

Effect of L(-)Threonine, 5-Hydroxytryptophane, and 5-Hydroxytryptamine on the Ceric-ion-initiated Grafting of Methyl Acrylate onto Cellulose

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SYNOPSIS

In order to study the effect of some radio protecting agents (RPA) such as L(-)threonine, 5-hydroxytryptophane (5-HT), and 5-hydroxytryptamine on ceric-ion-initiated grafting onto cellulose, attempts have been made to graft copolymerize methyl acrylate (MA) in aqueous medium in the presence and absence of RPA. Percentage of grafting has been determined as functions of concentration of (i) ceric ion, (ii) H₂SO₄, (iii) monomer, (iv) RPA, (v) reaction time, and (vi) reaction temperature. Maximum grafting percentage was obtained at [MA] = 5.53×10^{-2} mol/L within 180 min at 45°C in the absence of RPA. Grafting reactions were found to be suppressed in the presence of different RPAs. A plausible mechanism is suggested to explain the observed behavior of RPAs in grafting reactions. The graft copolymers have been characterized by IR spectroscopic and thermogravimetric methods. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

When cellulose is exposed to vinyl monomers in the presence of redox systems under the conditions which permit the decomposition of redox initiators to free radicals, the monomer becomes attached to the backbone of the polymer to produce a graft. Initiation of grafting of vinyl monomers onto cellulose with Ce⁴⁺ ions was first introduced by Mino and Kaizermann.¹ They found that certain ceric salts, such as nitrate and sulfate, formed very effective redox systems in the presence of organic reducing agents, such as alcohols, glycols, aldehydes, etc. By using this technique in both aqueous and emulsion systems, Mino and Kaizermann¹ prepared grafts of acrylamide, acrylonitrile, and methyl acrylate onto cellulose. Richards and others confirmed the validity of the method by preparing cellulose-*g*-polyacrylonitrile, cellulose-*g*-polystyrene,² and starch-*g*-polyacrylonitrile.³ Ceric ion initiation method has been extensively investigated with a large number of cellulosic systems, and many details of this reaction have been elucidated.⁴ Using ceric ammonium ni-

trate as redox initiator, Ide and Takayama prepared graft copolymers of vinyl acetate,⁵ methyl methacrylate,⁶ and styrene⁷ to cellulose. Schwab et al.⁸ studied grafting of acrylamide, acrylonitrile, and some acrylic and methacrylic esters to paper. Bergheim et al.⁹ have reviewed the method of grafting monomers onto cellulose and described the grafting of acrylic monomers onto wood cellulose by the ceric ion method. Patil et al.¹⁰ studied grafting of acrylamide on dihydroxypropyl cellulose (DHPC) by using ceric ion as initiator. Okeimen et al.¹¹ made the comparative study of grafting methyl acrylate onto cellulose and thiolated holocellulose by using the ceric ion initiation technique and concluded that grafting of poly(methyl acrylate) was lower in the thiolated holocellulose. Earlier, Misra and Chandel¹² studied ceric-ion-initiated grafting of vinyl monomers onto wool in the presence of different amines and reported that grafting occurs through a free radical mechanism involving prior complex formation between ceric ion and amine. Effect of various radio protecting agents on ceric-ion-initiated grafting of vinyl monomers onto cellulose has not been reported.

A lot of controversy exists regarding the mechanism of action of radio protecting agents. It is not

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known whether the radio protecting agents are capable of reacting with free radicals. In order to examine this aspect, attempts have been made to study effect of several radio protecting agents upon ceric-ion-initiated grafting of MA onto cellulose. Ceric-ion-initiated grafting of vinyl monomers onto cellulose is known to proceed through the formation of free radicals. If the radio protecting agents are capable of reacting with free radicals, then ceric-ion-initiated grafting will be significantly affected in their presence.

EXPERIMENTAL

Materials and Methods

Pure microcrystalline cellulose powder was dried in an oven at 40°C. Methyl acrylate was distilled and dried over anhydrous sodium sulfate. Nitrogen gas was purified by passing through freshly prepared alkaline pyrogallol solution to remove traces of oxygen.

Graft Copolymerization

Pure microcrystalline cellulose powder (200 mg) was dispersed in a definite amount of water in a three-necked flask placed in a water bath. The reaction flask was flushed with purified nitrogen for 30 min, and then a continuous supply of nitrogen was maintained throughout the reaction period. A known amount of ceric ammonium sulfate (CAS) and H₂SO₄ (6*N*) were added slowly to the reaction flask. A definite amount of monomer (methyl acrylate) was added dropwise to the reaction mixture from the dropping funnel. The graft copolymerization was carried out at 30, 45, and 75°C for various time periods under stirring by a magnetic stirrer in the presence and absence of a definite amount of radio protecting agents. After a definite time period, the reaction mixture was filtered, and the homopolymer was removed by extraction with benzene. The grafted sample was dried to a constant weight, and percentage of grafting (%G) was calculated from the increase in the initial weight of cellulose in the following manner:

$$\%G = \frac{W_2 - W_1}{W_1} \times 100$$

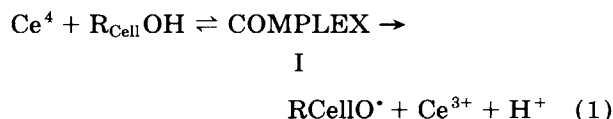
where W_1 denotes the weight of original cellulose powder and W_2 the weight of grafted cellulose after benzene extraction.

Evidence of Grafting

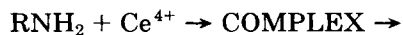
1. The IR spectrum of the grafted cellulose showed a strong absorption at 1730 cm⁻¹ attributed to C=O of poly(methyl acrylate), which was not present in the IR spectrum of pure cellulose.
2. When cellulose-*g*-PMA was hydrolyzed with 57% HBr, a resinous mass was obtained which was purified, and the isolated polymer showed in IR spectrum an absorption band at 1730 cm⁻¹ assigned to C=O of poly(methyl acrylate). Isolation of homopolymer (PMA) after hydrolysis of the graft indicated that poly(methyl acrylate) was covalently attached to cellulose.
3. A physical mixture of 100 mg cellulose dispersed in 100 mL of water and 500 mg of poly(methyl acrylate) in benzene was stirred at room temperature for 3 h. The physical mixture was filtered, and the residue extracted with benzene for 48 h. Quantitative recovery of cellulose indicated that the homopolymer is completely removed from a physical mixture by solvent extraction.
4. Thermogravimetric analysis data: The TGA was performed using a DuPont instrument. The cellulose powder and cellulose-*g*-PMA samples were heated from 32 to 707°C at a heating rate of 10°C/min. Primary thermograms were obtained by plotting the percentage residual weight against the temperature. The initial decomposition temperature (IDT) and the final decomposition temperature (FDT) were estimated. Upon grafting, IDT of cellulose is raised from 300 to 350°C, indicating that grafting of PMA improves the thermal stability of cellulose.

RESULTS AND DISCUSSION

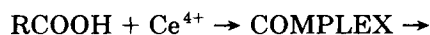
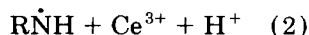
Ceric ion is known to form a complex with hydroxyl groups, and the complex can dissociate via one electron transfer to give free radicals.³ Since cellulose is a polyhydric alcohol, complex formation between the hydroxyl groups of cellulose and ceric ions occurs, and the complex undergoes dissociation to generate active sites onto cellulose backbone:



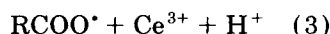
Grafting of appropriate vinyl monomers can occur onto the macroradical sites. Amines and carboxylic acids are also known to form complexes with ceric ion, and these complexes can decompose to generate free radicals, which can influence grafting:



II



III



In view of the fact that amino (NH_2) and carboxylic function (COOH) can generate free radicals by interaction with ceric ion, it was considered worthwhile to study grafting of MA onto cellulose in the presence of various radio protecting agents containing both amino and carboxylic functions.

Effect of Ceric Ion Concentration

Figure 1 shows the effect of concentration of CAS on the grafting of MA. The formation of complex I is dependent upon [CAS]. At lower [CAS], grafting is low and essentially remains constant. Maximum grafting (600%) is obtained at [CAS] = 26.28×10^{-3} mol/L. Further increase in [CAS] leads to

the decrease in percentage of grafting. It appears that at higher [CAS], the monomer preferentially forms a complex with Ce^{4+} , leading to the production of homopolymer at the expense of the graft. Further, Ce^{4+} at higher concentration promotes termination of growing grafted chains.¹³

Effect of Monomer Concentration

It is observed from Figure 2 that the percentage of grafting increases with increasing monomer concentration and reaches maximum at [MA] = 5.33×10^{-2} mol/L. At higher monomer concentration, homopolymerization of MA via the complex formation between the monomer and Ce^{4+} becomes the preferred process, leading to a decrease in grafting. Similar behavior was observed by Misra et al.¹⁴ during grafting of vinyl monomers in the presence of ceric ammonium nitrate (CAN) and HNO_3 onto wool.

Effect of Time

Figure 3 represents grafting of MA onto cellulose at 45°C as a function of time. Percentage of grafting increase with increase in time and maximum grafting is obtained within 180 min. Further increase in time leads to the decrease in grafting, presumably due to mutual annihilation of growing grafted chains.

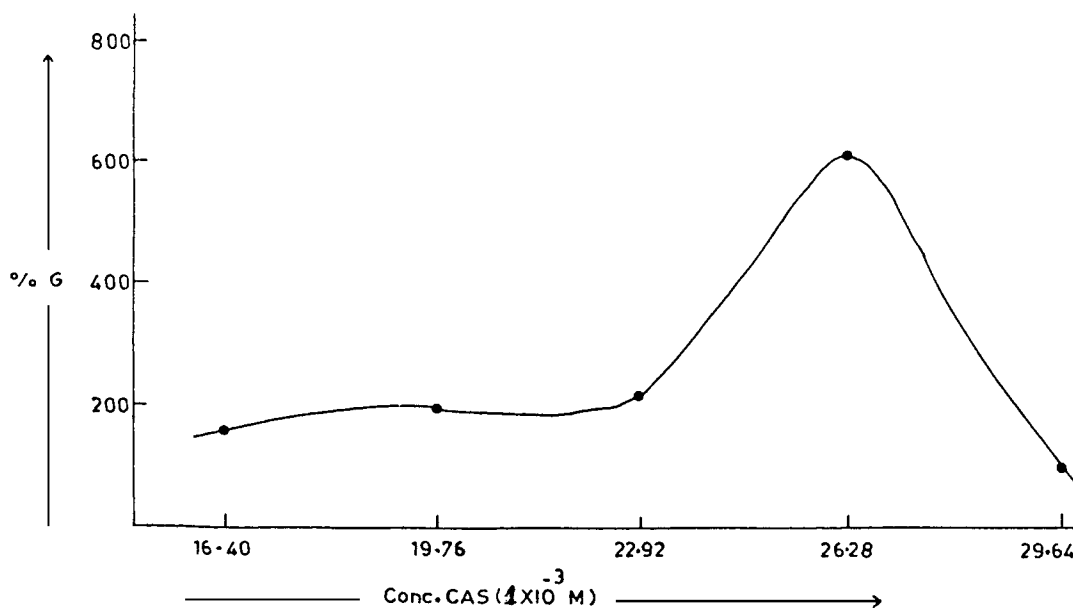


Figure 1 Cellulose = 100 mg; [MA] = 5.53×10^{-2} mol/L; [H_2SO_4] = 2.33×10^{-3} mol/L; water = 125 mL; temperature = 45°C ; reaction time = 120 min.

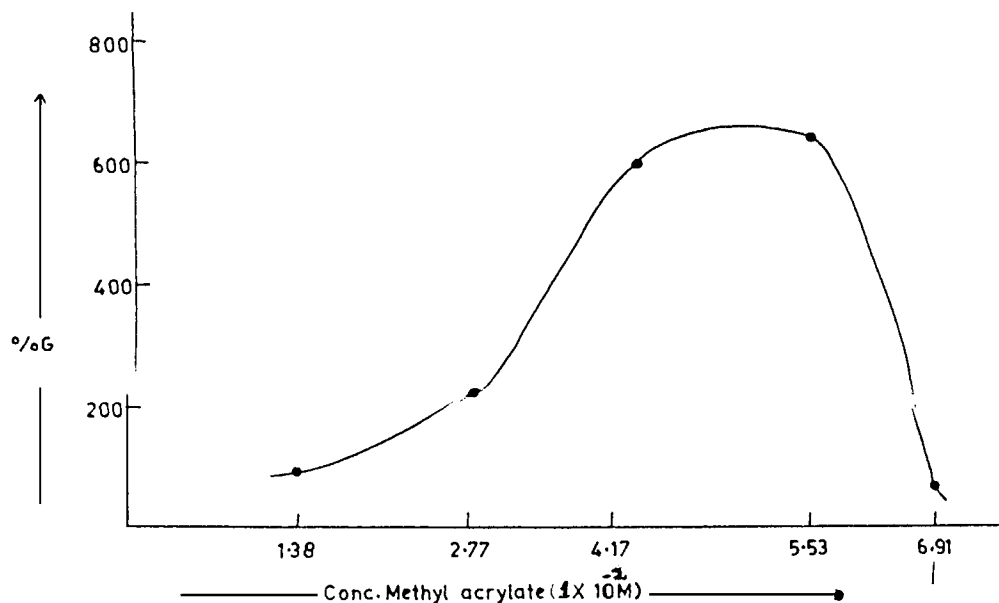


Figure 2 Cellulose = 100 mg; [CAS] = 26.28×10^{-3} mol/L; [H₂SO₄] = 2.33×10^{-3} mol/L; water = 125 mL; temperature = 45°C; reaction time = 120 min.

Role of Sulfuric Acid

It is observed that certain amount of sulfuric acid is required as a catalyst to give maximum grafting. The role of sulfuric acid is explained as follows:

In aqueous medium, Ce⁴⁺ is believed to combine with water in the following manner:

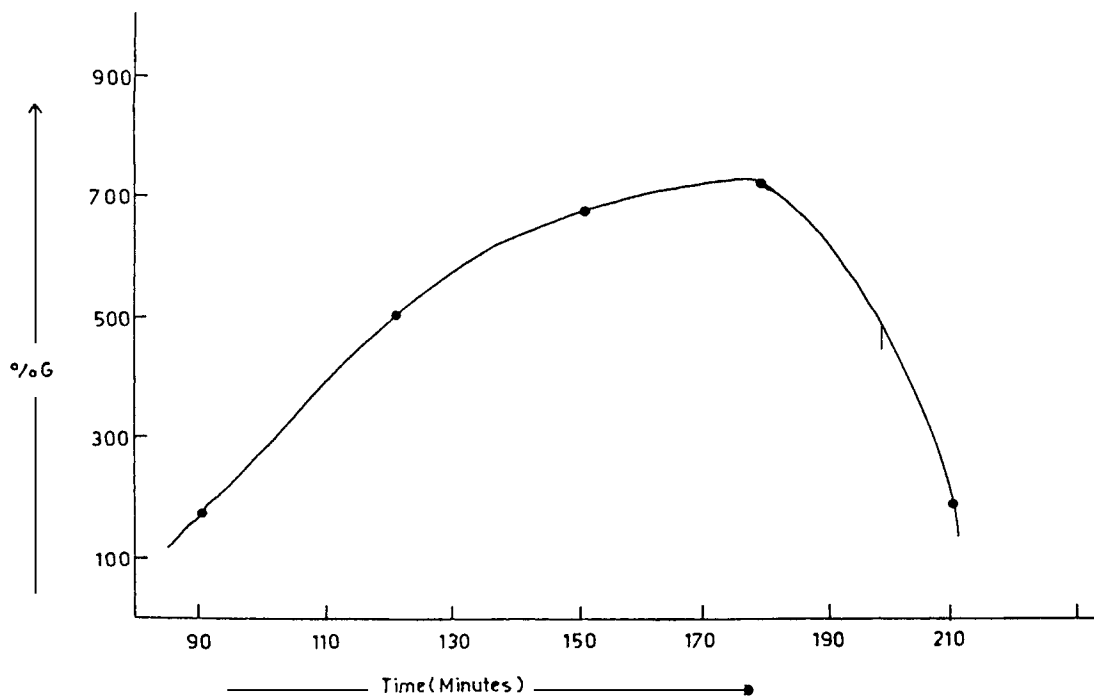
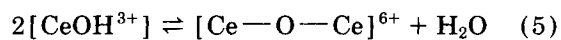
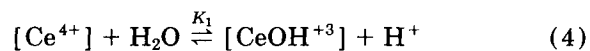


Figure 3 Cellulose = 100 mg; [MA] = 5.53×10^{-2} mol/L; [CAS] = 26.28×10^{-3} mol/L; [H₂SO₄] = 2.33×10^{-3} mol/L; water = 125 mL; temperature = 45°C.

Thus Ce^{4+} exists as Ce^{4+} , $[\text{CeOH}^{3+}]$, and $[\text{Ce}-\text{O}-\text{Ce}]^{6+}$ in water solution. Concentration of these species vary with the concentration of acid in the manner described:

From eq. (4),

$$[\text{CeOH}]^{3+} = K_1[\text{Ce}]^{4+}/[\text{H}^+] \quad (6)$$

The effective $[\text{Ce}^{4+}]$ in the solution is given by

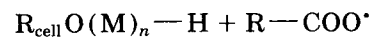
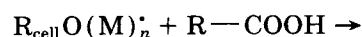
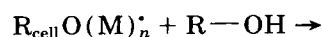
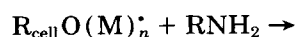
$$[\text{Ce}^{4+}]_E = [\text{Ce}^{4+}]_T - K_1[\text{Ce}^{4+}]_T/[\text{H}^+]$$

where $[\text{Ce}^{4+}]_E$ = concentration of ceric ion which is not complexed and $[\text{Ce}^{4+}]_T$ = total concentration of ceric ion.

It is clear that the $[\text{Ce}]_E^{4+}$ increases in solution with increasing $[\text{H}^+]$, and facilitates the formation of a complex with cellulose. With the increase in $[\text{H}_2\text{SO}_4]$, the equilibrium (4) and (5) shift towards formation of more and more of $[\text{CeOH}]^{3+}$ and $[\text{Ce}]_T^{4+}$. These species having smaller sizes facilitate the formation of a complex between ceric ion and cellulose, resulting in an increase in percentage of grafting (Fig. 4). Beyond optimum $[\text{H}_2\text{SO}_4]$, a considerable amount of $[\text{Ce}^{4+}]$ and $[\text{CeOH}]^{3+}$ is formed. These species at higher concentrations accelerate the termination of growing grafted chains, resulting in a decrease in percentage of grafting. Termination of growing chains at higher $[\text{Ce}]^{4+}$ has been reported by Saha and Chaudhuri.¹⁵

Effect of Radio Protecting Agents

The effect of various amines on ceric-ion-initiated grafting of vinyl monomers onto wool was studied by Misra and Chandel.¹² Reactivity of various amines towards grafting was found to be dependent on steric requirement, nucleophilicity, and basicity of amines. L-threonine possesses $-\text{OH}$, $-\text{NH}_2$, and $-\text{COOH}$ groups capable of forming complexes with ceric ion. Percentage of grafting of MA was found to increase with increasing concentration of L-threonine (Fig. 5). At higher concentration, L-threonine decreases grafting due to the enhanced rate of abstraction of the hydrogen atom by growing grafted chains:



In the presence of 5-hydroxytryptophane and 5-hydroxytryptamine as additives, grafting was found to be suppressed. This is explained by the fact that the phenolic OH groups present in these additives inhibit both polymerization and grafting. This may

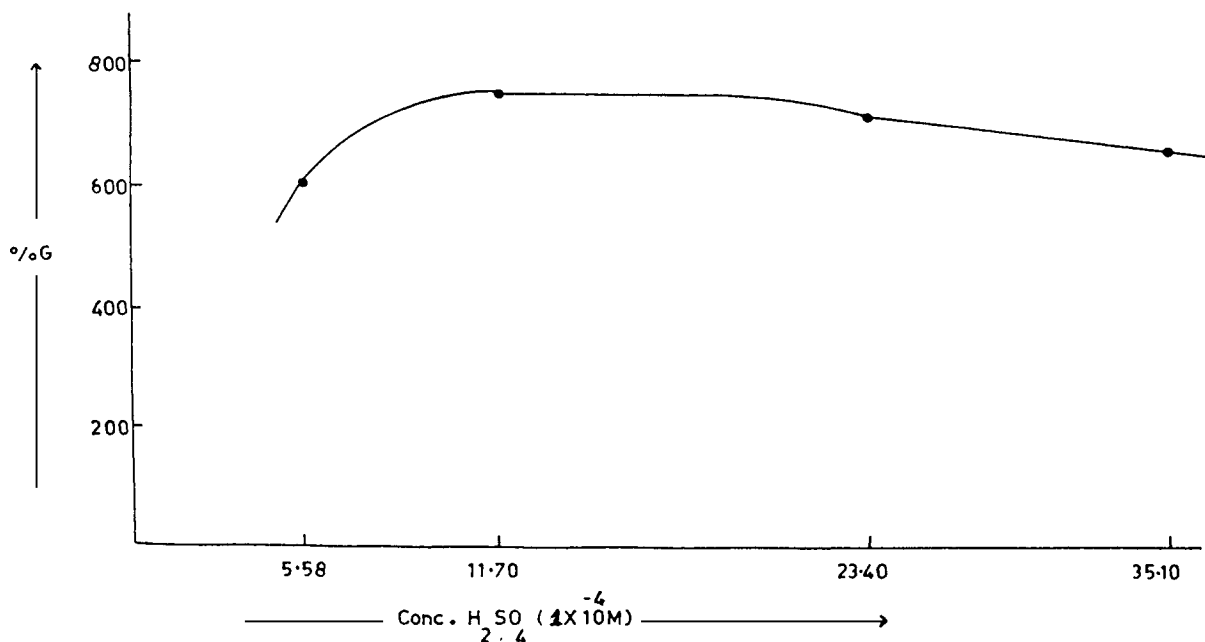


Figure 4 Cellulose = 100 mg; $[\text{MA}] = 5.53 \times 10^{-2}$ mol/L; $[\text{CAS}] = 26.28 \times 10^{-3}$ mol/L; water = 125 mL; temperature = 45°C; reaction time = 180 min.

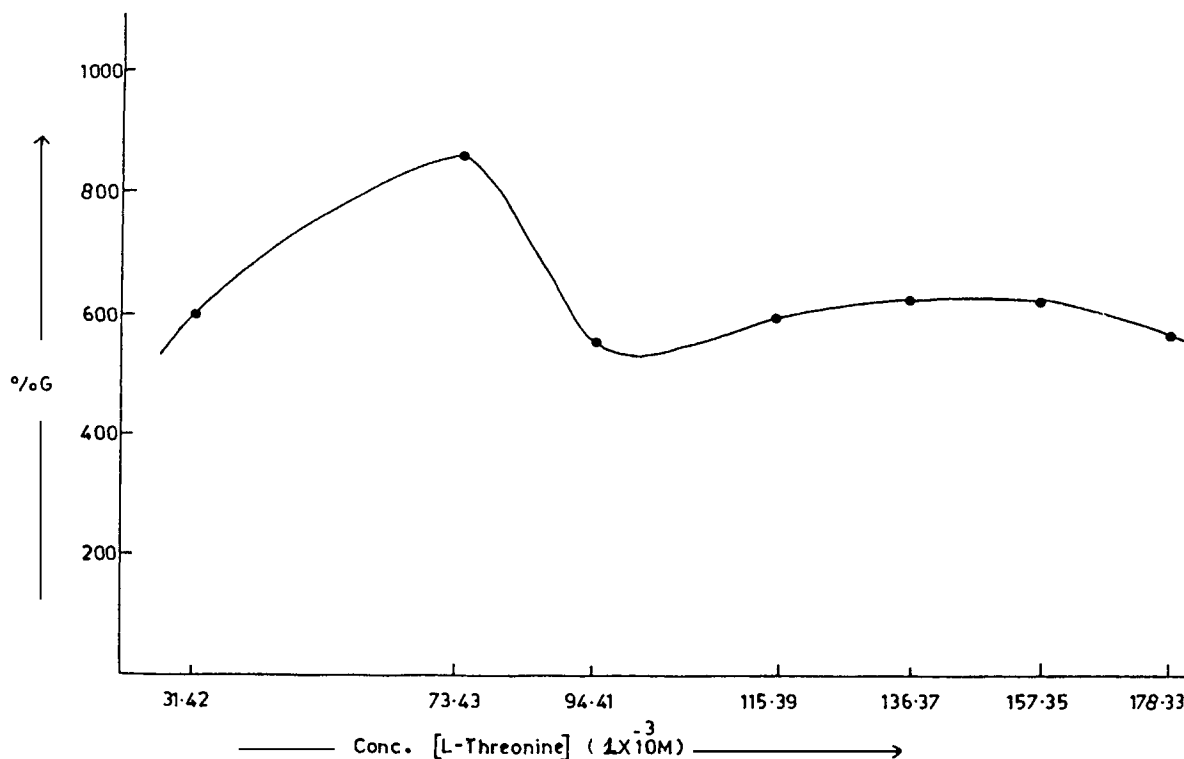


Figure 5 Cellulose = 100 mg; [MA] = 5.53×10^{-2} mol/L; [CAS] = 26.28×10^{-3} mol/L; water = 125 mL; temperature = 45°C; reaction time = 180 min.

tend to indicate that radio protecting agents involve free radical mechanism in their mode of action.

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