

Grafting Vinyl Monomers onto Cellulose. IV. Graft Copolymerization of Methyl Methacrylate onto Modified Cellulose using Peroxydiphosphate as the Initiator

SUBASINI LENKA, PADMA L. NAYAK, and MUNMAYA K. MISHRA,
*Laboratory of Polymers and Fibres, Department of Chemistry, Ravenshaw
College, Cuttack-753 003, Orissa, India*

Synopsis

The graft copolymerization of methyl methacrylate onto modified cellulose was studied at 60° causing peroxydiphosphate as the initiator. The rate of grafting in case of different modified cellulose was determined by varying peroxydiphosphate, monomer, nature of substrate, and temperature. The molecular weight of the isolated polymer has been determined, and the mechanism of grafting is discussed.

INTRODUCTION

Graft copolymerization of vinyl monomers onto cellulose has been studied extensively using a variety of methods, e.g., chain transfer,¹ high-energy radiation,²⁻⁹ low-energy radiation in the presence of a sensitizer,^{10,11} mechanical degradation,¹²⁻¹⁴ and redox systems.¹⁵⁻¹⁸ The mechanisms involved in the grafting reactions have been reviewed in detail.¹⁹

Peroxydiphosphate (PP) is a very good initiator. Recently, Nayak et al.²⁰⁻²² have reported the use of PP as an initiator for grafting methyl methacrylate (MMA) onto a number of natural and synthetic fibers. We have reported the graft copolymerization of MMA onto cellulose using V^{5+} —as the initiator.²³

This paper presents the results of graft copolymerization of MMA onto modified cellulose using PP as an initiator.

EXPERIMENTAL

Egyptian cotton slivers were purified by our previous procedure.²³

Sodium hydroxide treated cotton (NaOH-cotton) was prepared by treating the purified cotton slivers with aqueous sodium hydroxide (12*N*) at room temperature for 1 h followed by washing and drying in air at room temperature.

Cyanoethylated cotton was prepared by impregnating it with 0.5*N* sodium hydroxide for 1 h followed by padding to a pickup of about 100%. At this point, the sample was treated with acrylonitrile at 60° C for various lengths of time. Finally, the sample was scoured with dilute acetic acid, washed thoroughly with water, and dried at ambient conditions.

The crosslinked cellulose was prepared by immersing it and wetting it out in a solution containing specified concentrations of formaldehyde and 2% ammo-

mium chloride. Excess solution was removed by squeezing the materials to a wet pickup of 90–95%. The samples were dried at 60° C for 7 min and then heated in an oven at 120° C for 5 min.

Zinc-chloride-treated cellulose was prepared by immersing the cellulose in 70% (w/w) zinc chloride solution at 20° C for 1 h.

The method of grafting and the calculation of the percent graft have been reported in our earlier publications.^{20–23}

RESULTS AND DISCUSSION

Figure 1 shows the results of graft yield obtained when MMA was grafted onto cellulose using PP as the initiator. The graft yield increases with increasing the concentration of MMA from $28.16 \times 10^{-2} M$ to $122.21 \times 10^{-2} M$ in case of all the modified celluloses. The accelerated grafting at higher monomer concentration could be associated with the gel effect,²⁴ i.e., an increase in viscosity of the medium. Since poly(methyl methacrylate) is soluble in its own monomer, the viscosity of the medium would be higher at higher monomer concentration. Hence, at higher viscosities, bimolecular termination of the growing chains is hindered, whereas the other steps in the graft polymerization process, like initiation, propagation, and radical chain processes, are not affected to the same degree by increasing viscosity because the mobility of the polymer chains is restricted by the cellulose structure. In addition, the gel effect²⁴ causes swelling of cellulose and thus assists diffusion of monomer to the growing chains and active sites on the cellulose, thereby enhancing grafting.

Figure 2 shows the effect of PP concentration on the extent of grafting with MMA on different modified cellulose. Obviously, increasing the initiator concentration up to $100 \times 10^{-4} M$ causes a rapid increment in the graft yield. Further, increase in the PP concentration causes a decrease in the amount of graft formation. The reasons have been explained in our previous communication.²⁰

Figures 3 and 4 shows the effect of temperature on grafting within the range

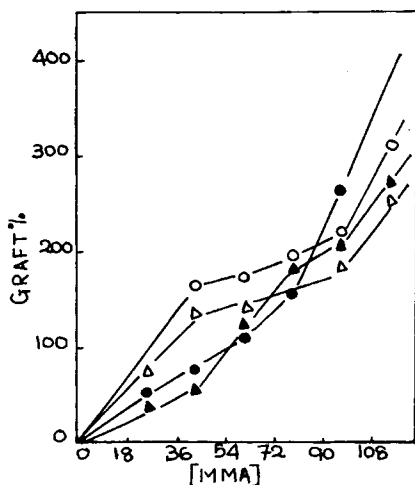


Fig. 1. Effect of [MMA] on graft yield: [PP] = 100×10^{-4} mol/L; temperature = 60° C; time = 8 h; *M:L* = 1:100; (O) NaOH-cell; (Δ) ZnCl₂-cell; (●) cyanoethylated-cell; (▲) crosslinked-cell.

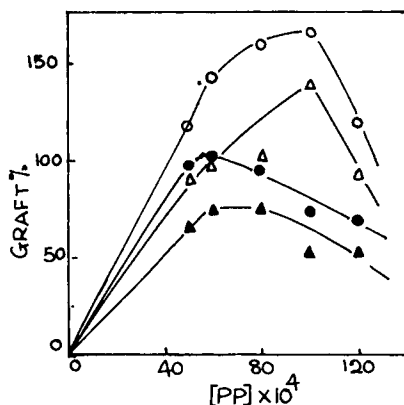


Fig. 2. Effect of [PP] on graft yield: [MMA] = 46.94×10^{-2} mol/L; temperature = 60°C ; time = 8 h; $M:L = 1:100$; (O) NaOH-cell; (Δ) ZnCl_2 -cell; (\bullet) cyanoethylated-cell; (\blacktriangle) crosslinked-cell.

$55\text{--}65^\circ\text{C}$. It is evident from the result that the graft yield increases with increasing temperature in case of zinc-chloride-treated, cyanoethylated, crosslinked cellulose. This is expected since increasing the temperature would favorably influence the swellability of cellulose, solubility of monomer, diffusion of both monomer and initiator, rate of PP decomposition, and initiation and propagation of the graft. The net effect of all these parameters leads to high grafting.

It is evident from Figure 5 that the percentage of graft yield decreases by cyanoethylation of cellulose. Nayak et al.²⁰ postulated that PP decomposes in the initial stages producing a number of free radicals like HPO_4^- , and PO_4^{2-} . These radicals interact with the hydroxyl groups present in the backbone of the cellulose-producing new free radicals capable of initiating grafting. Kantouch et al.,²⁵ while grafting acrylonitrile onto modified cellulose using the ceric ion method have predicted that Ce^{4+} forms a complex with the C_2 and C_3 hydroxyl groups

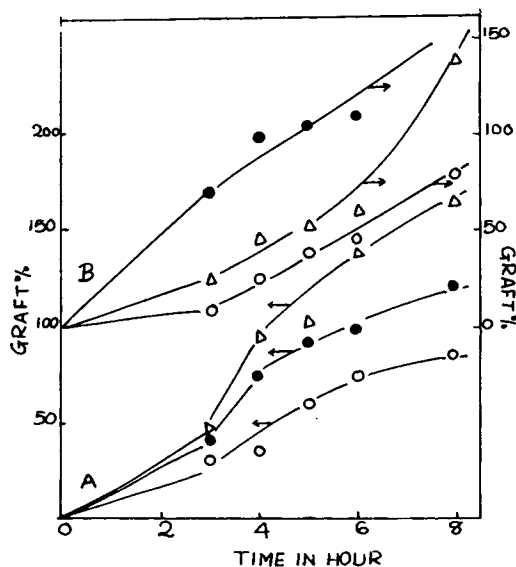


Fig. 3. Effect of temperature on graft yield: [PP] = 100×10^{-4} mol/L; [MMA] = 46.94×10^{-2} mol/L; $M:L = 1:100$; A = NaOH-cell; B = ZnCl_2 -cell; (O) temperature = 55°C ; (Δ) temperature = 60°C ; (\bullet) temperature = 65°C

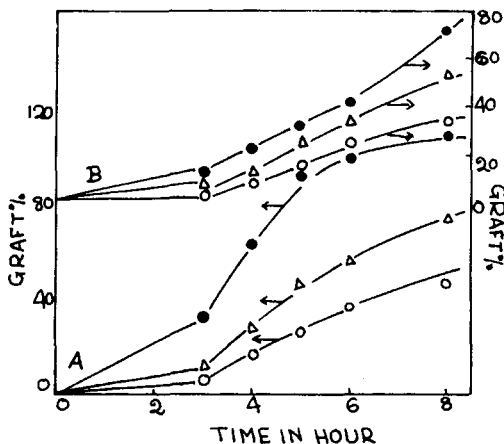


Fig. 4. Effect of temperature on graft yield: $[PP] = 100 \times 10^{-4}$ mol/L; $[MMA] = 46.94 \times 10^{-2}$ mol/L; $M:L = 1:100$; (A) cyanoethylated-cell; (B) crosslinked cell; (O) temperature = 55°C ; (Δ) temperature = 60°C ; (\bullet) temperature = 65°C .

of the cellulose molecule. This complex breaks down in a unimolecular fashion producing a free radical mostly at the C_2 of the anhydroglucose unit of the cellulose molecule. Etherification studies have shown that the C_2 group is etherified twice as fast as the C_3 group. Sonnerskoj²⁶ reported the preferential reactivity of C_2 of the anhydroglucose unit of cellulose. Hence, cyanoethylation most probably occurs through the C_2 -OH groups. Presence of such groups at the C_2 position will certainly decrease the extent of formation of free radicals on the cellulose backbone, thereby inhibiting the graft yield.

Crosslinking cellulose by formaldehyde decreases the extent of grafting, compared to the control. This is expected since the crosslinking reaction takes place in highly disordered regions. Besides blocking some of the cellulose hydroxyls, the crosslinks result in a measurable reduction in fibre swellability probably by restricting mobility of the cellulose molecules during grafting. Thus, low swellability of the crosslinked cellulose could impede diffusion of monomer and initiator, thereby adversely affecting the grafting reaction.

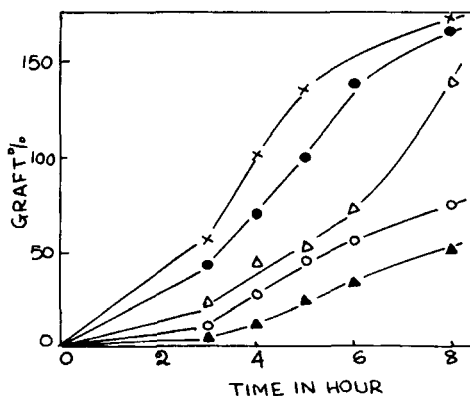


Fig. 5. Nature of substrate on graft yield: $[PP] = 100 \times 10^{-4}$ mol/L; $[MMA] = 46.94 \times 10^{-2}$ mol/L; temperature = 60°C ; $M:L = 1:100$; (x) untreated-cell; (\bullet) NaOH-cell; (Δ) $ZnCl_2$ -cell; (O) cyanoethylated-cell; (\blacktriangle) crosslinked-cell.

TABLE I
Percentage Graft, Molecular Weight, and Degree of Polymerization for Modified Cellulose

Nature of substrate	Graft %	$\bar{M}_w \times 10^{-5}$	$\bar{DP} \times 10^{-3}$
NaOH-cell	43.95	12.12	12.12
	101.10	18.32	18.32
	166.05	24.13	24.13
ZnCl ₂ -cell	25.35	8.32	8.32
	53.3	18.12	18.12
	140.6	20.31	20.31
Cyanoethylated	11.95	6.34	6.34
	46.7	8.79	8.79
	75.35	10.32	10.32
Crosslinked	26.1	12.31	12.31
	34.3	8.93	8.93
	54.05	7.65	7.65

When cellulose is treated with zinc chloride, probably it forms a chelate type of complex with the C₂ and C₃ hydroxyl groups of the cellulose molecule as is reported in case of ceric ion.²⁵

The availability of the free hydroxyl groups is reduced considerably for the interaction of the PP free radicals to create grafting sites on the cellulose backbone and hence the graft yield decreases.

When cellulose is treated with sodium hydroxide, sodium salt of the cellulose (sodium cellulosate) is formed. Hence, the hydroxyl group is blocked and it would be difficult to create free radicals on the cellulose backbone thereby decreasing the extent of grafting.

The average molecular weight \bar{M}_w , and degree of polymerization of the grafted poly(methyl methacrylate) was determined by using the relationship

$$[\eta] = 9.6 \times 10^{-5} \bar{M}_w^{0.69}$$

The perusal of the result (Table I) indicates that the average molecular weight as well as the degree of polymerization increases with increasing graft on percentage in case of cyanoethylated, sodium-hydroxide- and zinc-chloride-treated cellulose, but in case of crosslinked cellulose it decreases percentage of graft. This is because, in the former cases, the termination might be mutual, whereas, in the latter cases, the termination is linear.

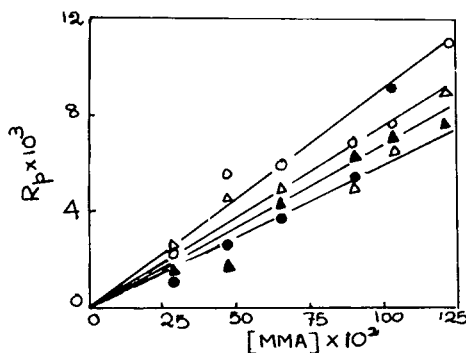
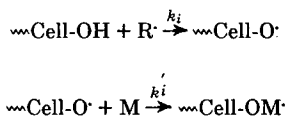


Fig. 6. Plot of R_p vs. $[M]$: (O) NaOH-cell; (Δ) ZnCl₂-cell; (\bullet) cyanoethylated-cell; (\blacktriangle) Cross-linked-cell.

Mechanism: The free radicals like $\text{H}_2\text{PO}_4^\cdot$, $\dot{\text{O}}\text{H}$, and $\text{HPO}_4^{\cdot-}$, which are produced during the reaction, interact with the hydroxyl groups present in the cellulose backbone-producing cellulose macroradicals which initiates grafting. The reaction scheme is presented below.

Initiation:



M = methyl methacrylate monomer, R \cdot = $\text{H}_2\text{PO}_4^\cdot$, $\dot{\text{O}}\text{H}$, and $\text{HPO}_4^{\cdot-}$, cell-OH = cellulose, $\sim\text{Cell-O}^\cdot$ and $\sim\text{Cell-OM}^\cdot$ = cellulose radicals

This initiation is being followed by the steps such as propagation and termination, resulting in the grafted polymer.

Applying steady-state assumptions, the rate of polymerization, R_p , may be expressed as $R_p = k_p (k_i/k_t)^{1/2} [\text{cell-OH}]^{1/2} [\text{M}]$. The plot of R_p , vs. $[\text{M}]$ (Fig. 6) is linear, indicating the dependence of order unity with respect to monomer concentration.

This project is financed by C.S.I.R., New Delhi, by Project No. 14(12)/76, EMR.II.

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, September 1960.
3. J. C. Arthur, *Text. Res. J.*, **29**, 759 (1959).
4. E. H. Immergut, *Encyclopedia of Polymer Science and Technology*, H. F. Mark, N. G. Gaylord, and N. M. Bakler, Eds., Interscience, New York, 1959, Vol. 3, p. 242.
5. J. J. Hermans, *Pure Appl. Chem.*, **5**, 147 (1962).
6. R. J. Demint, J. C. Arthur, Jr., A. R. Markezich, and W. F. Mcsberry, *Text. Res. J.*, **32**, 918 (1962).
7. H. Yasuda, J. A. Wray, and V. Stannett, *J. Polym. Sci. C*, **2**, 387 (1963).
8. F. A. Blouin and J. C. Arthur, Jr., *Text. Res. J.*, **33**, 727 (1963).
9. R. E. Kasting and V. Stannett, *Makromol. Chem.*, **65**, 248 (1963).
10. N. Geacintov, V. Stannett, and E. W. Abrahamson, *Makromol. Chem.*, **36**, 52 (1959).
11. N. Geacintov, V. Stannett, E. W. Abrahamson, and J. J. Hermans, *J. Appl. Polym. Sci.*, **3**, 54 (1960).
12. W. Deters and D. Huang, *Faserforsch Textiltechn.*, **14**(5), 183 (1963).
13. N. V. de Battafshe Petroleum Maatschappij, British Patent 679,563 (1962).
14. R. J. Ceresa, *Block and Graft Copolymer*, Butterworths, London, 1962, p. 325.
15. W. V. Smith and H. N. Cambell, *J. Chem. Phys.*, **15**, 338 (1947).
16. P. D. Bartlett and K. Nozaki, *J. Polym. Sci.*, **3**, 216 (1948).
17. D. J. Bridgeford, Am. Chem. Soc. 138th Annual Meeting, New York, September 1960.
18. G. N. Richards, *J. Appl. Polym. Sci.*, **5**, 539 (1961).
19. A. Hebeish, *Kolorisztikai Ertesito*, **13**(1-2), 12 (1971).
20. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Appl. Polym. Sci.*, **25**, 63 (1980).
21. S. Lenka, P. L. Nayak, and M. K. Mishra, *Angew. Makromol. Chem.*, **84**, 183 (1980).
22. P. L. Nayak, S. Lenka, and M. K. Mishra, *J. Polym. Sci.*, **A-1**, **XX**, xxx (1981).
23. S. Lenka, P. L. Nayak, and M. K. Mishra, *J. Appl. Polym. Sci.*, **25**, 1323 (1980).
24. S. Dilli, J. L. Garnett, E. C. Martin, and D. H. Phvoc, *J. Polym. Sci. C*, **37**, 57 (1972).
25. A. Kantouch, A. Hebeish, and M. H. El-Rafie, *J. Appl. Polym. Sci.*, **15**, 1007 (1971).
26. S. Sonnerskoj, *Svensk Papperstidn* **51**, 50 (1948).

Received October 10, 1980

Accepted March 13, 1981