Graft Copolymerization Kinetics of Ethyl Acrylate onto Hydroxypropyl Methylcellulose Using Potassium Persulphate as Initiator in Aqueous Medium

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Abstract

Potassium persulphate (KPS) has been used as efficient initiator for graft copolymerization of the ethyl acrylate (EA) onto hydroxypropyl methylcellulose (HPMC) at 60 ± 0.1°C. Graft copolymerization of EA onto HPMC has taken place through the radical initiation process. The grafting parameters have been evaluated by varying concentration of EA from 0.097 to 0.376 mol/L, KPS from 1.772 to 5.316 mmol/L and HPMC from 0.117 to 0.468 mmol/L. Evidence of grafting was obtained from IR spectroscopic measurements, SEM, and TGA studies of the grafted and ungrafted HPMC. The rate of graft copolymerization has shown 1, 0.5, 0.5 order with respect to the concentrations of the EA, KPS, and HPMC, respectively. The graft copolymerization data obtained at different temperatures were used to calculate the energy of activation which has been found to be 41.7±1.2 kJ/mol within the temperature range from 50 to 65°C. On the basis of the experimental observations, initiating steps have been proposed and a suitable rate expression for graft copolymerization has been derived.

Introduction

Graft copolymerization is a useful technique for modifying the properties of the synthetic and natural polymers. Graft copolymers are finding their applications in the development of selective permeable membranes [1], outstanding sorption agents [2], and in fabrication of drug delivery systems [3,4]. Cellulose is one of the most plentiful natural renewable sources. It has been widely applied in drug, textile, and food industries. Although cellulose has good

Key Words:

graft copolymerization; hydroxypropyl methylcellulose; ethyl acrylate; graft copolymerization rate.

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properties, it has some undesirable ones such as high moisture regain, low tensile strength, and low strength against microbial attack. Hence, grafting of synthetic polymers on cellulose eliminates these drawbacks and allows the acquisition of the additional properties of grafted polymers without destroying its own properties. The grafting of synthetic polymers may be accomplished by attaching performed polymers onto cellulose, but the rate and the extent of grafting by this method are usually low due to hindered diffusion of performed polymers. The products obtained by performed polymers or oligomers show inhomogeneous distribution of grafted chains onto cellulose in comparison with the graft copolymers obtained by copolymerization of monomers onto cellulose. The graft copolymerization of various alkylacrylates onto cellulose using different initiating agents [5-27] has been reported frequently but, the investigations about grafting of ethyl acrylate monomer onto cellulose is limited [28]. In addition, the extent of grafting is also affected by the physical structure of cellulose.

In present work, we choose hydroxypropyl methylcellulose as matrix, which is one of the useful kinds of cellulose derivates. The properties of grafted cellulose also depend on the weight of the grafted chains and their number. The molecular weight of grafted chains could be controlled by experimental conditions. Therefore, in these investigations, an effort has been made to study the grafting of ethyl acrylate onto HPMC under various experimental conditions and characteristic grafting parameters have been determined in the presence of potassium persulphate (KPS) as initiator.

EXPERIMENTAL

Materials
Hydroxypropyl methylcellulose (Molecular weight: 8.17×10⁴, Taian Ruitai Cellulose Co., Ltd, Shandong, China) was dried in a vacuum desiccator on calcium chloride. Ethyl acrylate (Tianjin Chemical Reagent Co., Inc, Tianjin, China) was washed with 5% sodium hydroxide and stored below 5°C after vacuum distillation. The potassium persulphate was reagent grade and used after recrystallization.

Graft Copolymerization
The graft copolymerization of EA onto HPMC has been carried out by adding a calculated amount of HPMC (6 g) in a three-necked round-bottom flask containing a known amount of distilled water. The flask was fitted with an electrically operated stirrer and kept in a water bath maintained at 60±1°C. The solution was purged with nitrogen gas for about 30 min before adding KPS (0.15 g) into the flask. Then, EA (6 g) was charged into the flask to initiate the graft copolymerization after KPS interacting with HPMC for 5 min. The reaction mixture was stirred at a constant rate to avoid the adverse effect of stirring on graft copolymerization. The reactants were allowed to react about 3 h before the reaction was terminated. The rough product was dried to a constant weight at 60°C in a vacuum. The dried product was extracted by acetone in a Soxhlet apparatus within 72 h for the removal of the homopolymer PEA, and the extracted product was finally dried and weighed.

Definition of some Parameters
Percentage of grafting (PG) and grafting efficiency (GE) were calculated by the following equation after the HPMC-g-PEA, PEA chains, and the HPMC were weighed:

\[ \text{PG} (%) = \frac{\text{Weight of grafted PEA}}{\text{Weight of HPMC}} \times 100 \]  
\[ \text{GE} (%) = \frac{\text{Weight of grafted PEA}}{\text{Weight of reacted EA}} \times 100 \]

The rate of the graft copolymerization (R_g) was calculated by the following equation:

\[ R_g \text{ (mol/L.min)} = \frac{\text{Amount of branch PEA grafted}}{M_{EA} \times \text{Reaction time} \times \text{Volume}} \]

where, \( M_{EA} \) represents the molecular weight of EA.

Determination of Molecular Weight of the PEA Grafted
The purified HPMC-g-PEA was hydrolyzed in a \( \text{H}_2\text{SO}_4 \) solution 72% at 30°C for 4 h to obtain the grafted side chains. The viscosity of the grafted chains solution was determined with an Ubbelohde viscometer at 25°C using acetone as solvent. The molecular weight was calculated according to the
equation below [29]:

\[ [\eta] = kM^\alpha \] (4)

where, \( k = 0.051 \) and \( \alpha = 0.59 \).

Characterization
The IR spectra of HPMC and grafted HPMC were recorded on KBr pallets using Nicolet 5DX fourier transform infrared spectrophotometer. Thermal analysis of HPMC and grafted HPMC have been carried out by recording thermogravimetric (TG) curve using Perkin Elmer Pyris 6 system at a heating rate of 10°C/min under nitrogen atmosphere. Micrographs of grafted and ungrafted HPMC were obtained by scanning electron microscopy technique on a SEM (Philips XL30), the samples were covered with gold before the analysis in order to avoid electrostatic charge.

RESULTS AND DISCUSSION

Identification of Grafting
IR Spectroscopy is an effective way of identifying organic compounds or polymers, especially for newly formed chemical bonds during a reaction. Figure 1 shows the IR spectra of HPMC and purified HPMC-g-PEA. The spectrum A of HPMC shows the characteristic absorption at 2900~3500 cm\(^{-1}\). The spectrum B of the grafted copolymer shows the characteristic absorption of HPMC at 2900~3500 cm\(^{-1}\) and also an absorption band at 1739 cm\(^{-1}\) corresponding to an ester carbonyl group (\(>\text{CO}\)) of the ethyl acrylate which was initially absent in pure HPMC (spectrum A). The presence of new absorption band at 1739 cm\(^{-1}\) has provided evidence for grafting of ethyl acrylate onto the HPMC.

Thermogravimetric analyses (TGA) were carried out in order to evaluate the effect of the chemical modification on the thermal stability of HPMC. Figure 2 shows thermograms for (a) HPMC and (b) HPMC-g-PEA, respectively. Primary thermograms were obtained by plotting the percentage of residual weights against the temperature. The initial decomposition temperature (IDT) was calculated from the end of the initial straight-line portion of the curve from where the actual decomposition is believed to occur. It can be observed that IDT of HPMC is raised from 320°C to 335°C upon grafting. Increase in IDT of HPMC after grafting copolymerization indicates that chemical change in HPMC has been occurred upon grafting.

Figure 3 shows two electron micrographs of HPMC, which were taken before and after the grafting process, as it is observed that there are evident differences in their appearance depending on the experimental stage. Figure 3a shows the pure HPMC before the graft copolymerization and Figure 3b shows the same HPMC after the graft copolymerization process. It can be seen from Figure 3a that the surface of pure HPMC is relatively smooth. On the other
hand, Figure 3b, which was taken after 72 h of acetone extraction, shows the presence of well-defined agglomerates whose texture is different from that of the pure HPMC. Such agglomerations were found on the surface of the grafted HPMC and, of course, not on the ungrafted ones. This result indicates that a considerable amount of PEA is grafted on to HPMC.

**Effect of EA Concentration**

The graft copolymerization has been recorded at different concentrations of EA ranging from 0.097 to 0.376 mol/L at constant concentrations of KPS (2.658 mmol/L) and HPMC (0.351 mmol/L) at 60.0±0.1°C. The PG and GE have shown an increase trend with the increasing of EA concentration (Figure 4). Similar results were reported by Subasini et al. [11]. The rate of grafting (Rg) at different concentrations of EA has been used to determine the order of reaction by drawing a plot between rate of graft copolymerization (Rg) and concentration of EA. In the EA concentration range of 0.097-0.376 mol/L, Rg apparently increased as the EA concentration grew [10] (Figure 5) because the local EA concentration in or around the soluble HPMC increased. This helped the diffusion of the monomer molecules into the radical centers on the backbone.

In addition, the high affinity of EA for grafting onto cellulose in comparison with MA and MMA has been attributed to the length of the ester alkyl group [30] which its reactivity has been increased by grafting onto cellulose through electronpumping capacity of
ester ethyl group. The formation of small amount of homopolymer during graft copolymerization of EA is an indication that EA has more affinity for grafting than the formation of homopolymer.

**Effect of KPS Concentration**

The graft copolymerization of EA onto HPMC has been studied at KPS concentration range 1.772 - 4.430 mmol/L and constant concentrations of EA (0.191 mol/L) and HPMC (0.351 mmol/L). On varying the concentration of KPS, the increasing trends have been seen in PG (or GE) (Figure 6). The increasing trends in grafting parameters have been attributed to the formation of more active sites on HPMC with the increasing concentration of KPS in the reaction mixture. The produced active sites were consumed in the formation of grafted chains on HPMC, which is apparent from the increasing trend in the PG and GE magnitudes. In addition, the initiating process for KPS in graft copolymerization is similar to that of those common free-radical initiators, which first decompose and form free radicals and then these free radicals react with the monomers and start the propagation of the chains.

The rate of graft copolymerization ($R_g$) calculated at different concentrations of KPS was used to determine the order of reaction with respect to the concentration of KPS as shown in Figure 7. In Figure 7, there is a linear relation between the rate of graft copolymerization ($R_g$) and sub-duplicate concentration of KPS [31], indicating half order with respect to the concentration of KPS. This half order dependence of concentration of KPS has suggested the termination of grafted and ungrafted chains by bi-molecular coupling of two growing chains.

**Effect of HPMC Concentration**

The graft copolymerization of EA onto HPMC has been carried out at different concentrations of HPMC ranging from 0.117 to 0.468 mmol/L but at constant concentrations of EA (0.191 mol/L) and KPS (2.658 mmol/L). Effect of the concentration of HPMC on PG and GE were plotted in Figure 8. The results show that PG was reduced if the amount of HPMC...
was increased because, the ratio of the EA to HPMC was lowered. This led to a decrease in the EA concentration in every HPMC molecule, even though the graft rate becomes fast because of the greater number of radical centers formed on the backbone as a whole [18]. With EA and KPS concentrations specified, the relationship between \( R_g \) and the HPMC concentration is also illustrated in Figure 9. \( R_g \) Had the increasing trend with sub-duplicate concentration of HPMC, increasing as the HPMC concentration grows [32].

In summary, the rate of the graft copolymerization of EA onto HPMC by KPS at a comparatively lower initiator concentration can be derived as follows:

\[
R_g = K [\text{KPS}]^{1/2}[\text{EA}][\text{HPMC}]^{1/2}
\]

\( (5) \)

**Effect of Reaction Temperature**

The graft copolymerization of EA onto HPMC has also been studied by varying the reaction temperature from 50 to 70°C at constant concentration of EA (0.191 mol/L), KPS (2.658 mmol/L) and HPMC (0.351 mmol/L).

To compare the effect of temperature, PG and GE recorded at different temperatures were used to calculate grafting parameters as shown in Figure 10. PG and GE have shown an increasing trend up to 65°C. On increase of the temperature, the kinetic energy of monomer molecules has been increased which ultimately it has increased the concentration of monomer molecules nearby to the active sites onto the HPMC due to the enhanced rate of diffusion of monomer molecules from the reaction mixture to the HPMC. This positive effect of temperature has been decreased by further increasing of the reaction temperature beyond 65°C due to the substantial increase in the rate of chain transfer and chain termination reactions between grafted chain and chain.

**Table 1.** Molecular weight of grafted and ungrafted chains

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( M_{n\text{GP}a} \times 10^{-4} ) (g/mol)</th>
<th>( M_{n\text{HPb}} \times 10^{-4} ) (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>131.1</td>
<td>44.7</td>
</tr>
<tr>
<td>60</td>
<td>147.5</td>
<td>45.4</td>
</tr>
</tbody>
</table>

(a) GP stands for graft polymer. (b) HP stands for homopolymer.

\[ R_g = K [\text{KPS}]^{1/2}[\text{EA}][\text{HPMC}]^{1/2} \]
monomer molecules. This is evident from the observed decreasing value in molecular weight of grafted chains as well as ungrafted chains (Table 1).

When the reaction temperature was changed in the range of 50-65°C, the grafting rate grew as the temperature was raised (Figure 11). The Arrhenius equation describes the relationship between the grafting rate and the reaction temperature:

$$\log R_g = \log K - \left(\frac{E_{ag}}{2.303R}\right)(1/T)$$  \hspace{1cm} (6)

The apparent activation energy of graft copolymerization ($E_{ag}$) can be determined from the Arrhenius equation. Figure 12 gives the plot of $\log R_g$ versus 1/T, by which $E_{ag}$ was roughly calculated from the slope of the line:

$$E_{ag} = 41.7 \pm 1.2 \text{ kJ/mol}$$  \hspace{1cm} (7)

The relatively lower energy of activation of graft copolymerization of EA onto HPMC is also an indication of the higher affinity of EA for grafting onto HPMC.

**Effect of Pre-interacting Time on the Grafting Ability of HPMC**

Calculated amount of HPMC was added in to a four-necked flask, KPS was added, the pre-interacting reaction was allowed for a period of time, and then EA was poured into the flask to start the graft copolymerization. Figure 13 shows the effect of the pre-interacting time on the grafting ability of HPMC. The data show that the pre-interacting time obviously affects the grafting ability of HPMC. PG and GE increase with the increasing of pre-interacting time. When KPS was added to the HPMC solution, some of the hydroxide groups (-OH) on the HPMC backbone were oxidized into free radicals. The produced free radicals reacted with EA, so the graft copolymerization could be carried out. As the pre-interacting time got longer, many more free radicals on the backbone were produced, so the grafting ability of HPMC was higher.

**Graft Mechanism**

Radical formation on HPMC macromolecules is a key issue in discussing the graft mechanism. On the basis of the observed experimental data for graft copolymerization of EA onto HPMC in the presence of KPS, the creation of free radicals during the graft copolymerization of EA onto HPMC may be described by the following equations:

$$S_2O_8^{2-} \rightarrow 2SO_4^-$$  \hspace{1cm} (8)

$$S_2O_8^{2-} + \text{Cell-H} \rightarrow \text{HSO}_4^- + \text{SO}_4^- + \text{Cell}$$  \hspace{1cm} (9)

$$\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{HSO}_4^-$$  \hspace{1cm} (10)

$$\text{SO}_4^- + \text{Cell-H} \rightarrow \text{Cell} + \text{HSO}_4^-$$  \hspace{1cm} (11)
Here, Cell and Cell’ are radical from HPMC and product of its two-electron oxidation, respectively. The produced free radicals consequently initiate the polymerization of the monomer EA and introduce EA branch chains onto the HPMC backbone:

\[
\text{Cell} + \text{EA} \rightarrow \text{graft copolymer}
\]  

CONCLUSION

We can conclude as follows:
- The KPS has been found to be an efficient initiator for graft copolymerization of EA onto HPMC in aqueous medium.
- The extent of grafting of EA onto HPMC has shown dependence on concentration of EA, KPS, HPMC, and the reaction temperature of graft copolymerization.
- Free radical formation steps for graft copolymerization were described. The reaction rate for the graft copolymerization of EA onto HPMC under the initiation of KPS was according to the equation of

\[
R_g = K \cdot [\text{KPS}]^{1/2} \cdot [\text{EA}] \cdot [\text{HPMC}]^{1/2}
\]

REFERENCES


