Grafting ethyl methacrylate onto partially hydrolysed starch using ceric ion as initiator

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Poly(ethyl methacrylate) has been grafted onto partially hydrolysed starch (84.04% conversion) by using ceric ion redox initiator in an aqueous medium at 29°C. The extent of graft polymer formation was measured in terms of conversion of monomer to polymer, graft level, molecular weight of grafted polymer chains and grafting frequency as a function of ceric ion concentration. It was found that an eight-fold increase in ceric ion concentration was accompanied by marked changes (of about three-fold in graft level, six-fold in molecular weight of grafted polymer chains and four-fold in grafting frequency) in the values of the measured grafting parameters. A ten-fold increase in the polymeric substrate to dispersion medium ratio was found to increase the extent of graft polymer formation onto partially hydrolysed starch.

Varieties of biopolymers are being utilized either alone or in blends and as grafted copolymers for many industrial applications. Starch stands out as one of the most widely used biopolymer on account of its low cost and availability of large feedstocks1. Modification of properties of starch through graft copolymerization may enhance their potential for use as improved viscosifiers in secondary petroleum oil recovery processes, as flocculants in the beneficiation and treatment of industrial wastewaters2-4, in paper manufacture, etc. An important advantage of graft polymerization is that the grafted polymer chains are held together by chemical bonding, allowing the two polymers to be intimately associated. The polymer that is grafted is expected to be distributed on the backbone polymer chains and also to impart beneficial effects on the properties of the composites. The chemical, physical, mechanical and rheological properties of graft copolymers correlate well with the size and distribution pattern of the grafts on the backbone polymer. Thus a major focus in graft copolymerization studies is the optimization of frequency of grafting and control of the molecular weight of grafted polymer chains. In previous studies5, the grafting characteristics of vinyl monomers on cellulose and its water-soluble derivative, carboxymethyl cellulose have been examined and it was reported that chemical modification was accompanied by marked increase in the extent of graft polymer formation. In this paper, the preparation of partially hydrolysed starch (dextrin), its graft copolymerization and the effects of dilution on the grafting characteristics are described.

Experimental Procedure

Materials

Ethyl methacrylate (BDH) was purified by extraction with aqueous sodium hydroxide/sodium chloride solution to remove the hydroquinone distilled and the middle fraction was collected as pure monomer. Ceric ammonium nitrate (BDH) was used without further purification. Dextrin was prepared from cassava starch with 0.2 wt% hydrochloric acid6. Partially hydrolysed starch of 83.04% conversion was used for graft copolymerization.

Graft copolymerization

The graft copolymerization procedure was based on the method described by Lepoutre and Hui7. A known amount of the partially hydrolysed starch was dispersed in 100 mL of distilled water containing a known quantity of ceric ion. The mixture was purged with nitrogen for 5 min; the initiator was allowed to interact with the backbone for 30 min and the monomer was added to the mixture over 10 min with stirring. The mixture was again purged with nitrogen for 5 min and the reaction was allowed to proceed for 2 h and then was stopped by the addition of hydroquinone solution (2 mL. of 5 wt%) to the reaction mixture. The mixture was diluted two-fold with distilled water with stirring poured into a large excess of methanol; allowed to stand for 8 h and then
filtered. The residue was air-dried and weighed. Grafting reactions were carried out by (a) using constant amount of ethyl methacrylate monomer and starch dispersed in 100 mL of distilled water with varied amounts of ceric ion initiator, (b) using varied amounts of ceric ion and monomer to maintain constant concentrations of 0.035 and 0.40 mol L\(^{-1}\) respectively, taking 1 g of starch dispersed in different volumes of distilled water.

The ungrafted poly(ethyl methacrylate) homopolymer was removed by soxhlet extraction with isopropanol\(^{12}\) and the residue obtained was air-dried and weighed.

**Isolation of grafted products and determination of their molecular weights**

The grafted poly(ethyl methacrylate) chains were extracted from the backbone polymer by treatment with dilute hydrochloric acid\(^{14}\). A portion of the graft copolymer was dispersed in 5 mL of deionised water at room temperature. 5 mL of dilute HCl were added and the mixture heated on a steam bath for 1 h. The mixture was poured into a large excess of ethanol and filtered. The residue was washed with deionised water, followed by dil. NaOH solution and finally with deionised water and then air-dried. The isolated poly(ethyl methacrylate) sample was purified by dissolution in isopropanol and precipitation with methanol, filtered and air-dried. IR spectra of the isolated poly(ethyl methacrylate) run as KB pellets showed as detectable fragments of carbohydrate. Dilute solution viscosity measured in isopropanol of the isolated poly(ethyl methacrylate) samples were carried out at 37°C. The average molecular weights of the isolated polymer samples were determined from the measured intrinsic viscosity values using the relationship\(^\text{13}^\text{)}.

\[
\log[\eta] = \log 4.75 \times 10^6 + 0.5 \log M_n
\]

**Grafting parameters**

The grafting parameters were determined using the following relationship\(^\text{15}^\text{)}.

\[
\text{Total conversion, } \% C_p = \text{wt of polymer formed per } 100 \text{ g of monomer in the reaction mixture}
\]

\[
\% \text{ conversion grafted, } C_g = \text{wt of grafted polymer per } 100 \text{ g of monomer in the reaction mixture}
\]

\[
\text{Graft level (\%) } P_g = \frac{\text{wt of grafted polymer per } 100 \text{ g of the backbone polymer}}{\text{wt of dextrin}}
\]

where \(N_g\) is the number of grafted polymer chain and AGU is anhydroglucose unit.

**Results and Discussion**

**Grafting characteristics of poly(ethyl methacrylate) on partially hydrolysed starch. Effect of ceric ion concentration**

The results of the grafting characteristics of poly(ethyl methacrylate) on partially hydrolysed starch are given in Table 1. The results show that monomer conversion to polymer is generally low (< 10\% conversion). A large proportion \(C_p > 70\%\) of the polymer formed is grafted onto the partially hydrolysed starch; and the graft levels are generally high \(P_g > 70\%\). The values of \(P_g\) increase with increase in ceric ion concentration, then level off and decrease at higher initiator concentration. It is observed that graft polymerization of ethyl

**Table 1—Effect of ceric ion concentration on the grafting parameters of poly(ethyl methacrylate) on partially hydrolysed starch**

<table>
<thead>
<tr>
<th>Ceric ion concentration (mmol L(^{-1}))</th>
<th>Monomer conversion (%)</th>
<th>Graft level (%)</th>
<th>Molecular weight of grafted polymer (10(^3) M(_n))</th>
<th>Frequency of grafting (F(_g) (Ng/AGU))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>4.10</td>
<td>77.73</td>
<td>5.32</td>
<td>2.4</td>
</tr>
<tr>
<td>10.0</td>
<td>5.38</td>
<td>83.03</td>
<td>6.20</td>
<td>2.2</td>
</tr>
<tr>
<td>15.0</td>
<td>6.95</td>
<td>110.55</td>
<td>4.53</td>
<td>4.0</td>
</tr>
<tr>
<td>25.0</td>
<td>6.99</td>
<td>106.50</td>
<td>4.10</td>
<td>4.5</td>
</tr>
<tr>
<td>30.0</td>
<td>6.94</td>
<td>109.30</td>
<td>3.20</td>
<td>5.5</td>
</tr>
<tr>
<td>35.0</td>
<td>6.51</td>
<td>102.48</td>
<td>2.02</td>
<td>8.2</td>
</tr>
<tr>
<td>40.0</td>
<td>5.09</td>
<td>82.88</td>
<td>1.03</td>
<td>10.3</td>
</tr>
</tbody>
</table>

\(\text{a) Monomer concentration } 0.16 \text{ mol L}^{-1}, \text{ reaction time } 2 \text{ h, temp. } 29°C\)
Dilution of starch with reactive concentrations considers combination of growing homopolymer chains with reactive sites on the backbone polymer as the main reaction leading to the formation of polymer grafted. The grafting frequency of poly(ethyl methacrylate) onto partially hydrolysed starch are relatively low (with at least 100 AGU separating two grafted polymer chains) when compared with the values of about 100 AGU separating two grafted polymer chains reported for grafting acrylonitrile onto partially hydrolysed starch using comparable monomer and initiator concentrations. It is thought that if grafted polymer chain formation was by way of propagation of radicals formed on the backbone polymer, then at comparable reaction conditions, the grafting frequency of vinyl monomers should be of about the same order of magnitude. Thus, a variation in frequency of grafting with monomer type and concentration is further evidence that graft polymer formation may not be due to propagation of radicals formed on the backbone polymer by the oxidative interactions with cationic ions.

**Dilution effect**

Table 2 shows the results of the effect of dilution of the backbone polymer on the grafting parameters. The grafting of poly(ethyl methacrylate) on partially hydrolysed starch is enhanced upon dilution of the latter, as the ten-fold dilution of the backbone polymer resulted in eighteen-fold increase in $P_c$, about two-fold increase in the molecular weight of grafted polymer chains and on eight-fold increase in frequency of grafting. Graft polymerization of partially hydrolysed starch in dilute aqueous dispersions leads to marked increase in grafting frequency which may be explained in terms of enhanced accessibility of the backbone polymer to reactant molecules.

### Table 2: Effect of dilution of partially hydrolysed starch on the grafting characteristics of poly(ethyl methacrylate)

<table>
<thead>
<tr>
<th>Concentration of partially hydrolysed starch (%)</th>
<th>Graft level of grafted polymer (P_c)</th>
<th>Molecular weight (10^3)</th>
<th>Frequency of grafting (N/10^2 AU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1390</td>
<td>5.28</td>
<td>42.65</td>
</tr>
<tr>
<td>0.4</td>
<td>1240</td>
<td>4.88</td>
<td>37.31</td>
</tr>
<tr>
<td>0.6</td>
<td>200</td>
<td>3.89</td>
<td>24.98</td>
</tr>
<tr>
<td>0.8</td>
<td>190</td>
<td>2.91</td>
<td>11.13</td>
</tr>
<tr>
<td>1.0</td>
<td>120</td>
<td>2.21</td>
<td>8.84</td>
</tr>
<tr>
<td>2.0</td>
<td>74</td>
<td>2.21</td>
<td>5.42</td>
</tr>
</tbody>
</table>

* Monomer concentration 0.4 mol L⁻¹; cationic ion concentration 0.035 mol L⁻¹.

**Conclusion**

The results of this study show that graft polymer formation in cationic ion initiated copolymerization occurs mainly due to the combination of growing homopolymer chains on the backbone polymer. The inherent heterogeneous nature of the polymerization system appears to determine the upper limits of the extent of graft polymer formation. Efforts aiming at improving the grafting frequency onto polysaccharides in addition to seeking to create more reactive sites on the backbone polymer and to extend the homogenous regime of the reaction system should modify/alter the physical state/state of aggregation of the backbone polymer to make it more accessible to the reactants.

**References**