

Pentavalent Vanadium Ion–Cellulose Thiocarbonate Redox-System Induced Grafting of Methyl Methacrylate and Other Vinyl Monomers Onto Cotton Fabric

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SYNOPSIS

Cellulose thiocarbonate was prepared by reacting cotton cellulose fabric with carbon disulphide in the presence of sodium hydroxide. The treated fabric formed, with pentavalent vanadium ion, an effective redox system capable of initiating grafting of methyl methacrylate (MMA) and other monomers onto the cotton fabric. The dependence of grafting on vanadium concentration, pH of the polymerization medium, temperature and duration of grafting, nature and concentration of monomer, and solvent/water ratio was studied. The results indicated that increasing the pentavalent vanadium (V^V) concentration up to 60 mmol/L was accompanied by enhancement in the rate of grafting; the latter was not affected by further increase in V^V concentration. Maximum grafting yield was achieved at pH 2; grafting fell greatly at higher pH. The rate of grafting followed the order: 70° > 60° > 50°C. The graft yield increased significantly by increasing the MMA concentration from 0.5 to 5%. Of the solvents studied, *n*-propanol and isopropanol enhanced the grafting rate provided that a solvent/water ratio of 5 : 95 was used; a higher solvent ratio decreased the magnitude of grafting. Other solvents, namely, methanol, ethanol, *n*-butanol, and acetone, in any proportion, decreased the rate of grafting. With the monomer used, the graft yield followed the order: methyl methacrylate > methyl acrylate > methacrylic acid > ethyl methacrylate > acrylic acid. Also reported was a tentative mechanism for vinyl-graft copolymerization onto cotton fabric using cellulose thiocarbonate- V^V . © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Vinyl-graft copolymerization onto celluloses and modified celluloses has been the subject of several publications.^{1–18} Recently, we reported on grafting of different vinyl monomers onto cotton fabric using cellulose thiocarbonate and different oxidants.^{19–21} Potassium bromate, potassium permanganate acid, and hexavalent chromium ion as oxidizing components were coupled with cellulose thiocarbonate as the reducing component. These stated systems were used to induce graft copolymerization of methacrylic acid and other vinyl monomers onto cotton fabric under a variety of polymerization conditions. The

optimum grafting conditions for these systems were also reported.

The present work deals with graft copolymerization of methyl methacrylate (MMA) onto cotton fabric using cellulose thiocarbonate–pentavalent vanadium (V^V) ion redox system. The ability of this initiation system to induce grafting of other vinyl monomers (acrylic acid, methacrylic acid, methyl acrylate, and ethyl methacrylate) onto the same substrate was also examined.

EXPERIMENTAL

Materials

Mill-scoured and bleached cotton fabric (23 picks × 23 ends/cm, Misr/Helwan Company, Egypt) for spinning and weaving was used as received without

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further purification. MMA, acrylic acid (AA), methacrylic acid (MAA), methyl acrylate (MA), and ethyl acrylate (EA) were purified before use. Carbon disulphide, sodium hydroxide, sulphuric acid, ammonium metavanadate, and methyl, *n*-propyl, isopropyl, and *n*-butyl alcohols and acetone were of reagent grade.

Preparation of V^V solution and estimation of its concentration were described elsewhere.²²

Thiocarbonation of Cotton Fabric

This was carried out by introducing a sample of cotton fabric in a 100-mL stoppered glass vessel containing a freshly prepared solution consisting of sodium hydroxide (1%, w/v) carbon disulphide (1%, v/v), keeping the thiocarbonation temperature at 30°C, and using material to liquor ratio of 1 : 50. The contents of the vessel were well shaken from time to time throughout the reaction period. After 2 h, the solution was drained and the sample was thoroughly washed with distilled water until the washing liquor acquired pH 7. The sample was then squeezed between two filter papers and dried before introducing to the grafting solution. The fabric in this form will be referred to as cellulose thiocarbonate.

Grafting Procedure

The cellulose thiocarbonate sample was placed in a 100-mL stoppered glass vessel containing the grafting solution at a specific temperature using a material to liquor ratio of 1 : 50. The grafting solution consisted of known concentrations of pentavalent vanadate ion and the monomer. The pH of the reaction medium was adjusted before starting the grafting reaction. The contents of the reaction vessel, throughout the reaction period, were shaken vigorously from time to time to avoid the precipitation of vanadate salts over the sample surface. After the desired polymerization time, the sample was washed thoroughly with water and repeatedly extracted with water or a proper solvent, depending upon the nature of the homopolymer to be removed. Extraction was repeated until constant weight. The grafted sample was then dried and weighed.

The percent graft yield was calculated as follows:

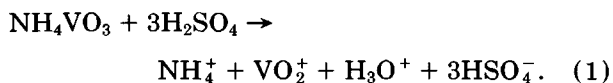
% graft yield

$$= \frac{\text{wt. of graft sample} - \text{wt. of original sample}}{\text{wt. of original sample}} \times 100.$$

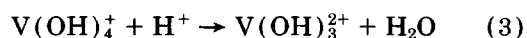
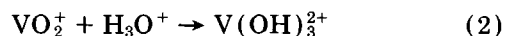
RESULTS AND DISCUSSION

Tentative Mechanisms of Grafting Reaction

Dissociation of ammonium metavanadate in a moderate concentration of sulphuric acid proceeds as follows²³:

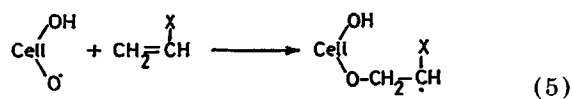
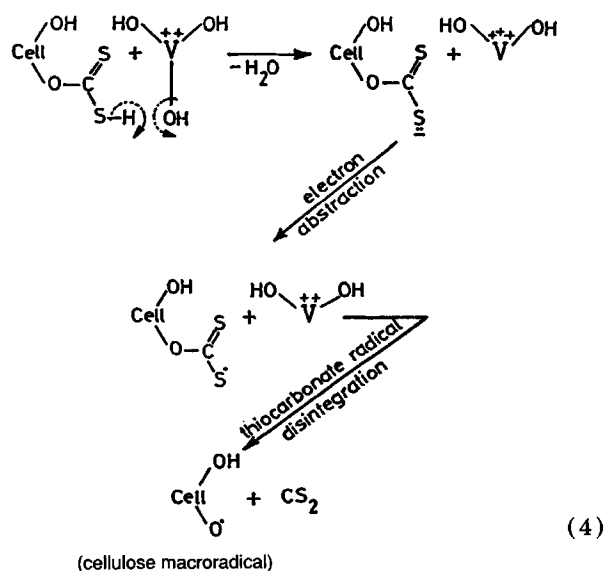


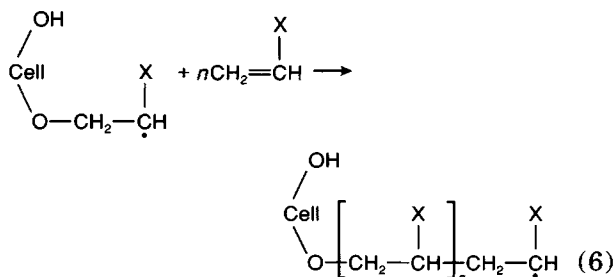
Formation of the active species $V(\text{OH})_3^{2+}$ is expected to occur according to either of the two routes suggested by eqs. (2), (3), or both:



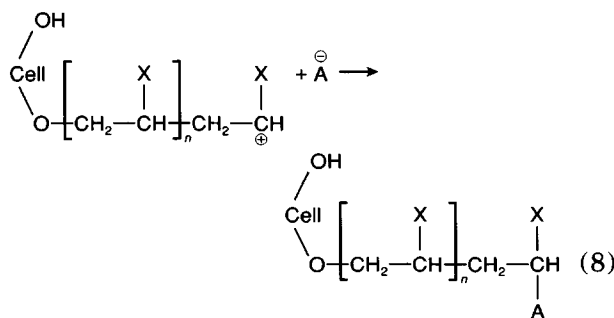
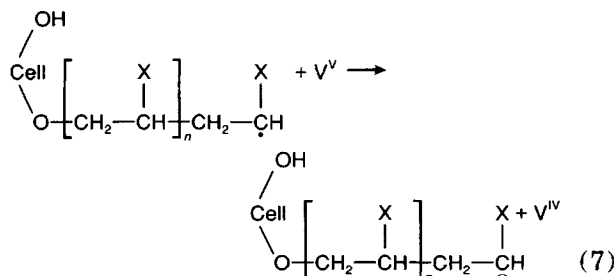
where the pervanadyl ion, $V(\text{OH})_4^+$, is the hydrated form of VO_2^+ . Once the active species $V(\text{OH})_3^{2+}$ ions are formed, they attack the cellulose backbone creating free radicals capable of initiating the polymerization. The most probable mechanism for generation of cellulose macroradicals may be written as shown in the reactions suggested by reactions (4)–(8).

Initiation



Propagation

where X is CN, COOH, CONH₂, COO-alkyl.

Termination

where A⁻ represents the vanadium anions such VO(HSO₄)₄⁻, V₂O₃(HSO₄)₅⁻, VO₂SO₄⁻, . . . etc. that may be produced during the course of the grafting reaction.

With the above in mind, experiments were designed to study major factors affecting the graft polymerization of MMA. Factors studied include vanadate concentration, pH of the polymerization medium, duration and temperature of grafting, nature and concentration of monomer, as well as the polymerization medium.

Vanadate Concentration

Figure 1 shows the effect of ammonium vanadate concentration on the graft yield. It is seen that the graft yield increases by increasing the vanadate concentration up to 60 mmol/L. Beyond this, no

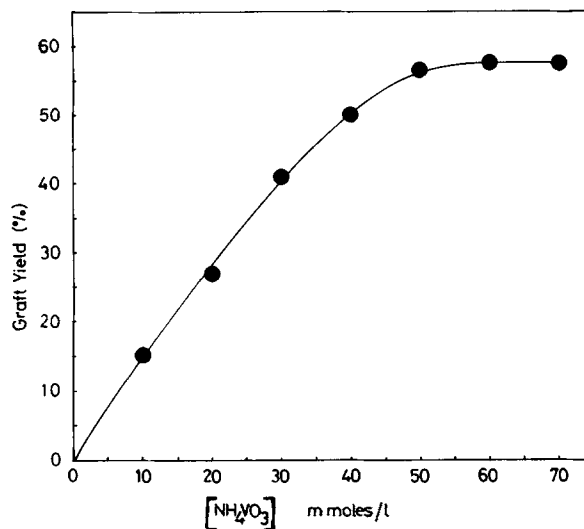
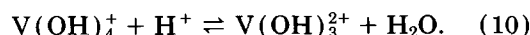
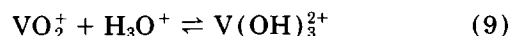


Figure 1 Effect of ammonium vanadate concentration on the graft yield: [MMA], 2%; pH, 2; grafting time, 3 h; grafting temperature, 60°C; material : liquor ratio, 1 : 50.

increment in the graft yield is observed. This suggests that increasing the vanadate concentration up to 60 mmol/L is accompanied by an enhancement in the production of the active species V(OH)₃²⁺ ions that are required for initiation of the grafting reaction. Above this concentration, an equilibrium may be established as shown under.^{24,25}



It is possible that the enhanced rate of initiation due to production of the active species V(OH)₃²⁺ observed at vanadate concentration up to 60 mmol/L is counterbalanced by a faster rate of termination owing to abundance of active species at higher vanadate concentrations.

pH of Polymerization Medium

Figure 2 shows the dependence of the graft yield of MMA on the acidity of the polymerization medium. It is clear that the graft yield increases significantly by changing the pH value to reach maximum at pH 2. Higher pH decreases the graft yield sharply; for instance the graft yield decreases from 56% at pH 2 to 10% at pH 3.

The dependence of the magnitude of grafting on the pH of the polymerization medium could be interpreted in terms of the amount of VO₂⁺ ions in the polymerization medium. Production of VO₂⁺ and,

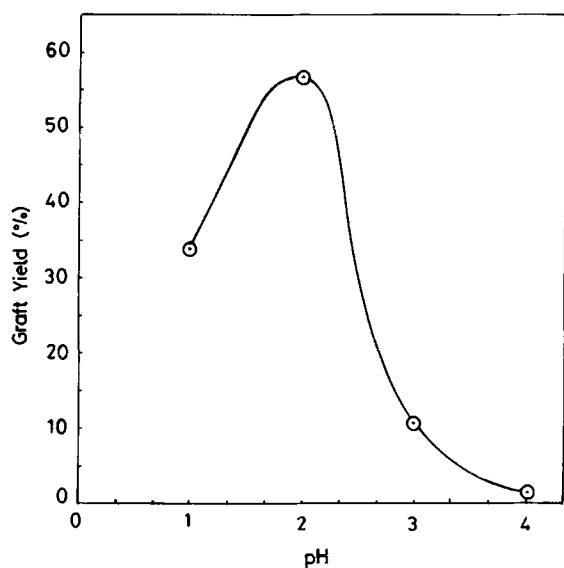
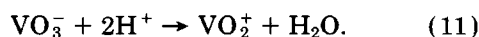


Figure 2 Effect of pH of the polymerization medium on the graft yield: [MMA], 2%; [NH_4VO_3], 50 mmol/L; grafting time, 3 h; grafting temperature, 60°C; material : liquor ratio, 1 : 50.

therefore, the production of the active species $\text{V}(\text{OH})_2^{3+}$ from the vanadate ions VO_3^- , is restricted by the moderate supply of H^+ ions available in the polymerization medium.²⁴



At higher acidity of medium, that is, $\text{pH} < 2$, less powerful species of V^{V} such as $\text{VO}_2\text{SO}_4^{3-}$, $\text{VO}(\text{HSO}_4)^-$, $\text{VO} \cdot \text{OH}^{2+}$, $\text{V}_2\text{O}_3(\text{HSO}_4)_5^-$, $\text{V}(\text{OH})_3(\text{HSO}_4)^+$, . . . etc. might be formed^{22,23} thereby reducing the oxidizing capacity of the quinquevalent vanadate ion. Stated in other terms, at lower acidity, $\text{pH} > 2$, the supply of H^+ ions will be very small and hence the amount of the active species will also be very small.

Monomer Concentration

Figure 3 shows the effect of MMA concentration on the graft yield. Obviously, the graft yield increases as the MMA concentration increases from 0.5 to 5%. Greater availability of MMA molecules in the vicinity of cellulose macroradicals at higher monomer concentrations would account for this. In addition, the gel effect, that is, the solubility of poly(methyl methacrylate) in its own monomer, may also contribute to the enhancement of grafting

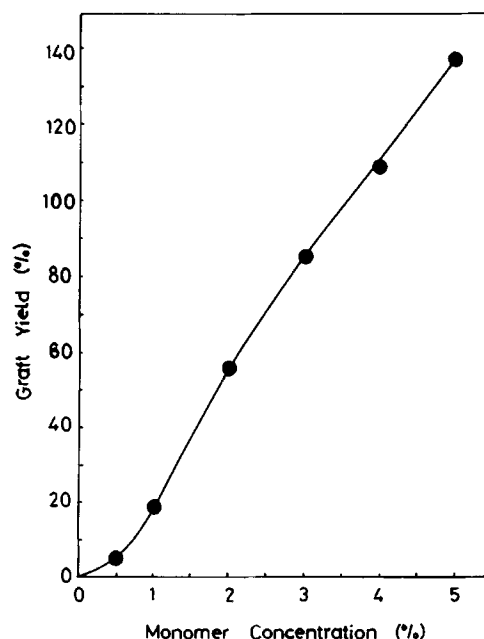


Figure 3 Effect of monomer concentration on the graft yield: [initiator], 50 mmol/L; pH, 2; grafting time, 3 h; grafting temperature, 60°C; material : liquor ratio, 1 : 50.

at higher monomer concentration through lowering the rate of termination.²⁶

Polymerization Temperature

Figure 4 shows the effect of polymerization temperature on the rate of grafting. It is seen that the rate of grafting is higher with higher polymerization

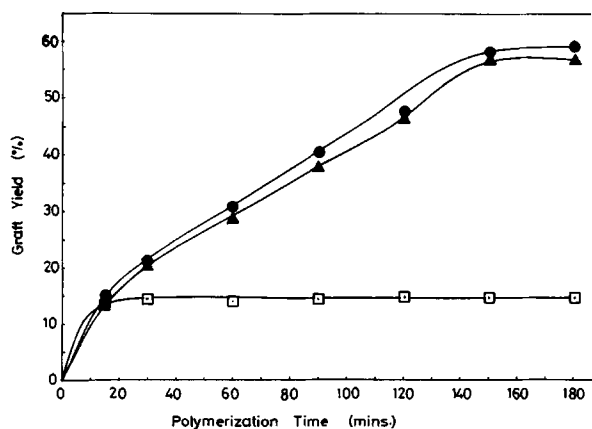


Figure 4 Influence of temperature on the rate of grafting: [MMA], 2%; [NH_4VO_3], 50 mmol/L; pH, 2; (□) 50°C; (▲) 60°C; (●) 70°C; material : liquor ratio, 1 : 50.

temperature. The rate of grafting follows the order: $70^{\circ} > 60^{\circ} > 50^{\circ}\text{C}$. This is logical because a higher temperature is expected to bring about:

1. speedy disintegration of the thiocarbonate groups;
2. greater activation energy;
3. enhanced oxidant efficiency;
4. enhancement of the solubility of the monomer and its diffusion from the solution phase to the fibre phase; and
5. higher rate of initiation and propagation of the graft.

Duration of Polymerization

The effect of duration of polymerization on the magnitude of grafting may be realized from Figure 4. As is evident, the graft yield increases significantly by increasing the duration of polymerization until a certain time after which these increments are marginal. This could be ascribed to depletion in both initiator and monomer concentrations as well as reduction in the available active sites on the cellulose backbone as the reaction proceeds.²⁰

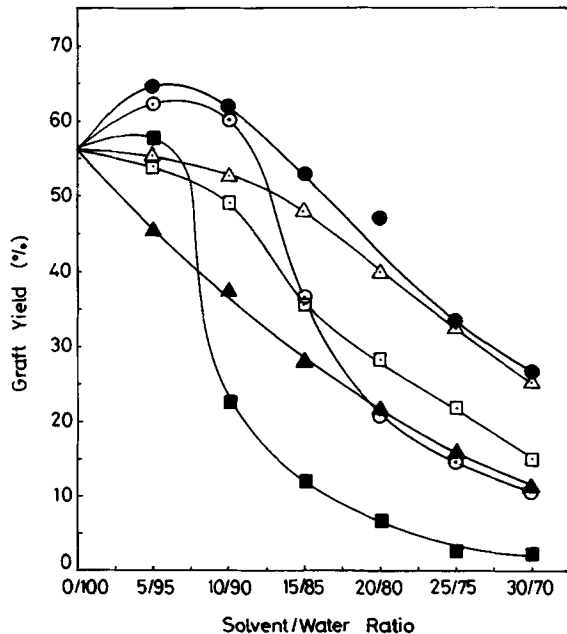


Figure 5 Effect of the polymerization medium on graft yield: (●) isopropanol; (○) *n*-propanol; (■) *n*-butanol; (△) ethanol; (□) methanol; (▲) acetone; $[\text{NH}_4\text{VO}_3]$ 50 mmol/L; [MMA], 2%; pH, 2; polymerization temperature, 60°C ; grafting time, 3 h; material : liquor ratio, 1 : 50.

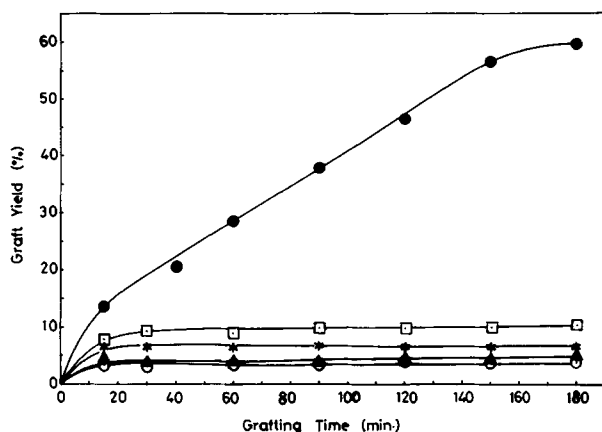


Figure 6 Dependence of the rate of graft yield on the nature of monomer: (●) MMA; (□) MA; (*) MAA; (▲) EA; (○) AA; $[\text{NH}_4\text{VO}_3]$, 50 mmol/L; [monomer], 2%; pH, 2; grafting temperature, 60°C ; material : liquor ratio, 1 : 50.

Polymerization Medium

The dependence of grafting upon the nature and concentration of solvents used in the polymerization medium is shown in Figure 5. It is obvious that mixtures of water and either *n*-propanol or isopropanol at a solvent to water ratio of 5 : 95 constitute the most favorable medium for grafting of MMA. As the ratio of the solvent in the solvent : water mixture increases, the grafting decreases. On the other hand mixing methanol, ethanol, *n*-butanol, or acetone with water in any proportions brings about lower graft yields. For the optimum solvent : water ratio of 5 : 95, the graft yield follows the order: isopropanol > *n*-propanol > *n*-butanol > ethanol > methanol > acetone.

Differences in the magnitude of grafting by nature and concentration of the solvent may be associated with differences in ability of the solvent with respect to:

1. miscibility of the monomer;
2. formation of solvent radicals from the primary radical species of the initiating system;
3. contribution of the solvent radical in formation of cellulose macroradical;
4. swelling of the fibres that favours diffusion of the monomer more toward the grafting site; and
5. termination of the growing grafted chains via chain transfer reactions.

The first four factors favour grafting, the last factor lowers it.²⁷

Nature of Monomer

Figure 6 shows the rate of grafting of AA, MAA, MA, ethyl methacrylate (EMA), and MMA onto cotton fabric using a cellulose thiocarbonate-pentavalent vanadium redox system. As is evident, MMA shows the highest rate of grafting and AA the lowest. Based on the rate of grafting the following order may be drawn for monomer reactivity: MMA > MA > MAA > EMA > AA.

Differences among these monomers with respect to polarizability of the vinyl double bond, miscibility and diffusion of monomer molecules, and ability of the monomers to convert to homopolymer may account for this.

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