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Influence of Monomer and Initiator Concentrations on the Simultaneous Grafting of Several Monomers onto Insoluble Collagen

S. Amudeswari[a]; C. Rami Reddy[a]; K. Thomas Joseph[a]
[a] Polymer Division, Central Leather Research Institute, Madras, India

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NOTE

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S. AMUDESWARI, C. RAMI REDDY, and K. THOMAS JOSEPH

Polymer Division
Central Leather Research Institute
Adyar, Madras 600020, India

ABSTRACT

Simultaneous grafting of 2-hydroxyethyl methacrylate and methyl methacrylate (3:1 and 3:2 mole ratios) onto insoluble collagen with ceric ammonium nitrate as initiator was attempted with a view to optimizing conditions for the preparation of hydrogels. The influence of monomer and initiator concentrations on the grafting reactions was investigated. The grafting results are discussed in the light of grafting efficiency and percentage of grafting. They were found to be lower when the 3:1 mole ratio of monomers was used.

INTRODUCTION

The redox method with ceric ion has been used for initiation of the graft copolymerization of vinyl monomers, and the kinetics and mechanism have been extensively studied [1-3]. Graft copolymers of collagen and poly(methyl methacrylate) have been studied in detail [4-6]. Ceric ion has been used by Rao and co-workers [7, 8] to graft various vinyl monomers onto collagen.

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Simultaneous grafting of polymers with several monomers is a better method of achieving the desired end properties. A limited number of such studies have been reported [9-12]. The physical properties of such graft copolymers are dependent both on the composition of the sidechain polymer and on the relative percentage with respect to the backbone polymer.

When collagen was grafted with mixtures of 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA), percent grafting and grafting efficiency were found to be maximum for 75 and 60 mol% HEMA in the monomer [13]. Hence, we report here graft copolymerization of those two mixtures onto insoluble collagen with ceric ammonium nitrate as initiator, as functions of various reaction parameters.

EXPERIMENTAL

Materials and Methods

2-Hydroxyethyl methacrylate (HEMA) (Fluka) was distilled under vacuum. Methyl methacrylate (MMA) (Rohm and Hass, U.S.A.) was distilled by the standard procedure [14]. The middle fractions of the monomers were used for the grafting reactions. Ceric ammonium nitrate was dissolved in 1 M nitric acid to the desired concentrations. Insoluble collagen prepared from the middle corium of buffalo hide was used.

The grafting procedure adopted and the isolation of the graft copolymer have been reported earlier [13, 15]. The tumbled bottle method was used for homopolymer extraction. The graft copolymer was separated from the ungrafted homopolymer or copolymer, using methanol as the solvent for poly(HEMA) and a mixture of methanol and acetone for poly(HEMA-co-MMA). The following quantities were calculated:

$$\text{Percent grafting} = \frac{\text{weight of the grafted side chain}}{\text{weight of insoluble collagen}} \times 100,$$

$$\text{Grafting efficiency} = \frac{\text{weight of the grafted side chain}}{\text{weight of grafted side chain} + \text{weight of ungrafted homopolymer or copolymer}} \times 100.$$

The IR spectra of pure insoluble collagen and the graft copolymer were taken in KBr on a Perkin-Elmer Model 337 grating IR spectrophotometer.

RESULTS AND DISCUSSION

The percent grafting is found to increase, but the grafting efficiency is more or less unaffected, when the backbone to monomer ratio was changed from 1:1 to 1:3 at a monomer ratio of 3:1 (Table 1). Above this ratio, the percent grafting remains unaffected whereas the grafting efficiency decreases. At lower monomer concentrations the formation of grafted chains is greater than the formation of ungrafted copolymer, hence the increase in the percent grafting. At higher monomer concentrations the rate of ungrafted copolymer formation seems to be higher compared to the rate of side chain grafting, resulting in reduction of the grafting efficiency.

As shown in Table 2, the percent grafting increases whereas the grafting efficiency decreases with increasing initiator concentration. The increase in the percent grafting is roughly linear up to 4.17 mmol/L and thereafter remains unchanged. The grafting efficiency continues to decrease. It may be assumed that the additional initiator facilitates the creation of active centers and the formation of ungrafted copolymer, hence the decrease in the grafting efficiency.

At a 3:2 monomer ratio the increase in percent grafting with increasing monomer concentration is identical to that at a 3:1 ratio (Table 1), but the grafting efficiency is found to increase slightly from the initial value up to a 1:3 ratio of backbone to monomer and decreases after this.

The IR spectra of insoluble collagen and the graft copolymer are shown in Figs. 1 and 2. The presence of a band at 1 750 cm^{-1}, which is characteristic of the ester carbonyl groups, and the characteristic amide absorption bands at 1 550 and 1 660 cm^{-1} in the graft copolymers supports the formation of collagen graft copolymers.

TABLE 1. Effect of Total Monomer Concentration[a]

Sample	Weight ratio of backbone: monomer	Monomer mole ratio 3:1		Monomer mole ratio 3:2	
		Percent grafting	Grafting efficiency	Percent grafting	Grafting efficiency
1	1:1	18	52	19	41
2	1:2	27	53	59	52
3	1:3	78	55	119	57
4	1:4	84	44	124	55

[a]Insoluble collagen = 0.5 g, [CAN] = 4.17 mmol/L, time = 3 h, temperature = 28°C, total volume = 37 mL.

TABLE 2. Effect of Initiator Concentration[a]

Sample	[CAN], mmol/L	Monomer mole ratio 3:1		Monomer mole ratio 3:2	
		Percent grafting	Grafting efficiency	Percent grafting	Grafting efficiency
1	2.09	7	100	36	98
2	3.13	24	67	95	80
3	4.17	78	55	119	57
4	6.26	78	50	112	47

[a]Insoluble collagen = 0.5 g, time = 3 h, temperature = 28°C, total volume = 37 mL.

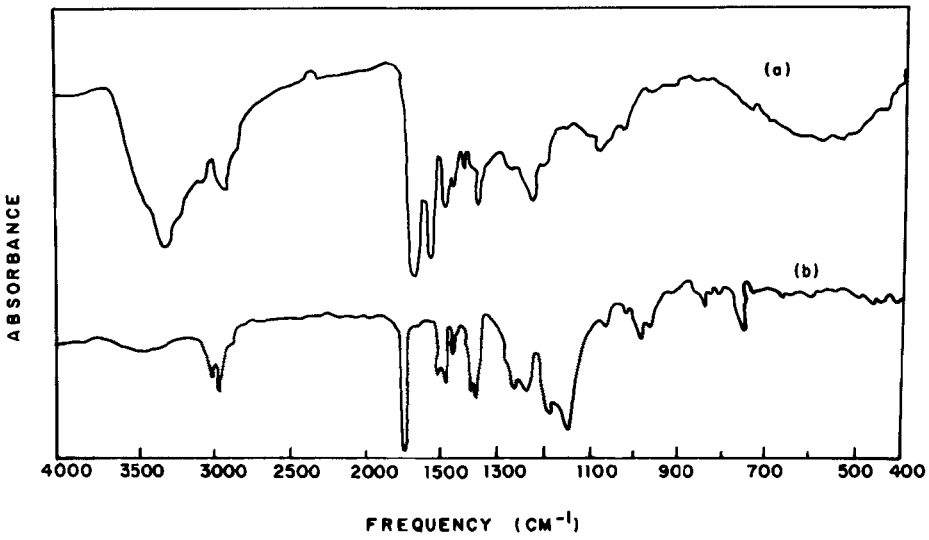

FIG. 1. IR spectra of (a) collagen (untreated sample) and (b) PMMA.

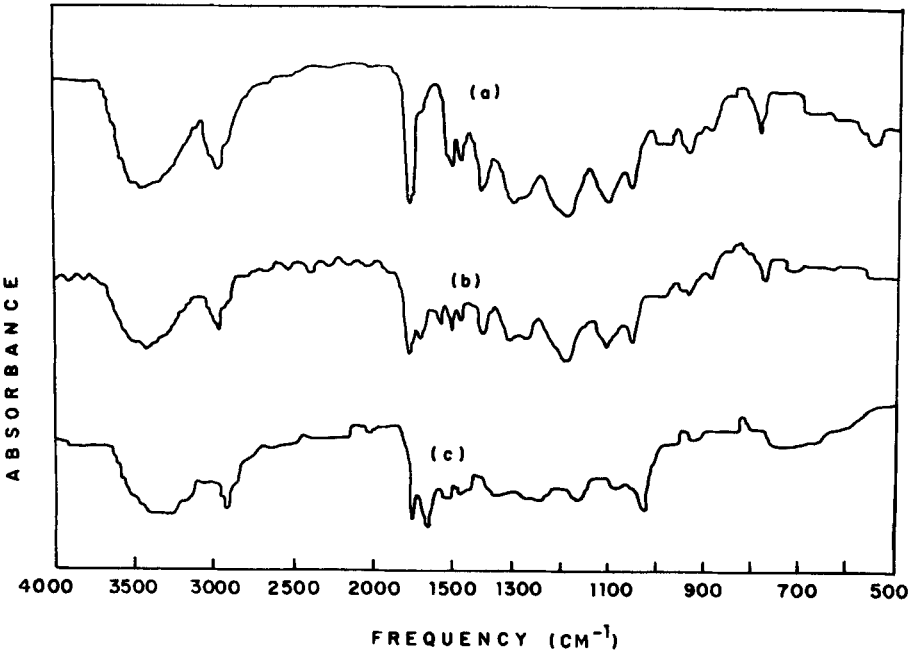

FIG. 2. IR spectra of (a) PHEMA, (b) collagen-g-HEMA, and (c) collagen-g-HEMA-co-MMA.

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