

Grafting Onto Wool. VI. Effect of Amines in Ceric Ion-Initiated Grafting of Poly(Vinyl Acetate)

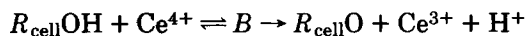
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Synopsis

Poly(vinyl acetate) has been graft copolymerized onto Himachali wool in the presence of ceric ammonium nitrate alone and in presence of amines in aqueous medium under a wide variety of reaction conditions. Nitric acid was found to catalyze the graft copolymerization. Maximum grafting under optimum conditions has been determined. Several grafting experiments were carried out in presence of triethylamine and triethanolamine. Both amines were found to reduce the extent of grafting. The decrease in the percent grafting in presence of amines has been explained in terms of a chain-transfer mechanism.

INTRODUCTION

As early as 1937, Flory discovered that polymers can be modified by grafting appropriate vinyl monomers in the presence of a variety of initiating systems. In the presence of radical initiators, grafting proceeds by a chain-transfer mechanism. Many synthetic polymers have been modified by using conventional radical initiators. However, it was shown that in the presence of radical initiators, grafting is often accompanied by formation of a large amount of homopolymer, separation of which from the grafted material presented a serious problem. Hence vigorous attempts were made to search for newer initiating systems which would selectively afford grafting or at least minimize the formation of homopolymer. Theoretically almost all the initiators known to effect polymerization of vinyl monomers are capable of producing graft in the presence of suitable preformed polymers. Attempts have been made to modify natural polymers such as cellulose in order to impart desirable properties. Conventional methods employing radical initiators such as BPO and AIBN were not very successful. Mino and Kaizerman¹ for the first time observed that oxidation of alcohols by ceric ion proceeds by a single electron transfer. Cellulose is a polyhydric alcohol and undergoes oxidation by ceric ions involving a one electron transfer as follows:



The macroradical generated in the presence of the ceric ion is expected to provide active sites for polymerization of suitable monomer. By applying this technique, Mino and Kaizerman¹ were able to graft acrylamide onto poly(vinyl alcohol). Since in this method free radicals are directly generated on the backbone polymer, grafting occurred without formation of homopolymer. Following the discovery of Mino and Kaizerman, many vinyl monomers have been grafted to cellulose by the ceric ion technique.

Wool is a natural polyamide containing numerous functional groups such as

-OH, -NH₂, -SH, -SS, -COOH and the imino group. It is well known that all these functional groups are capable of entering into redox reaction with ceric ion. Very little work has been reported on the modification of natural wool fiber by graft copolymerization using the ceric ion technique. Imai and Iwakura² were able to modify ovalbumin by graft copolymerization. Poly(ethyl acrylate) has been successfully grafted to gelatin³ by using persulfate as initiator. Recently Nayudamma and coworkers⁴ have reported on the grafting of poly(methyl methacrylate) onto collagen by ceric ammonium sulfate. Australian workers have reported that mineral acids promoted grafting of vinyl monomers in the presence of a swelling agent.⁵ Persulfates alone and in conjunction with reducing agents were found to graft vinyl monomers onto wool fiber.^{6,7} In recent years, Verma et al.^{8,9} have utilized the ceric ion technique for effecting grafting of various acrylates onto wool. Kantouch and coworkers¹⁰ observed that ceric sulfate is capable of producing grafts of wool and MMA and that the homopolymerization of MMA exceeded grafting in presence of wool. Recently Arai et al.¹¹ were able to graft MMA to wool without homopolymer formation by using a novel initiating system comprising LiBr-S₂O₈⁻². We have initiated a systematic research program on grafting of a wide variety of vinyl monomers onto wool by using different initiating system, which include (1) ceric ion,^{12,13} (2) radical initiator (BPO)¹⁴ in the presence of suitable pH modifier, (3) Fenton's reagent,¹⁵ and (4) the ceric-amine system.¹⁶

In a previous publication,¹⁶ we have reported that certain amines in the presence of Ce⁴⁺ promoted grafting of MA onto wool and that the percent grafting was dependent on the nature of amines used. In this paper, we report on the grafting of vinyl acetate, an electron-donating monomer onto wool as a function of various reaction variables. In order to study the effect of amines, several grafting reactions were carried out in presence of triethylamine and triethanolamine, and the results are presented in Tables I-III.

EXPERIMENTAL

Materials and Methods

Himachali wool is purified by extraction with acetone for 48-hr as reported earlier.^{13,14} Vinyl acetate (BDH) was freshly distilled, and the middle fraction was used. Ceric ammonium nitrate was used as received. Triethylamine was freshly distilled and triethanolamine (BDH) was used as such.

Graft Copolymerization

A gram of purified and dried wool was suspended in 200 ml de-aerated water. A known weight of CAN dissolved in a known volume of nitric acid was added to the reaction mixture. The reaction mixture was purged with nitrogen for 30 min. Monomer is added to the reaction mixture dropwise. To study the effect of amines, a known amount of amine is added to the reaction mixture consisting of CAN, HNO₃, and wool in water. The copolymerization was carried out under nitrogen atmosphere for various reaction periods. After completion of reaction, grafted material was separated and purified by the method described.¹⁵ Homopolymer was separated from the graft by extraction with acetone for 48 hr.

TABLE I
Effect of the Concentration of CAN, Monomer, Nitric Acid, Time, and Temperature in Ceric Ion-Initiated Grafting of Poly(Vinyl Acetate) Onto Wool^a

Sample	CAN, mol/l.	HNO ₃ , mol/l.	Monomer, mol/l.	Time, min	Temp., °C	Grafting, %	Efficiency, %
1	0.00125	9.0 × 10 ⁻²	16.1 × 10 ⁻²	30	45	0.88	0.31
2	0.00125	9.0 × 10 ⁻²	16.1 × 10 ⁻²	60	45	3.25	1.1
3	0.00125	9.0 × 10 ⁻²	16.1 × 10 ⁻²	90	45	6.78	2.4
4	0.00125	9.0 × 10 ⁻²	16.1 × 10 ⁻²	120	45	10.25	3.6
5	0.00125	9.0 × 10 ⁻²	16.1 × 10 ⁻²	150	45	12.53	4.4
6	0.00125	9.0 × 10 ⁻²	16.1 × 10 ⁻²	180	45	11.43	4.09
7	0.00125	9.0 × 10 ⁻²	16.1 × 10 ⁻²	150	40	5.69	2.04
8	0.00125	9.0 × 10 ⁻²	16.1 × 10 ⁻²	150	50	6.55	2.3
9	0.00125	9.0 × 10 ⁻²	16.1 × 10 ⁻²	150	60	3.64	1.3
10	0.00125	9.0 × 10 ⁻²	5.4 × 10 ⁻²	150	45	4.92	5.2
11	0.00125	9.0 × 10 ⁻²	27.0 × 10 ⁻²	150	45	8.25	1.7
12	0.00125	9.0 × 10 ⁻²	37.7 × 10 ⁻²	150	45	2.80	0.43
13	0.00125	9.0 × 10 ⁻²	48.6 × 10 ⁻²	150	45	0.33	0
14	0.00125	6.3 × 10 ⁻²	16.1 × 10 ⁻²	150	45	4.85	1.7
15	0.00125	8.1 × 10 ⁻²	16.1 × 10 ⁻²	150	45	2.02	0.73
16	0.00125	10.8 × 10 ⁻²	16.1 × 10 ⁻²	150	45	2.04	0.73
17	0.0015	9.0 × 10 ⁻²	16.1 × 10 ⁻²	150	45	32.26	11.5
18	0.002	9.0 × 10 ⁻²	16.1 × 10 ⁻²	150	45	20.10	7.2
19	0.003	9.0 × 10 ⁻²	16.1 × 10 ⁻²	150	45	9.42	3.3

^a Reaction conditions: wool, 1 g; water, 200 ml.

Percent grafting was determined from an increase in the weight of wool in the following manner:

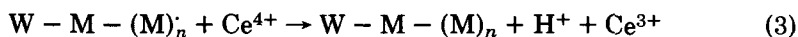
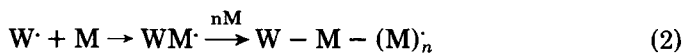
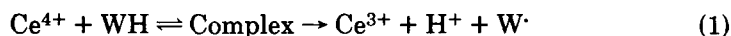
$$\text{Grafting (\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

$$\text{Efficiency (\%)} = \frac{W_1 - W_0}{W_2} \times 100$$

where W_0 , W_1 , and W_2 denote the weight of original wool, weight of wool after acetone extraction, and weight of monomer used, respectively. The infrared spectra of grafted material showed an absorption band at 1640 cm⁻¹, which was not present in wool. This was attributed to grafted poly(vinyl acetate).

RESULTS AND DISCUSSION

Grafting of vinyl monomers onto wool by ceric ion is believed to occur by the following mechanism:



In the above mechanism it is assumed that all the monomer goes to produce graft. This is true when acrylates are grafted to wool in presence of Ce⁴⁺. Very little homopolymer formation was observed in case of MA.¹² However, with vinyl acetate, it is observed that this monomer also undergoes homopolymerization,

TABLE II
Effect of the Concentration of CAN, Nitric Acid, Monomer, Triethylamine, Time, and Temperature on Ceric Ion-Initiated Grafting of Poly(Vinyl Acetate) Onto Wool^a

Sample	CAN, mol/l.	HNO ₃ , mol/l.	Amine, mol/l.	Monomer, mol/l.	Time, min	Temp., °C	Grafting, %	Efficiency, %
1	0.00125	9.0 × 10 ⁻²	1.77 × 10 ⁻²	16.1 × 10 ⁻²	30	45	0.1	0
2	0.00125	9.0 × 10 ⁻²	1.77 × 10 ⁻²	16.1 × 10 ⁻²	60	45	2.02	0.73
3	0.00125	9.0 × 10 ⁻²	1.77 × 10 ⁻²	16.1 × 10 ⁻²	90	45	5.23	1.8
4	0.00125	9.0 × 10 ⁻²	1.77 × 10 ⁻²	16.1 × 10 ⁻²	120	45	6.77	2.4
5	0.00125	9.0 × 10 ⁻²	1.77 × 10 ⁻²	16.1 × 10 ⁻²	150	45	8.88	3.1
6	0.00125	9.0 × 10 ⁻²	1.77 × 10 ⁻²	16.1 × 10 ⁻²	180	45	1.13	0.40
7	0.00125	10.8 × 10 ⁻²	1.77 × 10 ⁻²	16.1 × 10 ⁻²	150	45	0.89	0.31
8	0.00125	14.4 × 10 ⁻²	1.77 × 10 ⁻²	16.1 × 10 ⁻²	150	45	1.83	0.65
9	0.00125	18.0 × 10 ⁻²	1.77 × 10 ⁻²	16.1 × 10 ⁻²	150	45	4.03	1.4
10	0.0015	9.0 × 10 ⁻²	1.77 × 10 ⁻²	16.1 × 10 ⁻²	150	45	3.73	1.3
11	0.002	9.0 × 10 ⁻²	1.77 × 10 ⁻²	16.1 × 10 ⁻²	150	45	1.95	0.7
12	0.001	9.0 × 10 ⁻²	1.77 × 10 ⁻²	16.1 × 10 ⁻²	150	45	0	0
13	0.00125	9.0 × 10 ⁻²	1.77 × 10 ⁻²	5.4 × 10 ⁻²	150	45	0.89	0.95
14	0.00125	9.0 × 10 ⁻²	1.77 × 10 ⁻²	27.0 × 10 ⁻²	150	45	5.53	1.1
15	0.00125	9.0 × 10 ⁻²	1.77 × 10 ⁻²	37.7 × 10 ⁻²	150	45	2.59	0.39
16	0.00125	9.0 × 10 ⁻²	1.06 × 10 ⁻²	16.1 × 10 ⁻²	150	45	6.81	2.4
17	0.00125	9.0 × 10 ⁻²	2.49 × 10 ⁻²	16.1 × 10 ⁻²	150	45	11.88	4.2
18	0.00125	9.0 × 10 ⁻²	3.55 × 10 ⁻²	16.1 × 10 ⁻²	150	45	7.43	2.6
19	0.00125	9.0 × 10 ⁻²	2.49 × 10 ⁻²	16.1 × 10 ⁻²	150	40	3.51	1.2
20	0.00125	9.0 × 10 ⁻²	2.49 × 10 ⁻²	16.1 × 10 ⁻²	150	50	6.24	2.2
21	0.00125	9.0 × 10 ⁻²	2.49 × 10 ⁻²	16.1 × 10 ⁻²	150	60	7.37	2.6

^a Reaction conditions: wool, 1 g; water, 200 ml.

resulting in poor grafting. This then necessitates modification of the above mechanism so that the formation of homopolymer can also be accounted for. Table I shows that under the optimum conditions, vinyl acetate is only 32.26% grafted. Even the amines (triethylamine and triethanolamine) did not improve grafting. It appears that besides forming complex with wool, the ceric ion is also involved in reaction with vinyl acetate to give homopolymer. In order to explain satisfactorily the experimental data, the following modified mechanism is suggested:

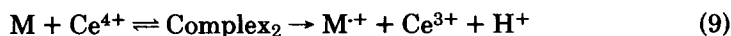
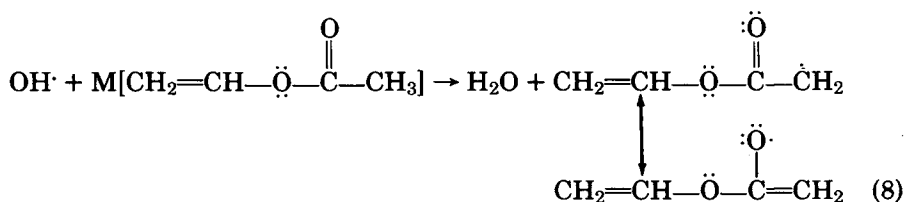
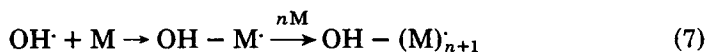
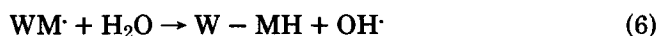
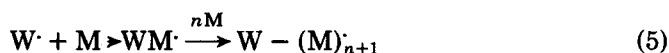
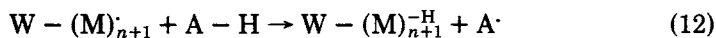


TABLE III
Effects of the Concentration of CAN, Nitric Acid, Monomer, Triethanolamine, Time, and Temperature on Ceric Ion-initiated Grafting of Poly(Vinyl Acetate) Onto Wool

Sample	CAN, mol/l.	HNO ₃ , mol/l.	Amine, mol/l.	Monomer, mol/l.	Time, min	Temp., °C	Grafting, %	Efficiency, %
1	0.00125	9.0 × 10 ⁻²	1.87 × 10 ⁻²	16.1 × 10 ⁻²	30	45	0.89	0.31
2	0.00125	9.0 × 10 ⁻²	1.87 × 10 ⁻²	16.1 × 10 ⁻²	60	45	1.48	0.53
3	0.00125	9.0 × 10 ⁻²	1.87 × 10 ⁻²	16.1 × 10 ⁻²	90	45	3.46	1.2
4	0.00125	9.0 × 10 ⁻²	1.87 × 10 ⁻²	16.1 × 10 ⁻²	120	45	1.17	0.40
5	0.00125	9.0 × 10 ⁻²	1.87 × 10 ⁻²	16.1 × 10 ⁻²	180	45	0.18	0
6	0.00125	9.0 × 10 ⁻²	1.87 × 10 ⁻²	16.1 × 10 ⁻²	90	40	2.82	2.0
7	0.00125	9.0 × 10 ⁻²	1.87 × 10 ⁻²	16.1 × 10 ⁻²	90	50	1.72	0.61
8	0.00125	9.0 × 10 ⁻²	1.87 × 10 ⁻²	16.1 × 10 ⁻²	90	60	0	0
9	0.00125	9.0 × 10 ⁻²	1.87 × 10 ⁻²	5.4 × 10 ⁻²	90	45	7.92	8.5
10	0.00125	9.0 × 10 ⁻²	1.87 × 10 ⁻²	27.0 × 10 ⁻²	90	45	11.60	2.5
11	0.00125	9.0 × 10 ⁻²	1.87 × 10 ⁻²	37.7 × 10 ⁻²	90	45	4.49	0.69
12	0.001	9.0 × 10 ⁻²	1.87 × 10 ⁻²	27.0 × 10 ⁻²	90	45	2.52	0.54
13	0.0015	9.0 × 10 ⁻²	1.87 × 10 ⁻²	27.0 × 10 ⁻²	90	45	8.24	1.7
14	0.002	9.0 × 10 ⁻²	1.87 × 10 ⁻²	27.0 × 10 ⁻²	90	45	4.54	0.97
15	0.00125	7.2 × 10 ⁻²	1.87 × 10 ⁻²	27.0 × 10 ⁻²	90	45	4.17	0.9
16	0.00125	10.8 × 10 ⁻²	1.87 × 10 ⁻²	27.0 × 10 ⁻²	90	45	7.74	1.6
17	0.00125	18.0 × 10 ⁻²	1.87 × 10 ⁻²	27.0 × 10 ⁻²	90	45	4.02	0.87
18	0.00125	9.0 × 10 ⁻²	1.12 × 10 ⁻²	27.0 × 10 ⁻²	90	45	0.56	0
19	0.00125	9.0 × 10 ⁻²	2.62 × 10 ⁻²	27.0 × 10 ⁻²	90	45	5.01	1.07
20	0.00125	9.0 × 10 ⁻²	3.75 × 10 ⁻²	27.0 × 10 ⁻²	90	45	6.03	1.3

^a Reaction conditions: wool, 1 g; water, 200 ml.



Effect of Concentration of CAN

In accordance with the above mechanism an increase in the concentration of CAN should afford higher grafting. In fact it is observed from Table I that with an increase in the concentration of CAN, the percent grafting increases up to a certain limit, indicating that there exists a critical concentration of CAN beyond which percent grafting decreases. Similar observations have also been reported with electron-attracting monomers such as MA,¹² EA,¹³ and MMA.¹⁰ But with all the acrylates, the percent grafting obtained using the optimum concentration of CAN was much higher than that obtained with vinyl acetate. This indicates that in the presence of the ceric ion, not all vinyl monomers are equally reactive towards grafting. Simultaneously with complex formation between Ce⁴⁺ and wool, another complex is also formed between vinyl acetate and Ce⁴⁺. This would be expected, since the highly electrophilic Ce⁴⁺ will show a strong tendency to combine with vinyl acetate, which is an electron-donating monomer. If this be the case, then it is not surprising that in the presence of vinyl acetate, some Ce⁴⁺ is consumed in forming the complex, which on decomposition forms M· outside the fiber matrix; this leads to the formation of homopolymer at the expense of grafting. Furthermore, since vinyl acetate shows a strong tendency to

complex with the Ce^{4+} , WM- which is generated does not find enough vinyl acetate in its vicinity to result in graft. Rather, WM- has enough time to react with water (reaction medium), resulting in the destruction of the active sites on the wool backbone. This will decrease the percent grafting. When Ce^{4+} exceeds the critical concentration, percent grafting decreases. This is explained by the fact that at higher concentration, Ce^{4+} is involved in terminating the growing grafted chains. The participation of Ce^{4+} in terminating the growing polymeric, as well as the grafted, chains has been reported.^{12,17} The poor grafting of vinyl acetate is further explained by the fact that the $OH\cdot$ is formed and it can abstract hydrogen atoms from suitable vinyl monomer, leading to the wastage of vinyl monomer. This assumes significance when vinyl acetate is used as monomer, since the hydrogen abstraction reaction with vinyl acetate is facilitated owing to resonance stabilization of the resulting radical species, as shown in step (8).

Effect of Monomer Concentration

Figure 1 shows the variation in the rate of grafting (R_p) with varying monomer concentrations. It is observed that with increases in the monomer concentration,

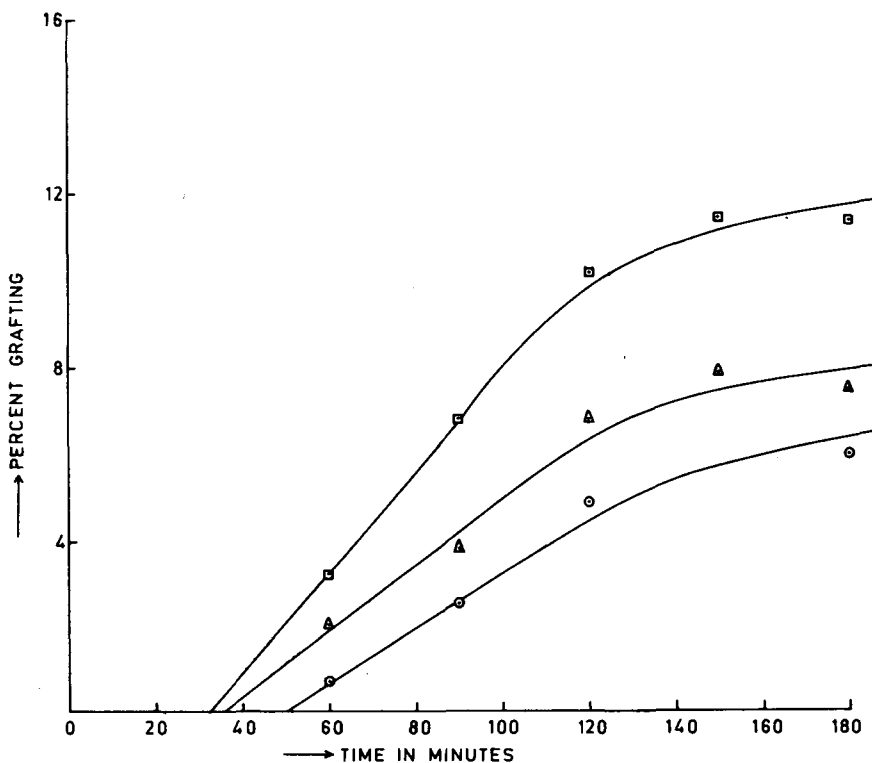


Fig. 1. Variation of the grafting rate, R_p , with the following monomer concentrations (in mol/liter): 5.4×10^{-2} (\circ), 27×10^{-2} (Δ), and 16.1×10^{-2} (\square). Conditions: wool, 1 g; H_2O , 200 ml; [CAN], 0.00125 mol/liter; $[HNO_3]$, 9×10^{-2} mol/liter; and $t = 45^\circ$.

TABLE IV
Effect of Total Initial Monomer Concentration on Percent Grafting^a

Initial monomer concentration mol/l.	Initial grafting rate (R_p), %/min	Induction period (I_p), min
5.4×10^{-2}	0.06	50
16.1×10^{-2}	0.11	32
27.0×10^{-2}	0.07	35

^a Wool, 1.0 g; H₂O, 200 ml; CAN, 0.00125 mol/liter; temp., 45°C; HNO₃, 9.0×10^{-2} mol/liter.

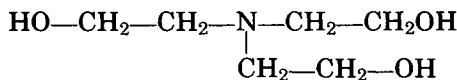
the percent grafting increases and then levels off. This indicates that within 150 min all the functional groups of wool are utilized in complex formation with Ce.⁴⁺ It is apparent from Figure 1 that there exists a critical monomer concentration beyond which R_p decreases. This tends to indicate that at higher monomer concentration, complex formation between monomer and Ce⁴⁺ assumes importance. Furthermore, when monomer concentration exceeds the optimum concentration, various chain-transfer processes leading to the wastage of monomer are occurring. The rate of grafting (R_p) has been calculated from the slopes of the plot of percent grafting versus time (Fig. 1) at the initial stages of reaction. Table IV shows that R_p is maximum (0.11%/min) at a total initial monomer concentration of 16.1×10^{-2} mol/l. The induction period (I_p) for grafting varies with the total initial monomer concentrations. It is apparent from Table IV that at a lower monomer concentration (5.4×10^{-2} mol/l.), I_p is at a maximum (50 min) and that I_p decreases as the concentration of monomer increases. When the total initial monomer concentration is 16.1×10^{-2} mol/l., I_p is at a minimum (32 min), and consequently R_p is maximum.

Effect of Temperature

It is apparent from Table I that the optimum temperature for maximum grafting was found to be 45°C. Beyond this temperature, chain-transfer processes are accelerated, resulting in poor grafting. It is, however, not clear why maximum grafting occurs at 45°C.

Effect of Amines

It is apparent from Tables II and III that both triethyl- and triethanolamines suppress grafting. However, with MA, it was observed that triethylamine of appropriate concentration promoted grafting onto wool.¹⁶ This was explained by assuming a complex formation between Ce⁴⁺ and triethylamine. Such complex formation between Ce⁴⁺ and triethylamine appears to show monomer selectivity. In the presence of vinyl acetate, complex formation between Ce⁴⁺ and triethylamine is inhibited; hence no acceleration in grafting occurs. In triethanolamine the oxygen atom at the beta-position,



reduces the electron density on the nitrogen

(—N—)

and hence complex formation between Ce^{4+} and triethanolamine is not favored. Besides, because of the large size, complex formation between triethanolamine and Ce^{4+} will be difficult. This is why neither grafting nor homopolymerization is favored in the presence of triethanolamine. Thus it appears that during grafting in presence of various Ce^{4+} -amine systems, both nucleophilicity and the size of amines are important; however, the relative contribution of each factor remains to be evaluated. In order to arrive at a relationship between the extent of grafting and nucleophilicity of amines, the percent grafting of various vinyl monomers in the presence of Ce^{4+} and various amines of known nucleophilicity is being investigated. In the presence of nitric acid, the amines will be in the protonated form. However, our arguments regarding the reactivity of amines remain valid.

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