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Synthesis of Casein-g-Poly(n-butyl Methacrylate)

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ABSTRACT

The graft copolymerization of n-butyl methacrylate onto casein initiated by peroxydisulfate in aqueous medium has been investigated and the results are discussed in the light of percent grafting, grafting efficiency, rates of conversion of monomer, and graft copolymerization.

INTRODUCTION

The properties of proteins can be modified effectively by grafting various acrylate monomers onto them. Modification of natural polymers [1-5] and synthetic polymers [6-8] by grafting technique has been extensively studied. Various initiating systems [4, 8-12] have been tried with varying degree of success. For efficient grafting onto natural polymeric backbones such as starch [13-15], cellulose [16, 17], and wool [18], various redox systems have been found to be effective. Persulfates [1-3] are found to be effective in initiating graft copolymerization. However, relatively few studies [1-5] have been carried out in the graft copolymerization of acrylate monomers onto casein. Hence, a systematic study on the graft copolymerization of n-butyl methacrylate onto casein has been investigated and the results are discussed in the light of percent grafting, grafting efficiency, rates of conversion of monomer, and graft copolymerization.

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EXPERIMENTAL

Materials

Casein (E. Merck, G.R.) and potassium peroxydisulfate (E. Merck, G.R.) were used as such in this investigation. Monomer, n-butyl methacrylate (n-BMA) (BDH, England) was purified by first washing with 6-8% sodium hydroxide solution to remove the inhibitor, then by distilled water, and dried over anhydrous calcium chloride. The monomer was distilled under vacuum and the middle fraction of the distillate was used for graft copolymerization.

Grafting Procedure

A known amount of casein was dispersed in water at constant stirring under nitrogen atmosphere and thermostated at the required temperature. After sufficient time, n-butyl methacrylate was added followed by the initiator, potassium peroxydisulfate. After a sufficient time interval, the reaction was quenched to 4° C and then the products were filtered through a weighed sintered crucible and dried in vacuum to a constant weight. The unbound homopolymer was then Soxhlet extracted using methyl ethyl ketone as solvent and dried in vacuo to constant weight. The infrared spectra of pure casein and the grafted casein were obtained with a Perkin-Elmer Model 337 grating spectrophotometer.

Calculations

The percent grafting (PG) and grafting efficiency (GE) were calculated as follows:

$$\text{Percent grafting (PG)} = \frac{\text{weight of poly(n-BMA) grafted}}{\text{weight of casein}} \times 100$$

$$\text{Grafting efficiency (GE)} = \frac{\text{weight of poly(nBMA) grafted}}{\text{weight of poly(nBMA) grafted} + \text{weight of unbound homopoly(nBMA)}} \times 100$$

RESULTS AND DISCUSSION

The influence of concentrations of monomer, initiator, and backbone, and the effect of temperature on the graft copolymerization of

n-butyl methacrylate onto casein were investigated and the results are discussed.

Effect of Monomer Concentration

The dependence of the grafting on the concentration of n-butyl methacrylate was studied within the range of 0.13-0.76 M and the results are depicted in Fig. 1. The percent grafting (PG), the rates of conversion of monomer (R_p), and the graft copolymerization (R_g) increase with the concentration of monomer. Similar observations were also made in our earlier investigations [1-5]. These may be due to the fact that a larger number of monomer radicals is available at higher concentrations of monomer and thereby increases PG, R_p, and R_g. Further, in concentrated monomer solution, the occurrence of chain transfer to monomer may take place, leading to increased formation of homopoly-(nBMA) and consequent loss of grafting sites [19] along casein. In addition, the solubility restriction might place a limit on the length of the grafted chain. From highly swollen polymers, graft removal is possible, leading to increased homopolymer formation [20-22]. As a result of this the rate of homopolymerization, R_h, is higher than that of graft copolymerization, R_g. Further, the relative increment in R_h is greater than that of R_g, resulting in an observed decrease in grafting efficiency.

Effect of Initiator Concentration

Percent grafting, grafting efficiency, the rates of conversion of monomer, and graft copolymerization were found to increase with the initial concentration of peroxydisulfate (Fig. 2), which is in good agreement with our earlier results [2, 4, 5]. With an increase in peroxydisulfate concentration, more active radicals such as $SO_4^{\cdot -}$ are created at higher rates, and they are utilized in graft copolymerization. However, beyond an optimum initiator concentration, annihilation of primary radicals is involved. Hence, R_p, R_g, and PG decrease. Further, the relative decrease in R_g is higher than that in R_h, leading to a downward drift in GE.

Effect of Backbone Concentration

The increase in the concentration of casein accelerates the rates of conversion of monomer, graft copolymerization, and percent grafting initially, while it increases the grafting efficiency continuously (Fig. 3),

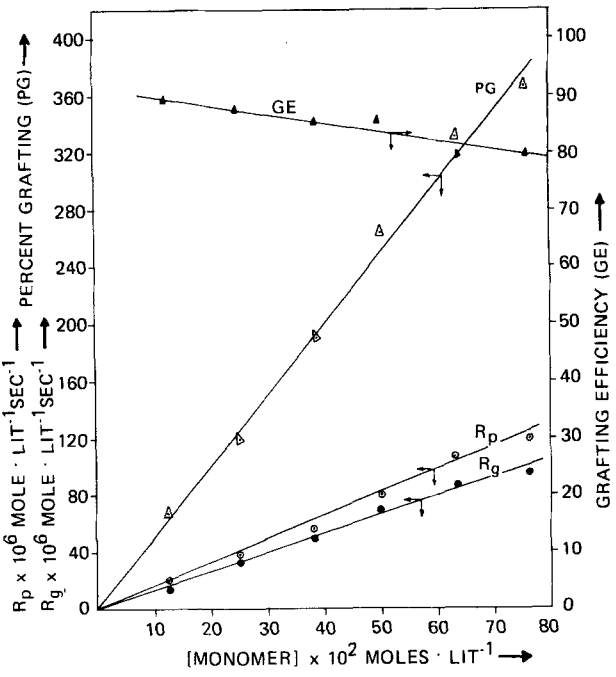

FIG. 1. PG: Plot of percent grafting versus monomer concentration (reaction conditions: $[S_2O_8^{2-}] = 1 \times 10^{-2}$ M, [casein] = 0.6667×10^{-3} M, total volume 50 mL, 60°C, and reaction time 90 min). GE: Plot of grafting efficiency versus monomer concentration (reaction conditions: [casein] = 0.6667×10^{-3} M, $[S_2O_8^{2-}] = 1 \times 10^{-2}$ M, total volume 50 mL, 60°C, and reaction time 90 min). R_p: Plot of rate of conversion of monomer versus monomer concentration (reaction conditions: $[S_2O_8^{2-}] = 1 \times 10^{-2}$ M, [casein] = 0.6667×10^{-3} M, total volume 50 mL, 60°C, and reaction time 90 min). R_g: Plot of rate of graft copolymerization versus monomer concentration (reaction conditions: $[S_2O_8^{2-}] = 1 \times 10^{-2}$ M, [casein] = 0.6667×10^{-3} M, total volume 50 mL, 60°C, and reaction time 90 min).

as in our earlier studies [1-5]. The increase in backbone concentration leads to a larger number of grafting sites along casein and thereby increases R_p, R_g, and PG initially. Further, the relative increment in R_g is higher than that of R_h. As a consequence of this, GE increases.

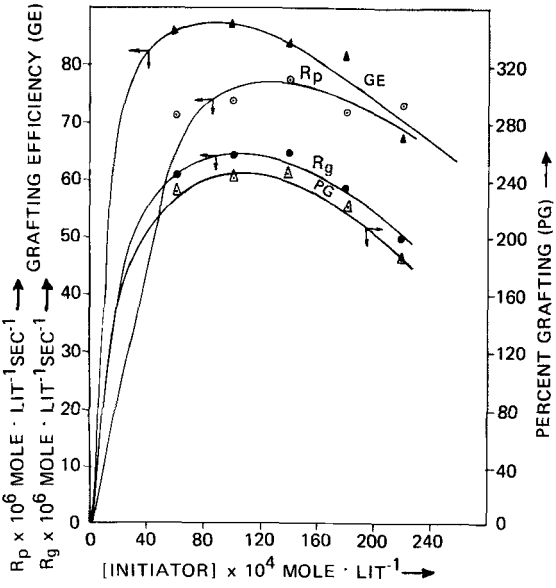

FIG. 2. PG: Plot of percent grafting versus initiator concentration (reaction conditions: [nBMA] = 0.4431 M, [casein] = 0.6667×10^{-3} M, total volume 50 mL, 60°C, and reaction time 90 min). GE: Plot of grafting efficiency versus initiator concentration (reaction conditions: [nBMA] = 0.4431 M, [casein] = 0.6667×10^{-3} M, total volume 50 mL, 60°C, and reaction time 90 min). R_p: Plot of rate of conversion of monomer versus initiator concentration (reaction conditions: [nBMA] = 0.4431 M, [casein] = 0.6667×10^{-3} M, total volume 50 mL, 60°C, and reaction time 90 min). R_g: Plot of rate of graft copolymerization versus initiator concentration (reaction conditions: [nBMA] = 0.4431 M, [casein] = 0.6667×10^{-3} M, total volume 50 mL, 60°C, and reaction time 90 min).

However, an increase in the concentration of casein beyond the optimum value leads to deactivation of the casein radical by mutual termination between backbone and primary radicals, which is reflected in the downward drift in R_p, R_g, and PG. Further, the relative decrease in R_g is smaller than that in R_h, resulting in a continuous increase in GE even beyond the optimum concentrations. Similar observations have been reported in literature [1-5, 13-15].

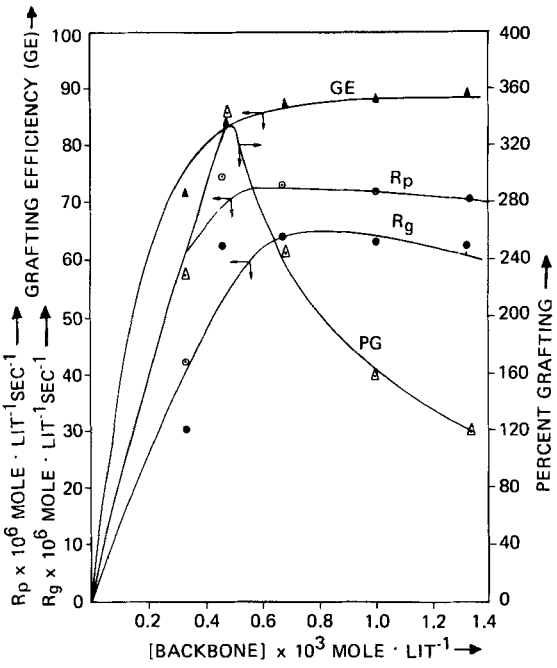

FIG. 3. PG: Plot of percent grafting versus backbone concentration (reaction conditions: [nBMA] = 0.4431 M, $[S_2O_8^{2-}] = 1 \times 10^{-2}$ M, total volume 50 mL, 60°C, and reaction time 90 min). GE: Plot of grafting efficiency versus backbone concentration (reaction conditions: [nBMA] = 0.4431 M, $[S_2O_8^{2-}] = 1 \times 10^{-2}$ M, total volume 50 mL, 60°C, and reaction time 90 min). R_p: Plot of rate of conversion of monomer versus backbone concentration (reaction conditions: [nBMA] = 0.4431 M, $[S_2O_8^{2-}] = 1 \times 10^{-2}$ M, total volume 50 mL, 60°C, and reaction time 90 min). R_g: Plot of rate of graft copolymerization versus backbone concentration (reaction conditions: [nBMA] = 0.4431 M, $[S_2O_8^{2-}] = 1 \times 10^{-2}$ M, total volume 50 mL, 60°C, and reaction time 90 min).

Effect of Temperature

An increase in temperature in the grafting of n-BMA onto casein, while keeping the concentrations of monomer, initiator, and backbone and time constant, was found to influence the rates of conversion of monomer and graft copolymerization, percent grafting, and grafting

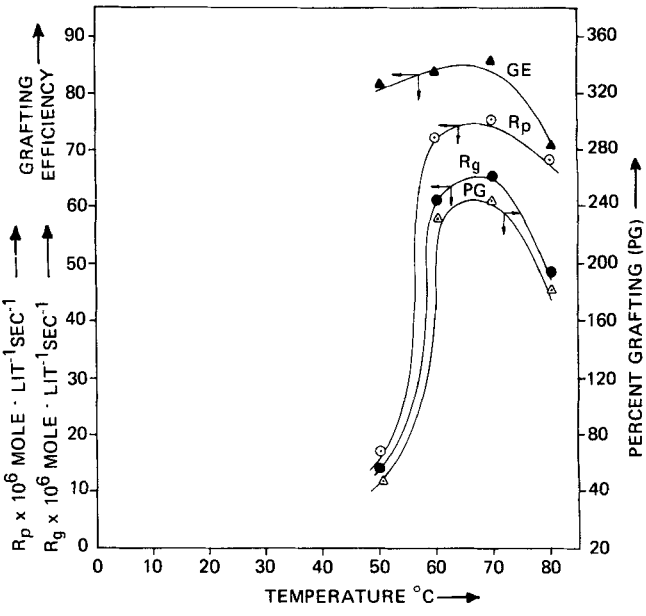

FIG. 4. PG: Plot of percent grafting versus temperature (reaction conditions: [nBMA] = 0.4431 M, $[S_2O_8^{2-}] = 1 \times 10^{-2}$ M, [casein] = 0.6667×10^{-3} M, total volume 50 mL, and reaction time 90 min). GE: Plot of grafting efficiency versus temperature (reaction conditions: [nBMA] = 0.4431 M, $[S_2O_8^{2-}] = 1 \times 10^{-2}$ M, [casein] = 0.6667×10^{-3} M, total volume 50 mL, and reaction time 90 min). R_p: Plot of rate of conversion of monomer versus temperature (reaction conditions: [nBMA] = 0.4431 M, $[S_2O_8^{2-}] = 1 \times 10^{-2}$ M, [casein] = 0.667×10^{-3} M, total volume 50 mL, and reaction time 90 min). R_g: Plot of rate of graft copolymerization versus temperature (reaction conditions: [nBMA] = 0.4431 M, $[S_2O_8^{2-}] = 1 \times 10^{-2}$ M, [casein] = 0.667×10^{-3} M, total volume 50 mL, and reaction time 90 min).

efficiency up to 70°C, as in normal polymerization (Fig. 4). Similar observations have also been cited in the literature [1-5]. However, an increase in temperature beyond 70°C leads to termination of growing radicals by primary radicals, and thereby decreases percent grafting, grafting efficiency, rates of conversion of monomer, and graft copolymerization.

Proof of grafting was obtained by comparing the infrared spectra

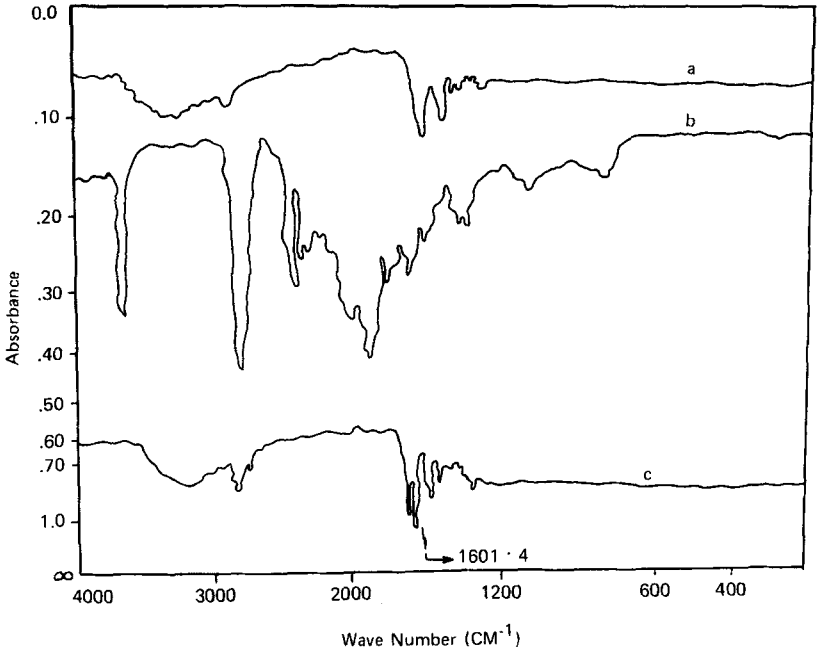

FIG. 5. (a) IR spectra of pure casein. (b) IR spectra of poly(n-butyl methacrylate). (c) IR spectra of casein-g-poly(n-butyl methacrylate).

of graft copolymerization and pure casein (Fig. 5). The additional peak at 1750 cm^{-1} in the grafted casein establishes proof of graft copolymerization of poly(n-butyl methacrylate) onto casein. Further proof of grafting was obtained from the ninhydrin test and selective solvent extraction [1-5, 23].

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