Eur. Polym. J. Vol. 28, No. 4, pp. 415–417, 1992
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0014-3057/92 $5.00 + 0.00

GRAFT COPOLYMERIZATION OF METHYL ACRYLATE ON DEXTRIN

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(Received 25 July 1991)

Abstract—Graft copolymerization of methyl acrylate on dextrin in an aqueous medium was studied at 29° using various concentrations of ceric ion as initiator. The dependence of the rate of grafting and extent of graft polymer formation on initiator concentration suggests that termination of graft copolymerization proceeds mainly by reaction of ceric ion with grafted chains. The relatively high frequency of grafting (up to 40 grafts per 10^4 units of anhydroglucose) indicate that dextrin is reactive towards graft polymer formation.

INTRODUCTION

Ceric ion has been used to initiate graft copolymerization of many monomers on various substrates [1–5]. Grafting is generally considered to result from propagation by radical sites generated on the polymer substrate. The low efficiency and frequency of grafting associated with ceric ion initiated graft copolymerization do not support this mechanism of initiation of grafting and have led to the suggestion that initiation sites for grafting, other than reactive sites formed on the polymeric substrate, may be important [6]. It is now accepted that the nature and reactivity of the polymeric substrate towards initiation, the reactivity of the reactive sites formed on the backbone polymer towards propagation, the nature of termination reactions in the polymerization and the solubility of the monomer and polymeric substrate in the reactions medium influence the extent of graft polymer formation. Several workers [7–14] have reported on graft copolymerization on starch. Graft copolymers of polysaccharides are of interest because of their potential as improved viscosifiers for use in enhanced oil recovery applications [15]. This communication examines some aspects of graft copolymerization on dextrin.

EXPERIMENTAL PROCEDURES

Methyl acrylate (MA) (BDH Ltd) was washed with aqueous NaCl/NaOH solution, dried over $CaCl_2$ and distilled. The middle fraction was collected. Ceric ammonium nitrate (BDH Ltd) was used without further purification. Dextrin (yellow) was prepared from cassava starch using 2% (v/v) hydrochloric acid [16].

Graft copolymerization of MA on dextrin was carried out using various concentrations of initiator. The procedure was based on the method described by Lepoutre and Hui [17] for grafting onto wood pulp. The substrate (0.5 g) was dissolved in 100 ml of deionized water containing a known amount of ceric ion. The initiator was allowed to interact with dextrin for 30 min and then a definite amount of monomer was added dropwise. The polymerization was allowed to proceed for 4 hr and then stopped by the addition of 2 ml of 1% (w/v) hydroquinone solution. The reaction mixture was poured into excess methanol and then filtered. The residue was air-dried and weighed. The ungrafted poly(methyl acrylate) (PMA) homopolymer was sochlet extracted with benzene. The grafted dextrin was then air-dried and weighed. The percentage of grafting (P_g), the rates of graft copolymerization (R_g), of homopolymerization (R_h) and total polymerization (R_p) were calculated from the weights of dextrin and grafting products as follows:

$$P_g = \frac{\text{weight of grafted PMA} \times 100}{\text{weight of dextrin}} \tag{1.1}$$

$$R_g = \frac{\text{weight of grafted PMA} \times 1000}{M_w \text{ of MA} \times \text{reaction time(sec)} \times \text{reaction volume (ml)}} \tag{1.2}$$

$$R_h = \frac{\text{weight of homo-PMA} \times 1000}{M_w \text{ of MA} \times \text{reaction time (sec)} \times \text{reaction volume (ml)}} \tag{1.3}$$

$$R_p = R_g + R_h. \tag{1.4}$$

The grafted PMA chains were isolated from the backbone polymer by treatment with hydrochloric acid [8]. The isolated PMA was purified by solution in benzene and precipitation with methanol. The average molecular weight of the isolated PMA grafts was determined from viscosity measurements in toluene at 30° using the relationship [18]

$$\log[\eta] = \log 7.79 \times 10^{-5} + 0.069 \log \bar{M}_v. \tag{2.1}$$

The frequency of grafting (F_g) defined as the number of PMA grafts per 10^4 anhydroglucose units (AGU) was calculated using the relationship:

$$F_g = \frac{\text{wt of grafted PMA} \times M_w \text{ of AGU}}{M_w \text{ of grafted PMA}} \times 10^4. \tag{2.2}$$

RESULTS AND DISCUSSION

The variation of P_g with ceric ion concentration using 0.44 M MA is shown in Fig. 1. The results show that the initial increase in P_g with ceric ion concentration attained a maximum value of *ca* 260% at 5.0×10^{-2} M ceric ion, and then decreased with further increase in ceric ion concentration. The decrease in P_g at high ceric ion concentration has been associated with the formation of a complex of

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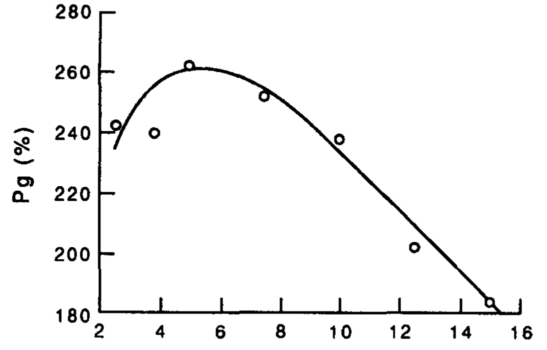

Fig. 1. Grafting methyl methacrylate on dextrin at 29° [MA] = 0.44 M.

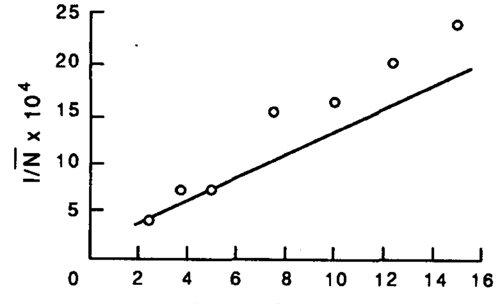

Fig. 4. Chain transfer to ceric ion in the graft copolymerization of MA on dextrin.

ceric ion with the backbone polymer [19, 20] which reduces both the number of grafting sites on the backbone polymer and the amount of ceric ion available to initiate graft polymer formation. The results in Fig. 1 clearly show that dextrin grafts more readily than starch in aqueous medium confirming the suggestion that the state of aggregation and swellability of the backbone polymer are important factors regulating the extent of grafting [10–12].

The relation between the rate of grafting and ceric ion concentration is shown in Fig. 2. The rates of grafting and homopolymerization increase with ceric ion concentration up to 0.05 M Ce(IV) and decrease at higher concentrations. This behaviour suggests the possibility of termination of graft copolymerization by combination of growing graft polymer chains at low ceric ion concentration and that termination of graft copolymerization might proceed by the interaction of ceric ion with the growing graft. A similar mechanism of termination has been reported for the grafting of acryamide on dextrin [21] and for the grafting of butyl acrylate on gelatin [22]. It is well recognized that, in such systems where the rates of mutual termination of growing polymer chains are low, the May relationship [23]

$$1/\bar{N} = 1/\bar{N}_0 + k_A[\text{Ce(IV)}]/k_p[\text{M}] \qquad (3)$$

would allow the chain transfer constant k_A/k_p to be determined. Here $\bar{N}$ and $\bar{N}_0$ are the average degrees of graft copolymerization in the presence and absence of ceric ion respectively. From the slope of the plot of $1/N$ against [Ce(IV)] (Fig. 4), the value of 1.08×10^{-2} was obtained for k_A/k_p.

Figure 5 shows the variation of F_g with ceric ion concentration. The number of grafted PMA mol-

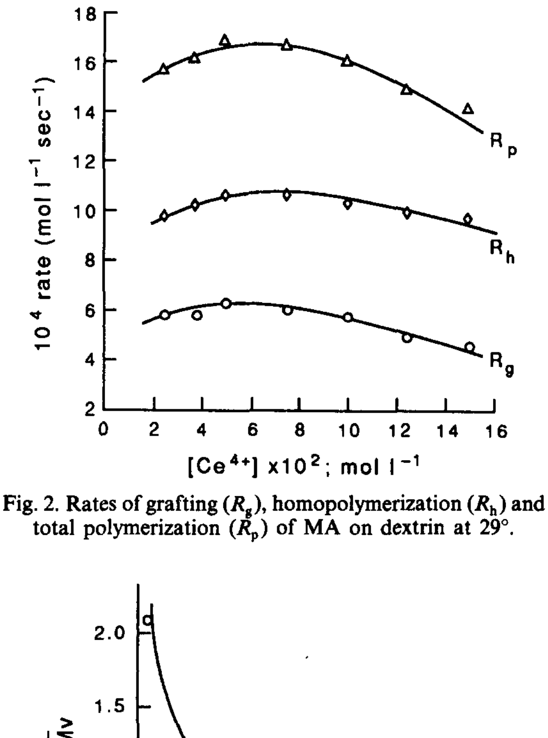

Fig. 2. Rates of grafting (R_g), homopolymerization (R_h) and total polymerization (R_p) of MA on dextrin at 29°.

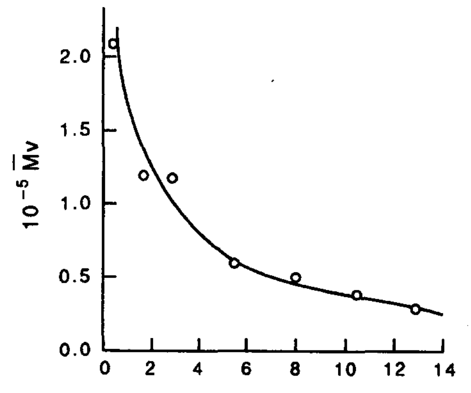

Fig. 3. Variation of molecular weight of grafted PMA with ceric ion concentration.

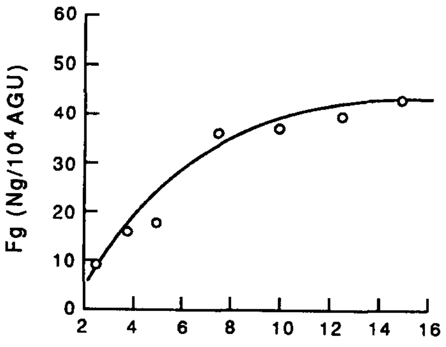

Fig. 5. Frequency of grafting MA on dextrin using ceric ion initiator at 29°.

ecules per 10^4 AGU varies from nine to more than 40. This result might be considered to indicate a reasonably high frequency of grafting compared to the values reported for starch [14]. Dextrinization is partial hydrolysis of starch and would be expected to result in the production of reactive end-groups. This process would explain the observed higher reactivity of dextrin than starch towards graft polymer formation. However the reported values of F_g show that $<1\%$ of AGU are effective in the initiation of graft copolymer formation.

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