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Grafting onto Cellulose. VI. Graft Copolymerization of Vinyl Acetate by Use of Metal Chelates as Initiators

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ABSTRACT

Graft copolymerization of vinyl acetate (VAc) onto cellulose has been studied in an aqueous medium in the presence of $Fe(acac)_3$, $Al(acac)_3$, and $Zn(acac)_2$ as initiators. Percentage of grafting has been determined as a function of concentration of initiators and monomer, reaction time, and temperature. The reactivities of different metal chelates toward grafting of VAc on cellulose have been determined and were found to follow the order: $Zn(acac)_2 > Al(acac)_3 > Fe(acac)_3$. A plausible mechanism for grafting involving complex formation between metal chelates and vinyl monomer has been suggested. Several grafting experiments were carried out in presence of CCl_4, $CHCl_3$, $CH_3CH_2CH_2SH$ and Et_3N. All these additives with the exception of Et_3N were found to suppress grafting.

INTRODUCTION

Graft copolymerization of a variety of vinyl monomers onto cellulose has been extensively studied [1, 2]. Various methods that have been tried with varying degree of success include: initiation by photo chemicals [3], redox systems [4, 5], gamma irradiation [6], chain transfer [7], and ring-opening reactions [8]. Metal derivatives are capable of initiating vinyl polymerization in a nonaqueous medium. It was shown by Bamford and co-workers [9] that many derivatives of transition metals in low oxidation states, in association with organic halides, are active sources of free radicals which initiate vinyl polymerization. Initiation was believed to occur through electron transfer from metal to halide. Bamford and co-workers have also reported [9] that chelates of transition metals are capable of initiating vinyl polymerization, and that generation of free radicals follows a different mechanism. No halide is necessary for initiation. The ability of certain metal chelates to produce free radicals when heated was first pointed out by Arnett and Mendelsohn [10, 11] in the course of investigation on oxidation of these compounds. The same workers [11] observed that at 110°C some chelates are able to initiate polymerization of styrene, they gave the following order of rates of polymerization in presence of 0.32 mole % of various acetyl acetonates: V(III) $<$ Cr(III) $\approx$ Al(III) $<$ Fe(III) $<$ Co(III) $<$ Ce(IV) $<$ Mn(III). Kasting, Naarman, Reis, and Berding [12] reported that of simple acetyl acetonates, those of Mn(III) and Co(III) are most active initiators. Indicator and Linder [13] reported that Co(II), Co(III), Cr(III), and Fe(III) acetyl acetonates in the presence of tert-butyl hydroperoxide can be used as initiators for polymerization of styrene. Recently, Nandi et al. [14] have been able to effect polymerization of MMA by using $Fe(acac)_3$ as initiator.

The use of metal acetyl acetonates in graft copolymerization has not been extensively investigated. Misra et al. [15] were able to effect grafting of MMA and styrene onto cellulose and cellulose derivatives in aqueous medium by using $Fe(acac)_3$ and $Mn(acac)_3$ as initiators. In order to initiate a detailed study on the utilization of metal chelates as graft initiators, an attempt has been made to effect grafting of vinyl monomers onto cellulose by using a variety of metal chelates as initiators. In this paper we report on grafting of poly(vinyl acetate) onto cellulose in presence of $Zn(acac)_2$, $Al(acac)_3$ and $Fe(acac)_3$ as initiators. Percentage and efficiency of grafting have been determined as functions of concentrations of initiators and monomers. Effect of CCl_4, $CHCl_3$, $CH_3CH_2CH_2SH$, and Et_3N upon percent grafting has been studied. Results are presented in Tables 1-4.

EXPERIMENTAL

Materials and Methods

Pure cellulose powder (Carl Scheir and Schull, Selecta) has been used in all experiments. Vinyl acetate (BDH) was freshly distilled and the middle fraction was used. Carbon tetrachloride, chloroform, and triethylamine were freshly distilled. Propane-1-thiol (BDH) was of reagent grade and used without further purification.

TABLE 1. Effect of Concentration of Monomer on Percent Grafting[a]

No.	Monomer concn × 10^2 (mole/liter)	Grafting % Fe(acac)$_3$	 Al(acac)$_3$	 Zn(acac)$_2$
1	3.3	7.40	7.40	4.01
2	5.5	-	16.75	6.22
3	6.6	12.75	-	-
4	8.8	6.10	12.10	10.25
5	11.0	4.10	10.50	17.85
6	16.5	3.92	8.68	20.00
7	22.0	3.90	4.00	25.19
8	26.5	-	-	31.95
9	33.0	-	0.90	32.96
10	38.5	-	-	

[a] Reaction conditions: time, 120 min; temperature = 60 ± 1°C; [Fe(acac)$_3$] = 0.249×10^{-2} mole/liter; [Al(acac)$_3$] = 0.214×10^{-2} mole/liter; [Zn(acac)$_2$] = 1.0×10^{-2} mole/liter.

Acetyl acetonates of Fe(III) and Al(III) were prepared by methods previously described [16-18].

Zn(acac)$_2$ was obtained from Dr. Acira Akimoto (Central Research Lab., Toyo Soda Manufacturing Co. Ltd., Japan).

Nitrogen was purified by passing through freshly prepared alkaline pyrogallol solution.

Graft Copolymerization

Pure cellulose powder (1.0 g) was dispersed in 100 ml of deaerated water (40°) in a three necked flask. The flask was purged with purified nitrogen for about 30 min. A weighed amount of metal chelates dissolved in minimum amount of appropriate solvents was added to the reaction mixture. The temperature of the water bath was raised and adjusted at 60 ± 1°C. A measured amount of vinyl acetate was added dropwise, and graft copolymerization was carried out under stirring in nitrogen atmosphere for various reaction periods. The separation and purification of graft were performed by the method described elsewhere [15]. The percentage of grafting was calculated by the equation:

TABLE 2. Effect of Concentration of Catalyst on Percent Grafting[a]

No.	Chelate	Catalyst concn × 10^2 (mole/liter)	Grafting (%)
1	$Fe(acac)_3$	0.1246	0.00
		0.2496	2.30
		0.4986	6.44
		0.7478	3.90
		0.9970	3.86
		1.1216	3.88
2	$Al(acac)_3$	0.107	11.82
		0.214	16.73
		0.321	6.25
		0.428	5.90
		0.535	6.00
		0.642	6.12
		0.749	6.00
3	$Zn(acac)_2$	0.25	8.20
		0.50	10.22
		1.00	17.85
		1.50	8.40
		2.00	8.51
		2.50	8.46

[a] Reaction conditions: monomer concentrations, 5.55×10^{-2} mole/liter; time, = 120 min; temperature, $60 \pm 1^\circ C$.

$$\% \text{ Grafting} = [(W_2 - W_1)/W_1]\ 100$$

where W_1, W_2, and W_3 denote, respectively, the weight of cellulose, weight of grafted cellulose, and monomer (vinyl acetate).

The percentage of grafting was expressed as a function of the concentration of metal chelates, concentration of vinyl acetate, and reaction time. Results are presented in Tables 1-4.

TABLE 3. Effect of Time on Percent Grafting[a]

No.	Time (min)	Grafting (%) Fe(acac)$_3$	Grafting (%) Al(acac)$_3$	Grafting (%) Zn(acac)$_2$
1	60	0.00	8.68	7.90
2	90	0.00	11.52	14.20
3	120	2.30	16.20	18.60
4	150	-	14.00	10.49
5	180	7.80	10.80	6.72
6	210	-	10.69	6.90
7	240	10.40	10.75	6.78
8	270	10.20	-	-
9	300	10.45	-	-

[a] Reaction conditions: [Fe(acac)$_3$] = 0.249×10^{-2} mole/liter; [Al(acac)$_3$] = 0.214×10^{-2} mole/liter); [Zn(acac)$_2$ = 0.5×10^{-2} mole/liter; monomer concentration, 5.5×10^{-2} mole/liter; temperature = 60 ± 1°C.

Evidence of Grafting

The IR spectrum of grafted samples showed an absorption at 1710 cm^{-1} (C=O) which was attributed to grafted vinyl acetate; no such band was present in the IR spectrum of cellulose.

An intimate physical mixture of cellulose (1.0 g) and poly(vinyl acetate) (1.0 g) in benzene was stirred at room temperature for 3 hr. The mixture was filtered, and the residue was extracted with benzene for 24 hr. Quantitative recovery of cellulose (0.99 g) indicated that all the poly(vinyl acetate) was removed by benzene extraction. Thus the poly(vinyl acetate) present in the grafted product must have been covalently bonded.

RESULTS AND DISCUSSION

Metal chelates are known to decompose upon heating to generate free radicals that can initiate polymerization of vinyl acetate and generate active sites onto cellulose by hydrogen abstraction. The active sites on cellulose, however, can also be generated by abstraction of hydrogen atom by the growing polymeric chain. Since only a

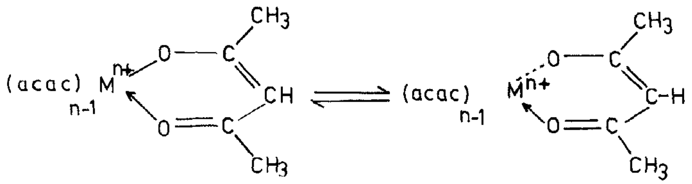
TABLE 4. Effect of Chain-Transfer Agents on Grafting[a]

Chain transfer agent		Grafting (%)		
Type	Vol (ml)	$Fe(acac)_3$	$Al(acac)_3$	$Zn(acac)_2$
CCl_4	2	5.29	3.00	8.23
	4	0.00	0.00	2.0
	6	0.00	0.00	6.0
$CHCl_3$	2	4.40	0.00	4.05
	4	0.00	0.00	4.0
	6	0.00	0.00	0.0
$CH_3CH_2CH_2SH$	1	0.00	0.00	0.00
	2	0.00	0.00	0.00
	3	0.00	0.00	0.00
$(C_2H_5)_3N$	2	15.40	18.62	20.02
	4	11.27	10.00	14.50
	6	6.00	4.10	7.20

[a] Reaction conditions: $[Fe(acac)_3] = 0.2493 \times 10^{-2}$ mole/liter; $[Al(acac)_3] = 0.107 \times 10^{-2}$ mole/liter; $[Zn(acac)_2] = 1.0 \times 10^{-2}$ mole/liter; monomer concentration, 5.55×10^{-2} mole/liter; time = 120 min; temperature = 60 ± 1°C.

very small amount of the initiator is present, generation of active sites onto cellulose primarily occurs by abstraction of hydrogen by the growing polymeric chain. The mechanism shown in (Eqs. 1-6) is suggested for grafting of VAc onto cellulose in presence of metal chelates.

In this mechanistic scheme, it is postulated that upon heating the metal chelates first loosen the metal-oxygen bond; this is followed by decomposition into free radical by a one-electron transfer process.



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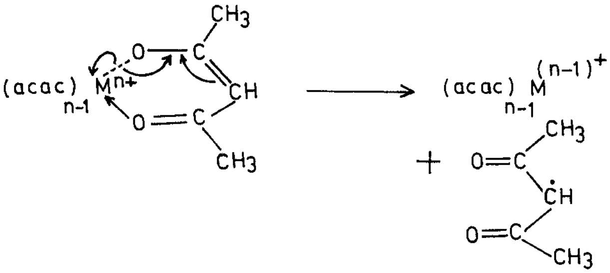

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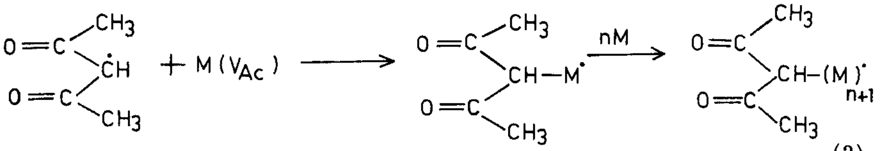

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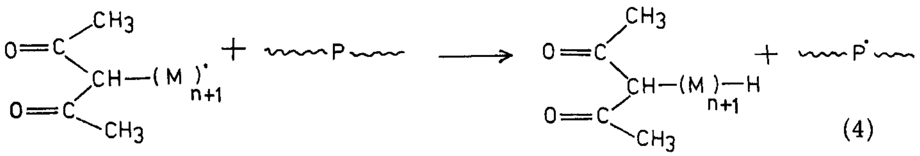

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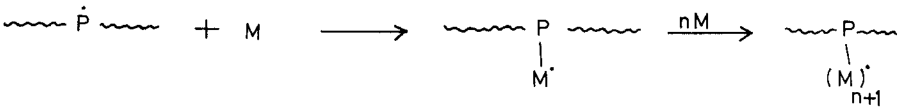

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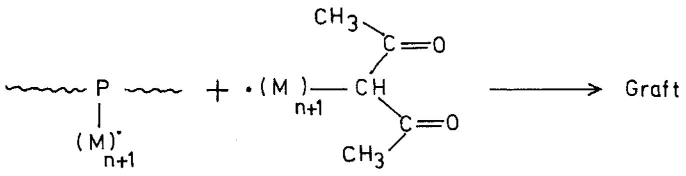
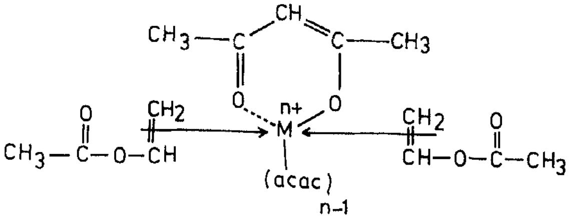


(6)

The free radical species thus generated is responsible for grafting. However, this seems unlikely, since all grafting experiments were carried out at 60°C, much below the decomposition temperature of the chelates. Further it is observed from Table 2 that not all chelates are equally reactive in producing grafts. It appears that different reactivity of metal chelates is due to varying ease of decomposition of chelates that may depend upon the nature of central metal atom. It is apparent from Table 1 that with increase in monomer concentration, percent grafting increases significantly with $Zn(acac)_2$. With $Fe(acac)_3$ and $Al(acac)_3$, increased monomer concentration initially leads to a small increase in percent grafting and at higher monomer concentration percent grafting decreases with both $Fe(acac)_3$ and $Al(acac)_3$. The dependence of percent grafting upon concentration of vinyl monomer indicates that metal chelates undergo monomer assisted decomposition into free radicals. This can occur at low temperature (60°C). In view of these facts, the above mechanism [Eqs. (1-6)] for grafting requires modification. It is assumed that the chelates instead of undergoing spontaneous decomposition by step (2) receive some assistance from the monomer. In other words, chelates combine with VAc to form a complex (I),



I

which then undergo decomposition to generate free radical species. Prior complex formation between the monomer and the chelates is supported by the fact that grafting occurs at 60°C much below the decomposition temperature of the chelates.

Evidence for Formation of Metal Chelate Monomer Complex

An attempt was made to isolate the complex I. Upon treatment of VAc with $Zn(acac)_2$, a solid residue was obtained which was extracted with benzene to remove the poly(vinyl acetate). The IR spectrum of the solid residue showed an absorption band at 450 cm^{-1} which was not present in the IR spectrum of $Zn(acac)_2$. This new band was assigned to the Zn-C bond. The complex of VAc and $Fe(acac)_3$ and $Al(acac)_3$ also showed the presence of the metal-carbon bond in IR spectrum. The complex of $Zn(acac)_2$ and VAc was dissolved in benzene and the percent transmission of benzene solution was determined in a UV spectrophotometer as a function of wavelength. The UV spectrum of $Zn(acac)_2$ was compared with that of the $Zn(acac)_2$-VAc complex. The band at 240 nm of $Zn(acac)_2$ was shifted to 298 nm in the $Zn(acac)_2$-VAc complex. Further, a new band at 440 nm was observed with $Zn(acac)_2$-VAc complex which was not present in the UV spectrum of $Zn(acac)_2$. The new band at 440 nm was due to formation of $Zn(acac)_2$ -VAc complex. The UV spectrum of $Fe(acac)_3$-VAc complex and $Al(acac)_3$-VAc complex showed bands at 440 and 430 nm, respectively.

Table 1 shows that with increasing monomer concentration percent grafting increases with $Zn(acac)_2$ and reaches a maximum value (32.96%) at a monomer concentration of 33.0×10^{-2} mole/liter. Further increase in monomer concentration does not have any effect on percent add on. With $Al(acac)_3$ and $Fe(acac)_3$ maximum grafting was obtained at 5.5×10^{-2} and 6.6×10^{-2} mole/liter, respectively. A further increase in monomer concentration results in decrease in percent grafting with both $Fe(acac)_2$ and $Al(acac)_3$. This indicates that homopolymer formation becomes predominant at a higher monomer concentration in $Fe(acac)_3$ and $Al(acac)_3$ initiated grafting.

Table 2 shows that with increase in the concentration of metal chelates, percent grafting initially increases and reaches maximum value of 6.44% for $Fe(acac)_3$, 16.73% for $Al(acac)_3$, and 17.85% for $Zn(acac)_2$ at initiator concentrations of 4.9×10^{-3}, 2.14×10^{-3}, and 1.0×10^{-2} mole/liter, respectively. A further increase in concentration of metal chelates leads to decrease in percent grafting. It seems that metal chelates at higher concentration participate in terminating the growing grafted chains.

It is observed from Table 3 that $Zn(acac)_2$ and $Al(acac)_3$ produce maximum grafting within 120 min, while $Fe(acac)_3$ affords maximum grafting at a higher reaction period (240 min).

Several grafting reactions were carried out in presence of CCl_4, $CHCl_3$, $CH_3CH_2CH_2SH$ and Et_3N. Table 4 shows that all these additives, with the exception of Et_3N, suppress grafting; the effect however is much greater with propane-1-thiol. This is expected since propane-1-thiol having a large chain transfer constant value suppresses both polymerization and grafting completely. Et_3N, on the other hand, promotes grafting with all the metal chelates studied. This indicates that Et_3N, being an efficient nucleophile assists in the decomposition of vinyl acetate-chelates complex. Thus it appears that during polymerization and grafting metal acetyl acetonates undergo monomer assisted decomposition through complex I. If such complex formation is actually involved, then it will be worthwhile to study grafting of electron withdrawing monomer onto cellulose in presence of metal chelates. Such studies are in progress and results will be reported in due course.

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