Graft Copolymerization of Styrene onto Casein Initiated by Potassium Diperiodatonickelate (IV) in Alkaline Medium

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ABSTRACT: A novel redox system, potassium diperiodatonickelate (Ni(IV))-casein is used to initiate graft copolymerization of Styrene onto casein under different conditions in aqueous alkaline solution. Graft copolymers with both high grafting efficiency (>98%) and percentage of grafting(>300%) are obtained, which indicated that (Ni(IV))-casein redox pair is an efficient initiator for this grafting. The effects of reaction parameters, such as monomer-to-casein weight ratio, initiator concentration, pH, time, and temperature, are investigated. A tentative initiation mechanism is proposed. The structures and properties of the graft copolymer are characterized by Fourier transform infrared Spectroscopy, X-ray diffraction diagrams, and Scanning Electron Microscope. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4247–4251, 2006

Key words: radical polymerization; initiators; graft copolymers; redox polymers

INTRODUCTION

The casein, namely milk protein, which abounds in the world as a natural polymer, contains hydrobonds between C—O and —NH groups, resulting in negative influence on the flexibility of the films formed. Graft copolymerization is one of the methods to modify casein to give new and desirable properties. Most of the usual initiators adopted are free radical initiators, such as $K_2S_2O_8$ alone or as part of a redox system[1–4] and Fe^{2+}-H_2O_2, by which homopolymerization is so easily initiated as to decrease grafting efficiency. And they are mainly used to initiate the graft polymerization of acrylate monomer onto macromolecule. Although ceric ion can initiate polymerization with high grafting efficiency,[5] acidic medium conditions and high price limit its applications.

Recently more and more considerable attentions have been paid to the basic theoretical research and application on supernormal valence transitional metal, which can form a redox system with the characteristic reductive group on the natural or synthetic macromolecule to initiate the graft copolymerization of vinyl monomer onto macromolecule directly with high grafting efficiency. In our previous studies supernormal valence transitional metals, such as diperiodatonickelate(IV),[6–9] diperiodatoargentate(III),[10–12] and Diperiodatocuprate(III),[13–15] have been applied to modify the macromolecular mainly with acrylate monomer, and some achievements have been obtained. On the basis of the experiments it has been demonstrated that Ni(IV) is an efficient and cheap initiator for the grafting. However there are no reports on graft copolymerization of Styrene onto macromolecular using Ni(IV) as initiator so far.

In this paper, graft copolymerization of styrene (St) onto casein has been carried out using Ni(IV)-casein redox initiating system in alkaline medium. The effects of the reaction variables, such as monomer-to-casein weight ratio, initiator concentration, pH, time and temperature, on graft parameters have been investigated. And the grafting conditions are optimized (monomer-to-casein weight ratio, 3.06; [NI(IV)] = 1.123×10^{-2} mol/L; time, 3 h; temperature, 55°C; pH, 12.83). A two-step, single-electron-transfer mechanism is proposed to explain the formation of radicals and the initiation. The structures and the properties of casein and casein-*g*-polystyrene (casein-*g*-PSt) are characterized by the Fourier transform infrared (FTIR) Spectroscopy, X-ray diffraction, and Scanning Electron Microscopy (SEM). Ni(IV)-casein system is found to be an efficient redox initiator for this graft copolymerization.

EXPERIMENTAL

Materials

Styrene is separated from inhibitor, dried and distilled, and then collected for use in the investigation.

Casein (Beijing Shuangxuan Microbe Culture Medium Products Factory, 02–08 BR) was dried under vacuum at 60°C for 10 h before used. The solution of Ni(IV) was synthesized and measured according to the reported procedure.[16] The other reagents and solvents (analytical grade) are used without any further purification.

Graft copolymerization and treatment of copolymer

Required amount of casein (0.2 g) is dissolved in 0.5% KOH aqueous solution with constant stirring and then the monomer (1.0 mL) is added in. After being deaerated sufficiently by nitrogen, Ni(IV) aqueous solution (1.5 mL) is dripped into the reaction system with the total volume settled to be 20 mL. After a period of reaction time, the reactant is cooled and terminated by a little aqueous hydrochloric acid solution, then poured into excess of methanol to precipitate the polymer. The precipitated product is filtered through weight sintered glass funnel and dried to a constant weight under vacuum at 60°C. The homopolymer of styrene is removed completely from the graft copolymer by exhaustive soxhlet extraction with toluene for 48 h. The final graft copolymer is dried to a constant weight under vacuum. The graft copolymerization is performed repetitively on the conditions of different monomer-to-casein weight ratio, Ni(IV) concentration, pH, time, and temperature. And the product is treated as mentioned earlier.

The grafting parameters, including total conversion (TC), grafting efficiency (GE), and percentage grafting (PG), are defined and calculated as follows

TC(%)

= (Total weight of PSt/Weight of St charged)

$$\times\ 100\%$$

GE (%)

= (Weight of PSt grafted/Total weight of PSt)

$$\times\ 100\%$$

PG (%)

= (Weight of PSt grafted/Weight of casein) $\times$ 100%

Measurements

FTIR spectroscopy

The FTIR spectra of casein and casein-g-PSt are recorded on a FTS-40 IR spectrometer (Bio-Rad) by the potassium bromide pellet method.
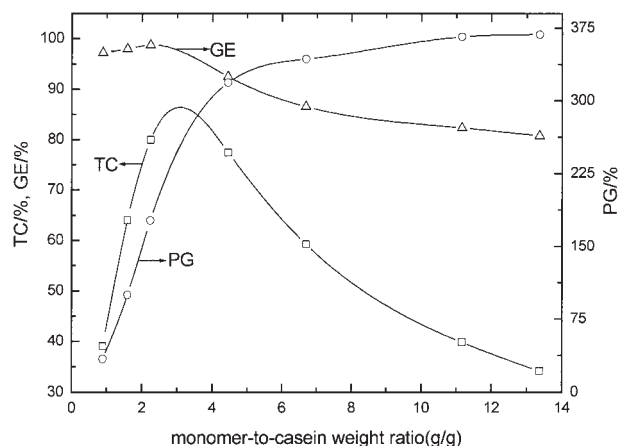
Figure 1 Effect of monomer-to-casein weight ratio on graft parameters: [Ni(IV)] = 1.123×10^{-2} mol/L, time, 3 h; temperature, 50°C; and pH, 12.77.

X-ray diffraction

X-ray diffraction of the casein and casein-g-PSt is carried out with a Y-2000 X-ray diffraction instrument (Dandong Ray Apparatus Corp., Jilin Province, China).

SEM

The surface shape of dried casein and casein-g-PSt are investigated by KYKY-1000B Scanning Electron Microscope (Scientific Apparatus Factory of Chinese Academy of Science, Beijing, China).

RESULTS AND DISCUSSION

To search further for the reaction mechanism of grafting of polystyrene onto casein, the effects of synthetic variables such as monomer-to-casein ratio, Ni(IV) concentration, pH, time, and temperature are investigated.

Effect of monomer-to-casein weight ratio

Keeping all other variables unchanged, the effect of monomer-to-casein ratio on graft copolymerization of St onto casein is investigated. The result is depicted in Figure 1. Initially, TC and PG increase continuously with the augment of St-to-casein ratio and GE even reaches to about 98% although styrene has little solubility in water. This may be due to the surface-activity and self-emulsifying properties of casein-g-PSt and casein,[17] which assists the proximity of monomer to the growing chains and active sites on the casein. This is in accordance with heterogeneous graft polymerization.[18] However, beyond St-to-casein (g/g) = 3.06, PG increases continuously while TC and GE decline. This may be explained as follows: with the increase of
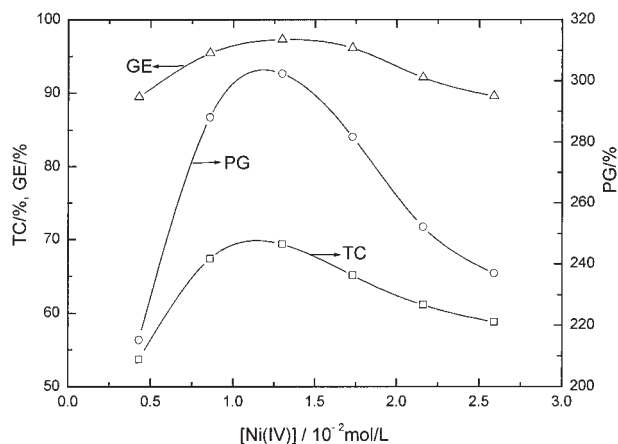
Figure 2 Effect of Ni(IV) concentration on graft parameters: monomer-to-casein weight ratio, 4.55; time, 3 h; temperature, 50°C; and pH, 12.77.

Figure 3 Effect of pH on graft parameters: monomer-to-casein weight ratio, 4.55; [NI(IV)] = 1.296 × 10^{-2} mol/L; time, 3 h; and temperature, 50°C.
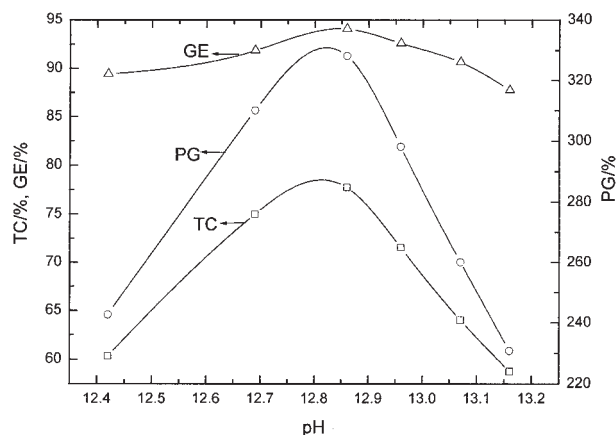
St-to-casein ratio, the adsorption amount of monomer onto casein is consumedly enhanced, which interferes largely with the approach of both Ni(IV) and casein that is necessary for initiation and finally leads the radical chain transfer reaction to St to be accelerated. As a result, the homopolymerization rate is enhanced and GE declines correspondingly. And the amount of PSt is decreasing oppositely to the St charged, though the PSt increases all the time, and so TC declines when St-to-casein ratio is beyond 3.06.

Effect of Ni(IV) concentration

The effect of Ni(IV) concentration on grafting parameters, with the total volume, the weight ratio of St-to-casein, PH, reaction temperature, and time are kept invariable, is shown in Figure 2. With increasing Ni(IV) concentration, TC, PG, and GE have a continuous increase trend at the beginning, then decrease obviously when the Ni(IV) concentration was beyond the optimum point of 1.123 × 10^{-2} mol/L. In the reaction system, when Ni(IV) concentration is lower, the Ni(IV) is mainly used to produce radicals, and initiate graft copolymerization. Thus all the grafting parameters increase continuously. However, a further increase of Ni(IV) concentration makes the radicals superfluous, which may accelerate the reaction of Ni(IV) with radicals and terminate the chain propagation reaction. On the other hand, the superabundant radicals can consumedly enhance the chance of homopolymerization. As a result, TC, PG, and GE decrease obviously when Ni(IV) concentration was beyond the optimum point.

Effect of pH

Figure 3 shows the effect of pH on graft parameters when all the other conditions are made invariable. The

alkalinity in the reaction solution is regulated by potassium hydroxide and hydrochloric acid. As is seen in the figure the TC, PG, and GE presents a first-increase-and-then-decrease trend. In alkaline medium, aqueous Ni(IV) exists mainly in the form of [Ni(H$_3$IO$_6$)$_2$ (OH)$_2$] and [Ni(H$_2$IO$_6$)$_2$ (OH)$_2$],[2–19]which directly influences the amount of radicals produced in the redox reaction system. In the pH-range studied the ratio of the two form changes with the increase in pH,[20,21] and then reaches a optimum value, enabling Ni(IV) to produce the maximum amount of radicals, and so the graft parameters have a peak value. It is found that the optimum pH-range of the reaction is 12.5–13.0.

Effect of time

The influence of the reaction time on grafting parameters is illustrated in Figure 4. As shown in the figure,
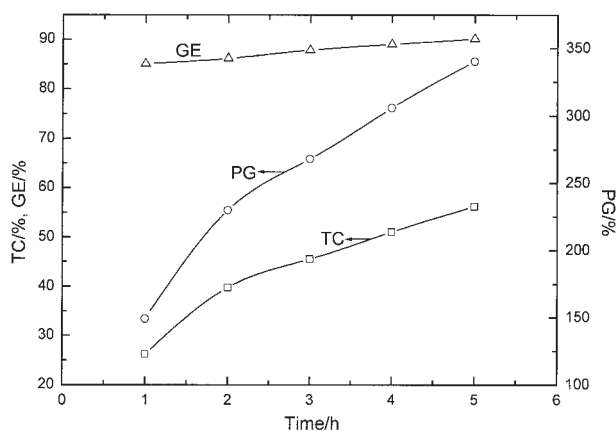
Figure 4 Effect of time on graft parameters: monomer-to-casein weight ratio, 6.82; [Ni(IV)] = 1.123 × 10^{-2} mol/L; temperature, 40°C; and pH, 12.77.
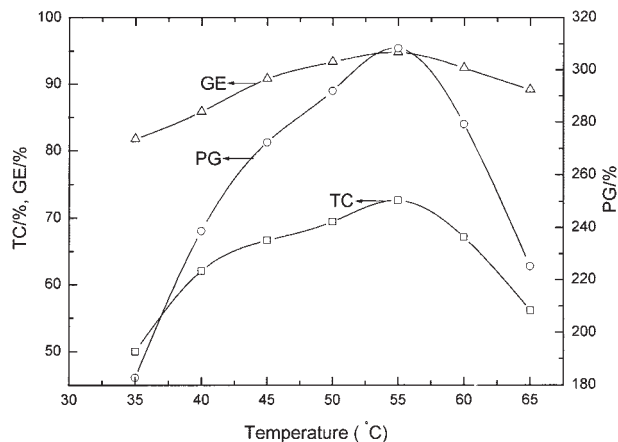
Figure 5 Effect of temperature on graft parameters: monomer-to-casein weight ratio, 4.55; [Ni(IV)] = 1.296×10^{-2} mol/L; time, 3h; and pH, 12.77.

GE changes little with the reaction time prolonged, while PG and TC increase all along, which is in accordance with the general rule of conventional radical polymerization. So the optimum reaction time of the reaction is 3 h.

Eeffect of temperature

When the other conditions are invariable, the graft copolymerization are carried out and investigated at different temperatures. The effect of reaction temperature on graft parameters is shown in Figure 5. As can be seen from the figure, TC, PG and GE present a tendency of durative increase before 55°C and then decrease with the continuous raise in temperature. Lower temperatures are a benefit for the initiating reaction and the chain propagation reaction. Although the generating rate of free radical increases at higher temperatures, the rate of radical termination reaction through oxidation by Ni(IV) increases simultaneously. Thus the grafting parameters increase initially then decrease with the continuous increase in temperature.

FTIR spectroscopy

The proof of graft copolymerization is obtained from the FTIR spectra of pure casein [Fig. 6(a)] and casein-g-PSt [Fig. 6(b)]. The FTIR spectrogram in Figure 6(a) shows characteristic absorption bands of casein at 3298.95 (ν_{N-H}), 1655.35, and 1060 cm^{-1}. However, the spectrogram of graft copolymer [Fig. 6(b)] has some additional peaks, when compared with that of pure casein, at 1601.52, 1532.80, 757.18, and 697.87 cm^{-1}, which are considered to belong to the characteristic absorption bands of phenyl group of polystyrene.
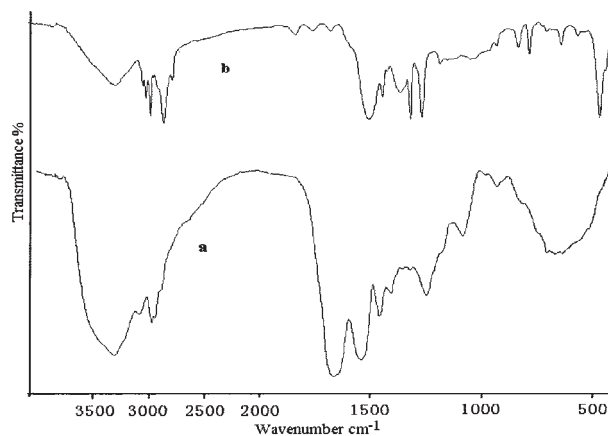
Figure 6 FTIR spectra of casein (a) and casein-g-PSt ((b), GE (%) = 83.26%).
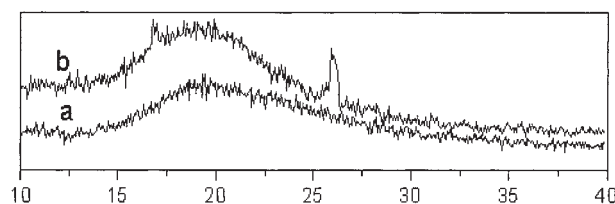
X-ray diffraction

The X-ray diffraction spectra of pure casein and casein-g-PSt are measured and, shown in Figure 7. From the figure we can see that the spectrum of pure casein [Fig. 7(a)] has no distinct peaks and is more convex than that of casein-g-PSt [Fig. 7(b)]. The crystallinity value of pure casein and casein-g-PSt is calculated to be 0.3639 and 0.3401, respectively, which elucidates the incorporation of PSt, with casein reduces the crystallinity of casein.

Scanning electron microscopy

The scanning electron micrographs of pure casein [Fig. 8(a)] and casein-g-PSt (Fig. 8b) were shown in Figure 8. The morphology of casein-g-PSt changes remarkably when compared with the facies shape of pure casein. As can be seen from the figure, the surface of pure casein is very rough and brittle with angular-chunk-shaped sandwich structure whereas the surface of casein-g-PSt becomes more uneven, pliable with numerous little tensible protuberances. The change may be due to the fact that PSt is successfully grafted onto the backbone of casein.

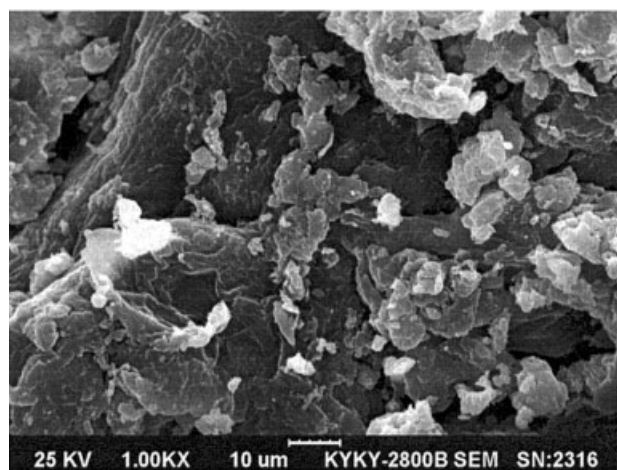### Discussion of the initiation mechanism

From different sides FTIR spectroscopy, X-ray diffraction, and SEM attest to the fact that St has been grafted

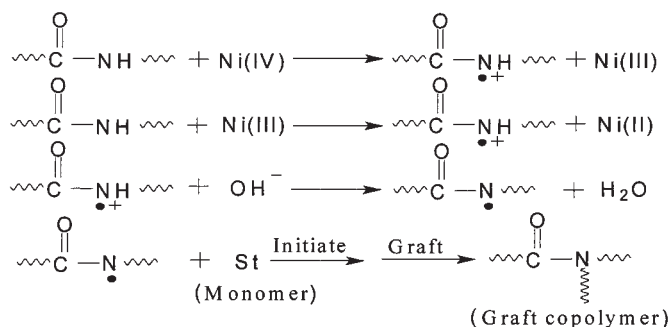Figure 7 X-ray diffraction spectra of casein (a) and casein-g-PSt ((b), GE (%) = 83.26%).
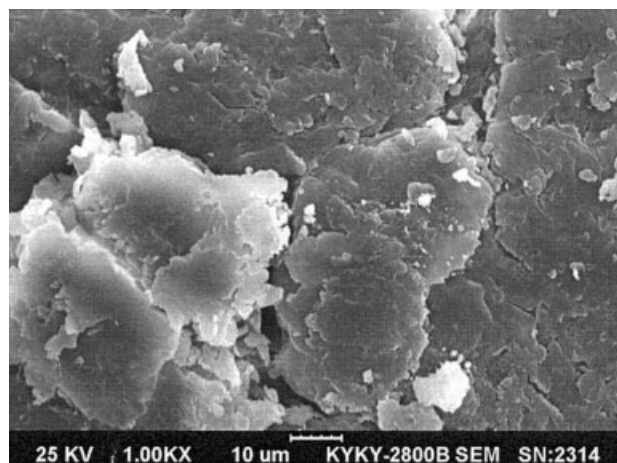
(a)

(b)

Figure 8 SEM of casein (a) and casein-*g*-PSt ((b), GE (%) = 83.26%).

onto casein triumphantly, to again verify that Ni(IV) can successfully initiate the graft copolymerization of vinyl monomers onto natural or synthetical macromolecule, which is considered to be a free radical polymerization.

The FTIR spectra also show that the characteristic absorption peaks of —CONHR belong to casein in (a) only present itself as weak peaks and almost disappear

in (b), which illustrates that the graft copolymerization proceeds on nitrogen atom. Thus a two-step, single electron transfer mechanism is proposed as is shown.

CONCLUSIONS

With satisfactory results, polystyrene has been grafted onto casein successfully under mild conditions in alkaline medium by using Ni(IV)-casein as initiator. Graft copolymers with high grafting efficiency (>98%) and percentage of grafting (>300%) have been obtained. The reaction parameters in the experimental condition have been optimized as follows: monomer-to-casein weight ratio, 3.06, [NI(IV)], 1.123×10^{-2} mol/L, time, 3 h, temperature, 55°C, and pH, 12.83. The proof of grafting was obtained from FTIR spectroscopy, X-ray diffraction, and SEM tests. It is confirmed that Ni(IV) is able to initiate the graft copolymerization of styrene as well as vinyl monomers on natural or synthetic macromolecular. And Ni(IV)-casein is testified to be an efficient and practical redox initiator for the graft copolymerization. A two-step single electron transfer mechanism is proposed to explain the formation of radicals and the initiation.

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