Notes

Grafting Vinyl Monomers onto Cellulose. V. Graft Copolymerization of Methyl Methacrylate onto Cellulose Using a Hexavalent Chromium Ion

Grafting of vinyl monomers onto cellulose[1] has been the subject of extensive investigations during the last several years. Chromium (VI) has been used by Nayak et al. as an initiator for graft copolymerization[2,3] as well as for homopolymerization.[4] Recently, we have reported the results of graft copolymerization of methyl methacrylate (MMA) onto cellulose[5] using V^{5+} as the initiator. This communication presents the result of grafting MMA onto cellulose using Cr^{6+} ion as the initiator.

EXPERIMENTAL

The cellulose was scored by the usual procedure.[5] MMA was purified by the method described in previous papers.[2,3] Potassium dichromate (AR Sarabhai M. Chemicals), perchloric acid (GR, E. Merck, 60%) were used. Cr^{6+} concentration was estimated by titrimetry. The graft copolymerization was carried out according to our previous procedure[2,3] using Cr^{6+} (8.3×10^{-4}–$83.0 \times 10^{-4}M$) in $HClO_4$ (1.12×10^{-1}–$3.75 \times 10^{-1}M$) at 50–65°C. The graft yield was calculated as the percentage increase in weight over the original weight of the polymer.

RESULTS AND DISCUSSION

The effect of chromium (VI) concentration on the grafting of methyl methacrylate onto cellulose has been studied near $8.3 \times 10^{-4}M$. Increasing the Cr^{6+} concentration up to $24.9 \times 10^{-4}M$, the graft yield increases; thereafer it decreases. This finding could be explained as follows. In the initial stages, with increasing Cr^{6+} concentration there will be abundance of cellulose macroradicals, hence the rate of grafting increases. At higher concentration of Cr^{6+}, the free radicals produced on the backbone of the cellulose might be oxidized to give rise to the oxidation products, and hence the graft percentage decreases. At higher concentrations of Cr^{6+}, the metal ion might interact with the monomer to produce homopolymer, thereby decreasing grafting. The percentage of grafting increases with increasing monomer concentration from 28.16×10^{-2}–$103.26 \times 10^{-2}M$. The effect of perchloric acid concentration on grafting was investigated by varying the concentration from 1.12×10^{-1} to $3.75 \times 10^{-1}M$. The percentage of grafting increases with increasing acid concentration up to

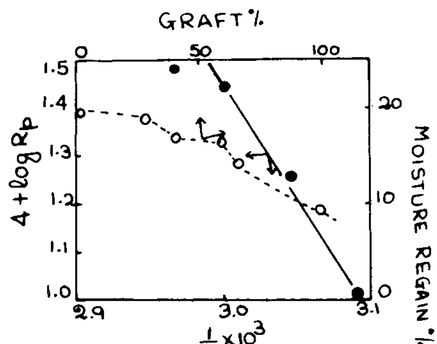

Fig. 1. Arrehenius plot of $\log R_p$ versus $1/T$: $[Cr^{6+}] = 24.9 \times 10^{-4}$, $[HClO_4] = 3.0 \times 10^{-1}$, [MMA] $= 46.94 \times 10^{-2}$ mol/l; M:L = 1:100; time 4 h. Plot of moisture regain (%) versus graft (%).

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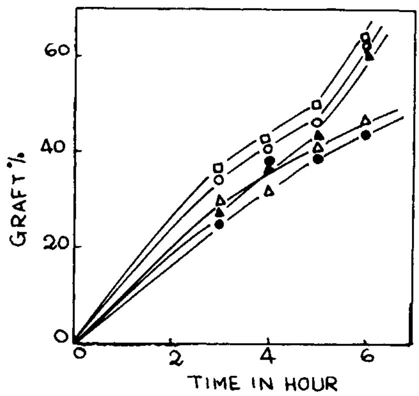

Fig. 2. Effect of nature of substrate on graft yield: $[Cr^{6+}] = 24.9 \times 10^{-4}$, $[HClO_4] = 3.0 \times 10^{-1}$, $[MMA] = 46.94 \times 10^{-2}$ mol/l; $T = 60°C$; M:L = 1:100. (○): NaOH cell; ▲: $ZnCl_2$ cell; ●: periodate-oxidized cell; △: $K_2Cr_2O_7$-H_2SO_4-oxidized cell; □: unmodified cell.

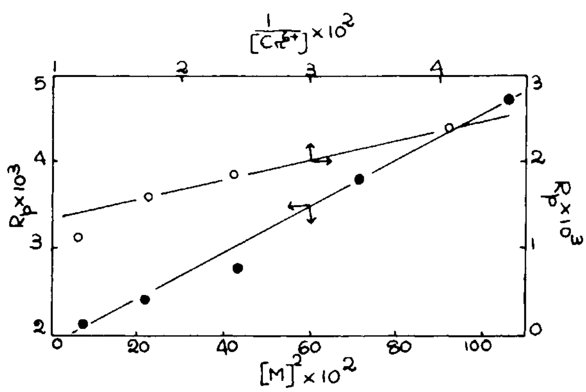

Fig. 3. Plot of R_p versus $[M]^2$: $[Cr^{6+}] = 24.9 \times 10^{-4}$, $[HClO_4] = 3.0 \times 10^{-1}$ mol/l; $T = 60°C$; M:L = 1:100; time 5 h. Plot of R_p versus $1/[Cr^{6+}]$: $[HClO_4] = 3.0 \times 10^{-1}$, $[MMA] = 46.94 \times 10^{-2}$ mol/l; $T = 60°C$; M:L = 1:100; time 5 hr.

$3.0 \times 10^{-1}M$ and decreases thereafter. A similar observation has been noted by Nayak et al.[3] while grafting MMA onto silk. The grafting reaction was carried out at four different temperatures ranging from 50 to 65°C. The graft yield increases with increasing temperature. From the Arrhenius plot of $\log R_p$ vs $1/T$ (Fig. 1), the overall activation energy was computed to be 36.2 kcal/mol. In the case of modified cellulose (Fig. 2), the graft percentage follows the following sequence: untreated cell → NaOH cell → $ZnCl_2$ cell → $K_2Cr_2O_7$-H_2SO_4-oxidized cell → periodate-oxidized cell. Furthermore, the percentage of moisture regain decreases with increasing graft percentage (Fig. 1).

The mechanism for grafting MMA onto cellulose using Cr^{6+} is illustrated below.

Initiation:

$$Cr^{6+} + H^+ + \text{cell} - H \rightarrow Cr^{4+} + \text{oxidation product}$$

$$Cr^{4+} + \sim\text{cell} - H \underset{}{\overset{K}{\rightleftharpoons}} \text{complex} \xrightarrow{k_d} \sim\text{cell}^{\cdot} + Cr^{3+} + H^+$$

$$\sim\text{cell}^{\cdot} + M \xrightarrow{k_i} \sim\text{cell} - M^{\cdot}$$

Propagation:

$$\sim\text{cell} - M^{\cdot} + M \xrightarrow{k_p} \sim\text{cell} - M_n^{\cdot}$$

Termination:

$$\sim\text{cell} - M_n^{\cdot} + Cr^{6+} \xrightarrow{k_t} \sim\text{cell} - M_n + Cr^{4+} + H^+$$

$$\text{~~~cell}^{\cdot} + Cr^{6+} \xrightarrow{k_0} \text{oxidation product} + Cr^{4+} + H^{+}$$

where ~~~cell − H denotes cellulose and ~~~cell· a cellulose macroradical; M is a monomer, K is an equilibrium constant; and k_i, k_p, k_t, and k_0 are rate constants. Considering the steady-state principle, the rate of polymerization was found to be

$$R_p = \frac{k_p}{k_t}[M]^2 \frac{Kk_d[\text{cell} - H]}{[M] + (k_0/k_i)[Cr^{6+}]}$$

The plots of R_p vs $[M]^2$ and R_p vs $1/[Cr^{6+}]$ (Fig. 3) were linear, supporting the above scheme.

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MUNMAYA K. MISHRA
ATANU K. TRIPATHY
SUBASINI LENKA
PADMA L. NAYAK

Laboratory of Polymers & Fibers
Department of Chemistry
Ravenshaw College
Cuttack-753 003, Orissa
India

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