Co(III) Acetylacetonate-Complex-Initiated Grafting of *N*-Vinyl Pyrrolidone on Cellulose in Aqueous Media

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ABSTRACT: The graft copolymerization of *N*-vinyl pyrrolidone (*N*-VP) onto cellulose was carried out with a cobalt acetylacetonate complex $Co(acac)_3$ as an initiator under a nitrogen atmosphere at 50 ± 0.1°C. The graft yield percentage (%*G*) obtained as a function of the concentrations of *N*-VP and $Co(acac)_3$ and the temperature was used to calculate various other grafting parameters and the grafting rate dependence on the concentrations of monomer, $Co(acac)_3$ and reaction temperature. The energy of activation (ΔE_a) for the grafting of *N*-VP onto cellulose was 22.7 kJ/mol within 40–60°C. The molecular weights of the grafted chains and homopolymers were determined viscometrically with a Ubbelohde-type viscometer. Graft yield (%*G*) in the presence of various additives such as sodium lauryl sulfate, cetyltrimethylammonium bromide, and methanol was studied, and the results are suitably explained. On the basis of the experimental results, a reaction scheme for graft copolymerization is proposed, and a kinetic rate expression is presented. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2286–2296, 2001

Key words: *N*-vinyl pyrrolidone; cobalt acetylacetonate; grafting; copolymerization; cellulose

INTRODUCTION

The grafting of synthetic polymers onto cellulose is an effective technique for modifying its properties. Grafting may be accomplished by the reacting of preformed polymers onto cellulose, but the rate and extent of grafting are usually very low because of hindered diffusion of the preformed polymers at the surface of the cellulose; hence, grafting through the polymerization of monomers at reactive sites on cellulose is highly preferred. Grafting on cellulose is a heterogeneous reaction; therefore, the physical structure[1] and state[2] of the cellulose also play an important role in the extent of grafting. The grafting yield (%*G*) decreases with increasing crystallinity and hydrogen bonding between the cellulose chains. The extent of the grafting of vinyl monomers on cellulose in the presence of appropriate solvents such as water has been found to be considerably high in comparison with solvents with less swelling power. To diversify the properties of cellulose as an adsorbent for the noble metal ions, Bojanic et al.[3] grafted 4-vinyl pyridine. To increase the hydrophilicity of cellulose, monomers containing hydrophilic groups have been grafted onto cellulose,[4,5] but the grafting of *N*-vinyl pyrrolidone (*N*-VP) on cellulose has hardly been reported in the literature.[6,7] Recently, it was reported that poly(vinyl pyrrolidone)-grafted silica could significantly alter the adsorption of water-soluble polymers.[8] The radiation grafting of *N*-VP on poly(tetrafluoroethylene) and poly(tetrafluoroethylene-hexafluropropylene) was carried out in benzene,

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and the yield was very low.[9] The free radical polymerization of *N*-VP in nonaqueous solvents generally leads to the formation of oligomers. The radiation-induced grafting of *N*-VP on poly(vinylidine fluoride) film in an aqueous medium was reported,[10] but no details about the various grafting parameters were given. Poly(vinyl pyrrolidone) is a nontoxic, hydrophilic, and biocompatible polymer, and its properties have been the focus of numerous investigations involving surface grafting.

Poly(vinyl pyrrolidone)-surface-grafted synthetic fibers[11] and liquid fractionation membranes[12,13] have shown greatly enhanced hydrophilicity. Poly(vinyl pyrrolidone)-grafted silica[14] and polystyrene resins[15] have been used as chromatographic supports for virus purification[14] and size exclusion chromatography.[15] Biocompatible rubber hydrogels have been prepared with poly(vinyl pyrrolidone) grafting.[16] Cellulose modified with biocompatible polymers such as poly(vinyl pyrrolidone) has been shown to have suitable applications for various pharmacological activities,[17] such as sustained therapy, slow drug release, prolonged activity, and decreased drug metabolism and excretion. Cellulose grafted with various types of vinyl monomers has also been shown to have potential applications as a temperature-responsive material.[18] During graft copolymerization, the radical formation of the initiation reaction can occur either on the cellulose backbone or on the monomer used for grafting. The radical formation on the monomer results in homopolymerization; hence, initiators capable of forming radicals at the cellulose backbone are usually preferred. Depending on the type of monomers, the graft copolymerization on cellulose has been initiated with radiation,[19] a magnetic field,[20] metal ions,[21] and metal chelates.[5] Among the various methods of initiation, the metal chelates have been well suited for the grafting of vinyl monomers. Initiation with metal chelates occurs through radicals formed by the homolytic fission of the metal–oxygen bond.[22] In this work, the graft copolymerization of *N*-VP on cellulose was studied with a cobalt acetylacetonate complex $Co(acac)_3$ in aqueous media.

EXPERIMENTAL

Chemicals

The cellulose powder (Loba Chemie, Mumbai, India, number-average molecular weight (M_n) = 2.3 $\times$ 10^4) was washed with methanol, acetone, and deionized water and was vacuum-dried over phosphorous pentoxide at room temperature. The $Co(acac)_3$ complex was prepared by the reaction of cobalt carbonate with acetylacetone at 40°C as reported in the literature.[23] *N*-VP (Fluka, Switzerland) was distilled under reduced pressure to remove the mixed potassium hydroxide inhibitor and was dried with calcium hydride. The fraction with a boiling point of 60°C was used for the radical polymerization. The nitrogen was purified by passage through an alkaline pyrogallol solution and concentrated sulfuric acid before it was used in graft copolymerization.

Graft Copolymerization

A purified and vacuum-dried cellulose sample (1.0 g) was dispersed in 100 mL of distilled water and placed in a three-necked, round-bottom flask fitted with an electrically operated stirrer maintained at 50 $\pm$ 0.1°C with a thermostat. A calculated amount of $Co(acac)_3$ was added to the flask before the addition of the monomer and was purged with nitrogen for about 30 min. Finally, a calculated volume of the monomer was added dropwise into the reaction flask, and the bubbling of nitrogen in the reaction mixture was maintained until the end of reaction. The reaction was finally stopped with the addition of a 5.0% solution (w/v) of hydroquinone. Finally, the crude-grafted cellulose was filtered and washed with hot and then cold water to extract the homopolymer and the monomer until a constant weight was obtained.

Conversion Measurement

The total conversion of the monomer to the polymer was determined by the absorbance being recorded at λ = 196 nm for the carbonyl group (ϵ = 3.64 $\times$ 10^{-6} cm^2/mol) and λ = 233 nm for the vinyl group (ϵ = 1.23 $\times$ 10^{-5} cm^2/mol) with an ultraviolet–visible spectrophotometer (Shimadzu-1601 PC, Japan) and with the following equation:

$$\text{Conversion} = 1 - \frac{A_t(233\text{ nm})}{A_t(196\text{ nm})} \Big/ \frac{A_0(233\text{ nm})}{A_0(196\text{ nm})} \quad (1)$$

where A_0 and A_t are the absorbances at reaction time t = 0 and time t, respectively. The amount of homopolymer formed was determined by the filtrate being poured into excess methanol. The pre-

cipitated homopolymer was vacuum-dried until it reached a constant weight. Thus, from the percentage conversion and the amount of the homopolymer obtained, the percent yield (%G) and the homopolymer formed was determined.

Extraction of Ungrafted Cellulose

To obtain the percentage of true grafting (%G_T), the ungrafted cellulose was extracted by the graft-polymerized cellulose being immersed in a cuoxam solution containing 1.2% $NaHSO_3$.[24] After 8 h, the filtered residue was washed with water and vacuum-dried until it reached a constant weight.

Degrafting of Poly(vinyl pyrrolidone):

To separate the grafted poly(vinyl pyrrolidone) from the surface of the cellulose, the cellulose-extracted samples were acid-hydrolyzed as reported elsewhere.[25] The separated grafted chains of poly(vinyl pyrrolidone) were subsequently characterized for molecular weight. The extracted chains and the homopolymers were water-soluble; hence, the probability of the formation of crosslinks in the polymer chains was discarded.

Molecular Weight of the Poly(vinyl pyrrolidone)

The molecular weights of the homopolymers and grafted polymers were determined viscometrically in a sodium acetate solution with a Ubbelohde-type viscometer with the following equation:[26]

$$[\eta]_{25^\circ C} = 8.86 \times 10^{-5} M_v^{0.74}$$

where $[\eta]$ is the intrinsic viscosity and M_v is viscometric molecular weight.

RESULTS AND DISCUSSION

N-VP usually forms oligomers in ionic polymerization and in organic solvents; hence, the grafting of this monomer onto cellulose in organic solvents or in the presence of ionic initiators would lead to the formation of grafted chains with low molecular weights. In this investigation, the free radicals were formed because of the interaction of $Co(acac)_3$ with cellulose. The formation of active sites on the cellulose backbone suppressed the formation of homopolymers, which are not usually observed with the initiators, which generate the free radicals at the monomers. To analyze the effect of experimental variation on grafting, the grafting parameters were determined at different concentrations of *N*-VP and $Co(acac)_3$ at a constant weight of cellulose. The rate of grafting (R_p) at 120 min was monitored as a function of monomer and initiator concentrations. The kinetic parameters were used to propose the reaction steps of the graft copolymerization of *N*-VP onto cellulose.

Effects of the Concentration of *N*-VP

The graft copolymerization of *N*-VP onto cellulose was studied at 50 ± 0.1°C with $Co(acac)_3$ as an initiator and with a variation of monomer concentration of 5.0 to 40.0 $\times$ 10^{-3} mol dm^{-3}. The apparent percent yield (%G) showed an increasing trend up to 30.0 $\times$ 10^{-3} mol dm^{-3} *N*-VP (Fig. 1) and decreased sharply beyond this point. This initial increase in percent graft yield (%G) may be assumed to be caused by the high rate of diffusion of *N*-VP from the bulk to the surface of the cellulose, where it is aligned appropriately to facilitate percent graft yield (%G). The initial increase in grafting could also be assumed to be caused by the gel effect of the monomer, which causes the swelling[27] of the cellulose and facilitates the diffusion of monomer molecules to the growing chains and other active sites on the cellulose. The decreasing trend in grafting on increasing *N*-VP beyond 30.0 $\times$ 10^{-3} mol dm^{-3} may be caused by the increase in the viscosity[28] of the medium because of a large number of monomer molecules and homopolymer formed in the reaction mixture, which ultimately decreases the rate of diffusion of the monomer molecules from the bulk to the active sites at cellulose and also causes the deswelling of the cellulose chains. The grafting parameters shown in Table I indicated that the percent graft conversion (%C_g) increased up to a monomer concentration of 30.0 $\times$ 10^{-3} mol dm^{-3}, but the increase in the homopolymer formation continued beyond 30.0 $\times$ 10^{-3} mol dm^{-3}. This indicates that beyond a monomer concentration of 30.0 $\times$ 10^{-3} mol dm^{-3}, *N*-VP started participating more actively in the formation of the homopolymer than in the formation of the graft copolymer. The decreasing trend in grafting efficiency (%G_E) and cellulose conversion (%C_c) further supports the decrease in the participation of monomer molecules in the formation of grafted chains beyond a monomer concentration of 30.0 $\times$ 10^{-3} mol dm^{-3}. The number of branches grafted per mole of cellulose (N_g) increased with the increase of the monomer con-

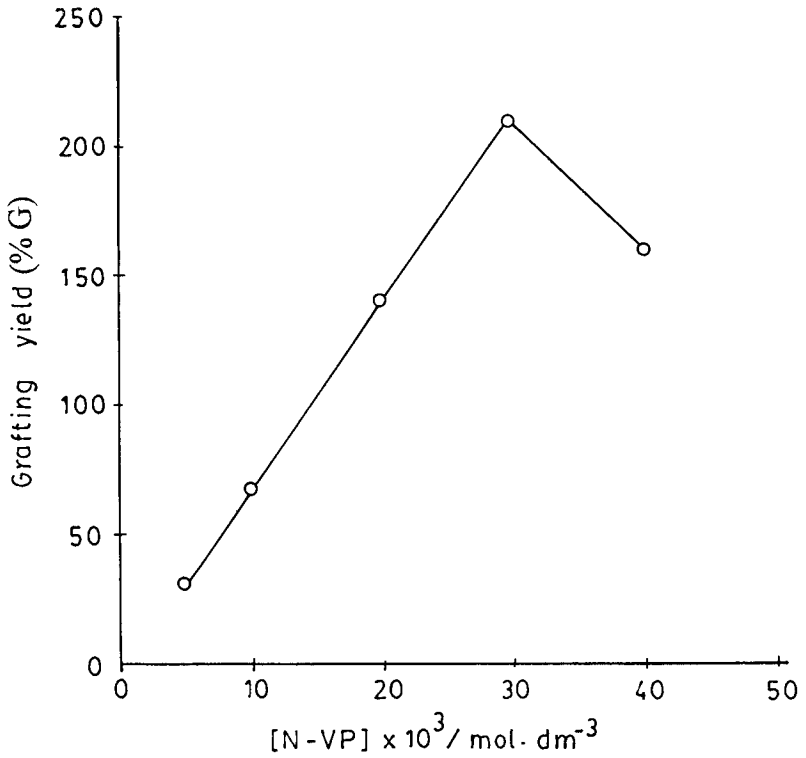

Figure 1 Graft yield (%*G*) as a function of [*N*-VP]. $[Co(acac)_3] = 10.0 \times 10^{-5}$ mol dm^{-3}; $[HClO_4] = 2.5 \times 10^{-3}$ mol dm^{-3}; [Cellulose] = 1.0 g; $T = 50°C$; $t = 120$ min.

centration (Table I). The almost constant molecular weight of the grafted chains beyond a monomer concentration of 30.0×10^{-3} mol dm^{-3} (Table I) further supports the idea that monomer molecules, after a certain concentration, start participating more actively in the growth of the homopolymer chains than in the growth of the grafted chains on cellulose. The R_p was obtained from the percentage conversion at 2 h and used to determine the order of reaction with respect to monomer concentration. The log–log plot (Fig. 2) of R_p versus monomer concentration clearly indicates that the R_p was directly proportional to the concentration of the monomer.

Table I Effect of Monomer Concentration on Grafting Parameters at 50°C

	[Monomer] $\times 10^3$ mol dm^{-3}				
	5.0	10.0	20.0	30.0	40.0
True grafting ($\%G_T$)	464.00	611.00	896.00	1140.00	1081.00
Total conversion ($\%C_t$)	62.90	69.80	72.52	74.05	48.42
Graft conversion ($\%C_g$)	54.00	60.00	62.60	63.06	36.03
Homopolymer conversion ($\%C_{hp}$)	9.00	9.50	10.00	11.00	12.50
Cellulose conversion ($\%C_c$)	23.00	23.50	24.00	25.00	22.00
Grafting efficiency ($\%G_E$)	85.83	86.45	86.87	87.50	74.41
Grafting frequency ($\%G_F$)	0.46	0.92	1.42	1.68	1.44
Grafted chains per cellulose unit (N_g) $\times 10^6$	4.50	9.25	14.60	18.26	13.79
Homopolymer chains (N_g) $\times 10^6$	1.40	2.20	2.80	4.30	5.20
Mol. wt. ($\overline{M}_n$) of grafted chains (G_p) $\times 10^{-3}$	65.00	72.00	95.00	115.00	116.00
Mol. wt. ($\overline{M}_n$) of homopolymer (H_p) $\times 10^{-3}$	35.00	48.00	79.00	85.00	105.00

$[Co(acac)_3] = 10 \times 10^{-5}$ mol dm^{-3}, $[HClO_4] = 2.5 \times 10^{-3}$ mol dm^{-3}, [Cellulose] = 1.0 g, $t = 120$ min.

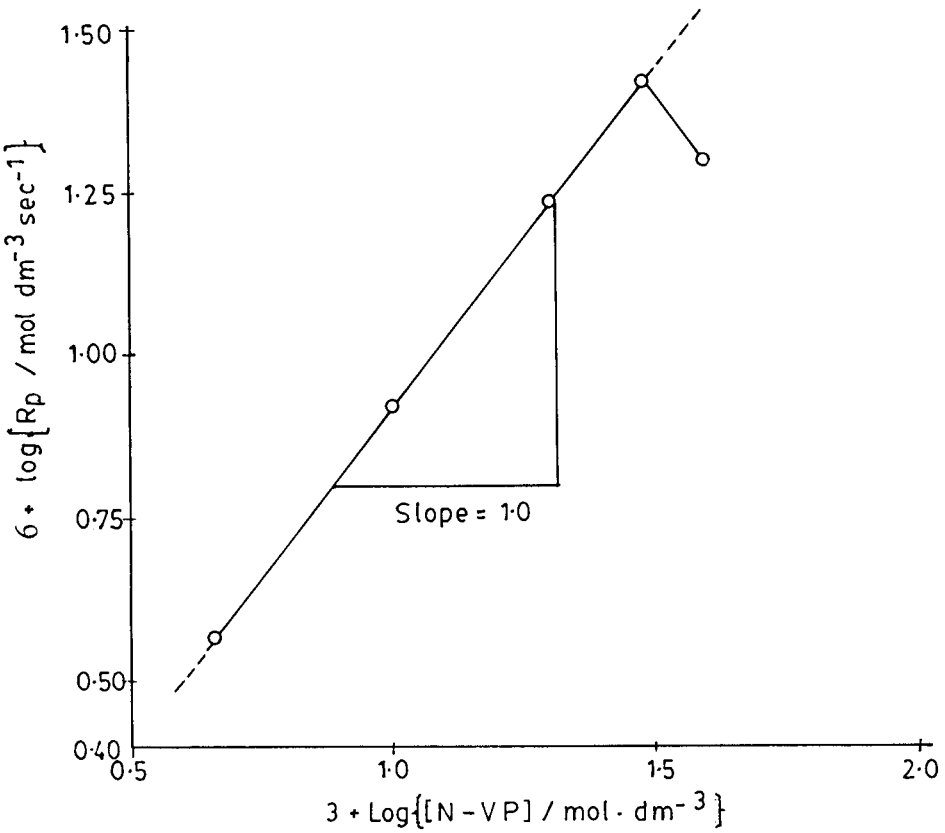

Figure 2 Double logarithmic plot between [*N*-VP] and R_p. [$Co(acac)_3$] = 10.0×10^{-5} mol dm^{-3}; [$HClO_4$] = 2.5×10^{-3} mol dm^{-3}; [Cellulose] = 1.0 g; T = 50°C, t = 120 min.

Effect of $Co(acac)_3$ Concentration

The percent yield (*%G*) of *N*-VP on cellulose was studied by the variation of the concentration of $Co(acac)_3$ from 2.0 to 20.0×10^{-5} mol dm^{-3}, with a 5.0×10^{-3} mol dm^{-3} concentration of the monomer at 50 ± 0.1°C. The data are shown in Figures 3 and 4 and Table II. The observed percent graft conversion ($\%C_g$) higher than percent homopolymer conversion ($\%C_{hp}$) clearly indicates that $Co(acac)_3$ promoted the formation of more active sites at the backbone of the cellulose than at the monomer molecules. The percent yield (*%G*) increased up to 15.0×10^{-5} mol dm^{-3} of $Co(acac)_3$ but showed a decreasing trend on the further increase of the concentration of $Co(acac)_3$ beyond 15.0×10^{-5} mol dm^{-3}. The percent cellulose conversion ($\%C_c$) (Table II) increased up to 15.0×10^{-5} mol dm^{-3} $Co(acac)_3$; hence, it is clear that up to this concentration of the initiator, $Co(acac)_3$ was involved exclusively in the formation of reacting sites on cellulose, but beyond this concentration, it started participating in the formation of radicals at monomer molecules in the solution. This retarding effect of $Co(acac)_3$ beyond a concentration of 15.0×10^{-5} mol dm^{-3} may have been caused by a decrease in the rate of diffusion of the complex at the surface of the cellulose; hence, the reactive sites were decreased. The decreasing trends in the number of grafted chains (N_g) and frequency of grafting (G_F) (Table II) again indicate that $Co(acac)_3$ at a higher concentration was unable to form active sites on cellulose but started participating in the termination of grafted growing chains at cellulose and homopolymer chains in solution. Above a concentration of 15.0×10^{-5} mol dm^{-3}, $Co(acac)_3$ participated actively in forming primary radicals by interacting with monomer molecules available in the solution. At a higher concentration of $Co(acac)_3$ ($>15.0 \times 10^{-5}$ mol dm^{-3}), the number of primary radicals was exceedingly higher; hence, the rate of termination was comparatively higher than the rate of propagation. The facile decomposition of the complex in the reaction mixture was assumed to be caused by the π-electrons of the monomer,[22] which help in increasing the

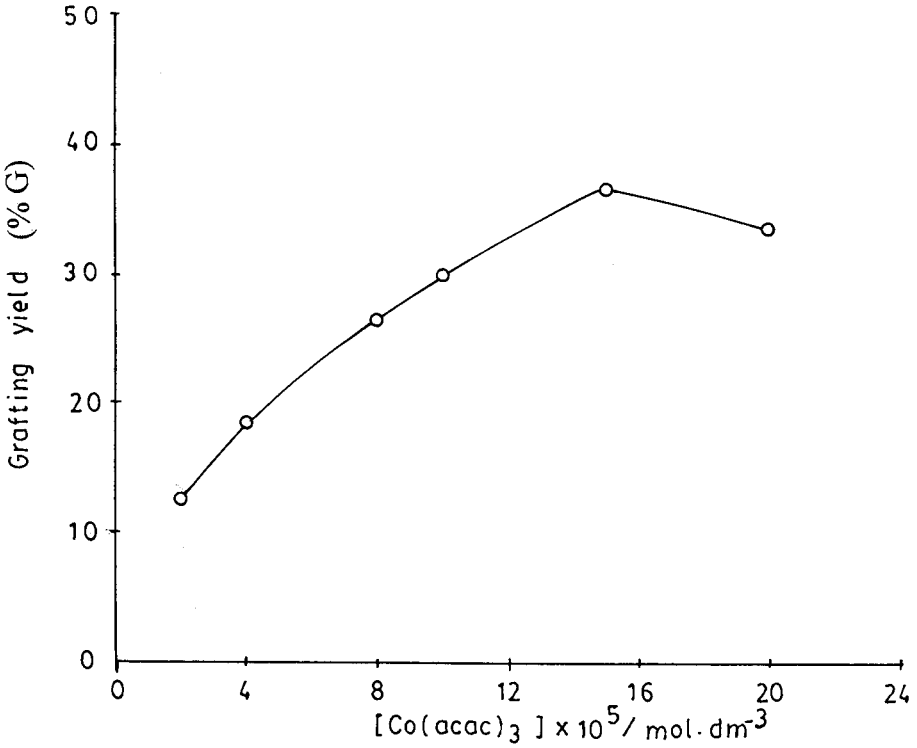

Figure 3 G as a function of $[Co(acac)_3]$. $[N\text{-VP}] = 5.0 \times 10^{-5}$ mol dm^{-3}; $[HClO_4] = 2.5 \times 10^{-3}$ mol dm^{-3}; [Cellulose] = 1.0 g; $T = 50$°C; $t = 120$ min.

homolytic fission of the metal–oxygen bond in the complex much below the decomposition temperature of the complex and generate free radicals responsible for grafting and homopolymerization. The log–log plot between R_p and $Co(acac)_3$ concentration (Fig. 4) shows a 0.5 order with respect to $Co(acac)_3$.

Effect of Temperature

To analyze the effect of temperature, we studied the grafting of *N*-VP on cellulose at different temperatures, ranging from 40 to 70°C; the results are shown in Table III and Figure 5. The graft yield (%G) and R_p increased up to 60°C, and at further high temperatures (>60°C), both graft yield (%G) and R_p decreased. The analysis of the grafting parameters shown in Table III clearly indicates that the increasing trend in graft efficiency (%G_E) and graft yield (%G) may have been caused by the formation of more reactive sites at the cellulose backbone and by the sufficient number of monomer molecules available at the growing end of the radicals. At higher temperatures, the rate of diffusion of the monomer molecules from the solution to the surface increased. This was made even more clear by the increasing trend in the molecular weight of the grafted and homopolymer chains obtained at higher temperatures (Table III). G_F also increased with the increase of temperature; hence, the increase in active sites at the backbone of the cellulose may have been caused by the high rate of decomposition of the complex and the formation of more sites on the cellulose. However, when the temperature was further increased beyond 60°C, the R_p and the molecular weights of grafted chains and homopolymer chains showed a decreasing trend that may have been caused by the high rate of termination of the immature growing chains because of mutual combination or chain transfer to the solvent or monomer molecules. The activation energy (ΔE_a) of grafting was calculated from an Arrhenius plot (Fig. 5); it was low (22.7 kJ/mol) in comparison with the value previously reported[5,25] for grafting on cellulose in the presence of cobalt (III) chelate; hence, our results support the suitability of the studied complex for the grafting of *N*-VP on cellulose.

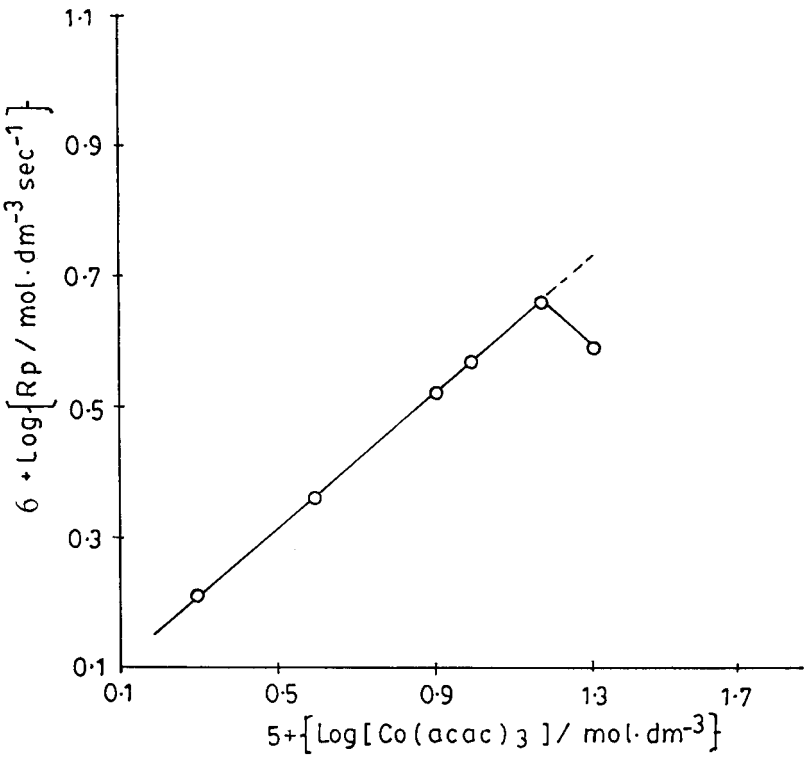

Figure 4 Double logarithmic plot between $[Co(acac)_3]$ and R_p. $[N\text{-VP}] = 5.0 \times 10^{-5}$ mol dm^{-3}; $[HClO_4] = 2.5 \times 10^{-3}$ mol dm^{-3}; [Cellulose] = 1.0 g; $T = 50°C$, $t = 120$ min.

Effect of Additives

To determine the effect of the reaction medium, we studied the graft copolymerization of *N*-VP on cellulose in the presence of different additives, and their effects were compared with a controlled experiment carried out at 10.0×10^{-3} mol dm^{-3} *N*-VP and 10.0×10^{-5} mol dm^{-3} $Co(acac)_3$ at 50°C in 2.5×10^{-3} mol dm^{-3} perchloric acid (Fig. 6). To evaluate the effect of surfactants on the grafting of *N*-VP on cellulose, we added sodium lauryl sulfate (NaLS) and cetyltrimethyl ammonium bromide (CTAB) to the reaction mixture just after the addition of monomer and initiator.

Table II Effect of $Co(acac)_3$ Concentration on Grafting Parameters at 50°C

	$[Co(acac)_3] \times 10^5$ mol dm^{-3}					
	2	4	8	10	15	20
True grafting ($\%G_T$)	438.00	448.00	460.00	464.00	466.00	456.00
Total conversion ($\%C_t$)	30.90	40.72	55.63	62.90	76.36	65.45
Graft conversion ($\%C_g$)	23.60	32.70	47.30	54.50	72.70	56.00
Homopolymer conversion ($\%C_{hp}$)	7.40	8.00	8.50	9.00	10.50	11.00
Cellulose conversion ($\%C_c$)	21.00	21.50	22.50	23.00	24.00	23.50
Grafting efficiency ($\%G_E$)	76.47	80.35	84.90	85.83	85.90	83.69
Grafting frequency ($\%G_F$)	0.14	0.24	0.35	0.46	0.59	0.55
Grafted chains per cellulose unit (N_g) $\times 10^6$	1.23	2.15	3.39	4.50	6.08	5.50
Homopolymer chains (N_g) $\times 10^6$	6.45	8.00	9.78	14.00	18.10	20.10
Mol. wt. ($\overline{M}_n$) of grafted chains (G_p) $\times 10^{-3}$	105.00	85.00	78.00	65.00	60.00	56.00
Mol. wt. ($\overline{M}_n$) of homopolymer (H_p) $\times 10^{-3}$	62.00	55.00	47.00	35.00	32.00	30.00

$[N\text{-VP}] = 5.0 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 2.5 \times 10^{-3}$ mol dm^{-3}, [Cellulose] = 1.0 g, $t = 120$ min.

Table III Effect of Temperature on Grafting Parameters at 50°C

	Temperature (°C)				
	40	45	50	60	70
True grafting ($\%G_T$)	563.00	583.00	611.00	675.00	660.00
Total conversion ($\%C_t$)	48.60	60.36	69.80	88.20	80.10
Graft conversion ($\%C_g$)	41.40	51.60	60.00	77.40	68.00
Homopolymer conversion ($\%C_{hp}$)	7.50	9.00	9.50	11.00	13.00
Cellulose conversion ($\%C_c$)	22.00	23.00	23.50	24.00	23.00
Grafting efficiency ($\%G_E$)	84.71	85.07	86.45	87.75	86.51
Grafting frequency ($\%G_F$)	0.85	0.89	0.92	0.99	1.05
Grafted chains per cellulose unit (N_g) $\times 10^6$	7.90	8.81	9.20	10.10	9.37
Homopolymer chains (N_h) $\times 10^6$	1.97	2.00	2.20	2.44	2.71
Mol. wt. ($\overline{M}_n$) of grafted chains (G_p) $\times 10^{-3}$	58.00	65.00	72.00	85.00	80.00
Mol. wt. ($\overline{M}_n$) of homopolymer (H_p) $\times 10^{-3}$	42.00	45.00	48.00	50.00	53.00

[*N*-VP] = 10×10^{-3} mol dm^{-3}, [$Co(acac)_3$] = 10×10^{-5} mol dm^{-3}, [Cellulose] = 1.0 g, t = 120 min.

The addition of an anionic surfactant (NaLS) caused a substantial increase in percent graft yield ($\%G$) and graft efficiency ($\%G_E$), whereas a cationic surfactant (CTAB) caused a decrease in percent graft yield ($\%G$). The decreasing trend in the presence of CTAB may have been caused by the formation of a cationic layer over the surface of the cellulose, which ultimately retarded the rate of polymerization of *N*-VP. It has been reported that *N*-VP polymerizes poorly in the presence of cationic species[29] and forms oligomers. The anionic micelles of lauryl sulfate form an

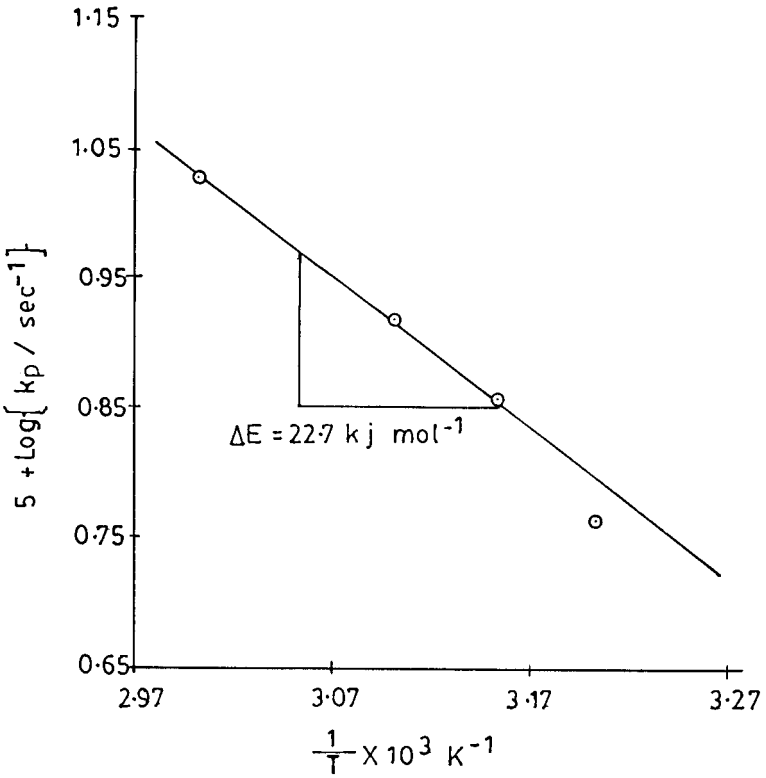

Figure 5 Arrhenius plot between log R_p and $1/T$. [*N*-VP] = 10×10^{-3} mol dm^{-3}; [$Co(acac)_3$] = 10×10^{-3} mol dm^{-3}; [Cellulose] = 1.0 g; T = 50°C; t = 120 min.

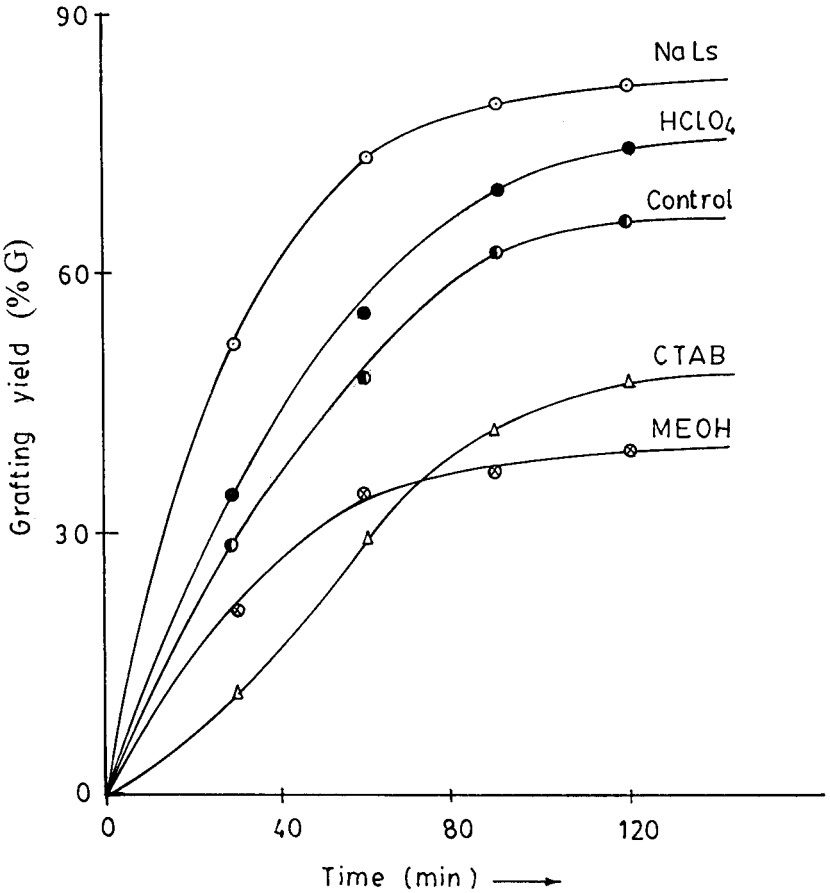

Figure 6 Effect of additives. [*N*-VP] = 10×10^{-3} mol dm^{-3}; [$Co(acac)_3$] = 10×10^{-3} mol dm^{-3}; [$HClO_4$] = 2.5×10^{-3} mol dm^{-3} (◐); [$HClO_4$] = 5.0×10^{-3} mol dm^{-3} (●); [NaLS] = 7.0×10^{-3} mol dm^{-3} (ȯ); [CTAB] = 1.5×10^{-3} mol dm^{-3} (△); [MeOH] = 5% (v/v) (⊗); [Cellulose] = 1.0 g; T = 50°C; t = 120 min.

adsorbed portion of the electrical double layer at the surface of the cellulose that prevents the participation of primary radicals and other growing homopolymer radicals in the premature termination of the growing chains at the cellulose; hence, percent graft yield (%*G*) increases in the presence of the anionic surfactants. Thus, cationic and anionic parts of the surfactants are adsorbed at the surface of the cellulose and form a part of a double layer that ultimately controls the concentration of the monomer and other species in the diffused part of the double layer. Thus, the overall R_p is controlled by the average time potential that exists between adsorbed and diffused portions of the double layer.[30] percent graft yield (%*G*) increased with the increasing concentration of perchloric acid from 2.5 to 5.0×10^{-3} mol dm^{-3} (Fig. 6). The effect of the addition of perchloric acid may be explained by the consideration of the effect of perchlorate anion (ClO_4^-) being similar to that of anions formed during the addition of NaLS. These perchlorate anions help in the growth of the grafted chains at the surface of cellulose. The increase in percent graft yield (%*G*) with the increase of perchloric acid may be caused by an increase in the crystallinity of cellulose in an acidic medium, which reduces the chances of the termination of the growing chains on the cellulose surface by restricting the diffusion of primary radicals or growing homopolymers chains; hence, percent graft yield (%*G*) increased with the increase of the concentration of perchloric acid. Percent graft yield (%*G*) decreased in the presence of added methanol (5% v/v) in the reaction mixture. The decreasing trend in the percent graft yield (%*G*) percentage in the presence of methanol was thought to be caused by the transfer of activity of the growing chain to the added alcohol molecules that produce radicals of low initiating power; hence, the overall percent graft yield (%*G*) de-

creased with the addition of methanol to the reaction mixture. The addition of methanol also contracted the cellulose molecules that prevented the propagation of the cellulose radicals, as reactive sites of the cellulose were insufficiently exposed to the monomer molecules; hence, percent graft yield (%*G*) decreased.

Reaction Scheme

On the basis of these experimental findings, the following reaction steps are proposed to derive a rate expression for the graft copolymerization of *N*-VP on cellulose.

Radical formation:

$$\text{Cellulose} - \text{H} + \text{Co(acac)}_3 \xrightarrow{k}$$

$$\text{acac–Cellulose}^{\bullet} + \text{Co(acac)}_2 \quad (2)$$

$$\text{Monomer} + \text{Co(acac)}_3 \xrightarrow{k}$$

$$\text{acac–Monomer}^{\bullet} + \text{Co (acac)}_2 \quad (3)$$

Initiation:

$$\text{acac} - \text{Cellulose}^{\bullet} + \text{Monomer} \xrightarrow{k_i}$$

$$\text{acac–Cellulose–Monomer}^{\bullet} \quad (4)$$

Propagation:

$$\text{acac–Cellulose} - \text{Monomer}^{\bullet} + \text{Monomer} \xrightarrow{k_p}$$

$$\text{acac–Cellulose–(Monomer)}_2^{\bullet}\text{-} \quad (5)$$

$$\text{acac–(Monomer)}_n^{\bullet}\text{-} + \text{Monomer} \xrightarrow{k_p}$$

$$\text{acac} - \text{(Monomer)}_2^{\bullet}\text{-} \quad (6)$$

Termination:

$$\text{acac–Cellulose} - \text{(Monomer)}_n^{\bullet}\text{-}$$

$$+ {}^{\bullet}\text{(Monomer)}_m\text{–acac} \xrightarrow{ktc} \text{Grafted Cellulose} \quad (7)$$

$$\text{acac–(Monomer)}_n^{\bullet}\text{-} + {}^{\bullet}\text{(Monomer)}_m\text{–acac} \xrightarrow{ktc}$$

$$\text{Homopolymer} \quad (8)$$

(n and m are the number of repeat units in the growing chains). From eqs. (2)–(8), which are involved in graft copolymerization, the following equation for the rate of graft copolymerization (R_p) is obtained:

$$R_p = k_p\left(\frac{k_i}{2k_{tc}}\right)^{1/2}[N - VP][\text{Co(acac)}_3]^{1/2} \quad (9)$$

where k, k_i, k_p, and k_{tc} are the rate constants for reactions involving radical formation, initiation, propagation, and termination through coupling, respectively. The derived rate expression of graft copolymerization shows close agreement with the experimental data; that is, R_p is directly proportional to the concentration of the monomer (Fig. 2) and the square-root dependence on the concentration of Co(acac)$_3$ (Fig. 4). The grafting of *N*-VP onto cellulose showed low energy of activation (ΔE_a). The agreement of the experimental results with the derived rate law supports the validity of the steps proposed in the reaction scheme of the graft copolymerization.

CONCLUSIONS

N-VP was grafted onto cellulose successfully with Co(acac)$_3$ as an efficient initiator at a low temperature. The proposed reaction steps of graft copolymerization and the derived rate law were in conformity with the experimental results, supporting the validity of the steps proposed in the reaction scheme.

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