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Copper-Mediated Graft Copolymerization of Methyl Methacrylate onto Casein

Pei Li*[1], Jiang Hong Liu[1], Qun Wang[1], and Chi Wu[2]

[1] Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon;
[2] Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T. Hong Kong

SUMMARY : This study describes copper-mediated graft-copolymerization of methy methacrylate (MMA) onto casein, which gives stable core-shell latex particles. The effects of Cu (II) to casein and MMA to casein ratios were examined systematically. In addition, reaction kinetics was studied at various temperatures. The research results suggested that the graft copolymerization might proceed through a radical polymerization mechanism. The casein-g-PMMA was isolated by solvent extraction, and was confirmed by FTIR studies. Finally, the particle size of the casein-g-PMMA latexes was found to decrease with the increase of percentage grafting, and a near linear relationship was noted. TEM micrographs revealed that a core-shell particle was formed, with a shell of casein and a core of PMMA.

Introduction

Graft copolymerizations of monomers onto various natural polymers have been the most popular method of making bioartificial polymeric materials. For example, grafting various monomers onto gelatin, wool, silk, collage, cellulose, starch, curdlan have been documented in details[1-6)]. Casein, a milk protein, is a very practicable biomaterial, easily available in high purity and at low cost. It also has an outstanding glazable property. Therefore, casein has long been used as a principal binder in leather finishing. Because of this importance, the grafting of casein with suitable monomers has been the subject of extensive studies aiming to modify the properties of casein. For example, Mohan *et al* studied the graft copolymerization of butyl acrylate, acrylamide, methyl acrylate, n-butyl methacrylate, and ethyl acrylate using potassium persulfate as an initiator in order to overcome the brittleness and hydrophilicity problems of casein.[7)] Villiappan *et al* found that polymerizations of vinyl compounds with casein gave stable graft-copolymers, which were compatible with formaldehyde and dyes when used as a glaze finish for leather.[8)] It was also reported that acrylonitrile and acrylamide grafted casein easily formed into glazable films.[9)] However, all of the above graft copolyemrizations were achieved by employing reagents, such as potassium persulfate, alone or as part of a redox system with ascorbic acid. In addition, there have been

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reports on the use of H_2O_2-Fe^{2+} redox system and ceric ions[5,6]. However, such use often resulted in low grafting efficiency and a formation of a significant amount of homopolymer. Moreover, casein is easily oxidized in the presence of these initiators, producing yellowish products. Therefore, the development of new grafting methods to improve the grafting efficiency and overcome the oxidative problems is highly desirable. In 1982, Imoto and Ouchi[10] reported that many natural and synthetic polymers such as silk, collagen fiber, nylon, starch, polyethylene glycol could initiate polymerization of MMA in the presence of Cu (II) ions in a water medium. A radical polymerization mechanism involving complexes between the polymer and MMA on copper ion was suggested. In recent years, numerous fundamental researches on solution properties of casein have demonstrated that casein forms stable colloidal particles of approximately spherical shape, known as casein micelles. Small-angle neutron scattering has indicated that an average micellar radius is about 100-120 nm with a polydispersity of about 40-59%.[11] These literature results has prompted us to determine whether Cu (II) ion could induce the graft copolymerization of MMA onto casein, and form stable core-shell latex particles in the absence of surfactant.

Experimental

Materials. Commercial casein (Arcos Organics) (50 g) was refluxed in 1% EDTA aqueous solution (200 ml) for 24 hours in order to remove small amount of metal ions in casein. Methyl methacrylate (Aldrich) was freed from inhibitor by washing with 5% sodium hydroxide solution, then deionized water until the pH of the monomer dropped to 7. Other chemicals such as $CuCl_2 \cdot 2H_2O$ (Aldrich), EDTA (Guangzhou Chemicals) and ammonia solution (Aldrich) were used without further purification.

Graft Copolymerization of Methyl Methacrylate onto Casein. Casein (0.5 g) was first dissolved in 5 ml of 10% ammonia solution at 90^0C, followed by the addition of deionized water and copper chloride solution to make up a total 50 mL solution. The mixture was stirred for 30 minutes prior to the addition of 2.5 g of purified methyl methacrylate. The polymerization was carried out for 3 hours with continuous stirring, and a stable emulsion was obtained.

Percent Grafting. Casein / PMMA mixture obtained by precipitating the latex dispersion in 10% aqueous acetic acid solution and drying to a constant weight in vacuum, was extracted in a Soxhlet extractor with chloroform for 48 hours to remove any PMMA homopolymer formed during the polymerization. The resultant copolymer was dried in vacuum for 48 hours at 50^0C, and characterized by FTIR. Homopolymer of PMMA was isolated after removing the chloroform and drying the residue to a constant weight. Conversion and percentage grafting were then calculated according to following formulas:

$$\text{Conversion} = \frac{\text{MMA polymerized}}{\text{MMA added}} \text{ x } 100\%$$

$$\text{Percentage grafting} = \frac{\text{Weight of PMMA grafted}}{\text{Weight of casein}} = \frac{\text{MMA polymerized - PMMA}}{\text{Weight of casein}} \text{ x } 100\%$$

Determination of Particle Size of Casein-g-PMMA Latexes. Polymerization was stopped after 3 hours, and the unreacted MMA monomer in the emulsion was evaporated at 90^0C. The resulting dispersion was then diluted with deionized water to about 0.3% (w/v), and the particle size and its distribution were measured by Zeta Plus (Brookhaven Instruments Corp.).

Results and Discussion

In order to optimize the conditions for grafting, The effects of Cu (II) to casein and MMA to casein ratios have been examined. Table 1 shows that increasing copper ion to casein ratio from 0.75 to 7.5 : 10000 had little influence on both of the conversion of MMA and the percentage grafting. When copper ion to casein ratio was 9.5 : 10000, the conversion of MMA was significantly raised to 60%, but lower grafting percentage was actually obtained due to the increase of PMMA homopolymer. Further increases of copper ion to casein ratios to 1.1 : 1000 and 1.9 : 1000 were also examined. In these two cases, particles became very unstable, and a large amount of PMMA homopolymer precipitated out. On the other hand, the polymerization of MMA did not take place in the absence of Cu (II) ions. These results suggested that only a trace of copper ions were required to induce the graft copolymerization of methyl methacrylate onto the casein.

Table 1. Effect of Cu (II) Ions to Casein Ratios[1]

Cu (II) / Casein (w/w)	Conversion of MMA (%)	Grafting (%)
0.75 : $1\text{x}10^4$	40	200
2 : $1\text{x}10^4$	39	195
4 : $1 \text{ x } 10^4$	38	190
7.5 : $1 \text{ x } 10^4$	37	183

[1] Casein : MMA = 1 : 5, [Casein] = 1%, reactions were all carried out at 90^0C for 3 hours.

Table 2 demonstrates the effect of methyl methacrylate (MMA) to casein ratio on conversion and percentage grafting. The conversion decreased considerably with increasing MMA/casein ratio. The higher the MMA to casein ratio, the slower the reaction underwent. These results suggest that casein may interact with copper ions to initiate the graft copolymerization of MMA. Higher casein concentration provides a more reactive site to initiate the copolymerization, thus giving higher conversion. In contrast, percentage grafting increased with the increase of MMA to casein ratio. When MMA/casein ratio was lower than 2:1, PMMA homopolymer was detected.

Table 2. Effect of Methyl Methacrylate to Casein Ratios[1]

MMA / Casein (w/w)	**Conversion of MMA (%)**	**Grafting (%)**
1 : 1	95	80
2 : 1	89	160
3 : 1	54	162
4 : 1	45	180
5 : 1	40	200

[1] [Casein] = 1%, Cu^{2+}/Casein = 0.75 : 10000, reactions were all carried out at 90^0C for 3 hours.

The effect of reaction temperatures ranging from $60\text{-}80^0$C is demonstrated in Figure 1. It was found that the conversion of MMA increased remarkably when the reaction temperature was elevated from 60^0C to 70^0C. A further increase of temperatures from 70^0C to 75^0C, then to 80^0C enhanced only the initial conversion, but not the overall conversion.

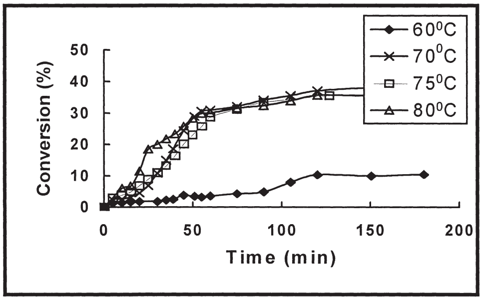

Fig 1. Graft copolymerization of MMA onto casein in the presence of Cu^{2+} at various temperature ([MMA]=3%, [casein]=1%, [Cu^{2+}]=7.5ppm)

The kinetic behavior of this graft copolymerization system at 70°C is illustrated in Figure 2. Two stages of reaction were observed: first, the polymerization rate increased monotonically and reached a maximum; second, the polymerization rate decreased from the maximum and leveled off. This was a typical kinetic behavior for radical polymerization confined in a pre-formed micro-environment. This finding is in agreement with the proposed mechanism by Imoto and Ouchi$^{10)}$.

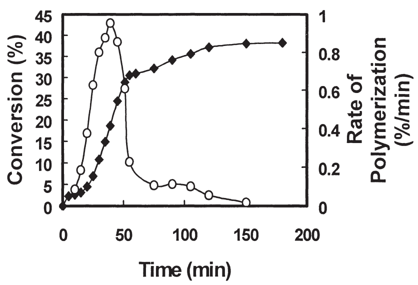

Fig 2. Conversion (◆) and rate of polymerization (o) vs reaction time ([MMA]=3%,[casein]=1%, [Cu^{2+}]= 7.5ppm, 70°C)

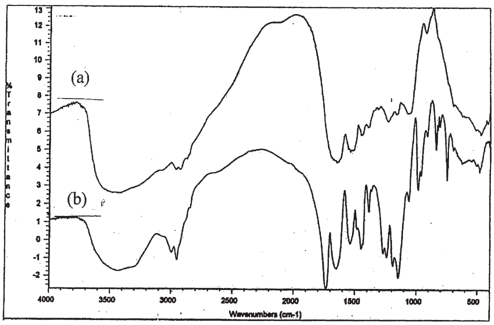

Fig 3. FTIR spectra of: (a) pure casein, and (b) casein-g-PMMA.

FTIR spectra of the pure casein and casein-g-PMMA obtained after solvent extraction are compared in Figure 3. A strong absorption band at 1735 cm^{-1} is observed for the grafted casein. ^{1}H-NMR studies of standard PMMA and grafted PMMA obtained after hydrolysis indicated that they had comparable peaks. These results proved that the grafted material was casein-g-PMMA.

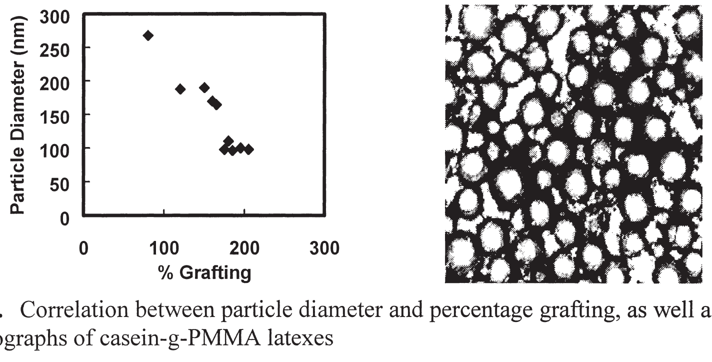

Fig 4. Correlation between particle diameter and percentage grafting, as well as TEM micrographs of casein-g-PMMA latexes

An interesting correlation between the particle size of the casein-g-PMMA latexes and the percentage grafting has been found as demonstrated in Figure 4. The diameter of casein-g-

PMMA latexes decreased with the increase of percentage grafting, but the particle size remained nearly constant when the percentage grafting was higher that 180%. TEM micrographs revealed that these latex particles (mean diameter = 96 nm) had a core-shell morphology, with a shell of casein molecules and a core of grafted PMMA branches.

Conclusion

Synthesis of core-shell latexese of casein-g-poly(methyl mthacrylate) has been successfully achieved through the graft copolymerization of methyl methacrylate onto the casein induced by a trace of copper ions. This study demonstrates a convenient method of producing core-shell particles of casein-g-PMMA under mild conditions. In addition, formation of homopolymer and oxidative problems could be overcome. Finally, these core-shell particles may find many potential applications in leather, textiles industries, and in the area of biocompatible materials.

Acknowledgement

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