

# Graft Copolymerization onto Rubber. VII. Graft Copolymerization of Methyl Methacrylate onto Rubber Using Potassium Peroxydisulfate Catalyzed by Silver Ion

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## Synopsis

The graft copolymerization of methyl methacrylate onto natural rubber (NR) was carried out varying the concentration of monomer, initiator, thiourea, and silver nitrate over a wide range. The grafting reaction was temperature-dependent. From the Arrhenius plot, the overall energy of activation was computed. A suitable reaction scheme and rate expression for the rate of polymerization was suggested.

## INTRODUCTION

The ability of peroxydisulfate ion to initiate polymerization of certain vinyl monomers was reported by Bacon<sup>1</sup> as early as 1946. This is one of the oldest initiating reagents reported in the literature. Peroxydisulfate ion when coupled with monovalent silver ion acts as better initiator, since  $\text{Ag}^{2+}$ , which is produced during the reaction, is a more powerful initiator than peroxydisulfate. Morgan<sup>2</sup> reported the polymerization of acrylonitrile initiated by peroxydisulfate with ferrous ammonium sulfate as reductant. Schulz and co-workers<sup>3</sup> and Whitby et al.<sup>4</sup> reported the kinetics of the polymerization of acrolein initiated by the peroxydisulfate– $\text{Ag}^+$  redox system. Recently, Kagiya and co-workers<sup>5</sup> reported the kinetic features of the redox polymerization of acrolein with the potassium persulfate–silver nitrate redox system. Arai and co-workers<sup>6–10</sup> have studied the graft copolymerization of vinyl monomers onto wool and silk fibers using the peroxydisulfate–lithium bromide redox system. Nayak and co-workers<sup>11</sup> reported the graft copolymerization of methyl methacrylate onto wool fiber using peroxydiphosphate ion as the initiator. Though a number of metal ions have been used<sup>12,13</sup> for grafting vinyl monomers onto natural rubber, non-metal ion like peroxydisulfate has not been used. This communication presents the graft copolymerization of methyl methacrylate onto crepper natural rubber using potassium peroxydisulfate catalyzed by silver ion.

## EXPERIMENTAL

Crepper natural rubber with ash content = 0.6% and acetone extract = 2.2% was obtained as a gift sample from Dr. S. K. De of IIT, Kharagpur. The purification of monomers, preparation of stock solution of potassium

peroxydisulfate, thiourea, silver nitrate, and the method of rate measurements were discussed in our previous communication.<sup>11</sup> Extraction of the grafted product was carried out in cold benzene by percolation to remove the homopolymer completely. The percentage of grafting was calculated by using the following expression:

$$\% \text{ graft yield} = \frac{\text{wt grafted polymer}}{\text{dry wt organic natural rubber}} \times 100$$

## RESULTS AND DISCUSSION

The graft copolymerization of methyl methacrylate onto rubber was studied using the potassium peroxydisulfate–thiourea redox system in the presence of silver nitrate solution. The percentage of grafting was maximum at 5 h known from time conversion curve (Fig. 1).

Figure 2 shows the effect of monomer concentration on grafting. It was observed that, with increase of monomer concentration up to 1.4082 mol/L, the graft yield increases and, with further increase of monomer concentration, the graft yield decreases. A similar trend was noticed in case of graft copolymerization of methyl methacrylate onto wool using peroxydisulfate ion.<sup>11</sup>

The effect of peroxydisulfate concentration on the rate of grafting was shown in Fig. 3. The graft yield increases with increasing the peroxydisulfate concentration up to  $2.5 \times 10^{-2}$  mol/L and with further increase of the initiator concentration the graft yield decreases.

Thiourea and *N*-substituted thiourea have been used for initiation of aqueous vinyl polymerization during the last few years.<sup>14-16</sup> In all initiating

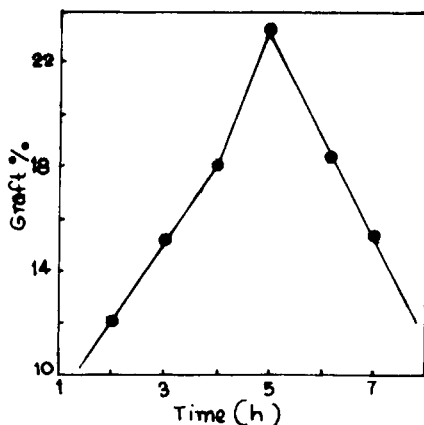


Fig. 1. Time conversion: [PS] =  $2.0 \times 10^{-2}$  mol/L; [MMA] = 0.9388 mol/L; [AgNO<sub>3</sub>] =  $5.0 \times 10^{-3}$  mol/L; [TU] =  $5.0 \times 10^{-3}$  mol/L; temp = 50°C.

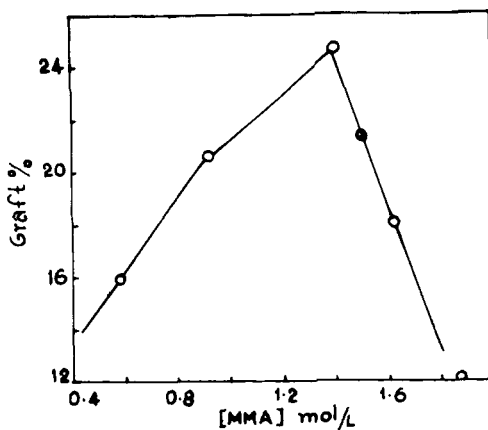
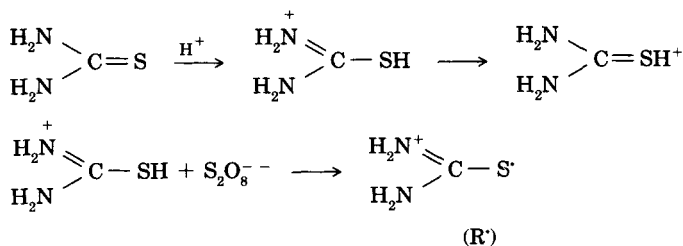


Fig. 2. Effect of [monomer]: [PS] =  $2.0 \times 10^{-2}$  mol/L; [AgNO<sub>3</sub>] =  $5.0 \times 10^{-3}$  mol/L; [TU] =  $5.0 \times 10^{-3}$  mol/L; temp = 50°C; time = 5 h.

systems containing thiourea, the redox component is isothiurea, a thiol existing in a tautomeric equilibrium with thiourea as the reductant:



The isothiocarbamido radicals (R<sup>·</sup>) abstract hydrogen from rubber to form rubber macroradicals which initiate graft copolymerization. The isothiocarbamido radical might also react with the monomer to give rise the mono-

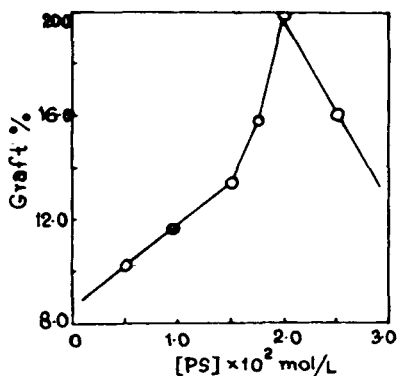


Fig. 3. Effect of [PS]: [MMA] = 0.9388 mol/L; [TU] =  $5.0 \times 10^{-3}$  mol/L; [AgNO<sub>3</sub>] =  $10.0 \times 10^{-3}$  mol/L; time = 5 h; temp = 50°C.

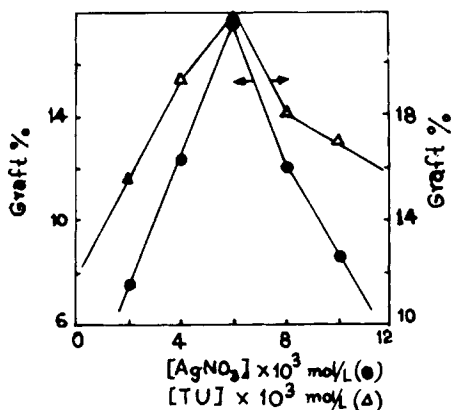


Fig. 4. Effect of [TU] ( $\Delta$ ): [PS] =  $2.0 \times 10^{-2}$  mol/L; [MMA] = 0.9388 mol/L; [AgNO<sub>3</sub>] =  $5.0 \times 10^{-3}$  mol/L; time = 5 h; temp = 50°C. Effect of [AgNO<sub>3</sub>] ( $\bullet$ ): [PS] =  $2.0 \times 10^{-2}$  mol/L; [TU] =  $5.0 \times 10^{-3}$  mol/L; [MMA] = 0.9388 mol/L; time = 5 h; temp = 50°C.

mer radicals which initiate homopolymerization. The percentage of grafting increases by increasing thiourea concentration up to  $6 \times 10^{-3}$  mol/L, and with further increase of the activator the graft yield decreases (Fig. 4). The lower graft yield at higher thiourea concentrations might be due to the following reasons: (a) the increased amount of free radical inhibitor in thiourea which is always present in it, (b) the increased amount of thiourea might be facilitating the formation of disulphide decreasing the concentration of isothiurea radical, and (c) at higher concentration of thiourea some species might be generated which might be acting as radical scavenger.

The graft copolymerization was carried out at four different temperatures ranging from 45 to 60°C. A perusal of results indicates that with increasing temperature the percentage of graft-on increases, which might be due to swellability of rubber, solubility of monomer and its high diffusion rate. From the Arrhenius plot of  $\log R_p$  vs.  $1/T$  (Fig. 5) the overall activation energy was found to be 67,490 J/mol.

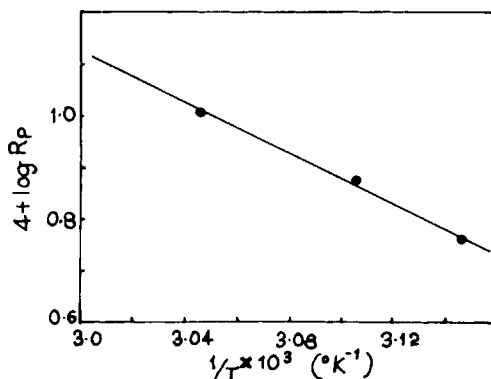
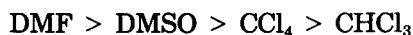


Fig. 5. Arrhenius plot of  $\log R_p$  vs.  $1/T$ .

The effect of  $\text{CuSO}_4$  concentration on grafting is quite interesting. It is observed that with increasing  $\text{CuSO}_4$  concentration, the graft yield first increases, and, with further increase of  $\text{CuSO}_4$ , the graft yield decreases (Fig. 6). A similar occurrence was noticed by us while grafting methyl methacrylate onto wool using peroxydisulfate ion as the initiator.<sup>11</sup>

The graft copolymerization was studied varying  $\text{AgNO}_3$  concentration over a wide range ( $2.0\text{--}10 \times 10^{-3}$  mol/L). In the initial stage, the graft percentage increases, and with further increase of  $\text{AgNO}_3$  concentration the graft-on percentage decreases (Fig. 4). This might be due to the formation of homopolymer at higher concentration of  $\text{AgNO}_3$ .

Solvent plays an important role for graft copolymerization. The grafting reaction was studied in the presence of different solvents. The order of reactivity follows the sequence



The graft copolymerization was also studied by using a number of organic sulphur compounds. The graft copolymerization increases in the following order:

cysteine hydrochloride > thioglycollic acid

> thiourea > thioacetamide

Different monomers were used for grafting reaction. It was observed that methyl methacrylate is more reactive than other monomers. The order of reactivity shows the following sequence:

methyl methacrylate > butyl acrylate

> acrylic acid > ethyl methacrylate

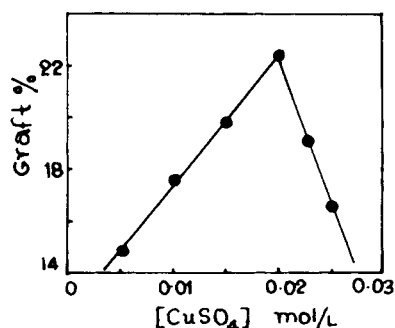
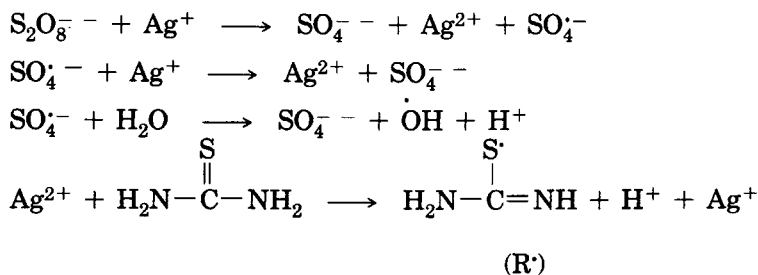


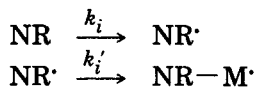
Fig. 6. Effect of  $[\text{CuSO}_4]$ :  $[\text{PS}] = 2.0 \times 10^{-2}$  mol/L;  $[\text{MMA}] = 0.9388$  mol/L;  $[\text{TU}] = 5.0 \times 10^{-3}$  mol/L;  $[\text{AgNO}_3] = 5.0 \times 10^{-3}$  mol/L; time = 5 h; temp =  $50^\circ\text{C}$ .

*Mechanism:* In a system consisting of peroxydisulphate, silver ion, thiourea, MMA, and rubber, the following reaction scheme may be suggested:

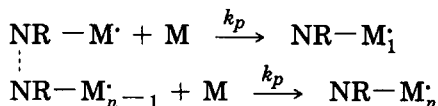


$\text{R}^{\cdot}$ ,  $\dot{\text{O}}\text{H}$ ,  $\text{SO}_4^{\cdot-}$  interact with rubber, producing rubber macroradicals. The rubber macroradicals react with monomer resulting grafting as represented below.

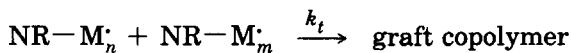
*Initiation:*



*Propagation:*



*Termination:*



By applying steady state principle, the rate of polymerization was found to be

$$\begin{aligned}
 R_p &= k_p[\text{NR}-\text{M}_n^{\cdot}][\text{M}] \\
 &= k_p(k_i/k_t)^{1/2}[\text{NR}]^{1/2}[\text{M}]
 \end{aligned}$$

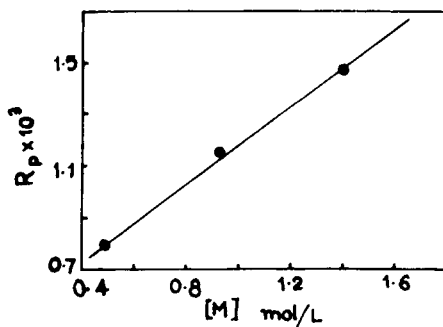


Fig. 7. Plot of  $R_p$  vs.  $[\text{M}]$ .

Thus the plot of  $R_p$  vs.  $[M]$  was linear, passing through the origin (Fig. 7), which satisfies the above-proposed mechanism.

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