

Grafting of Vinyl Monomers onto Natural Rubber. I. Graft Copolymerization of Methyl Methacrylate onto Natural Rubber Using Quinquevalent Vanadium Ion as the Initiator

Rubber occupies a dominant position among natural macromolecules being modified for commercial use by copolymerization with synthetic polymers. Copolymers of natural rubber are prepared and characterized by techniques applicable to wholly synthetic copolymers, and their properties could be duplicated by the characteristics of an appropriate synthetic rubber.

The successful grafting of vinyl monomers onto natural rubber involves the creation of free radical on the backbone of rubber. This can be achieved by several methods, such as chemical¹⁻⁴ and irradiation.⁵⁻⁸ Out of all these methods, the chemical method has attracted attention in recent years. Graft copolymerization of vinyl monomers onto natural rubber has been studied by using benzoyl peroxide as the initiator.⁹

In the recent past, we have used a multitude of chemical initiators for grafting vinyl monomers onto a number of natural and synthetic fibers. This paper presents the results of studies of graft copolymerization of MMA onto natural rubber using V^{5+} ion as the initiator.

EXPERIMENTAL

Crepe natural rubber with ash content = 0.6% and acetone extract = 2.2% was obtained as a gift sample from Dr. S. K. De, IIT, Kharagpur. The purification of monomers, preparation of solution of V^{5+} , and the method of rate measurements were discussed in our previous papers.^{10,11} Extraction of the grafted product was carried out in benzene to remove the homopolymer completely. The percentage of grafting and percent efficiency were calculated according to our previous procedure.

Effect of Monomer Concentration

The effect of monomer concentration on the extent of grafting was investigated by changing the monomer concentration within the range of 0.005–0.035*M* and keeping the concentration of all other reagents constant. From Figure 1 it can be seen that as the monomer concentration increases, there is an increase in the percentage of grafting in the lower concentration range; it reaches a maximum value at 0.02–0.025*M*, and thereafter it decreases. At higher monomer concentration, reactions that are competitive to grafting probably take place in solution, i.e., homopolymerization is more favored than grafting at higher monomer concentrations. On the other hand, the rate of monomer diffusion is bound to be progressively affected by the polymer deposit formed, which, of course, grows most rapidly when high concentrations of monomer are used. Similar observations have been noted by Nayak et al. in the case of grafting of methyl methacrylate onto wool by hexavalent chromium¹² ion.

Effect of $[V^{5+}]$ on Graft Yield

The effect of concentration of V^{5+} ion on grafting of MMA onto rubber is shown in Figure 2. The rate of grafting has been investigated by changing the V^{5+} concentrations within the range of 0.02–0.04*M*. The data indicate that increasing $[V^{5+}]$ up to 0.035*M* is accompanied by a significant increase in graft yield while further increase cause a marked fall in the graft yield. This could be ascribed to a faster rate of termination at higher initiator concentrations.

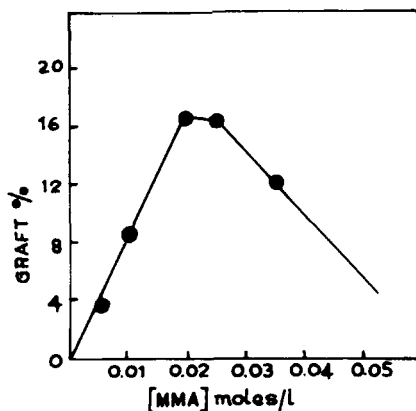


Fig. 1. Plot of graft % vs. [MMA]: $[V^{5+}] = 0.035M$; $[H_2SO_4] = 1.29M$; temperature = $50^\circ C$; time = 6 h.

Effect of Temperature

The graft copolymerization was carried out at four different temperatures ranging from $45^\circ C$ to $66^\circ C$, keeping the concentrations of all other reagents constant. A perusal of result indicates that with increasing temperature, the percentage of graft-on increases. The dependence of the rate of grafting on temperatures could be ascribed to the greater activation energy, the swellability of rubber, solubility of monomer, and its diffusion rates are enhanced by increasing the reaction temperature. From the Arrhenius plot of $\log R_p$ vs. $1/T$ (Fig. 3), the overall activation energy was computed to be 18.4 kcal/mol. Using the value of $(E_p - \frac{1}{2}E_t) = 4-5$ kcal/mol given by Tobolsky,¹³ where E_p and E_t are values of energy of propagation and termination, respectively. The value of the activation energy of initiation, E_d , was calculated as follows: $E_d = 2E_a - (2E_p - E_t)$, where E_a is the overall activation energy and $E_d = 25.8$ kcal/mol for total conversion reaction of MMA to PMMA.

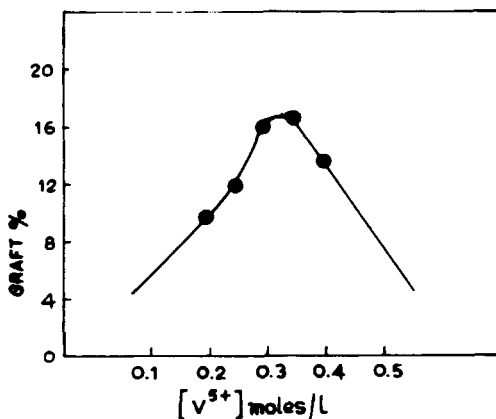


Fig. 2. Plot of graft % vs. $[V^{5+}]$: $[H_2SO_4] = 1.29M$; $[MMA] = 1.408M$; temperature = $50^\circ C$; time = 6 h.

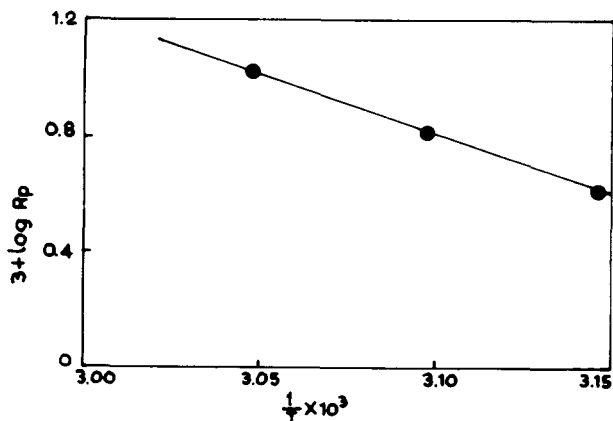


Fig. 3. Arrhenius plot of $\log R_p$ vs. $1/T$.

Effect of $[\text{CuSO}_4]$ on Graft Yield

The effect of CuSO_4 concentration on grafting is quite interesting (Fig. 4). It is observed that, with increasing $[\text{CuSO}_4]$, the graft yield increases and then decreases. The initial increase in graft yield might be due to fact that the presence of Cu^{2+} ions in the vicinity of rubber certainly favors grafting since the involvement of Cu^{2+} ion in a rubber-monomer complex should be easier. Furthermore, the creation of free radical species under the presence of Cu^{2+} ions would be in the proximity of rubber, thus assisting formation of rubber macroradicals. The drop in the graft yield with higher concentrations of cupric sulfate could be attributed to a variety of reasons. First is termination of free radicals in solution, on homopolymer, and/or on rubber, the Cu^{2+} ions seem to act as radical trap. Second might be that a particular concentration of Cu^{2+} favors complexation of monomer with rubber and beyond this concentration of Cu^{2+} ions perturbed such complexation.

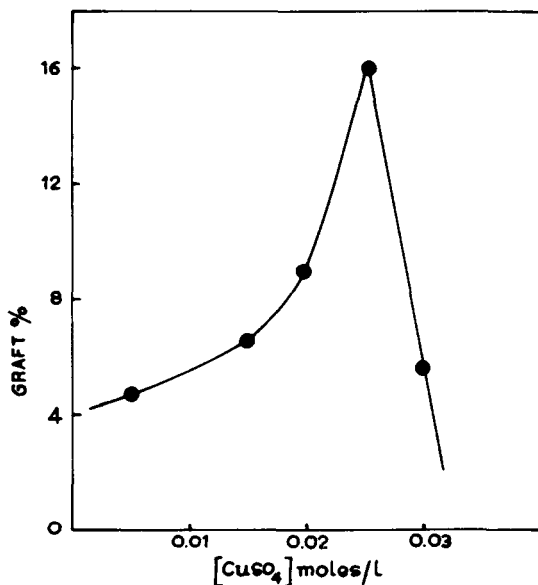
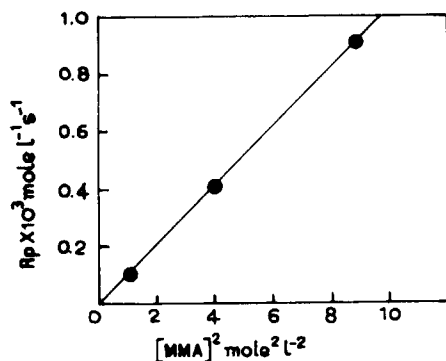


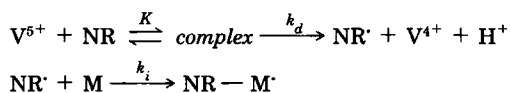
Fig. 4. Plot of graft % vs. $[\text{CuSO}_4]$: $[\text{V}^{5+}] = 0.025M$; $[\text{MMA}] = 0.02M$; $[\text{H}_2\text{SO}_4] = 1.29M$; temperature = 50°C ; time = 6 h.

Fig. 5. Plot of R_p vs. $[M]^2$.

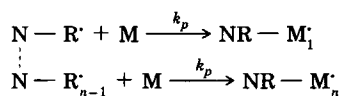
Mechanism

In a system consisting of NR, MMA, and V^{5+} , the following grafting mechanism has been suggested.

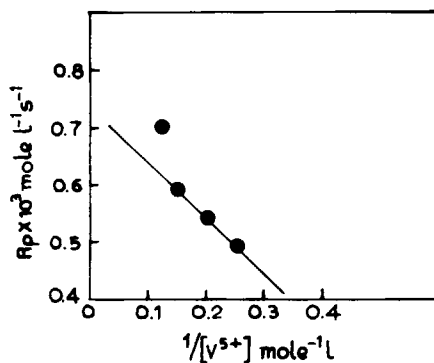
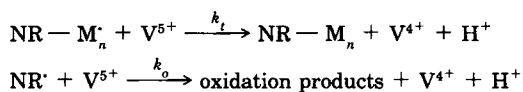
Initiation:



Propogation:



Termination:

Fig. 6. Plot of R_p vs. $1/[V^{5+}]$.

Here M is the monomer, K is equilibrium constant, and k_i , k_p , k_t , and k_0 are rate constants.

By applying steady state conditions to the concentrations [NR] and [NR—M], the overall rate of polymerization can be derived to be

$$R_p = \frac{k_p}{k_t} [M]^2 \frac{Kk_d[NR]}{[M] + (k_0/k_i)[V^{5+}]}$$

The above rate expression was verified by plotting R_p vs. $[M]^2$ (Fig. 5) and R_p vs. $1/[V^{5+}]$ (Fig. 6), which were linear.

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