Grafting onto Wool. IX. Graft Copolymerization of Vinyl Monomers by Use of Vanadium Oxyacetylacetonate as Initiator

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ABSTRACT

Methyl methacrylate (MMA), acrylic acid (AAc), and vinyl acetate (VAc) were graft copolymerized onto Himachali wool in an aqueous medium by using vanadium oxyacetyl acetonate as initiator. Graft copolymerization was studied at 45, 55, 65, and 75°C for various reaction periods. The percentage of grafting was determined as functions of concentration of monomers, concentration of initiator, time, and temperature. The maximum percentage of grafting with each monomer occurred at 55°. Several grafting experiments were carried out in the presence of various additives which include HNO_3, DMSO, and pyridine. Nitric acid was found to promote grafting of MMA. All these additives had adverse effects on grafting of VAc and AAc. MMA, VAc, and AAc were found to differ in reactivity toward grafting and followed the order MMA > AAc > VAc.

INTRODUCTION

As early as 1937 Flory [1] discovered that polymers can be modified by grafting appropriate vinyl monomers in the presence of suitable

initiator system. In the presence of radical initiators such as BPO and AIBN, grafting proceeds by a chain transfer mechanism. A variety of vinyl monomers has been grafted onto natural rubber [2, 3] and synthetic polymeric backbones [4] by using conventional radical initiators. However, it was shown that in the presence of radical initiators, grafting is often accompanied by the formation of large amount of homopolymer, separation of which from the grafted material involves considerable difficulty. Attempts were made to find newer initiating systems which would selectively afford grafting with a minimum of homopolymer formation. This problem was partly solved by Mino and Kaizerman who observed that in the presence of ceric ion, grafting occurs without homopolymer formation. Ceric ion is known to form complexes with alcohols, aldehydes, and amines. Cellulose and starch, which are polyhydric alcohols, combine with ceric ion to form complexes which disproportionate by a one-electron transfer process leading to the formation of free radical species on the polymeric backbone where grafting of appropriate vinyl monomer can occur.

$$RCellOH + Ce^{4+} \rightleftharpoons B \longrightarrow RCellO \cdot + Ce^{3+} + H^+$$
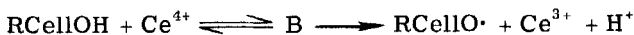
By applying this technique, Mino and Kaizerman [5] were able to graft acrylamide onto polyvinyl alcohol. Wool is a polypeptide that contains numerous functional groups such as –OH, –NH$_2$, imino, –SH, and –SS– linkages. All these functional groups are capable of entering into redox reaction with ceric ion. The present authors have been able to graft MA [6], EA [7], MMA [8], VAc [9], and AAc [8] onto Himachali wool by using the ceric ion technique. Other workers were also able to effect grafting of a variety of vinyl monomers onto wool [10-12] and collagen [13] by the ceric ion method. Very little work is reported on grafting of vinyl monomers onto wool by radical initiators. Recently Misra and Chandel [14] were able to successfully graft PS onto Himachali wool by using BPO in the presence of pyridine and acetic acid which acted as a pH modifier. Arai et al. [15] observed that grafting of MMA onto wool in the presence of the LiBr-S$_2$O$_8^{2-}$ system occurs without homopolymer formation. A comprehensive research program on grafting of a variety of vinyl monomers onto wool has been initiated in our laboratory. Different initiating systems that have been tried with varying degrees of success include ceric ion [6, 9], the ceric-amine system [16, 17], Fenton's reagent [18], and a radical initiator (BPO) in presence of a pH modifier [14].

In an attempt to find newer initiating system for effecting grafting onto wool, we have studied the suitability of metal chelates as graft initiators. Misra and Pande [19] were able to effect grafting of PS and PMMA onto cellulose and cellulose derivatives in the presence of Fe^{III}(acac)$_3$ and Mn^{III}(acac)$_3$ as initiators. Acetylacetonate of

various transition metals has been successfully used as an initiator for graft copolymerization [20]. Few studies on the use of vanadium chelates as initiators for polymerization have been reported. Recently Bamford et al. [21] have studied the photoinitiated polymerization of a number of vinyl monomers in the presence of chloro-oxobis (2,4-pentanedionato) vanadium (V), VO(acac)$_2$Cl. During the photo-initiation of MMA it was observed that it was actually responsible for vinyl polymerization. Use of vanadium oxyacetylacetonate VO(acac)$_2$ as the graft initiator has not been reported. For the first time we are reporting studies on the use of VO(acac)$_2$ as an initiator for grafting of vinyl monomers onto wool. The present paper describes the results of our studies on the grafting of MMA, VAc, and AAc onto Himachali wool by using VO(acac)$_2$ as the initiator under a wide variety of conditions. The effects of several additives such as HNO$_3$, DMSO, and Py on graft copolymerization have been studied.

EXPERIMENTAL

Preparation of Vanadium Oxyacetylacetonate

The chelate was prepared by the method reported in inorganic synthesis [23]:

$$2V_2O_5 + 9C_5H_8O_2 \longrightarrow 4VO(C_5H_7O_2)_2 + (CH_3CO)_2CO + 5H_2O$$
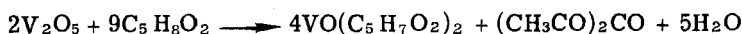
Five grams of technical vanadium (V) oxide is placed in a 200-mL round-bottomed flask which is attached to a reflux condensor through a ground glass joint, 100 mL of acetylacetone is added, and the mixture is refluxed for 24 hr. The suspension is filtered while hot and the filtrate is cooled. About 5 g of product separates as tiny blue crystals. The remaining acetylacetone is removed by evaporation in a stream of air. The solid product is washed with acetone and ether and dried at 110°C.

Analysis: Calculated for VO(C$_5$H$_7$O$_2$)$_2$: C, 45.28%; H, 5.28%; V, 19.25%. Found: C, 45.09%; H, 5.33%; V, 19.32%.

Materials and Methods

Methyl methacrylate was washed with 5% NaOH and dried over anhydrous sodium sulfate. Dried MMA was then distilled and the middle fraction was used.

Vinyl acetate was freshly distilled before use. Acrylic acid was freshly distilled under reduced pressure. DMSO, CCl$_4$, and chloroform were used as received. Pyridine was distilled over potassium hydroxide. Nitric acid of known strength was used. Nitrogen was

purified by passing it through freshly prepared alkaline pyrogallol solution.

Graft Copolymerization

One gram of purified wool is dispersed in 200 mL of deaerated water in a three-necked flask. A known weight of chelate is added. Prior to the addition of the monomer, purified nitrogen is passed through the reaction flask and then a continuous supply of nitrogen is maintained throughout the reaction period. Vinyl monomer is added dropwise to the reaction flask. The copolymerization reaction is carried out under stirring at temperatures ranging from 55 to 75°C for various reaction periods.

After the reaction is over, the reaction mixture is filtered and the residue is extracted with appropriate solvents. Benzene is used as a solvent for P(MMA) and acetone is used as a solvent for both P(VAc) and P(AAc).

The percentage and efficiency of grafting were calculated as follows:

$$\text{Percent grafting} = \frac{W_1 - W_0}{W_0} \times 100$$

$$\text{Percent efficiency} = \frac{W_1 - W_0}{W_2} \times 100$$

where W_0, W_1, and W_2 are the weight of the original wool, the weight of the grafted wool after extraction, and the weight of the monomer used, respectively.

Evidence of Grafting

W-g-P(MMA) is hydrolyzed with 6 $\underline{N}$ HCl at 115°C for 24 hr. After all the wool goes into solution, a resinous mass is obtained which is characterized as P(MMA) by IR spectroscopy.

In the case of P(VAc) and P(AAc), no such resinous mass is obtained, since under these conditions P(VAc) is hydrolyzed to poly(vinyl alcohol), and both poly(vinyl alcohol) and poly(acrylic acid) are soluble in water.

RESULTS AND DISCUSSION

When a metal is capable of existing in more than one valence state, the combination of an organic ligand with the higher valence state of

the metal may result in a single electron transfer to the metal. As a consequence of this electron transfer, initiation of vinyl polymerization may occur. Arnett and Mendelsohn [22] observed that certain transition metal chelates decompose upon heating to generate free radicals. When the decomposition of the metal chelates is carried out in the presence of a vinyl monomer and a backbone polymer, grafting may occur. The following mechanism is suggested to explain grafting of MMA, VAc, and AAc onto wool in the presence of VO(acac)$_2$.
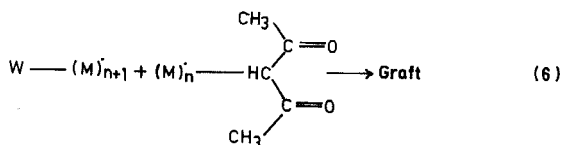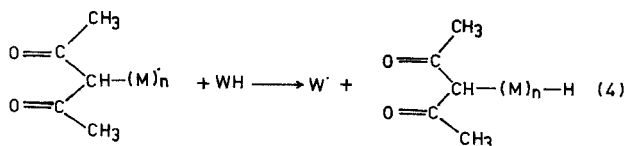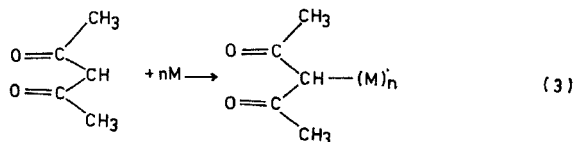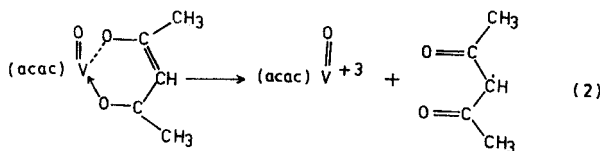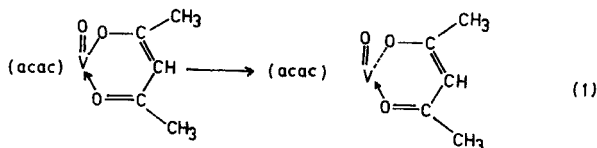
In the above postulated mechanism it is assumed that the metal chelate upon heating first loosens the V–O bond followed by transfer of one electron to generate the free radical species which are responsible for grafting. The above process is expected to occur at the decomposition temperature of the chelate. Decomposition of chelate normally

occurs at the higher temperature, but it is observed from Tables 2, 7, and 12 that maximum grafting occurred at 55°C, much below the decomposition temperature of the chelate. This indicates that during grafting VO(acac)$_2$ undergoes monomer-assisted decomposition at a lower temperature. The above mechanism (Eqs. 1-6) therefore requires modification. It is presumed that the chelate, instead of undergoing spontaneous decomposition by Step (2), first combines with the vinyl monomer to give a complex (I) which then dissociates at a lower temperature to generate the free radical species.

(I)

X = CH$_3$, y = COOCH$_3$
X = H, y = OCOCH$_3$
X = H, y = COOH
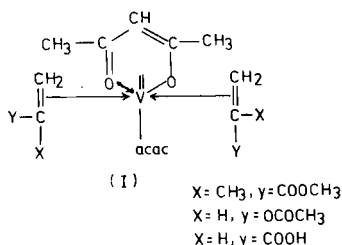
A similar mechanism involving complex formation between the metal chelates and vinyl monomer has been proposed by Misra et al. [20] for explaining grafting of vinyl acetate (VAc) onto cellulose. The formation of a complex between vinyl acetate and Fe(acac)$_3$, Al(acac)$_3$, and Zn(acac)$_2$ was established from spectroscopic evidence. It has not been possible to isolate and characterize the complex of vanadium oxyacetylacetonate and the vinyl monomers studied. However, it

TABLE 1. Effects of Concentration of Chelate on Percent Grafting of MMA onto Wool[a]

No.	[VO(acac)$_2$] $\times 10^2$ (mole/L)	% Grafting	% Efficiency
1	0.9	4.84	1.03
2	1.1	15.58	3.31
3	1.9	7.07	1.50
4	2.4	5.35	1.12
5	2.8	8.55	1.82

[a]Wool = 1 g, H$_2$O = 200 mL, [MMA] = 23.5 $\times 10^{-2}$ mole/L, time = 120 min, temperature = 55°C.

TABLE 2. Effect of Temperature on Percent Grafting of MMA[a]

No.	Temperature (°C)	% Grafting	% Efficiency
1	45	2.61	0.55
2	55	15.58	3.31
3	65	9.65	2.03
4	75	3.43	0.72

[a]Wool = 1 g, H_2O = 200 mL, [MMA] = 23.5×10^{-2} mole/L, time = 120 min, [$VO(acac)_2$] = 1.1×10^{-2} mole/L.

TABLE 3. Effect of Concentration of MMA on Percent Grafting[a]

No.	[MMA] $\times 10^2$ (mole/L)	% Grafting	% Efficiency
1	14.4	2.92	1.04
2	23.5	15.58	3.31
3	32.5	4.92	0.74

[a]Wool = 1 g, H_2O = 200 mL, time = 120 min, temperature = 55°C, [$VO(acac)_2$] = 1.1×10^{-2} mole/L.

TABLE 4. Effect of Time on Percent Grafting of MMA[a]

No.	Time (min)	% Grafting	% Efficiency
1	90	2.02	0.43
2	120	15.58	3.31
3	150	6.94	1.47
4	180	5.49	1.17

[a]Wool = 1 g, H_2O = 200 mL, temperature = 55°C, [MMA] = 23.5×10^{-2} mole/L, [$VO(acac)_2$] = 1.1×10^{-2} mole/L.

TABLE 5. Effect of Additives on Percent Grafting of MMA[a,b]

	No.	Additive (mL)	% Grafting	% Efficiency
HNO$_3$	1	1.25	48.65	10.35
	2	2.0	42.51	9.04
DMSO	3	3.0	0.89	0
	4	5.0	2.03	0.43
DMSO/HNO$_3$	5	5.0/1.25	37.75	8.03
Pyridine	6	0.5	2.91	0.61
	7	1.0	8.5	1.82

[a]Wool = 1 g, H$_2$O = 200 mL, $[$MMA$]$ = 23.5 × 10^{-2} mole/L, time = 120 min, temperature = 55°C, $[$VO(acac)$_2]$ = 1.1 × 10^{-2} mole/L.
[b]No grafting with CCl$_4$ and CHCl$_3$.

TABLE 6. Effect of Chelate Concentration on Percent Grafting of VAc onto Wool[a]

No.	$[$VO(acac)$_2]$ × 10^2 (mole/L)	% Grafting	% Efficiency
1	0.9	3.79	0.8
2	1.1	5.81	1.24
3	1.9	4.33	0.93
4	2.4	7.18	1.54
5	2.8	4.21	0.90

[a]Wool = 1 g, H$_2$O = 200 mL, time = 120 min, temperature = 55°C, $[$VAc$]$ = 27.3 × 10^{-2} mole/L.

TABLE 7. Effect of Temperature on Percent Grafting of VAc[a]

No.	Temperature (°C)	% Grafting	% Efficiency
1	45	5.78	1.23
2	55	7.18	1.54
3	65	2.33	0.50
4	75	0.89	0

[a]Wool = 1 g, H_2O = 200 mL, time = 120 min, $[VAc]$ = 27.3 × 10^{-2} mole/L, $[VO(acac)_2]$ = 2.4 × 10^{-2} mole/L.

TABLE 8. Effect of Time on Percent Grafting of VAc[a]

No.	Time (min)	% Grafting	% Efficiency
1	90	4.03	0.86
2	120	7.18	1.54
3	150	3.05	0.65
4	180	2.80	0.60

[a]Wool = 1 g, H_2O = 200 mL, temperature = 55°C, $[VAc]$ = 27.3 × 10^{-2} mole/L, $[VO(acac)_2]$ = 2.4 × 10^{-2} mole/L.

TABLE 9. Effect of Concentration of VAc on Percent Grafting[a]

No.	$[VAc] \times 10^2$ (mole/L)	% Grafting	% Efficiency
1	16.2	3.12	1.11
2	27.3	7.18	1.54
3	37.8	5.39	0.58
4	48.6	2.21	0.23

[a]Wool = 1 g, H_2O = 200 mL, time = 120 min, temperature = 55°C, $[VO(acac)_2]$ = 2.4 × 10^{-2} mole/L.

TABLE 10. Effect of Additive on Percent Grafting of VAc[a]

No.	HNO$_3$ (mL)	% Grafting	% Efficiency
1	1.25	0	0
2	2.0	2.15	0.46

[a]Wool = 1 g, H$_2$O = 200 mL, time = 120 min, temperature = 55°C, [VO(acac)$_2$] = 2.4×10^{-2} mole/L, [VAc] = 27.3×10^{-2} mole/L.

TABLE 11. Effect of Chelate Concentration on Percent Grafting of Acrylic Acid onto Wool[a]

No.	[VO(acac)$_2$ $\times 10^2$] (mole/L)	% Grafting	% Efficiency
1	0.9	4.4	0.84
2	1.1	12.24	2.35
3	1.9	10.59	2.00
4	2.4	10.74	2.04

[a]Wool = 1 g, H$_2$O = 200 mL, time = 120 min, temperature = 55°C, [AAc] = 36.4×10^{-2} mole/L.

TABLE 12. Effect of Temperature on Percent Grafting of AAc[a]

No.	Temperature (°C)	% Grafting	% Efficiency
1	45	7.24	1.37
2	55	12.24	2.35
3	65	3.14	0.60
4	75	2.00	0.38

[a]Wool = 1 g, H$_2$O = 200 mL, time = 120 min, [AAc] = 36.4×10^{-2} mole/L, [VO(acac)$_2$] = 1.1×10^{-2} mole/L.

TABLE 13. Effect of Concentration of Acrylic Acid on Percent Grafting[a]

No.	$[AAc] \times 10^2$ (mole/L)	% Grafting	% Efficiency
1	21.8	6.24	2.00
2	36.4	12.24	2.35
3	51.4	9.32	1.28
4	73.5	3.91	0.36

[a]Wool = 1 g, H_2O = 200 mL, temperature = 55°C, time = 120 min, $[VO(acac)_2]$ = 1.1 × 10^{-2} mole/L.

TABLE 14. Effect of Time on Percent Grafting of AAc[a]

No.	Time (min)	% Grafting	% Efficiency
1	90	4.03	0.76
2	120	12.24	2.35
3	150	8.49	1.61
4	180	3.14	0.60

[a]Wool = 1 g, H_2O = 200 mL, temperature = 55°C, $[AAc]$ = 36.4 × 10^{-2} mole/L, $[VO(acac)_2]$ = 1.1 × 10^{-2} mole/L.

TABLE 15. Effect of Additives on Percent Grafting of AAc[a]

	No.	Additive (mL)	% Grafting	% Efficiency
HNO_3	1	1.25	0.89	0
	2	2.6	6.92	1.12
	3	3.0	8.17	1.55
	4	4.0	2.23	0.42
DMSO	5	3.0	2.02	0.38
	6	5.0	0	0

[a]Wool = 1 g, H_2O = 200 mL, time = 120 min, temperature = 55°C, $[AAc]$ = 36.4 × 10^{-2} mole/L, $[VO(acac)_2]$ = 1.1 × 10^{-2} mole/L.

appears that in the present case also, vinyl monomers assist the decomposition of VO(acac)$_2$ through Complex I. If the vinyl monomers do indeed form complexes with VO(acac)$_2$ as assumed, then increasing the concentration of vinyl monomers should enhance grafting. In fact, it is observed from Tables 3, 9, and 13 that with an increase in the concentration of monomer, the percent grafting increases and reaches a maximum value at a monomer concentration of 23×10^{-2} mole/L for MMA, 27.3×10^{-2} mole/L for VAc, and 36.4×10^{-2} mole/L for AAc. A further increase in monomer concentration decreases the percentage of grafting. This indicates that at higher monomer concentrations the growing polymeric chain preferentially combines with the monomer to give homopolymer.

It is also observed from Tables 1, 6, and 11 that with an increase in the concentration of the chelate, the percent grafting increases and reaches a maximum at 1.1×10^{-2} mole/L for MMA, 2.4×10^{-2} mole/L for VAc, and 1.1×10^{-2} mole/L for AAc. Beyond these concentrations, graft yield decreases with all the monomers studied. This indicates that the chelate at higher concentrations participates in chain termination of the growing polymeric as well as the growing grafted polymeric chain.

Effect of Time and Temperature

Tables 4, 8, and 14 show that the maximum percent grafting of MMA, VAc, and AAc under optimum conditions occurs within 120 min. It is also observed from Tables 2, 7, and 12 that the percent grafting increases with an increase in temperature, and the maximum grafting is obtained at 55°C for all the monomers studied. A further increase in temperature leads to a decrease in percent grafting. This would be expected since, in the mechanism proposed (Eqs. 1-6), the growing polymeric chain abstracts a hydrogen atom from the wool backbone to generate active sites for grafting. Hydrogen abstraction reactions are usually promoted by a rise in temperature. Beyond 55°C it appears that termination reactions are accelerated, leading to a decrease in percent add-on.

Effect of Additives

In order to study the ligand-assisted decomposition of VO(acac)$_2$, several grafting experiments were conducted in the presence of DMSO and pyridine. It is observed from Tables 5, 10, and 15 that none of the additives promotes grafting. However, nitric acid was found to enhance grafting of MMA. In all our work on grafting of vinyl monomer onto wool by the ceric ion method, it was observed that a catalytic amount of nitric acid promoted grafting. It is not clear why nitric acid reduced the percent grafting of VAc and AAc in the present case. It seems that vinyl acetate, being much less reactive, is used

in side reactions, thus resulting in poor grafting. Both AAc and poly-(acrylic acid) are water soluble, and it appears that AAc preferentially undergoes homopolymerization in a homogeneous medium, resulting in a decrease in percent grafting.

ACKNOWLEDGMENTS

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