

Notes

Grafting Vinyl Monomers onto Cellulose. X. Graft Copolymerization of Methyl Methacrylate onto Cellulose Fibers Using Acetylacetonate Complex of Vanadium Ion

Graft copolymerization of vinyl monomers onto cellulose has been extensively studied using a variety of methods, e.g., chain transfer,¹ high energy radiation,^{2,3} low energy radiation in the presence of a sensitizer,⁴ mechanical degradation, and redox systems.^{5,6}

Nayak and co-workers have used quinquevalent vanadium ion as the initiator for graft copolymerization of vinyl monomers onto wool,⁷ silk,⁸ cellulose,⁹ and PET¹⁰ fibers. Recently the interest of many authors has been focused on the study of the kinetics and mechanism of initiation of radical polymerization of vinyl and diene monomers by metal chelates.^{11,12} This note presents the results of studies of graft copolymerization of methyl methacrylate onto cellulose using acetylacetonate complex of quinquevalent vanadium ion.

EXPERIMENTAL

Egyptian cotton slivers were purified by our previous procedure.⁹ The acetylacetonate complex of quinquevalent vanadium was prepared according to the literature procedure.¹³ The graft copolymerization was carried out according to our previous methods.⁷⁻¹⁰

RESULTS AND DISCUSSION

The effect of the initiator concentration on graft yield was investigated by varying the initiator concentration from 0.75×10^{-4} to $3.75 \times 10^{-4}M$ at different monomer concentrations. The results indicate that, with increasing chelate concentration, the graft yield increases. But, at very high concentration of chelates, a decreasing trend in the graft yield is noticed. This phenomenon has also been observed while grafting methyl methacrylate onto PET¹⁰ fibers using V^{5+} as the initiator. The effect of monomer concentration on the polymerization reaction was evaluated by changing the monomer concentrations within the range of 0.2816–1.032M at different initiator concentrations. It is observed that increasing the monomer concentration in the initial stages causes an outstanding enhancement in the graft yield. But as the concentration of monomer increases after certain stage, the graft yield decreases. The effect of sulphuric acid concentration was studied using acid concentration within the range of 1.5×10^{-3} – $5.0 \times 10^{-3}M$. It is observed that the graft yield increases up to $7.5 \times 10^{-3}M$ and thereafter the graft yield decreases with further increase in acid concentration (Fig. 1). The effect of raising the temperature from 50°C to 70°C is to bring about a significant

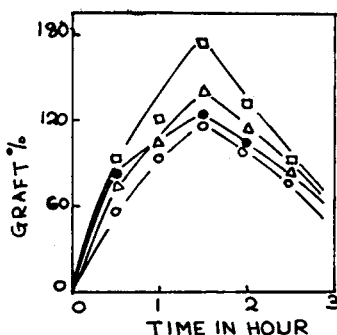


Fig. 1. Effect of acid concentration: [complex] = $2.5 \times 10^{-4}M$; [MMA] = $0.4694M$; temp = 70°C; M:L = 1:100; (○) $[H_2SO_4] = 1.5 \times 10^{-3}M$; (Δ) $[H_2SO_4] = 4.5 \times 10^{-3}M$; (□) $[H_2SO_4] = 7.5 \times 10^{-3}M$; (●) $[H_2SO_4] = 15 \times 10^{-3}M$.

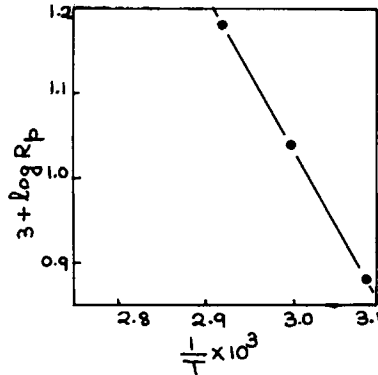
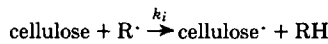
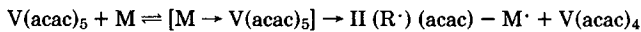
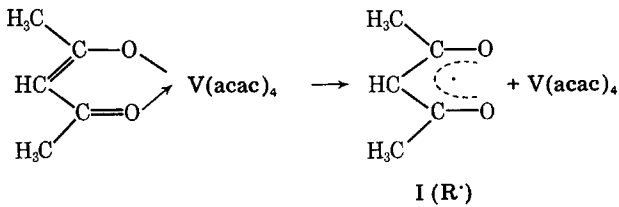


Fig. 2. Arrhenius plot of $\log R_p$ vs. $1/T$.

enhancement in the rate of grafting. Beyond 70°C the rate of grafting decreases. From the Arrhenius plot (Fig. 2) of $\log R_p$ vs. $1/T$, the overall activation energy was computed to be 5.2 kcal/mol.

Arnett and Mendelsohn¹⁴ and Bamford and Lind¹¹ have pointed out that the initiation mechanism by $\text{V}(\text{acac})_5$ is considered to occur through the homolysis of their metal-oxygen bonds forming acetylaceton radical or the radical in combination with the monomer ($\text{R}\cdot$) which initiates grafting:



Initiation:

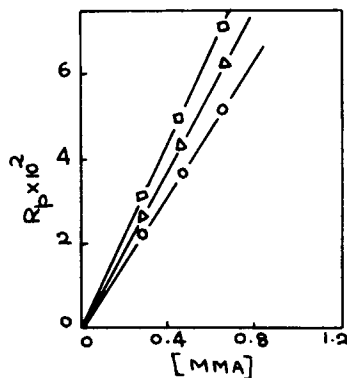
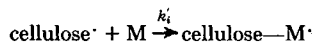


Fig. 3. Plot of R_p vs. $[\text{MMA}]$: (O) $[\text{complex}] = 1.75 \times 10^{-4}\text{M}$; (Δ) $[\text{complex}] = 2.5 \times 10^{-4}\text{M}$; (\square) $[\text{complex}] = 3.25 \times 10^{-4}\text{M}$.

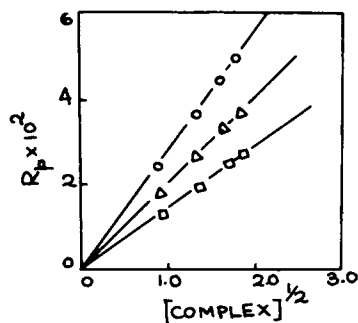
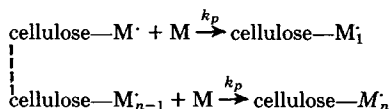
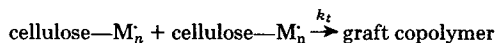


Fig. 4. Plot of R_p vs. $[\text{complex}]^{1/2}$: (\square) $[\text{MMA}] = 0.4694M$; (Δ) $[\text{MMA}] = 0.7041M$; (\circ) $[\text{MMA}] = 0.9388M$.

Propagation:



Termination:



Applying steady state assumptions to the growing radicals we have

$$R_p = k_p (k_i/k_t)^{1/2} [V(\text{acac})_5]^{1/2} [M]$$

Thus the plots of R_p vs. $[\text{MMA}]$ (Fig. 3), R_p vs. $[\text{complex}]^{1/2}$ (Fig. 4) were linear, indicating the validity of the above reaction scheme.

The rate of grafting was also studied in presence of two monomers, i.e., methyl methacrylate, acrylonitrile and methyl methacrylate, methyl acrylate. In both systems methyl methacrylate concentration was maintained constant. The perusal of the result indicates that, as the monomer concentration (acrylonitrile or methacrylate) increases, the graft-on percentage decreases. The effect of inhibitors like hydroquinone and picryl chloride was studied. As the concentration of inhibitor increases, the graft-on percentage decreases, and it becomes negligibly small at certain stages of inhibitor concentration.

This project is financed by C.S.I.R., New Delhi by Scheme No. 2 (135)/79 EMR-II. Two of the authors (S.L. and A.K.T.) are thankful to C.S.I.R., New Delhi for Research Associateship and JRF.

References

1. D. K. R. Chaudhari and J. J. Hermans, *J. Polym. Sci.*, **48**, 159 (1960).
2. W. H. Rapson, Am. Chem. Soc. 138th Meeting, New York, Sept. 1960.
3. J. C. Arthur, *Text. Res. J.*, **29**, 759 (1959).
4. N. Geacintov, V. Stannett, and E. W. Abrahamson, *Makromol. Chem.*, **36**, 52 (1959).
5. W. V. Smith and H. N. Cambell, *J. Chem. Phys.*, **15**, 338 (1947).
6. P. D. Bartlett and K. Nozaki, *J. Polym. Sci.*, **3**, 216 (1948).
7. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Makromol. Chem.*, **71**, 189 (1978).
8. P. L. Nayak, S. Lenka, and N. C. Pati, *Angew. Makromol. Chem.*, **68**, 117 (1978).
9. S. Lenka, P. L. Nayak, and M. K. Mishra, *J. Appl. Polym. Sci.*, **25**, 1323 (1980).
10. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Appl. Polym. Sci.*, **26**, (1981), to appear.
11. C. H. Bamford and D. J. Lind, *Chem. Commun.*, 792 (1966).

12. T. Otsu, N. Minamii, and Y. Nishikawa, *J. Macromol. Sci. Chem. A*, **2**(5), 905 (1968).
13. J. Kleinberg, Ed., *Inorganic Synthesis*, McGraw-Hill, New York, 1965, Vol. 5.
14. E. M. Arnett and M. A. Mendelsohn, *J. Am. Chem. Soc.*, **84**, 382 (1962).

SUBASINI LENKA
PADMA L. NAYAK
ATANU K. TRIPATHY

Laboratory of Polymer and Fibres
Department of Chemistry
Ravenshaw College
Cuttack-753003, Orissa, India

Received September 28, 1981
Accepted March 11, 1982