

# Grafting of *N,N'*-Methylenebisacrylamide onto Silk Fibers using the Vanadylacetylacetonate Complex in Aqueous Medium

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## Synopsis

The grafting of *N,N'*-methylenebisacrylamide (*N,N'*-MBA) onto mulberry silk fibers is reported using vanadylacetylacetonate (VO(acac)<sub>2</sub>) complex under inert atmosphere at 50°C. The effect of various variables like, concentration of *N,N'*-MBA and VO(acac)<sub>2</sub>, acidity of the medium and the surfactants on the percentage grafting have been investigated. The higher rate of radical formation has been explained due to the coordination of  $\pi$ -electrons of the *N,N'*-MBA with the metal chelate which has assisted in the cleavage of M—O bond to generate radical easily. A plausible mechanism for graft copolymerization involving cyclization of *N,N'*-MBA prior to the grafting has been proposed.

## INTRODUCTION

Although silk fibers have been used for graft copolymerization in presence of different vinyl monomers,<sup>1</sup> the appreciable dyeability effect of *N,N'*-MBA on natural fibers has prompted investigation of grafting of this monomer onto silk fibers in presence of metal chelate, where monomer facilitates the production of free radicals by enhancing the homolytic cleavage of M—O bond. However, Bamford<sup>2</sup> and Otsu et al.<sup>3,4</sup> have reported the polymerization of vinyl monomers by employing different metal acetylacetonates, the use of metal acetylacetonate in graft copolymerization is rather a recent recognition.<sup>5</sup> We have reported the kinetics of homopolymerization of *N,N'*-methylenebisacrylamide in presence of peroxydiphosphate and peroxydisulfate ions in our earlier work.<sup>6,7</sup> The present investigation describes the kinetics and mechanism of graft copolymerization of *N,N'*-methylenebisacrylamide onto mulberry silk fibers.

## EXPERIMENTAL

The chelate vanadylacetylacetonate was prepared by the method reported in inorganic synthesis.<sup>8</sup> *N,N'*-MBA (Koch-Light) was recrystallized from acetone at 40°C and the silk fibers have been purified as reported elsewhere.<sup>9</sup> The percentage grafting was calculated by the equation

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

where  $W_1$ ,  $W_2$  denote the weight of silk and weight of grafted silk, respectively.

## RESULTS AND DISCUSSIONS

The homopolymerization of  $N,N'$ -MBA has usually revealed the formation of gel at low percent polymerization and thereby hindered the formation of linear homopolymer. The results obtained during grafting onto silk have suggested ruling out the possibility of homopolymerization of  $N,N'$ -MBA due to lack of gel at lower concentration of monomer which is an indication of maximum participation of monomer in grafting process. Deviation in rate of grafting and formation of gel at higher concentration of monomer ( $> 10 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ ) have clearly indicated that monomer molecules are participating preferably in homopolymerization rather than grafting onto silk fibers.

## Effect of Vanadylacetylacetonate Complex Concentration

The rate of grafting of  $N,N'$ -MBA onto the silk fibrion has been investigated by varying the concentration of  $\text{VO}(\text{acac})_2$  from 1.0 to  $15.0 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ . The experimental results showed that the graft yield increased up to  $7.48 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$  of  $\text{VO}(\text{acac})_2$  concentration, but thereafter percentage grafting decreased appreciably (Fig. 1). The decomposition of chelates below the reported temperature<sup>10</sup> and the formation of radicals at ease in the present study is assured due to the monomer-assisted decomposition of chelate at 50°C, much below the decomposition temperature. The higher efficiency of  $N,N'$ -MBA in the present case can be assumed due to the presence of two vinyl groups in a single monomer molecule which has high nucleophilic affinity in comparison to other vinyl monomers. The retardation in graft yield at higher concentration on vanadylacetylacetonate ( $> 7.48 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ ) can be assumed to be due to the oxidation of silk radicals and the variation in ratio between monomer molecules and chelates.

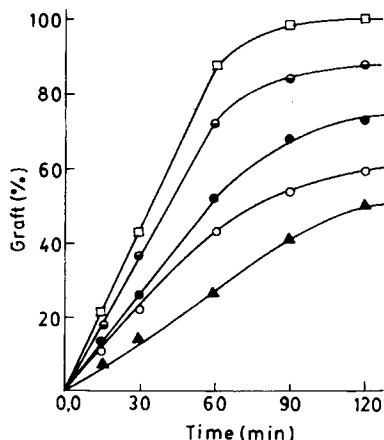
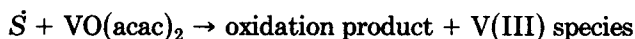


Fig. 1. Effect of  $[\text{VO}(\text{acac})_2]$  on graft yield.  $[N,N'$ -MBA] =  $5.0 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ ,  $[\text{HClO}_4]$  =  $6.0 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ , M:L = 1:100, Temp. 50°C.  $[\text{VO}(\text{acac})_2]$  = (▲)  $1.0 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ , (○)  $2.5 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ , (□)  $7.5 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ , (⊙)  $10.0 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ , (●)  $15.0 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ .

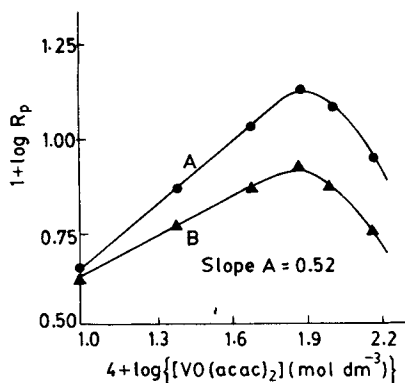
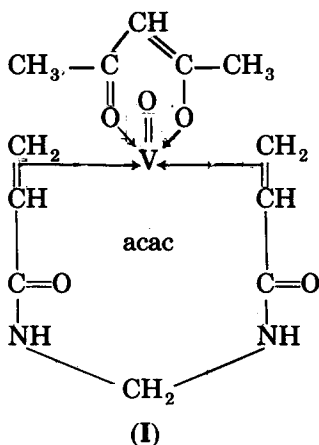


Fig. 2. Double logarithmic plot between  $[VO(acac)_2]$  vs.  $R_p$ : (●) 60 min; (▲) 120 min.

The formation of acetylacetonate radical is assisted by the solvent,<sup>11</sup> which presumably, forms hydrogen bond with the oxygen atom and facilitates the decomposition of  $M-O$  bond. The monomer molecules assist the formation of radicals through its  $\pi$  electrons which coordinate in the present system<sup>12</sup> as follows



However, the formation of this complex is prevented at higher concentration of vanadylacetylacetonate and thereby the retardation in rate is obvious (Fig. 2).

### Effect of Monomer Concentration

The concentration of  $N,N'$ -MBA has been changed from  $2.50-20.0 \times 10^{-3}$  mol  $\cdot$  dm<sup>-3</sup> (Fig. 3) and has been found that at lower concentration of monomer, the rate of grafting does not show deviation (Fig. 4) but does show appreciable deviation at higher concentration (Fig. 3) (beyond  $10.0 \times 10^{-3}$  mol  $\cdot$  dm<sup>-3</sup>). The monomer molecules which are not associated with the silk macroradicals participate actively in formation of cross linkages between side chains grafted onto backbone of silk fibers as well as in the linear homopolymer of  $N,N'$ -MBA with the occurrence of gel which retards the cyclization of

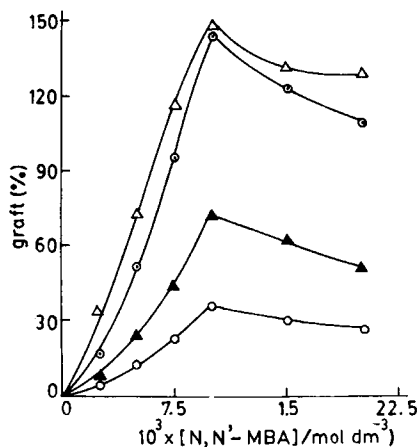


Fig. 3. Graft yield at different time intervals on varying the  $[N,N'-MBA]$ .  $[VO(acac)_2] = 3.3 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ,  $[HClO_4] = 6.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ,  $M:L = 1:100$ , Temp.  $50^\circ\text{C}$ : (○) 15 min; (▲) 30 min; (○) 60 min; (△) 120 min.

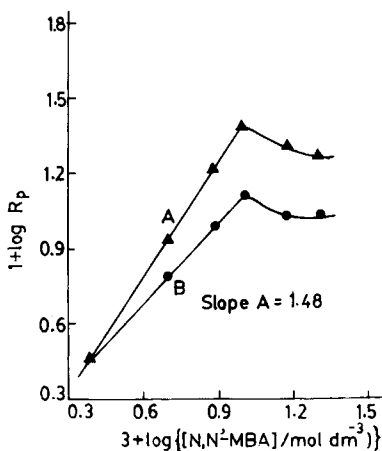


Fig. 4. Double logarithmic plot between  $[N,N'-MBA]$  vs.  $R_p$ : (▲) 60 min; (●) 120 min.

terminal monomer molecules present at the grafted side chains. But at lower concentration of monomer molecules the process of cyclization of monomer molecules has not been hindered, therefore, the regular increase in graft yield is maintained. The radicals formed by the  $N,N'$ -MBA at the silk backbone undergo cyclization process with the formation of a seven-membered ring with simultaneous production of radical at the terminal carbon atom of the second vinyl group of  $N,N'$ -MBA.<sup>13</sup> The process of cyclization which is helpful in linear propagation of chains, is prominent at lower concentration of monomer. Therefore, the graft yield increased at lower concentration of monomer, but as soon as the process of cyclization of terminal monomer molecules is prevented from formation of the pendant seven-membered ring, the process of cross linking is prevalent and the process of propagation of monomer molecules on the chains grafted on silk fibers became diffusion controlled<sup>14</sup> and decreased

the graft yield with the appreciable appearance of gel. The assumption of formation of seven-membered rings in this monomer has been presumed due to the suggestions given by Butler et al.<sup>15a</sup> and Gibbs et al.<sup>15b</sup> for dienes where the propagation has been reported through intra-intermolecular mechanism. The infrared absorption spectroscopy has revealed an absorption band at  $1720\text{ cm}^{-1}$  which is a characteristic of  $>\text{C}=\text{O}$  group present in cyclic rings containing more than six members. The absence of residual mass on dissolving the grafted silk in  $6N\text{ HCl}$  is another indication for discarding the possibility of propagation through intermolecular mechanism, only because, if propagation occurs via this process the second vinyl group participates actively in cross-linking processes which result in forming insoluble cross-linked polymer chains. The retardation in rate in the later period of reaction has been supposed to be due to the retardation in radical reactivity of the terminal group on the grafted side chains.

#### Effect of Temperature

The graft copolymerization has been studied in the temperature range from  $40$  to  $60^\circ\text{C}$ . The results clearly indicate that the graft yield increased on increasing the temperature which can be ascribed due to the greater ease of radical formation and the higher rate of diffusion of monomer molecules to the vicinity of the growing macroradicals. The overall energy of activation has been found to be  $49.8\text{ kJ/mol}$  (Fig. 5).

#### Effect of Additives

The grafting of  $N,N'$ -MBA onto silk fibers has been studied in presence of different additives. The graft yield has been increased on varying the concentration of perchloric acid from  $6.0\text{--}7.5 \times 10^{-3}\text{ mol} \cdot \text{dm}^{-3}$  (Fig. 6), which can be assumed due to the catalyzing effect of acid in decomposition of complex I to form radicals easily. The graft copolymerization has also been studied in presence of anionic surfactant sodiumlaurelsulfate and cationic surfactant, cetyltrimethylammonium bromide (CTAB). It has been observed

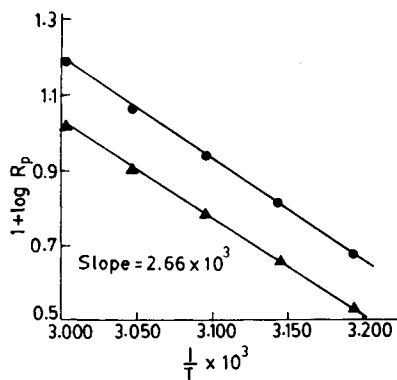


Fig. 5. Arrhenius plot of  $\log R_p$  vs.  $1/T$ , (●) 60 min, (▲) 120 min,  $[N,N'$ -MBA] =  $5.0 \times 10^{-3}\text{ mol} \cdot \text{dm}^{-3}$ ,  $[\text{VO}(\text{acac})_2]$  =  $3.3 \times 10^{-3}\text{ mol} \cdot \text{dm}^{-3}$ ,  $[\text{HClO}_4]$  =  $6.0 \times 10^{-3}\text{ mol} \cdot \text{dm}^{-3}$ , M : L = 1.100.

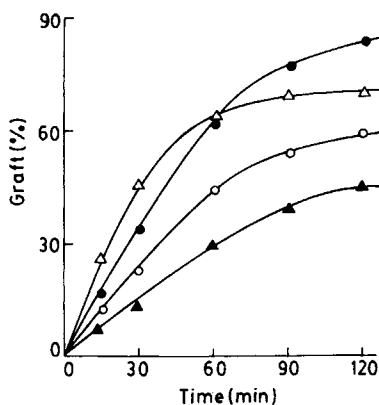


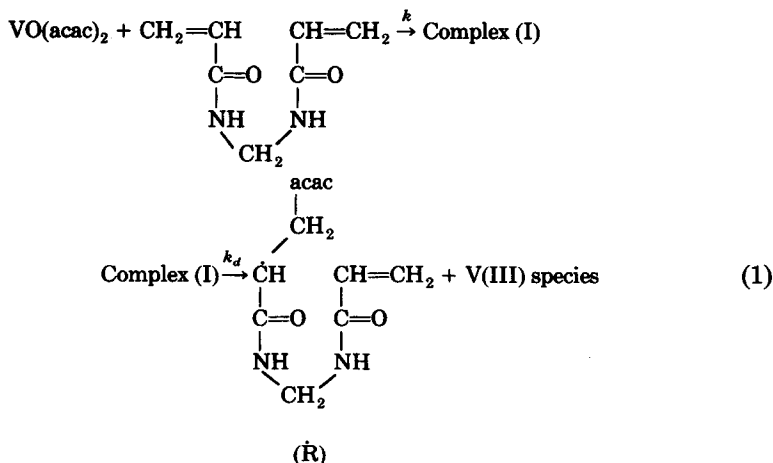
Fig. 6. Effect of additives  $[N,N'$ -MBA] =  $5.0 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ ,  $[\text{VO}(\text{acac})_2]$  =  $3.3 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ ,  $[\text{HClO}_4]$  = (○)  $6.0 \times 10^{-3}$ , (△)  $7.5 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ , M:L = 1:100, Temp. 50°C,  $[\text{NaLs}]$  (●) =  $6.6 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ ,  $[\text{CTAB}]$  (▲) =  $1.3 \times 10^{-3}$  mol  $\cdot$  dm $^{-3}$ .

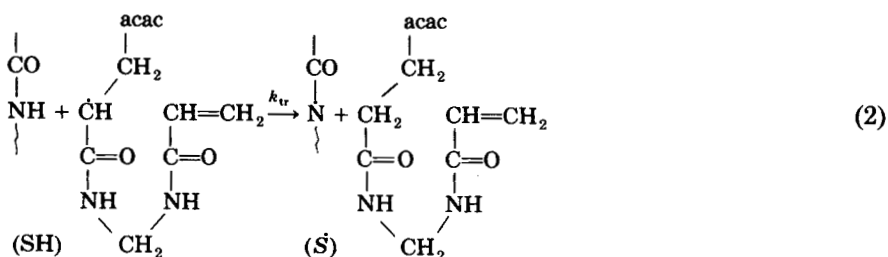
that the graft yield has increased in presence of anionic detergent (Fig. 6). The sulfate ions produced by the sodiumlaurelsulfate, have formed a Gouy-Chapman double layer<sup>16</sup> at the silk fibers, which facilitates the formation of charge transfer complex (I) with the chelate, therefore, enhancing the concentration of free radicals in the silk fiber matrix, which results in high percentage grafting. But, contrary results obtained in presence of CTAB are due to the presence of ammonia ions in the Gouy-Chapman layer, which decrease the tendency of chelate to form charge transfer complex with monomer molecules, thereby retarding the rate of graft copolymerization.

### REACTION MECHANISM

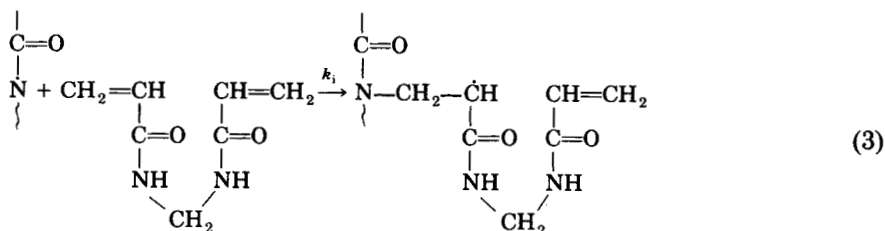
Considering all experimental observations, the following reaction steps have been proposed to explain the results.

Radical formation

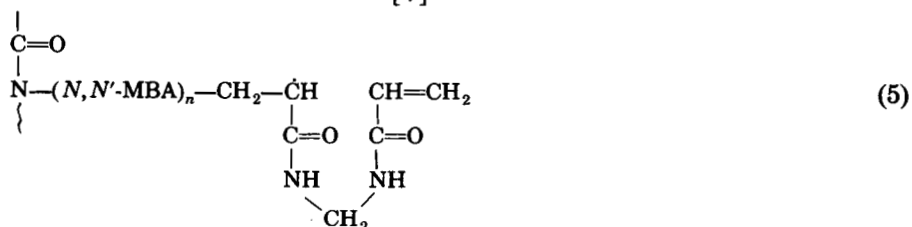
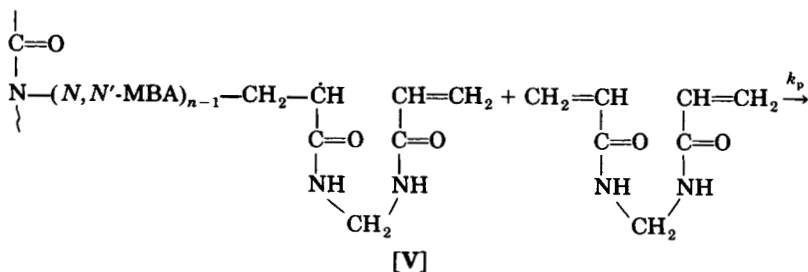
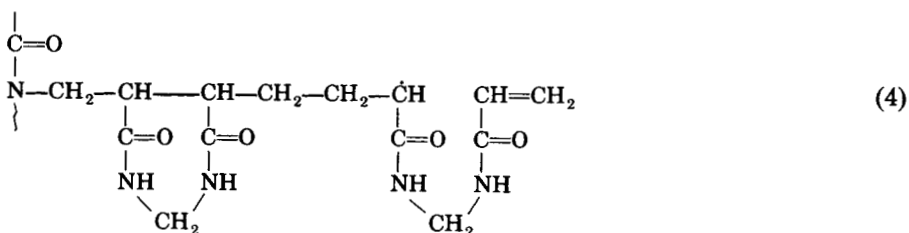
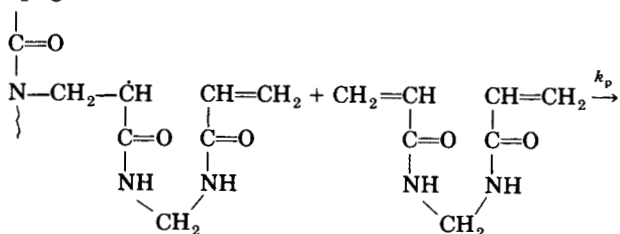


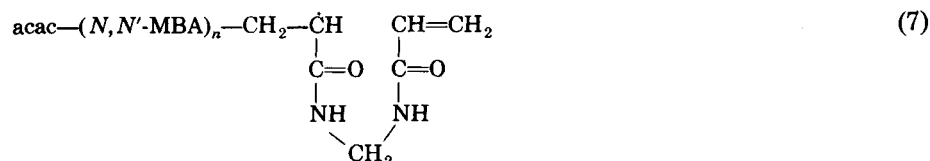
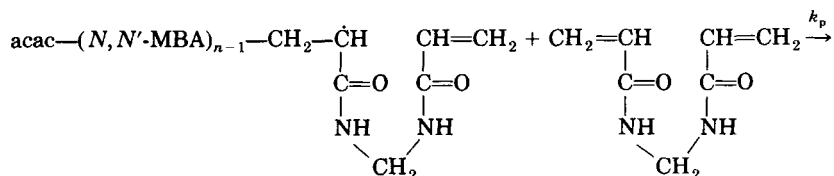
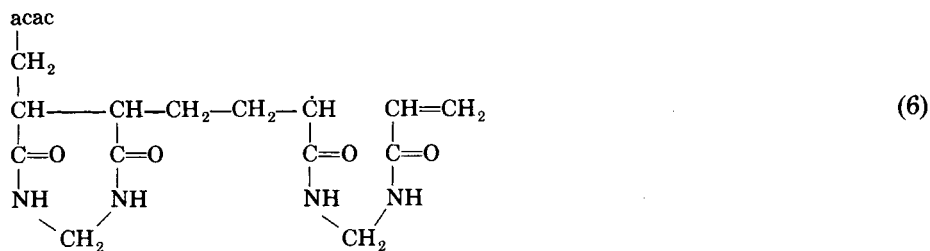
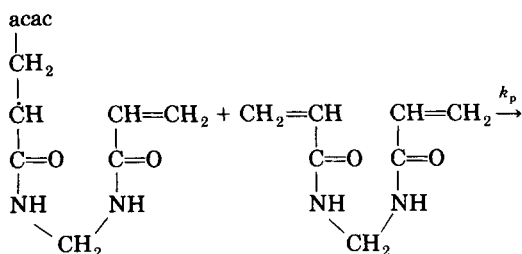


## Initiation

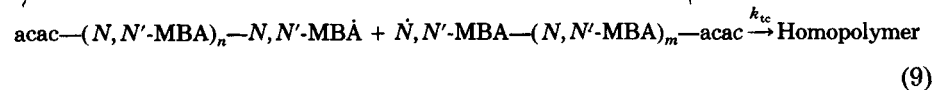
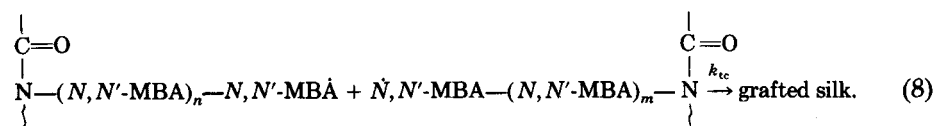


## Propagation





### Termination



Therefore, considering the above steps the rate law for graft copolymerization ( $R_p$ ) has been derived as follows.

$$R_p = k_p \left\{ \frac{k k_d}{2 k_t} \right\} [\text{VO}(\text{acac})_2]^{1/2} [\text{M}]^{3/2} \quad (10)$$

The rate law (10) suitably explains the experimental results. That is, the rate of grafting is dependent to one and a half concentration of  $\text{N}, \text{N}'\text{-MBA}$  (Fig. 4) and square-root dependence to metal chelate concentration (Fig. 2). Therefore, the proposed steps 1-9 may be assumed to be correct.



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