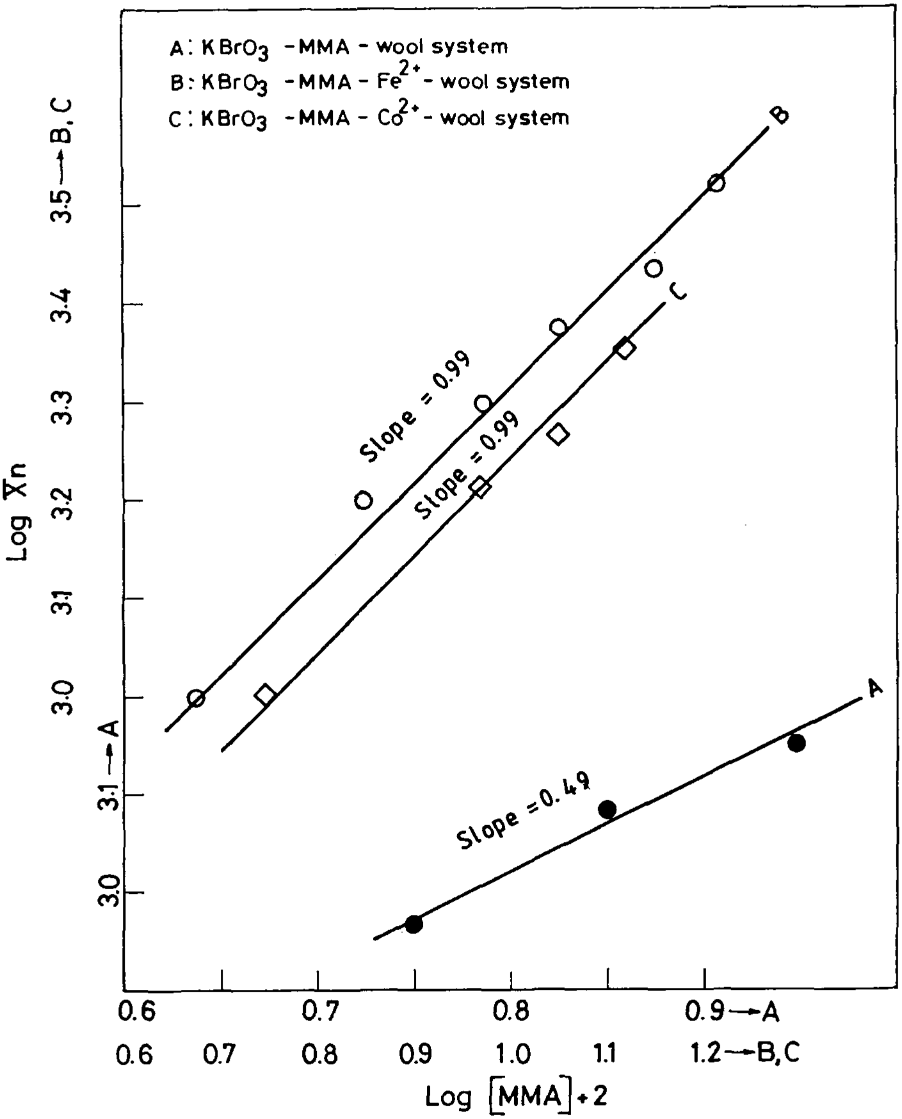

FIG. 3. Chain-length dependence. Log $\overline{X}_n$ vs log [MMA].

rate is increased. The half-order dependence of the rate on $KBrO_3$ concentration in all three systems (Fig. 5) pointed to mutual termination of the macroradicals. The inverse half-order dependence on $\overline{X}_n$ values further supported mutual termination (Fig. 6).

Effect of Metal Ions

An overall enhancement of R_g was observed in the presence of both metal ions [8, 9], and the bromate-Fe^{2+} ion couple gave the highest rate among the three systems studied. This may be due to:

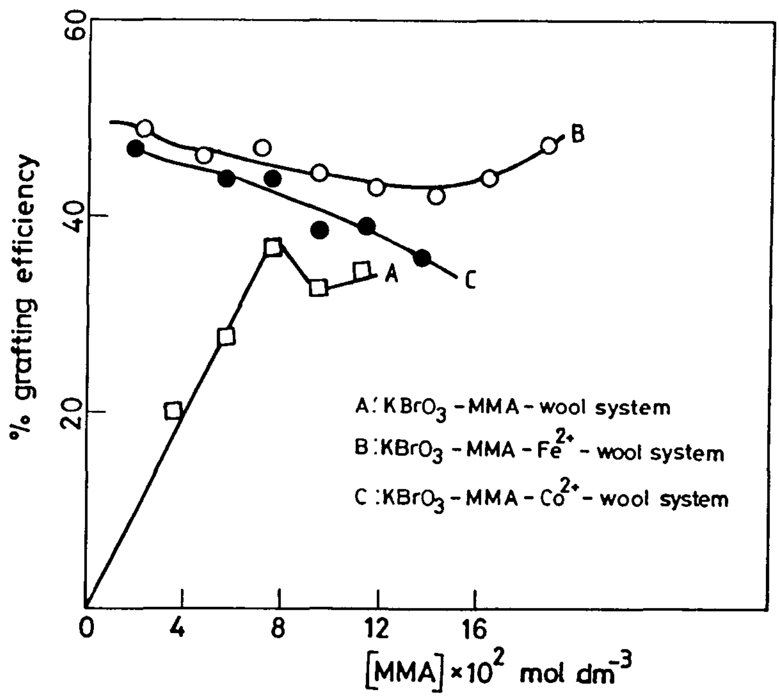

FIG. 4. Percentage grafting efficiency vs [MMA].

1. The capacity of the metal ion to facilitate the transfer of an electron from the "activator" to the "catalyst" in the redox pair system [10].
2. The involvement of the metal ion in the formation of a three center metal-MMA-wool complex or in the formation of metal-MMA and metal-wool adducts, possibly influencing the propagation step. This seems to find support from the interesting observation from chain-length measurements that higher molecular weight grafts were always obtained at higher Fe^{2+} concentrations.

In the case of the KBrO$_3$-Co^{2+} couple, however, the R_g increased only marginally and remained unaffected for an increase in the concentration of Co^{2+}, coupled with a decrease in chain length. It may be assumed that a part of Co^{2+} was involved in the radical production step.

These observations on the role of Fe^{2+} and Co^{2+} gain strength from a study of the plot of grafting efficiency as a function of metal ion concentrations (Fig. 7). While in the case of Co^{2+} there is an initial rise followed by constant grafting efficiency, Fe^{2+} registers a steady increase with an increase in Fe^{2+} concentration. This supports the contention that Fe^{2+} makes more and more monomer available during the propagation step, which is not the case with Co^{2+}.

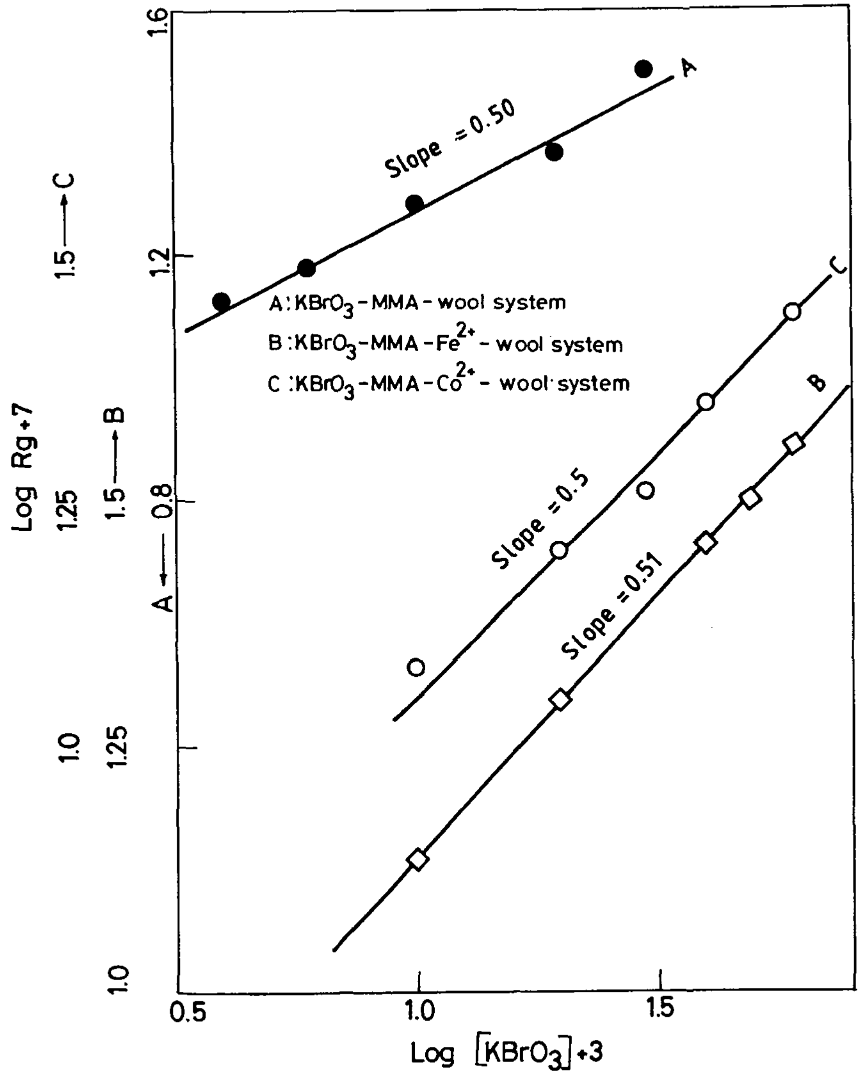

FIG. 5. $KBrO_3$ variation. Log $KBrO_3$ vs log R_g.

Effect of Wool

The amount of wool used in the reaction had a definite effect on the rate of grafting and on the chain lengths of the polyMMA formed. It also increased the percentage of grafting and the grafting efficiency. This showed that the polymerization of MMA took place preferentially in the wool matrix. With an abundance of wool in the medium, the integrated surface area of the fibers greatly affects diffusion of the monomer and free radical species while increasing the possibility of free radical formation on the wool backbone. The same explanation holds good for the reduction in chain-length values with larger amounts of wool (Figs. 8 and 9).

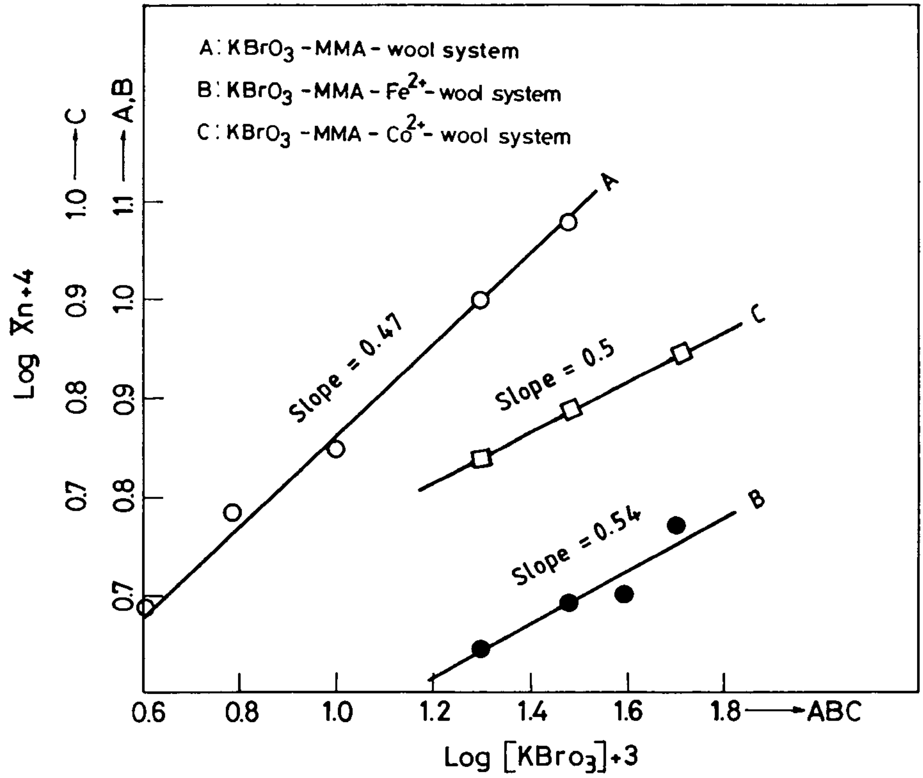

FIG. 6. Chain-length dependence. Log $\overline{X}_n$ vs log [$KBrO_3$].

Effect of pH

An optimum pH was needed for the reaction, and maximum rates were obtained at pH 1.1, 1.4, and 1.6 for Systems 1, 2, and 3, respectively. It is well known that wool swells in acid, and that maximum swelling takes place at pH 1. It was also found that salts could either increase or decrease the swelling [11]. This may be the reason for the shifting of pH from 1.1 (when BrO_3 alone was present) to 1.4 and 1.6 in the case of metal ion systems. Because of the swelling of wool fiber, the diffusion of reactants and reactive species into its matrix may be made easily. As the diffusion of monomer and radicals was facilitated, grafting could also be accelerated at pH values around 1.0. Any further lowering of pH probably hinders swelling, thus decreasing the rate of grafting of still higher acid concentrations (Fig. 10).

Effect of Temperature and the Overall Energy of Activation, E_a

The usual rise of rate with increasing temperature in heterogeneous polymerization is limited to a certain temperature range, the actual value of which is determined largely by the physical nature of the separating phase and by the rate of the initiating reaction. The usual trend of a rate–temperature plot is to exhibit a maxi-

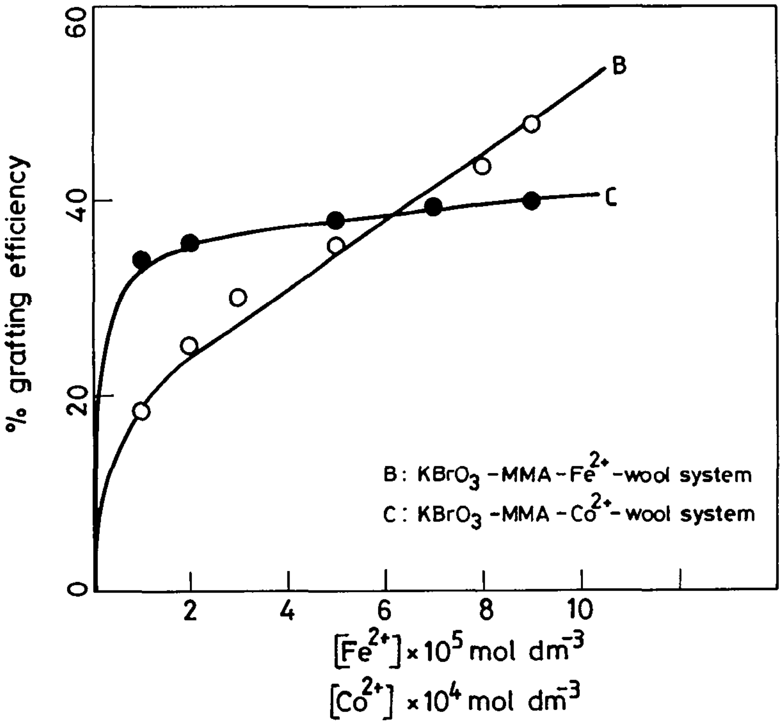

FIG. 7. Percentage grafting efficiency vs [metal ion].

mum after an exponential rise. The R_p begins to decrease at about 55°C [12]. In the present study also, R_g was found to decrease above 50°C. This is attributable to the rapid rise in the rate of coagulation of colloidal particles at this temperature, facilitating mutual termination of growing polyradical chains.

The overall activation energy was found to be highest when potassium bromate alone was present as the initiator (62.8 $\text{kJ}\cdot\text{mol}^{-1}$). When metal ions were present along with the oxidant, less activation energy (32.2 and 23.7 $\text{kJ}\cdot\text{mol}^{-1}$ for Systems 2 and 3, respectively) was needed to effect graft copolymerization.

Evidence for Grafting

Infrared spectra of the polymethyl methacrylate side chains isolated from the wool grafts showed bands typically characteristic of amino acid residues and those corresponding to polymethyl methacrylate. The characteristic amide I and II bands at 1650 and 1550 cm^{-1} and absorption peaks due to the polymethyl methacrylate C=O stretching vibration in the ester at 1730 cm^{-1} and C—O stretching vibration in the ester at 1080 cm^{-1} were also observed in the infrared spectra taken [13]. The ratio of isotactic, heterotactic, and syndiotactic triads was 9.7:39.0:51.4, respectively [14], from the characteristics peaks found at 7.2, 6.75, and 10.1 μ. The NMR spectrum of the polyMMA side chain showed peaks at 9.2, 9.0, 8.8, 8.2 and 6.4 τ values, providing evidence for graft copolymerization of methyl methacrylate onto

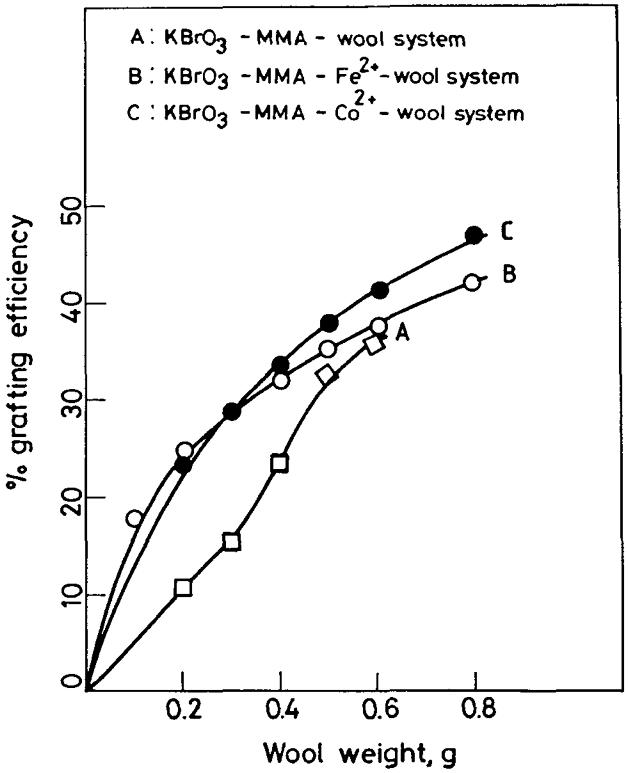

FIG. 8. Percentage grafting efficiency vs wool weight.

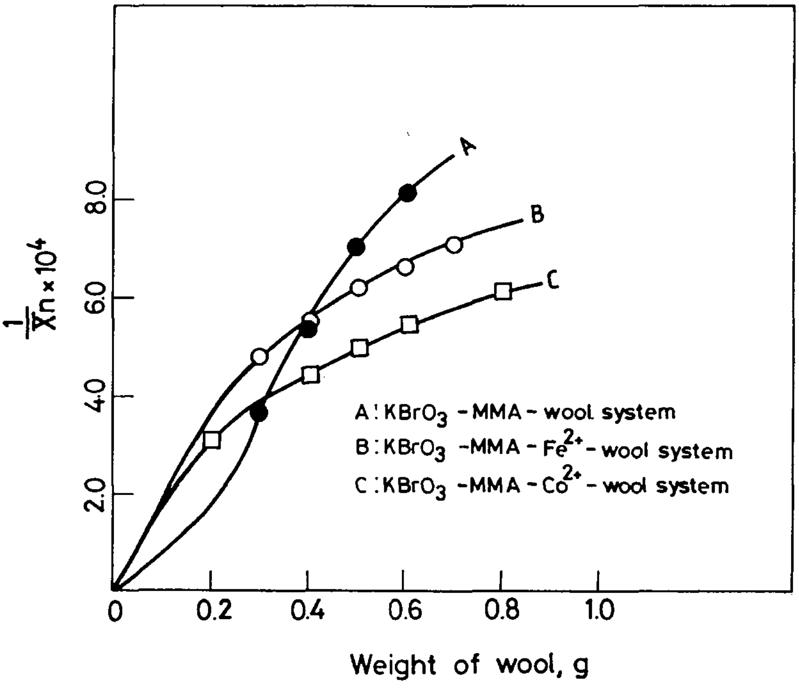

FIG. 9. $1/\overline{X}_n$ vs weight of wool.

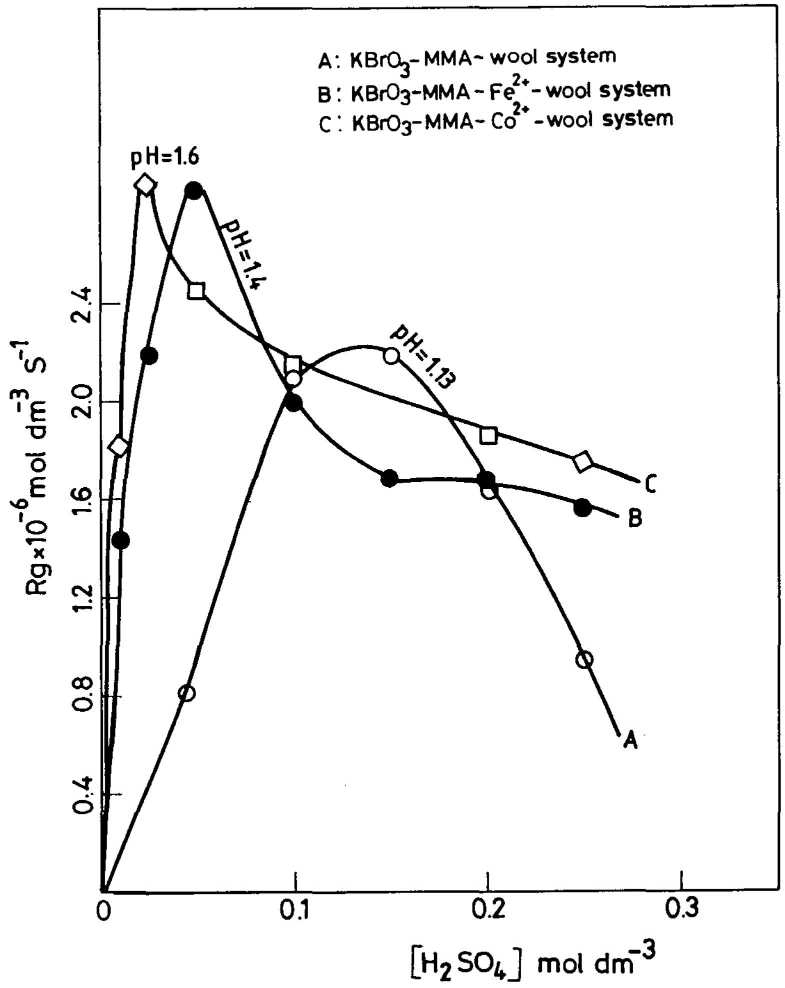

FIG. 10. R_g vs $[H_2SO_4]$.

TABLE 1. Amino Acid Analysis

	Amino acid residues/1000 g wool	
	Original fiber	Grafted fiber
Tyrosine	38	24
Phenylalanine	27	24

wool [15]. The ratio of isotactic, heterotactic, and syndiotactic triads was found to be 9.1:33.3:57.6, respectively, similar to that found for the homopolymer.

From IR and NMR data it was found that the ratio of isotactic, heterotactic, and syndiotactic triads was very much closer to 10:35:55 [which is characteristic of poly(MMA) initiated by a free radical mechanism]. This aspect also gave evidence for the free radical nature of the redox pairs.

Site of Grafting

The hydrolyzate of HCl digestion of original and grafted wool samples ($KBrO_3$-Fe^{2+} system) was taken by filtering the residue and was analyzed by buffered paper chromatography. From amino acid analysis it was found that tyrosine and phenylalanine content was less in the grafted samples than in the original sample (Table 1). The other amino acid contents remained the same in both samples. This analysis suggests the involvement of tyrosine and phenylalanine in the grafting reaction.

As this analysis was not applicable to cystine, evidence for the involvement of cystine by this method was not possible. However, a literature study has given proof for the oxidation of cysteine, cystine, and tyrosine by BrO_3^- [16].

Evidence for grafting also came from a study of the thermal and tensile properties of the grafted wool as well as from the dye uptake and resistance shown toward acid and alkali as discussed in earlier papers [17, 18].

CONCLUSION

This study clearly indicated the effect of Fe^{2+} and Co^{2+} ions on $KBrO_3$ -initiated graft copolymerization. The overall activation energy was found to be highest when potassium bromate alone was present as the initiator, but it was less for systems with metal ions. Improvement in the thermal and tensile properties of grafted wool, as well as the resistance shown toward acid and alkali as discussed in earlier papers [17, 18], gave evidence toward the end use properties of grafted wool.

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