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Graft Copolymerization of Methyl Methacrylate onto Casein Initiated by Potassium Ditelluratocuprate(III)

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ABSTRACT

A novel redox system, potassium ditelluratocuprate(III) (DTC)–casein was employed to initiate graft copolymerization of methyl methacrylate (MMA) onto casein in an aqueous alkali solution medium. The effects monomer concentration, initiator concentration, pH, temperature, and time were investigated. The grafting conditions were optimized by means of a series of copolymerization. The DTC–casein system was found to be an efficient redox initiator for this graft copolymerization. The structures and thermal stability of casein and casein-*g*-PMA were characterized by infrared spectroscopy (IR), thermogravimetric analysis (TGA), and scanning electron microscope (SEM). A mechanism is proposed to explain the formation of radicals and the initiation.

Key Words: Potassium diperiodatocuprate[Cu(III)]; Casein; Casein-*g*-PMA; Graft copolymer.

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INTRODUCTION

The milk protein, casein, contains hydrobonds between $>C=O$ and $-NH$ groups, which have a negative influence on the flexibility of the films formed. The technique of graft copolymerization has been used to modify casein to give desirable properties. Most of the initiators adopted are the free radical initiators, such as $K_2S_2O_8$ alone or as part of a redox system,^[1-4] $Fe^{2+}-H_2O_2$, with which homopolymerization is easily initiated, so as to decrease grafting efficiency. Although ceric ion can initiate polymerization with high grafting efficiency,^[5] high price and acidic conditions limit its broad applications.

The basic theoretical research and application on supernormal valence transitional metals have recently received considerable attention. In recent years, we have obtained some achievements on the polymerization and graft copolymerization of vinyl monomer initiated by supernormal valence transition-metals, such as diperiodatocuprate(III),^[6-8] diperiodatoargentate(III),^[9,10] and diperiodatonickelate(IV).^[11-14] It has been demonstrated that Cu(III) is an efficient and cheap initiator, but they only use the orthoperiodate as complexing agents. There were numerous references^[15-19] for strong oxidative behavior of dietelluratocuprate (DTC). In our last report,^[20] we have confirmed that DTC was a good radical initiator and was used to initiate radical homopolymerization. However, yet there are no reports on graft copolymerization of vinyl monomer onto macromolecular using DTC as the initiator. In this paper, graft copolymerization of methyl methacrylate (MMA) onto casein has been carried out using DTC-casein redox initiator in an alkaline medium. No matter how the conditions of the reaction system were changed, a high value of percent grafting was always attained. The effects of reaction variables on graft parameters have been investigated. The structures and the thermal stability of casein and casein-*g*-PMA were characterized by infrared spectroscopy (IR), scanning and electron microscope (SEM), and thermogravimetric analysis (TGA). A mechanism is proposed to explain the formation of radicals and their initiation.

EXPERIMENTAL

Materials

Methyl methacrylate was freed from inhibitor by washing successively with aqueous sodium hydroxide solution and distilled water, dried over anhydrous sodium sulfate, and distilled under reduced pressure. The distillate was collected and then used in the investigations. Casein was dried under vacuum at 60°C for 10 hr before use. The stock solution of DTC was prepared by the method given by Chandra and Yadava.^[21] The concentration of DTC was obtained by its absorption at $\lambda = 405$ nm using a Shimadzu UV-265 spectrophotometer (Shimadzu, Japan).

Synthesis and Purification of Graft Copolymers

Graft copolymerization was carried out in a 50 mL four-necked flask equipped with thermometer, condenser, stirrer, and gas inlet. In a typical reaction, 0.5 g casein was added with constant stirring under nitrogen. The required amount of monomer was added,



followed by a DTC aqueous solution and the total volume was made up to 15 mL with distilled water. The graft copolymerization was performed under different conditions of temperature, pH value, monomer concentration, initiator concentration, and time. After the completion of reaction, the reactants were cooled and poured into an aqueous hydrochloric acid solution, then filtered through a weight-sintered glass funnel and washed to neutral. It was then dried to a constant weight under vacuum at 60°C. The homopolymer of MMA poly methyl methacrylate (PMMA) was removed from a crude graft copolymer by soxhlet extraction with acetone, and then dried to a constant weight under vacuum.

Measurements

Casein-g-PMMA was characterized after exhaustive Soxhlet extraction to remove PMMA by IR analysis using an FTS-40 spectrophotometer (BIO-RAD, Co., USA) in the potassium bromide medium. Thermogravimetric analysis of casein (8.7 mg) and the copolymers (7.5 mg) were carried out on a Shimadzu DTA-TG apparatus DGC-40 (Shimadzu, Japan) in an oxygen atmosphere at a heating rate of 10°C/min. Dried casein and casein-g-PMMA samples were made into granules, whose morphology was investigated using an AMKAY-1000B (The Scientific Apparatus Factory of Chinese Academy of Sciences, China) scanning electron microscope.

RESULTS AND DISCUSSION

The grafting parameters, such as grafting efficiency (%*E*), percent grafting (%*P*), and total conversion percentage (%*C*) were defined and calculated as follows:^[22]

$$%E = (\text{weight of PMMA grafted} / \text{total weight of PMMA}) \times 100$$

$$%P = (\text{weight of PMMA grafted} / \text{weight of casein}) \times 100$$

$$%C = (\text{total weight of PMMA} / \text{weight of MMA charged}) \times 100$$

Effect of Temperature

When the other reaction conditions are invariable, the grafting parameters at various temperatures are shown in Fig. 1. In accordance with the general rule of radical polymerization, the grafting parameters, %*E* falls gradually and then levels off. %*P* increases greatly at first, and beyond 20°C the extent of increase is not much. %*C* increases with the increasing temperature, and this may be due to an increase in free radical generation with the increase of temperature that results in the increase of PMMA. Lower temperatures benefit in initiating the reaction and chain propagation reaction. At higher temperatures, the radical termination reaction through oxidation by DTC as well as rate of free radical generation increased.



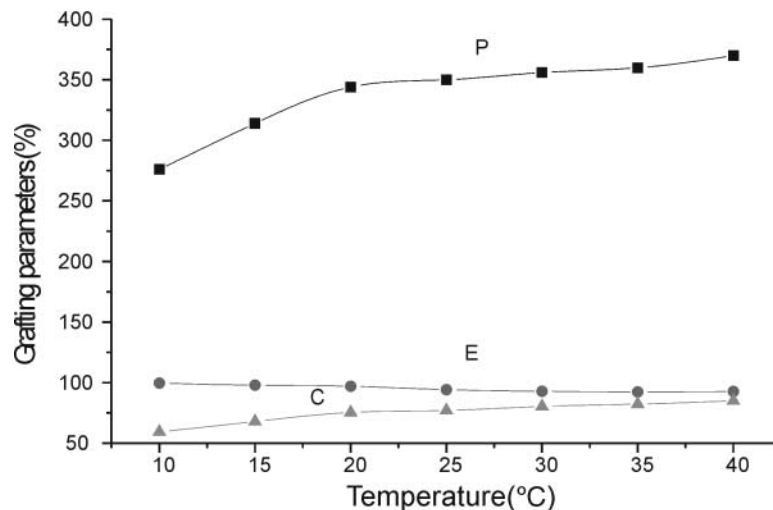


Figure 1. Effect of temperature on graft parameters. Casein: 0.5 g; MMA: 2.5 mL; [DTC]: 2.66×10^{-3} M; pH = 12.80; 60 min.

Effect of Monomer-to-Casein Ratio

The effect of monomer-to-casein ratio on graft copolymerization of MMA onto casein is depicted in Fig. 2. Methyl methacrylate was hardly soluble in water, but %P and %E still remained at a high level. This may be due to the surface activity and self-emulsifying properties of casein and casein-g-PMMA,^[23] which assist in the proximity of monomer to

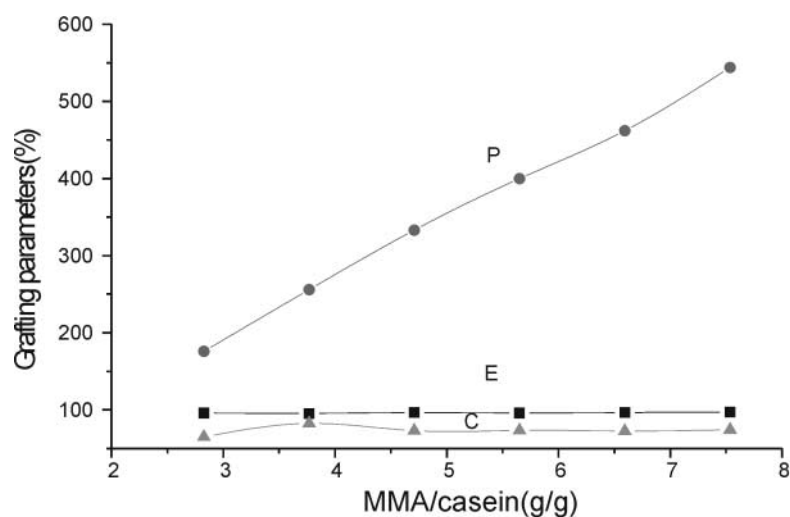


Figure 2. Effect of monomer-to-casein ratio on graft parameters. [DTC]: 2.66×10^{-3} M; 60 min; pH = 12.80; 20°C.



the growing chains and active sites on the casein. With an increase in MMA-to-casein ratio, %*P* increases continuously, %*E* remains constant, and %*C* decreases slightly, which is in accord with heterogenous graft polymerization.^[24–26] This can indicate that the DTC is an effective initiator and the redox system of DTC–casein has the characteristic of stability.

Effect of pH

Figure 3 shows the effect of pH on graft parameters. Potassium hydroxide and hydrogen chloride are employed to maintain the required alkalinity in the reaction solution. In the studied pH range, DTC exists mainly in the form of $[\text{Cu}(\text{OH})_2(\text{H}_4\text{TeO}_6)_2]^{3-}$ and $[\text{Cu}(\text{OH})_2(\text{H}_3\text{TeO}_6)_2]$.^[2–19] In the aqueous alkali solution, the ratio of the two forms changes with pH, which directly influences the amount of radicals produced in the reaction system. It is found that the optimum pH value is 12.80.

Effect of DTC Concentration

The effect of DTC concentration on grafting parameters was shown in Fig. 4. Grafting parameters, both %*C* and %*P* show the tendency of increasing at first and then decreasing with a further increase in DTC concentration. The higher %*P* (200–350%), and *E* (>90%), compared with the other systems,^[2–5] can be explained as follows: in the reaction system, the reduction of DTC involves only the formation of casein radicals, which activates the backbone to initiate polymerization. This can be confirmed by a contrast experiment, in where without casein PMMA cannot be obtained. The primary

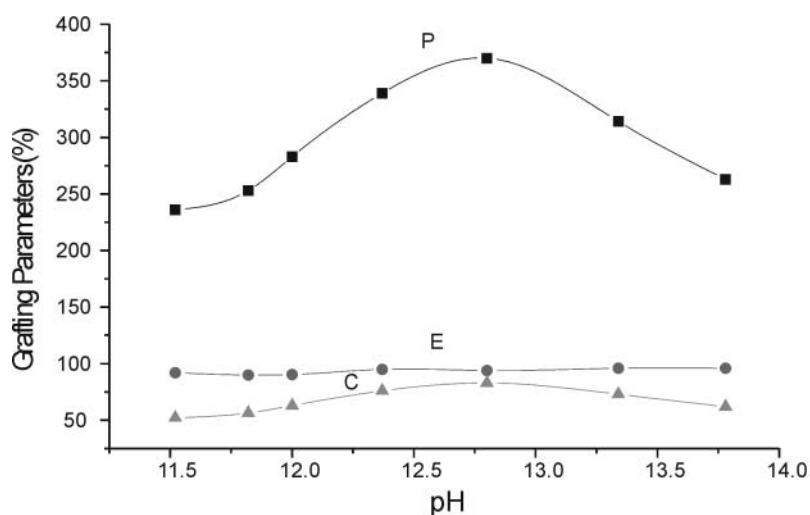


Figure 3. Effect of pH on graft parameters. Casein: 0.5 g; MMA: 2.5 mL; [DTC]: 2.66×10^{-3} M; 60 min; 20°C.



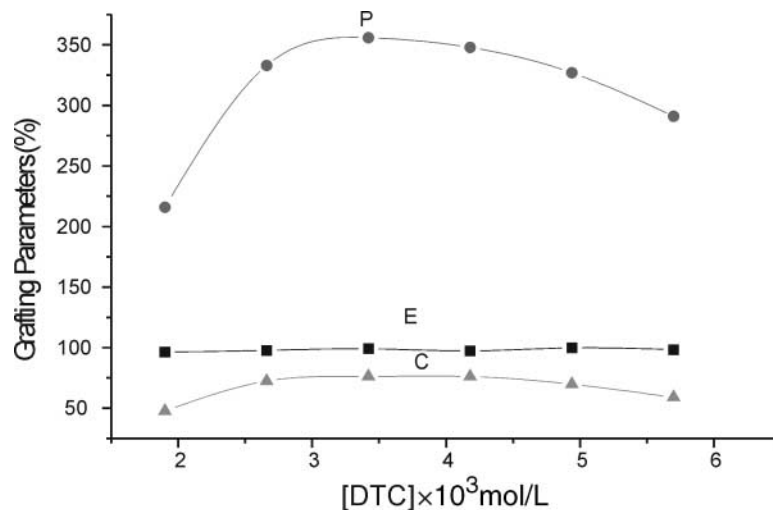


Figure 4. Effect of DTC concentration on graft parameters. Casein: 0.5 g; MMA: 2.5 mL; pH = 12.80; 60 min; 20°C.

radicals produced are mainly utilized for graft copolymerization, and DTC reacts with the characteristic group of casein, $\left(\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{NH}- \end{array} \right)$ to form a number of grafting dots, which initiate the polymerization of MMA. As a result, %C and %P increases. However, a further increase in the DTC concentration accelerates the reaction of DTC and radical which in turn terminates the chain propagation reaction. At the same time, the possibility of a transfer reaction due to a monomer increase and the homopolymerization of MMA was raised with an increase in DTC concentration. All these resulted in a decrease of the grafting parameter.

Effect of Time

Figure 5 illustrates the influence of the reaction time on grafting parameters. Both %P and %C increase with the prolonged reaction time and, after 60 min the tendency of increase declined and maintained a plateau, therefore, the optimum reaction time is 60 min.

Infrared Spectroscopy

The proof of grafting was obtained from the FTIR spectra of pure casein and casein-g-PMMA after an exhaustive Soxhlet extraction with acetone [Fig. (6)]. The FTIR spectra show characteristic absorption bands of casein [Fig. 6(a)] at 3300 cm^{-1} ($\nu_{\text{N-H}}$), 1665 and 1060 cm^{-1} . Compared with pure casein, graft copolymer (Fig. 6b) has an additional peak at 1745 cm^{-1} due to the ester carbonyl group of PMMA.



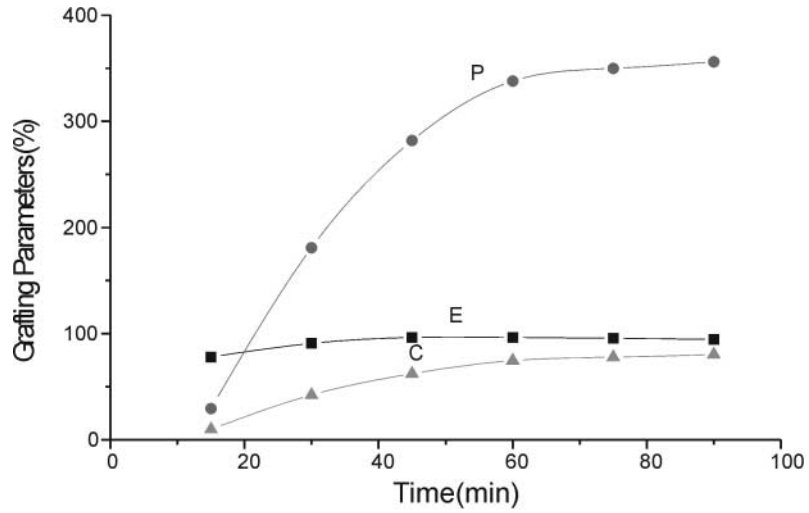


Figure 5. Effect of time on graft parameters. 0.5 g; MMA: 2.5 mL; [DTC]: 2.66×10^{-3} M; pH = 12.80; 20°C.

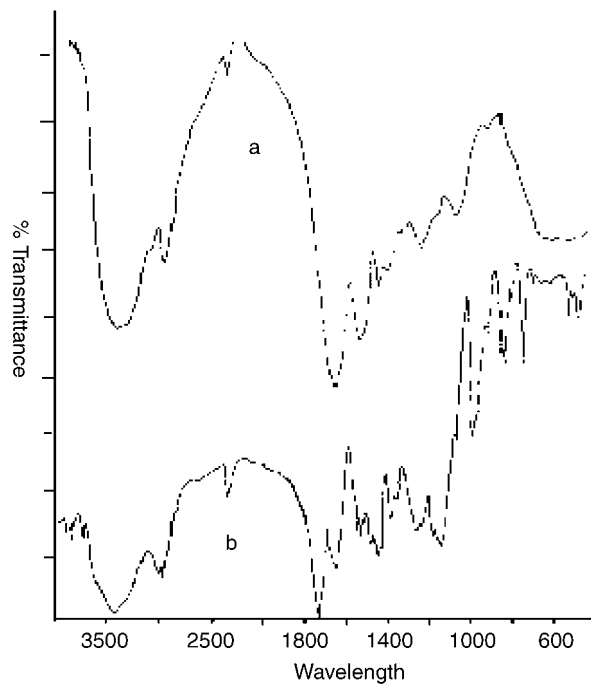


Figure 6. IR spectra of (a) casein and (b) casein-g-PMMA.

Thermal Analysis

Thermogravimetric analysis of pure casein and the grafted copolymer are shown in Fig. 7. In TGA of pure casein, the first stage ranges from 25°C to 98.1°C and shows about 7.41% wt loss. This may correspond to the loss of the absorbed and bound water. The second stage starts at 203°C and continues up to 425°C, during which there was 45.08% wt loss due to the degradation of the macromolecular chain. The TGA of the grafted product is different as the first stage ranges from 30°C to 84°C and shows about a 3.5% wt loss. At the same time, the decomposition temperature of grafted copolymer starts at 227.0°C, which is higher than that of the pure casein due to the effect of PMMA on casein. The temperature at 50% wt loss of the casein and casein-*g*-PMMA were 420°C and 348°C, respectively. It illustrated that the grafted copolymer has distinct thermal properties compared to pure casein.

Scanning Electron Microscopy

The scanning electron micrographs of pure casein and casein-*g*-PMMA are shown in Figs. 8 and 9. It is obvious that the surface of pure casein is very rough and not smooth, whereas the surface of casein-*g*-PMMA tends to be smoother and has almost turned into an integration. It is the graft reaction that brings about these changes. Compared with the morphology of pure casein, there is a significant increment in the coagulum formation on casein-*g*-PMMA.

The Initiation Mechanism of Grafting Reaction

The IR spectra, TGA, and SEM show that PMMA has been grafted onto casein. To test the nature of the polymerization, free radical inhibitors ferric chloride and

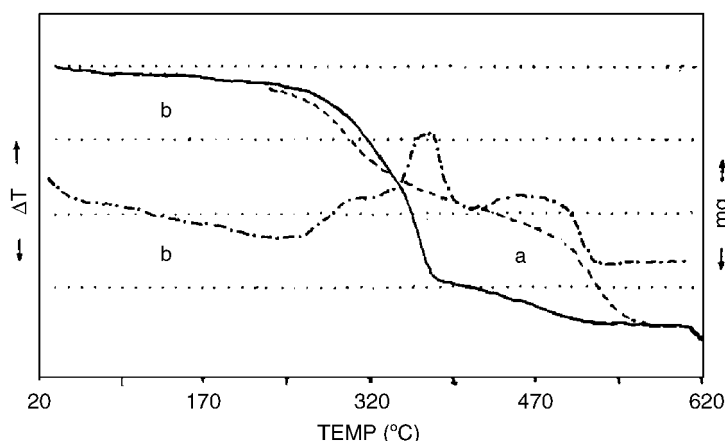


Figure 7. Thermal analysis for (a) casein and (b) casein-*g*-PMMA.



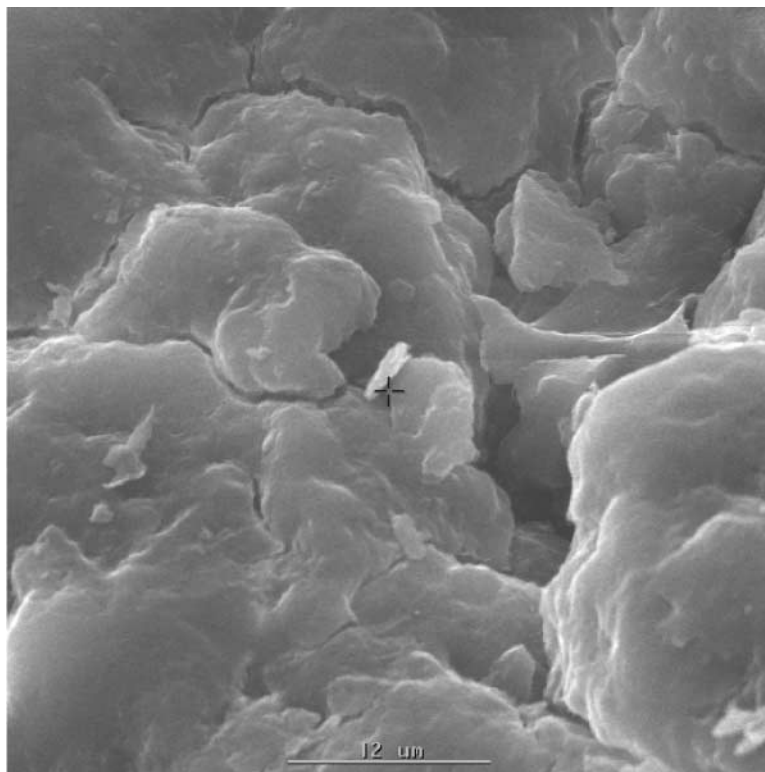
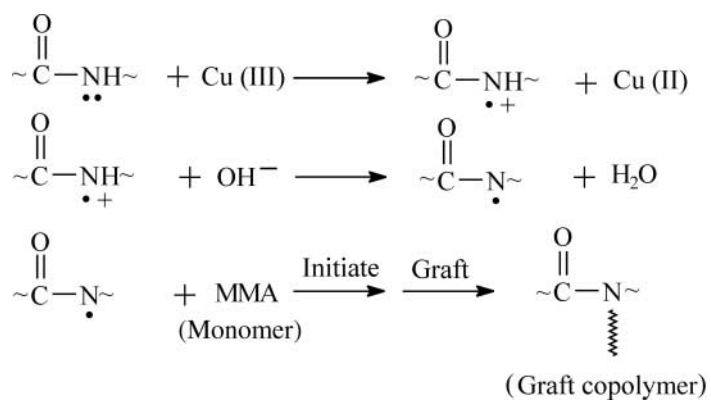


Figure 8. Scanning electron microscopy.

p-dihydroxy benzene (0.1% mol of MMA) were added to the reaction system separately and no polymerization occurred. So, it was considered to be a free radical polymerization. Referring to reports,^[6–8,20] the initiation mechanism belongs to a single-electron-transfer mechanism and is shown as follows:



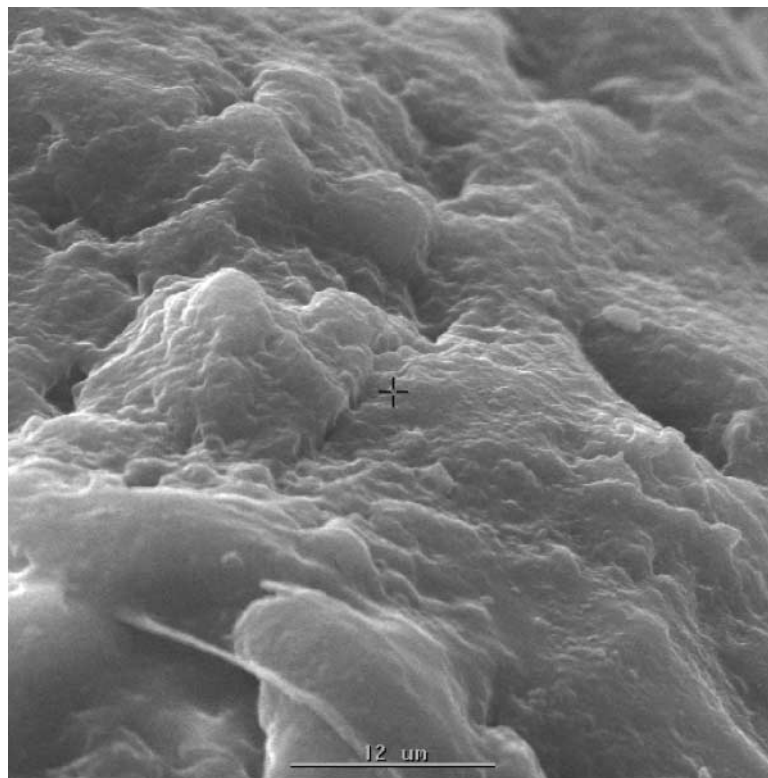


Figure 9. Scanning electron micrograph of casein-*g*-PMMA.

CONCLUSION

It was the first time that DTC was employed to initiate graft copolymerization of MMA onto casein in an aqueous alkaline medium. The proof of grafting was obtained from FTIR, TGA, and SEM. Compared to the morphology of pure casein, there is a significant increment in the coagulum formation on casein-*g*-PMMA.

In this work, the effects of reaction variables on grafting parameter have been investigated. Compared with the initiating systems of diperiodatocuprate (III),^[7,8] diperiodatoargentate(III),^[9] and diperiodatonickelate(IV),^[13,14] the conclusion shows the similar phenomenon. High levels of %P, %E, and %C have been obtained. However, we found no matter how the condition of the reaction was changed, %E always remained stable and at a high value (>90%), which was better than the redox system initiated by diperiodatocuprate(III),^[7,8] diperiodatoargentate(III),^[9] and diperiodatonickelate (IV).^[13,14] The DTC–casein system can be confirmed to be an efficient and staredox system for this graft copolymerization. Moreover, because the activation energy of the reaction employing DTC as an initiator is low,^[20] the graft copolymerization is carried out at a room temperature of 20°C and in an aqueous alkali medium, which is superior to other initiators. Thus, the DTC–casein redox system is considered to be a practical initiator and has a good foreground. Further work in this area is being carried out.



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