Grafting of *N*,*N*′-Methylenebisacrylamide onto Cellulose Using Co(III)-Acetylacetonate Complex in Aqueous Medium

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Received 29 July 1999; accepted 17 September 1999

ABSTRACT: The grafting of *N*,*N*′-methylenebisacrylamide (*N*,*N*′-MBA) onto cellulose is carried out using the cobaltacetylacetonate complex ($Co(acac)_3$) under nitrogen atmosphere at 40°C. The rate of graft copolymerization has been studied as a function of [*N*,*N*′-MBA], [$Co(acac)_3$], and temperature. The activation energy of grafting is found to be 156.0 k J mol^{-1} within the temperature range of 30–60°C. The effect of perchloric acid, methanol, and surfactants on graft yield has also been studied and results are suitably explained. The higher efficiency of the metal chelate in initiation of graft copolymerization has been assumed due to the coordination of the π electrons of the *N*,*N*′-MBA with the metal chelate, which facilitated the formation of the radicals through homolytic cleavage of metal–oxygen bond of the cobalt acetylacetonate complex. On the basis of the results, a suitable kinetic scheme for graft copolymerization is presented and rate expression is derived. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 906–912, 2000

Key words: *N*,*N*′-methylenebisacrylamide; cellulose; graft copolymerization; cobalt acetylacetonate; kinetics

INTRODUCTION

Cellulose is a naturally occurring polysaccharide and most abundant organic raw material. Graft polymerization has gained importance to modify chemical and physical properties of the cellulose. The graft polymerization is a heterogeneous reaction and strong hydrogen bonds between the cellulose chains hinder grafting of vinyl monomers in absence of the effective swelling agents such as water. Various vinyl monomers[1] have been used to modify the properties of the cellulose by graft copolymerization technique in presence of radiation,[2,3] metallic ions,[4] peroxidisulphate,[5] and peroxides.[6] A lot of work has been carried out using hydrophobic type of monomers such as methylmethacrylate,[7,8] styrene,[9] and acrylonitrile.[10,11] To improve the hydrophilicity,[12,13] and water absorbency,[14] the monomers containing hydrophilic group must be grafted onto cellulose. Grafting of a hydrophilic monomer onto cellulose in the presence of a magnetic field has been reported recently.[15] Hydrophilic monomers such as *N*,*N*′-methylenebisacrylamide possesses an appreciable dyeability effect and grafting of this monomer requires a special attention; otherwise, it easily forms a hydrophilic three-dimensional homopolymeric network, as reported in our previous studies of peroxidiphosphate initiated homopolymerization of this monomer.[16] Cellulose grafted with 4-vinyl pyridine acts as an efficient adsorbent.[17] The grafting on cellulose is normally a diffusion-sensitive process and the extent of grafting is usually low when hydrophobic monomers are used. In such a monomer, the further diffusion of initiator and monomer at the reaction sites is hindered due to the hydrophobic nature of the grafted chains on cellulose. The reported studies

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Journal of Applied Polymer Science, Vol. 76, 906–912 (2000)

have revealed that metal chelates are capable of producing free radical easily[18,19] and well suited for vinyl polymerization at low temperature. The initiation with metal chelate is believed to occur through homolytic fission of the metal oxygen bond as suggested by the Arnet et al.[18] The grafting of the cellulose has been carried out in the aqueous phase as it gets degraded in solvents such as sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_3). These solvents also react with the monomers, catalysts used in the grafting process, and prevent the formation of the graft copolymers. The interesting feature of the *N,N′*-methylenebisacrylamide has prompted us to study the kinetics and mechanism of its grafting on cellulose using the cobaltacetylacetonate complex as an initiator in aqueous medium.

EXPERIMENTAL

The cellulose powder (Loba Chemie, India) was washed with methanol, acetone, and deionized water, and vacuum dried at room temperature. The cobaltacetylacetonate complex ($Co(acac)_3$) was prepared by the reaction of the cobalt carbonate with acetylacetone as given in the literature.[20] The *N,N′*-methylenebisacrylamide (*N,N′*-MBA) was recrystallized from the acetone at 40°C and dried in vacuum over silica gel. For graft copolymerization of *N,N′*-MBA, the purified and dried cellulose (1.0 g) was dispersed in 100 mL distilled water in a three-necked round-bottomed flask fitted with electrically operated stirrer and maintained at the desired temperature. A known amount of the $Co(acac)_3$ complex was added in the flask prior to the addition of the monomer and a continuous supply of nitrogen was maintained throughout the reaction carried out at 40°C. The monomer solution was added dropwise into the reaction flask and the solution was kept under stirring conditions to obtain better results. Finally, the crude grafted cellulose was filtered and washed repeatedly to extract the homopolymer until constant weight was obtained. The ungrafted cellulose was extracted by immersing the samples in cuoxam solution and washing the filtered grafted cellulose residue with distilled water. Cellulose extracted graft copolymer was dried at 60°C under vacuum in a desiccator over phosphorous pentaoxide. The percent grafting (% G), true grafting (% G_T), grafting efficiency (% G_E), homopolymer conversion (% C_H), cellulose conversion (% C_C), and total conversion (% C_T) are calculated as reported elsewhere.[12,21]

RESULTS AND DISCUSSION

The cobaltacetylacetonate complex generates free radicals onto cellulose by hydrogen abstraction when a small amount of complex is taken ($<3.0\times 10^{-4}$ mol dm^{-3}). The *N,N′*-methylenebisacrylamide in the present system does not forms crosslinked homopolymers as no gel formation has been observed. This has clearly indicated that monomer either participates in the formation of linear grafted chains on the cellulose or in the formation of linear water-soluble homopolymer. However, at higher concentrations of monomer ($>5.0 \times 10^{-2}$ mol dm^{-3}), the gel formation was clearly observed. The graft copolymerization has been studied by varying the concentration of reactants, and the experimental data were used to calculate the percentage grafting and other grafting parameters.The rate of grafting (R_P) is calculated with percent yield at 120 min. and used to propose the reaction steps of the graft copolymerization.

Effect of Cobalt Acetylacetonate Complex Concentration

The rate of grafting of *N,N′*-methylenebisacrylamide on the cellulose has been studied by varying the concentration of the cobaltacetylacetonate complex from 2.5 to 25.0×10^{-5} mol dm^{-3} at 40°C. The percentage grafting has increased up to 15.0×10^{-5} mol dm^{-3} of $Co(acac)_3$ concentration, but thereafter no significant increase in the percentage grafting and rate of grafting was observed. In this system, the $Co(acac)_3$ complex is found to be capable of initiating graft copolymerization much below the reported decomposition of this metal chelate,[18] which is due to the presence of two single groups in the *N,N′*-methylenebisacrylamnide monomer that help in decomposition through its π electrons.[22] The homolytic decomposition of the metal–ligand bond of the complex generates free radicals with simultaneous reduction of the valency of the cobalt ion. The generated radicals, $CH_3C\dot{O}CHCOCH_3$ (acac$^{\bullet}$), attach on the cellulose backbone to produce macrocellulosic radicals that ultimately react with the monomer to yield the graft copolymers. The higher concentrations of $Co(acac)_3$ complex beyond 15.0×10^{-5} mol dm^{-3} has shown a retarding effect on the

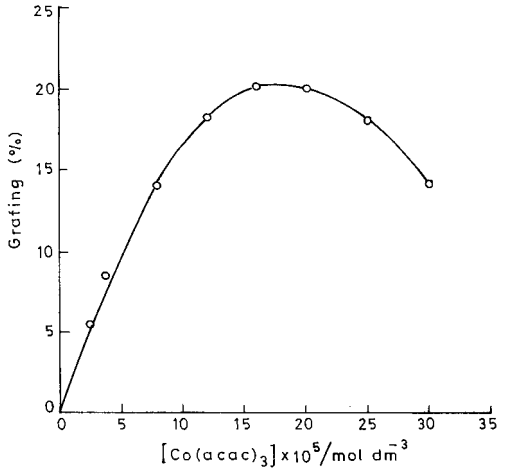


Figure 1 Effect of [co(acac)$_3$] on percent grafting, [*N*,*N*′-MBA] = 6.6 × 10^{-2} mol dm^{-3}, [$HClO_4$] = 8.0 × 10^{-3} mol dm^{-3}, M:L = 1: 100, temperature = 40°C.

percent grafting and overall rate of grafting (Figs. 1 and 2), which is due to the oxidizing effect of the metal chelate on macroradicals. The retardation may also occur due to the premature termination of the growing graft chains by the excess primary radicals (acac$^{\cdot}$) generated at higher concentrations of the cobalt acetylacetonate complex. The log–log plot (Fig. 2) of the rate of graft copolymerization versus concentration of the cobaltacetylacetonate has shown half-order dependence on the concentration of the cobaltacetylacetonate complex. The effect of concentration variation of the cobaltacetylacetonate on grafting parameters is shown in Table I, which clearly shows maximum efficiency (G_E) of grafting upto 15.0 × 10^{-5} mol dm^{-3} of the cobaltacetylacetonate.

Table I Effect of [Co(III)-Acetylacetonate] on Grafting Parameters[a]

[Co(acac)$_3$] × 10^5 mol dm^{-3}	G_T (%)	G_E (%)	C_H (%)	C_T (%)	C_C (%)
2.5	369	59.0	3.8	9.2	22.5
4.0	372	63.6	4.8	13.3	23.0
8.0	387	66.6	6.9	20.7	23.4
12.0	393	68.4	8.3	26.3	24.0
15.0	397	70.4	8.4	28.3	24.2
20.0	395	69.3	7.8	25.0	24.1
25.0	391	67.7	7.8	24.1	24.0
30.0	386	66.1	6.6	19.6	23.5

[a] [Monomer] = 6.6 × 10^{-2} mol dm^{-3}, [$HClO_4$] = 8.0 × 10^{-2} mol dm^{-3}, M:L = 1:100, temperature = 40°C.

Effect of Monomer Concentration

The graft copolymenization of *N*,*N*′-methylenebisacrylamide on to cellulose has been studied by varying monomer concentration from 2.0 to 20.0 × 10^{-2} mol dm^{-3} at constant concentration of the metal complex at 40°C in the presence of the nitrogen atmosphere (Fig. 3). The rate of grafting (R_P) has increased on increasing the concentration of the *N*,*N*′-methylenebisacrylamide (Fig. 4), which might be due to (a) the complexation of the monomer with cellulose in which monomer molecules are essentially aligned on the surface of the cellulose matrix to increase the grafting rate. The extent of these cellulose–monomer interactions

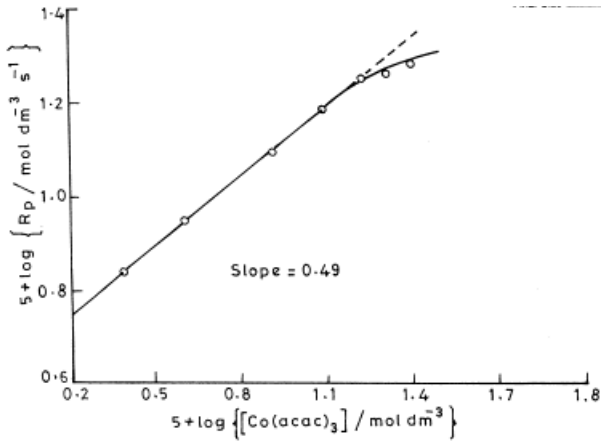


Figure 2 Double logarithmic plot between [Co(acac)$_3$] versus, R_p, [*N*,*N*′-MBA] = 6.6 × 10^{-2} mol dm^{-3}, [$HClO_4$] = 8.0 × 10^{-3} mol dm^{-3}, M:L = 1:100, temperture = 40°C, time = 120 min.

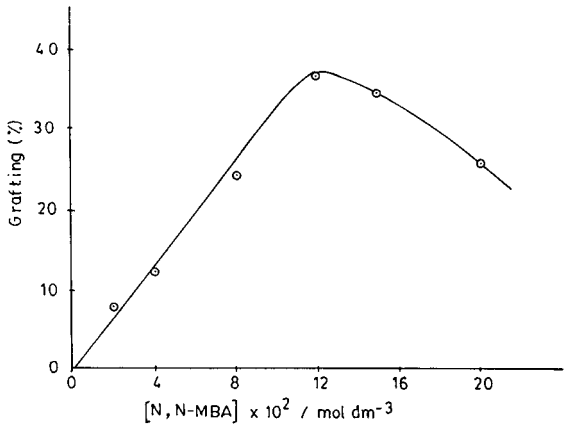


Figure 3 Effect of [*N*,*N*′-MBA] on percent grafting, [Co(acac)$_3$] = 12.0 × 10^{-5} mol dm^{-3}, [$HClO_4$] = 8.0 × 10^{-3} mol dm^{-3}, M:L = 1:100, temperature = 40°C.

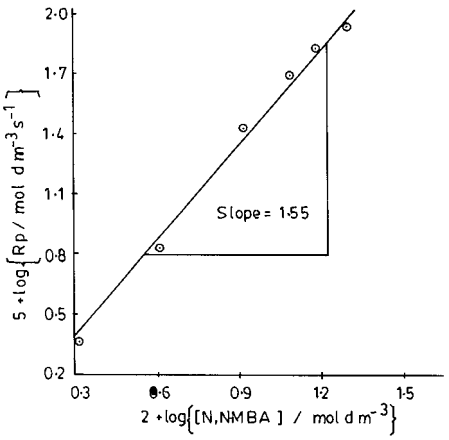


Figure 4 Double logarithmic plot between [*N,N′*-MBA] versus R_p, $[Co(acac)_3] = 12.0 \times 10^{-5}$ mol dm^{-3}, $[HClO_4] = 8.0 \times 10^{-3}$ mol dm^{-3}, M:L = 1:100, temperature = 40°C, time = 120 min.

ultimately depends upon the degree of the crystallinity of the cellulose as considered by the Gaylord et al.[23] (b) It also may be due to gel effect, i.e., the increase in viscosity of the medium owing to the solubility of the linear homopolymer of *N,N′*-methylenebisacrylamide in the solution of the *N,N′*-methylenebisacrylamide.

The gel effect causes the swelling of the cellulose, which facilitates the diffusion of the monomer molecules to the growing chains and other active sites on the cellulose to enhance the rate and percent of grafting. At higher concentrations of the monomer (>12.0 $\times$ 10^{-2} mol dm^{-3}), the solution lost the fluidity due to the formation of the semisolid transparent crosslinked gel, which clearly indicated that at and beyond 12.0 $\times$ 10^{-2} mol dm^{-3} of *N,N′*-methylenebisacrylamide, the formation of the crosslinked homopolymer is predominant over the propagation of growing chain by intra–intermolecular cyclization mechanism forming a seven-membered ring with simultaneous production of the radical at the terminal carbon atom of the second vinyl group of the added *N,N′*-methylenebisacrylamide.[24] This crosslinked state of the homopolymer significantly checks the diffusion of the monomer molecules[25] to the reactive sites on cellulose macroradicals; thus no further increase in the percent grafting and rate of grafting was observed. At lower concentrations of *N,N′*-methylenebisacrylamide, the propagation of the macroradical takes place through the intra–intermolecular mechanism as prevalent in diene monomers.[26,27] The decrease in the percent grafting at higher concentrations of *N,N′*-methylenebisacrylamide (>12.0 $\times$ 10^{-2} mol dm^{-3}) may also be assumed due to the participation of the monomer molecules in forming a three-dimensional network in the cellulosic chains, which ultimately reduces the diffusion of the monomer molecules for grafting on cellulose as explained by Liveshits[28] during the grafting of polyacrylonitrile on cellulose. The formation of the crosslinked cellulose was experimentally approved by putting the grafted cellulose in 72% sulfuric acid solution for about 6 h to hydrolyze the grafted chains, but no clear solution was obtained with the sulfuric acid except a swollen mass of the grafted cellulose. This swollen mass was then washed with distilled water and dried in vacuum, and its weight was compared with the original weight taken to digest in the solution of the sulfuric acid. The final weight was found to be almost equal to the original weight, which clearly indicated that at higher concentrations of the monomer, the *N,N′*-methylenebisacrylamide participated exclusively in the formation of the crosslinked net work rather forming a linear grafts as observed at low concentration of the *N,N′*-methylenebisacrylamide (<12.0 $\times$ 10^{-2} mol dm^{-3}). The experimental data on monomer concentration variation were further used to calculate the other grafting parameters, which are given in Table II. It is interesting to note that percent grafting and true grafting have shown an increasing trend (Fig. 3) on increasing the concentration of the monomer, hence the rate of grafting has also increased. The efficiency of grafting (G_E) and total conversion (C_T) have shown a decreasing trend on increasing the concentration of the monomer. This decrease in the efficiency of the grafting has indicated that homopolymer formation is favored over grafting because of the difficulties for the diffusion of the monomer to form a

Table II Effect of [Monomer] on Grafting Parameters[a]

[M] $\times$ 10^2 mol dm^{-3}	G_T (%)	G_E (%)	C_H (%)	C_T (%)	C_C (%)
2.0	414	89	3.2	29.0	21.0
4.0	421	82	4.2	23.5	21.5
8.0	444	72	8.1	26.8	22.8
12.0	486	62	12.2	31.5	23.2
15.0	478	53	13.5	27.5	23.0
20.0	455	38	14.5	22.3	22.5

[a] $[Co(acac)_3] = 12.0 \times 10^{-5}$ mol dm^{-3}, $[HClO_4] = 8.0 \times 10^{-2}$ mol dm^{-3}, M:L = 1:100, temperature = 40°C.

cellulose monomer complex to facilitate the propagation reaction of graft copolymerization. The increasing trend of the homopolymer conversion (C_H) also provided a support for the decreasing trend in the grafting efficiency. The cellulose conversion has shown an increasing trend on increasing the monomer concentration upto 12 $\times 10^{-2}$ mol dm^{-3}, but showed a decreasing trend on further increase in the concentration of the monomer, which is due to the overall decrease in the grafting yield beyond this concentration of the monomer, as clear from the data given the Figure 3.

Effect of Temperature

The grafting of *N,N′*-methylenebisacrylamide onto cellulose has been studied in the temperature range of 30–60°C. Variation in the rate of grafting as a function of temperature is shown in Figure 5. The rate of grafting (R_P) has increased on increasing the temperature, which suggests that the rate of grafting is diffusion controlled; thus it has shown a positive effect of the temperature on graft copolymerization. The overall energy of activation has been found to be 156.0 kJ mol^{-1}, which is comparatively low with cobalt (III) initiated grafting on cellulose by Kurlynakina et al.[29] The monomer helps in the production of the radicals at low energy of the activation due to facile decomposition of the initiator by π electrons of the studied monomer.[22]

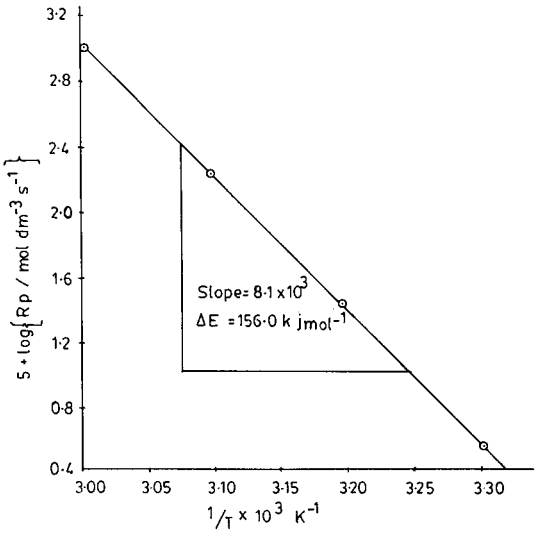


Figure 5 Arrhenius plot between log R_p versus 1/*T*, [*N,N′*-MBA] = 8.0 $\times$ 10^{-12} mol dm^{-3}, [Co (acac)$_3$] = 12.0 $\times$ 10^{-5} mol dm^{-3}, [$HClO_4$] = 8.0 $\times$ 10^{-3} mol dm^{-3}, M:L = 1:100, time = 120 min.

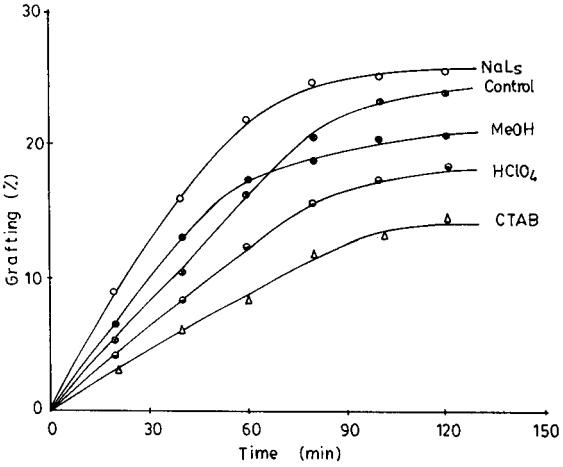


Figure 6 Effect of additives, [*N,N′*-MBA] = 8.0 $\times$ 10^{-12} mol dm^{-3}, [Co(acac)$_3$] = 12.0 $\times$ 10^{-3} mol dm^{-3}, [$HClO_4$] = 4.0 $\times$ x10^{-3} mol dm^{-3} (◒), [$HClO_4$] = 8.0 $\times 10^{-3}$ mol dm^{-3} (⊗), [NaLs] = 7.0 $\times$ 10^{-3} mol dm^{-3} (O), [CTAB] = 1.5 $\times$ 10^{-3} mol dm^{-3} (△), [MeOH] = 5% v/v (○). M:L =1:100, temperature = 40°C.

Effect of Additives

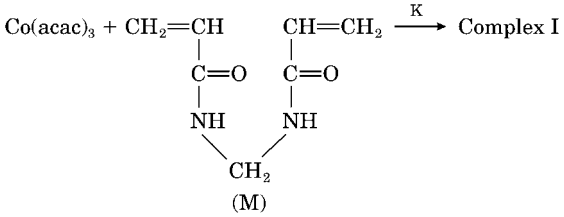
The grafting of *N,N′*-methylenebisacrylamide onto cellulose also has been studied in the presence of the additives, and the effect of the additives are shown in Figure 6. The percent grafting has increased on increasing the concentration of the perchloric acid from 4.0 to 8.0 $\times$ 10^{-3} mol dm^{-3}, which facilitated the formation of radicals (acac$^{\cdot}$) by the dissociation of the monomer–chelate complex I. The higher rate of the graft yield on higher concentrations of the perchloric acid may be assumed due to the increase in the cryastallinity in the cellulose, where the rate of termination is decreased. The addition of sodium laural sulphate (NaLs) has shown a positive effect on the graft yield, which is due to the formation of a layer of lauryl sulphate anion over the surface of the cellulose that enhances the concentration of the monomer–chelate complex I and free monomer molecules nearly to the surface of the cellulose to facilitate the propagation reaction at a faster rate. The addition of cetyltrimethylammoniumbromide (CTAB) has shown a decreasing effect on graft field in which the cationic part of the surfactant forms a layer over the surface of the cellulose and prevents the accumulation of monomer–chelate complex I and the monomer molecules due to the repelling effect. These results have clearly indicated the existence of the Gouy and Chapman type of double layer at the surface

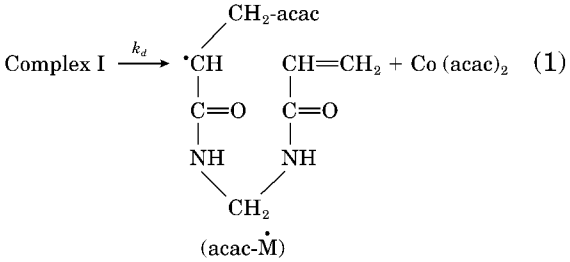
of the cellulose in which adsorbed layer is formed by the anionic or cationic parts of the added surfactants (NaLs and CTAB), and this adsorbed layer of the ions controls the concentration of the other species of the reaction mixture in the diffused portion of the double layer. The overall rate and graft yields are controlled by the time average potential of the electrical double layer.[30] The rate of grafting was also studied in presence of methanol (Fig. 6), which resulted in a decrease of the maximum graft yield. However, in the initial part of the reaction there seemed to be an increasing trend on graft yield, but as reaction proceeded further, a retarding effect was observed. The initial effect was due to the dielectric effect of the methanol, which facilitates the coordination of monomer molecule with the metal chelate to enhance the rate of formation of free radicals from the metal chelate, but ultimately these alcoholic molecules produce less active radicals by chain transfer reaction with the growing macroradicals. Consequently, the overall rate and yield of grafting are retarded. The addition of alcohol also contracts the cellulosic molecules and thereby prevents the propagation of the cellulose radicals due to the hindered access of the monomeric units to the active sites at the cellulosic backbone.

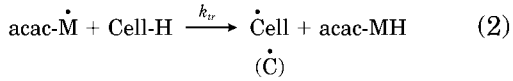
Reaction Mechanism

Considering the experimental observations, the following reaction steps have been proposed to derive a rate expression for the graft copolymerization.

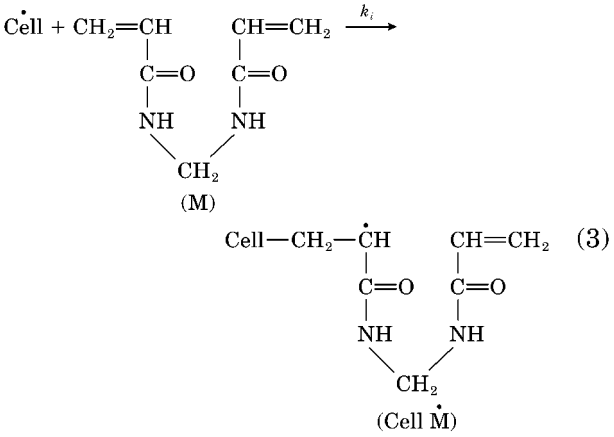
Radical Formation





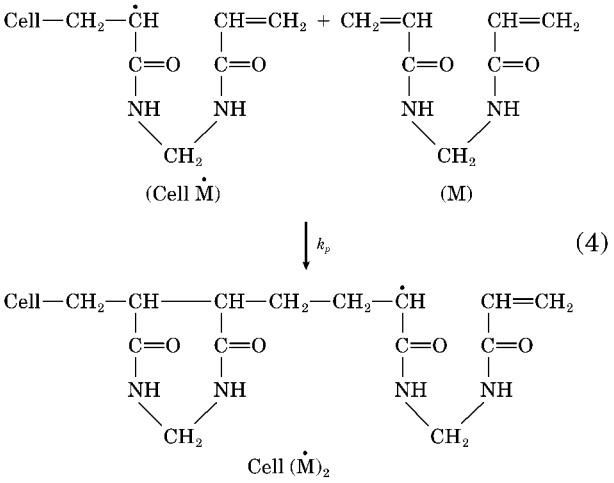


Initiation



Propagation

The propagation of the chain (cell-Ṁ) takes place through intra–intermolecular cyclization mechanism[18] and forming radical at the end of the second monomeric unit.



$$\text{Cell}\ (\dot{\text{M}})_{n-1} + \text{M} \xrightarrow{k_p} \text{Cell-}(\dot{\text{M}})_n \qquad (5)$$

Simultaneously, a small amount of homopolymer is also formed as

$$\text{acac} - (\dot{\text{M}}) + \text{M} \xrightarrow{k_p} \text{acac} - (\dot{\text{M}})_2 \qquad (6)$$

$$\text{acac} - (\dot{\text{M}})_{n-1} + \text{M} \xrightarrow{k_p} \text{acac} - (\dot{\text{M}})_n \qquad (7)$$

Termination

$$\text{Cell} - (\text{M})_n - \dot{\text{M}} + \dot{\text{M}} - (\text{M})_m - \text{Cell} \xrightarrow{k_{tc}}$$

Grafted Cellulose (8)

And termination for homopolymers

$$\text{acac} - (\text{M})_n - \dot{\text{M}} + \dot{\text{M}} - (\text{M})_m - \text{acac} \xrightarrow{k_{tc}}$$

Homopolymer (9)

Considering the steps involved in graft copolymerization, the following rate expression for the overall rate of graft copolymerization (R_p) is derived.

$$R_P = k_P\left\{\frac{Kk_ik_d}{2k_{tc}}\right\}^{1/2}[\text{M}]^{3/2}[\text{cell} - \text{H}]^{1/2}[\text{Co(acac)}_3]^{1/2} \quad (10)$$

where K, k_d, k_i, k_p, and k_{tc} are the equilibrium constant of complex formation between initiator and the monomer, rate constant of decomposition of the complex, rate constant of initiation, rate constant of propagation,and rate constant of termination through coupling respectively.

The derived rate law suitably explains the experimental results, i.e., the rate of grafting is dependent to one and a half concentrations of the monomer (Fig. 4) and square root dependence on the concentration of the cobaltacetylacetonate complex (Fig. 2). This agreement of the results supports the validity of the steps proposed in the mechanism of the graft copolymerization.

CONCLUSION

Cobaltacetylacetonate complex is found to be an useful initiator for the graft copolymerization of the *N*,*N*′-methylenebisacrylamide onto cellulose at low temperature without forming a crosslinked homopolymer of *N*,*N*′-methylenebisacrylamide under the studied experimental conditions.

One of the authors, Sujata Sahoo, is thankful to UGC, New Delhi, for the award of a fellowship. The authors also are thankful to the University of Roorkee for providing facilities to complete this work.

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