Synthesis of Chitosan-Modified Poly(methyl methacrylate) by Emulsion Polymerization

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ABSTRACT: Emulsion polymerization of methyl methacrylate (MMA) in the presence of chitosan was studied and a reaction mechanism was proposed. It was proved in the companion article that potassium persulfate (KPS) free radicals can degrade chitosan chains into chain free radicals. Therefore, it is possible to produce a chitosan copolymer when the monomer and the KPS initiator are added into the chitosan solution. According to the proposed mechanism, concentrations of different species such as the initiator, total free radicals, and degraded chitosan chain were calculated with the reaction time. All the results agreed with the experimental observation. The results showed that the polymerization rate varied with 0.83- and 0.82-order of the total free-radical concentration and chitosan repeating unit concentration, respectively. It was also verified that chitosan played multiple roles in the reaction system. If the monomer was added into the chitosan solution before the addition of KPS, chitosan served mainly as a surfactant. Consequently, the polymer particle number was increased with the chitosan addition and so was the polymerization rate. However, if the monomer was added into the solution where the chitosan was already degraded by KPS, the polymerization rate was decreased with the predegradation time of chitosan. In both cases, the final polymer particles consisted of the poly(methyl methacrylate) (PMMA) homopolymer and the chitosan–PMMA copolymer. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3047–3056, 2002

Key words: emulsion polymerization; chitosan; PMMA

INTRODUCTION

Chitosan is a high molecular weight polysaccharide composed mainly of β-(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units and partially of β-(1,4) linked 2-deoxy- 2-acetamido-D-glucopyranose. It is an environmentally friendly material with many superior properties and can be used in many areas, such as in wastewater treatment, food processing, pharmaceuticals, biomaterials, and agriculture.[1,2] Chitosan can be dissolved in an acid solution and then it becomes a cationic polymer due to the protonation of amino groups on the C-2 position of the pyranose ring. Therefore, it can be used as a cationic, polymeric surfactant in emulsion polymerization for the purpose of producing positively charged nanoparticles. In addition, polymeric surfactants offer the advantage of steric stabilization of dispersions while most low molecular weight surfactants operate only through electrostatic stabilization, meaning that chitosan can pro-vide electrosteric stabilization, a combination of both mechanisms of electrostatic and steric stabilization.[3,4]

In our laboratory, we found that when potassium persulfate (KPS) was added into the chitosan solution the solution viscosity was greatly decreased.[5] It was then proved that KPS free radicals can degrade the chitosan chain and a free-radical degradation mechanism was proposed. The details were described in the companion article[5] and only a brief description is given here: First, persulfate ions ($S_2O_8^{2-}$) in KPS are thermally dissociated into anionic radicals, which are attracted to the cationic amino groups (NH_3^+) in the chitosan. Subsequently, the anionic radical attacks the nearby C-4 carbon and transfers the radical to the C-4 carbon by subtracting the hydrogen from it. The presence of free radicals at the C-4 carbon results in the breakage of the C—O—C bond in the main chain. Therefore, the chitosan chain is degraded into two chain fragments: One has a terminal carbonyl group and the other has a free radical at the scission end. The reaction scheme is shown in Scheme 1.

From the reaction mechanism, it was expected that if KPS was used to initiate the monomer for polymerization in the presence of chitosan not only would degradation of chitosan occur, but also it would affect the polymerization kinetics as well as the final structures of the particles. A chitosan copolymer in addition to the homopolymer is expected to be produced during the reaction. This article describes the degra-
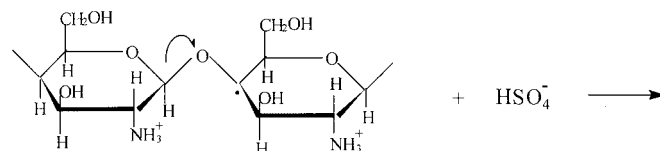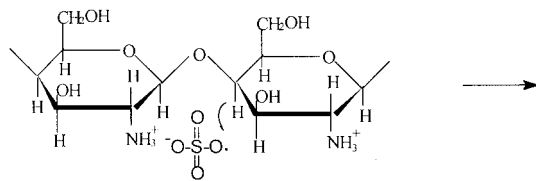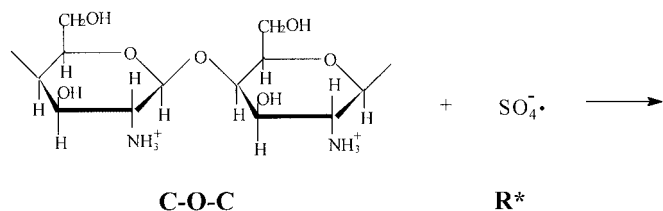
(1) Thermal dissociation of KPS

$$S_2O_8^{2-} \longrightarrow 2\ SO_4^- \bullet$$

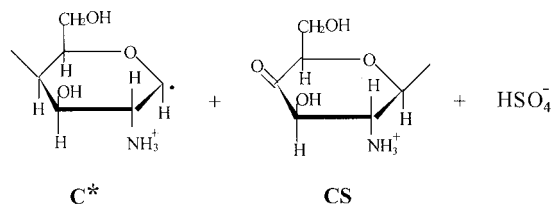**I**   **R***

(2) Persulfate ion was attracted to the cationic amino group and free radical was transferred to

the C-4 carbon

C-O-C   **R***

$+\ HSO_4^-\ \longrightarrow$

(3) Chain scission at the C-O-C bond

C*   **CS** $+\ HSO_4^-$

Scheme 1   Free-radial degradation of chitosan by KPS.

dation behavior of chitosan and the emulsion polymerization kinetics of methyl methacrylate (MMA) in the chitosan solution.

EXPERIMENTAL

Materials

Chitosan (Tokyo Chemicals Inc., Tokyo, Japan) was purified before use. It was first dissolved into a 2% acetic acid solution, then precipitated out by adding a concentrated NaOH solution. The precipitate was washed several times with a great amount of deionized water, until the pH had reached 7. The degree of deacetylation of chitosan was found to be 86% by the colloid titration method.[6] MMA from ACROS Organ-

ics (Geel, Belgium) was distilled under reduced pressure. Only the distillate obtained at the middle stage of distillation was used for the polymerization. Potassium persulfate (KPS) was reagent grade from Wako Pure Chemical Industries (Osaka, Japan). All the other chemicals were analytical grades or HPLC grades and used as received without further purification.

Emulsion polymerization

From a previous study, it is known that if KPS was used as an initiator for polymerization in the system with chitosan the degradation of chitosan by KPS would occur at the same time. To understand the effects of chitosan degradation on the polymerization

Reaction system	One-stage	Two-stage
MMA (g)	100	100
Chitosan (g)	0, 1, 2, 5, 10, 15	15
Predegradation time (min)	0	0, 5, 10, 20, 30
Acetic acid (g)	20	20
Deionized water (g)	1000	1000
KPS (g)	1.081	1.081
Stirring speed (rpm)	300	300
Temperature (°C)	70	70

kinetics, two reaction systems were undertaken, namely, one-stage and two-stage reaction systems: (1) one-stage reaction system: A specific amount of chitosan was first dissolved into 1 L of a 2% (w/w) acetic acid solution, followed by the addition of 100 g of the MMA monomer. The solution was heated to 70°C in an isothermal water bath. It was then stirred at a speed of 300 rpm and purged with nitrogen. Subsequently, 1.081 g of KPS was added to the solution for initiating the polymerization. In this system, KPS would initiate the polymerization and degrade the chitosan molecules at the same time. (2) Two-stage reaction system: Prior to the addition of the monomer, 1.081 g of KPS was added into the chitosan solution at 70°C and immediately started the degradation of chitosan. After a period of degradation time, 100 g of the MMA monomer was then added into the solution for polymerization. Therefore, degradation occurred before polymerization in this system. Table I lists the reaction conditions of the one-stage and two-stage reaction systems.

Measurement of conversion

During polymerization, 20 mL of the emulsion solution was drawn out at different times for the measurement of monomer conversion. The solution was poured into an ice-bathed beaker with a hydroquinone–methanol solution to inhibit the polymerization. Then, it was dried at 5°C in a circulation oven and then in a vacuum oven. The conversion was calculated by the following equation:

$$X\ (\%) = \frac{W_2 - W_1 \times P\ \%}{W_1 \times M_0\ \%} \times 100 \qquad (1)$$

In the equation, W_1 and W_2 are the weights of specimens drawn out from the emulsion solution before and after drying, respectively; $M_0\ \%$ and $P\ \%$ are the weight percentages of feeding the monomer and chitosan in the beginning, respectively.

RESULTS AND DISCUSSION

As KPS was added into the viscous chitosan solution with the MMA monomer, KPS dissociated into free radicals, which not only initiated the polymerization but also degraded the chitosan molecule. Every time the chitosan chain was degraded, two shorter chains were produced with a free radical at one scission end and a terminal carbonyl group at the other scission end (see Scheme 1). It was thus expected that the MMA monomer could grow on the chitosan chain radical and produce the chitosan copolymer. In addition, if the cationic chitosan chain could serve the role of a surfactant, it was expected that the polymerization rate should be increased. This is indeed observed in Figure 1, which shows that, for a one-stage reaction system, the polymerization rate was greatly enhanced by the presence of chitosan and increased with the amount of chitosan addition. The natural cationic surfactant of chitosan was verified by measuring the zeta potential of the latex particles, which is related to the surface charge of the particles. The measured zeta potential was positive and in the range of 20–40 mV, where the value was increased with the amount of chitosan addition.[7] On the contrary, the surface charge of the poly(methyl methacrylate) (PMMA) latex particles was negative in the emulsion polymerization of MMA with the KPS initiator without the addition of chitosan. This was due to the nature of the anionic KPS initiator.

In addition, it was found in the previous article[7] that the average particle size, measured from 50 latex particles, was decreased from 265 nm for pure PMMA to about 103 nm for the chitosan-modified PMMA and the nonuniformity was increased with the amount of chitosan addition. This agrees with the well-known fact that increasing the surfactant concentration would increase the particle number and decrease the particle size. The nonuniformity was due to the continuing production of the chitosan chain radical that could not be absorbed into the primary particles because of the high solution viscosity, which means that secondary nucleation occurred. Both these results provided evidence that the chitosan can serve as a role of the cationic surfactant.

Yet, if the monomer was added into the solution where chitosan was already predegraded by KPS first, the polymerization rate was found to be slower. Figure 2 shows that, with the same amount of chitosan addition, the polymerization rate was decreased as the predegradation time was increased. These results indicated that the degraded chitosan chains could inhibit the free radicals. Also, the extent of deactivation was related to the extent of predegradation of chitosan. A reasonable assumption is that the terminal ring structure with the carbonyl group in the degraded chain could inhibit the free radicals.[5] The reaction scheme is shown in Scheme 2.

It is also possible that the anionic persulfate was trapped and immobilized inside the degraded chitosan chains through electrostatic attraction as shown
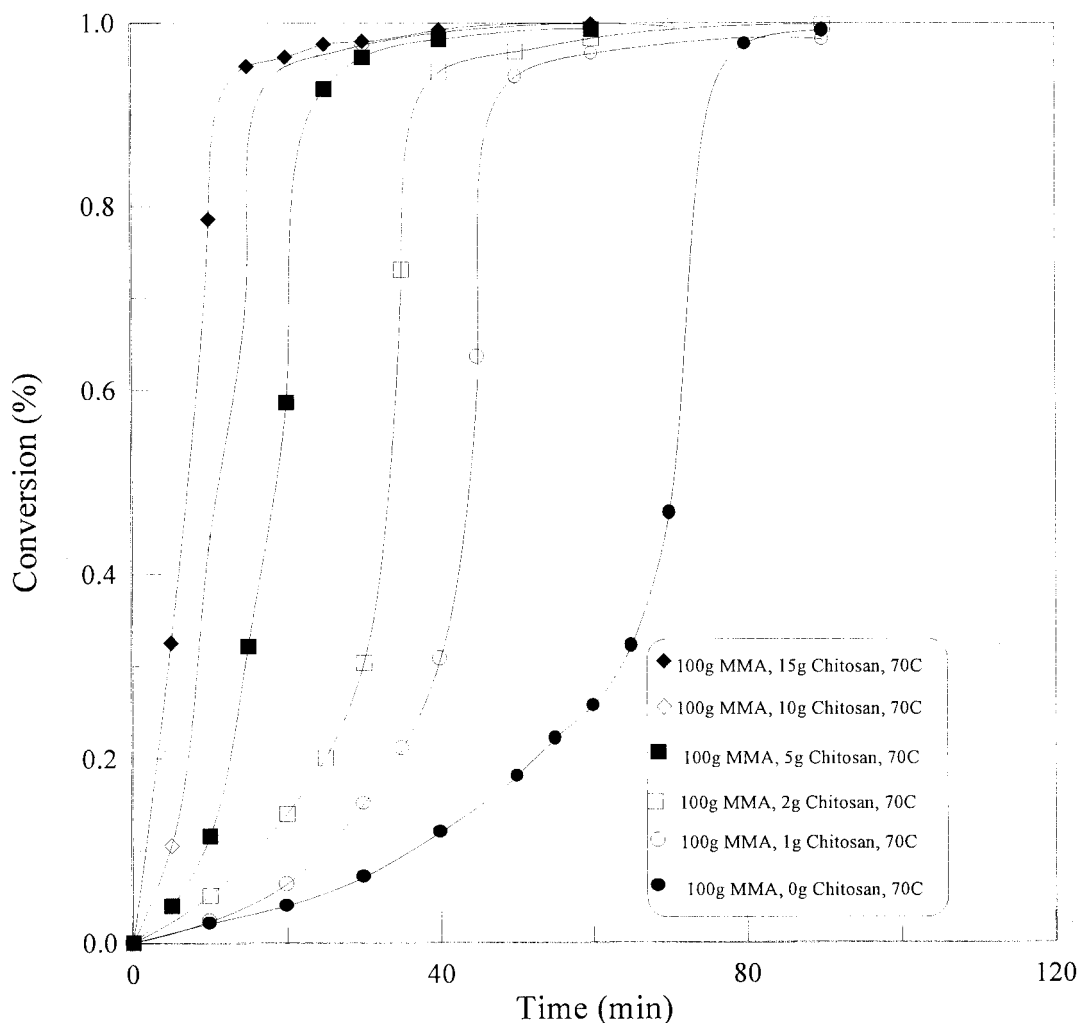
Figure 1 Conversion of MMA monomer with reaction time in the one-stage reaction system.

below. This would occur more easily when the chitosan chains were shorter and solution viscosity was smaller through the degradation of chitosan. This was just like the "cage effect," in which KPS could still decompose into two free radicals, but could not escape from the surrounding cationic chitosan chains (Scheme 3).

From the above results, it is known that chitosan plays multiple roles in the reaction system with the KPS initiator. In one way, it can increase the polymerization rate by serving as a surfactant; yet, in the other way, the degraded chitosan chain can inhibit the free radicals and slow down the polymerization. The major role of chitosan that plays in the system, surfactant, or inhibitor depends on whether the chitosan was predegraded, that is, is it a one-stage or two-stage reaction system. In a one-stage reaction system, it has the role mainly of a surfactant, whereas in the two-stage reaction system, it is mainly an inhibitor. As in the structure design, the degraded chitosan chain free radical provides the opportunity to produce the chitosan copolymer in both cases. According to the reac-

tion mechanism shown in the Introduction and the above discussion, the kinetic reactions and rate equations could then be expressed to calculate the concentration of various species. The theoretical concentrations were then used to compare them with the experimental results:

1. Initiation and deactivation of KPS:

$$I \xrightarrow{k_d} 2R^* \qquad (2)$$

$$I + CS \xrightarrow{k_{de}} CS \cdots I \qquad (3)$$
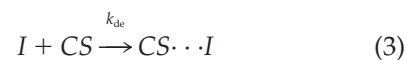
where I is the KPS initiator; R^*, the free radical produced from the KPS dissociation, CS, the degraded chitosan fragment with a terminal carbonyl group; $CS \cdots I$, the electrostatic immobilization of KPS; k_d, the dissociation rate constant of KPS (1/s); and k_{de}, the deactivation rate constant of KPS (L mol^{-1} s^{-1}).
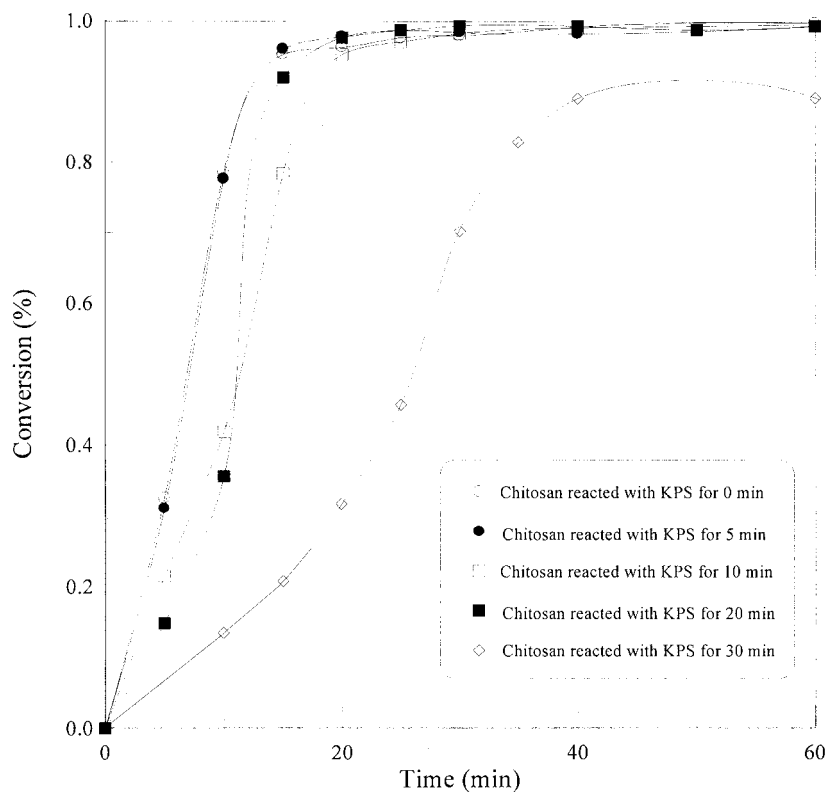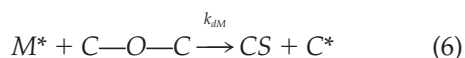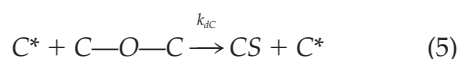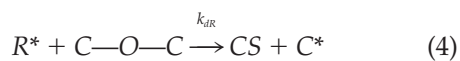
Figure 2 Conversion of MMA monomer with reaction time in the two-stage reaction system with 15-g chitosan addition. There was no conversion for the system in which chitosan was predegraded for 60 min.
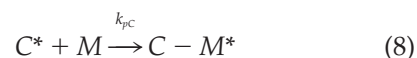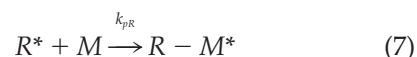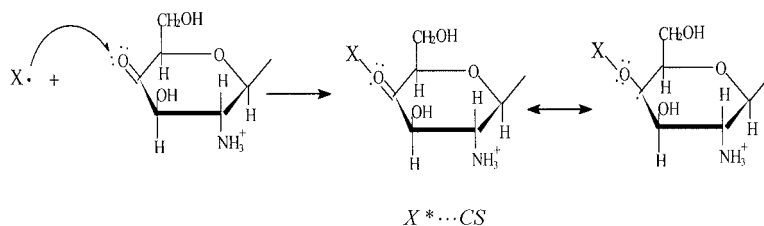
2. Degradation of chitosan chains:

$$R^* + C\text{—}O\text{—}C \xrightarrow{k_{dR}} CS + C^* \tag{4}$$

$$C^* + C\text{—}O\text{—}C \xrightarrow{k_{dC}} CS + C^* \tag{5}$$

$$M^* + C\text{—}O\text{—}C \xrightarrow{k_{dM}} CS + C^* \tag{6}$$

where $C\text{—}O\text{—}C$ is the β-(1,4)-linked glycosidic bond in the chitosan main chain; C^*, the degraded chitosan fragment with a free radical at the scission end; M^*, the propagating polymer chain with the terminal MMA radical; and k_{dR}, k_{dC}, and, k_{dM}, the degradation rate constants (L

$\text{mol}^{-1}\,\text{s}^{-1}$). The total free radicals (R_t^*) in the water consisted of anionic radicals from KPS, degraded chitosan chain radicals, and the propagating polymer chain radical, that is, $R_t^* = R^* + C^* + M^*$.
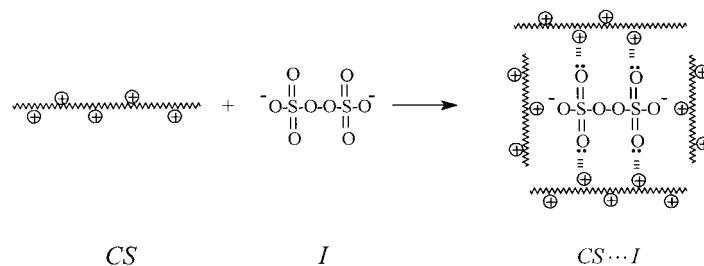
3. Polymerization of MMA monomer:

$$R^* + M \xrightarrow{k_{pR}} R - M^* \tag{7}$$

$$C^* + M \xrightarrow{k_{pC}} C - M^* \tag{8}$$

$$M^* + M \xrightarrow{k_{pM}} M - M^* \tag{9}$$

where M is the MMA monomer, and k_{pR}, k_{pC}, and, k_{pM}, the propagation rate constants (L $\text{mol}^{-1}\,\text{s}^{-1}$).

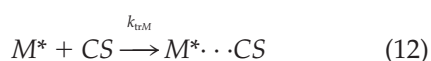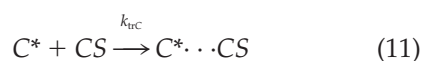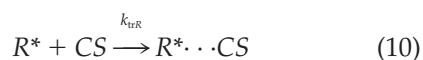$X^* \cdots CS$

Scheme 2 Inhibition of free radical by degraded chitosan with terminal carbonyl group.

$$CS \qquad\qquad I \qquad\qquad CS\cdots I$$

Scheme 3   Deactivation of persulfate ions by electrostatic immobilization.

4. The inhibition of free radicals by the degraded chitosan chains:

$$R* + CS \xrightarrow{k_{trR}} R*\cdots CS \qquad (10)$$

$$C* + CS \xrightarrow{k_{trC}} C*\cdots CS \qquad (11)$$

$$M* + CS \xrightarrow{k_{trM}} M*\cdots CS \qquad (12)$$

where $R*\cdots CS$, $C*\cdots CS$, and $M*\cdots CS$ are stable free radicals, and k_{trR}, k_{trC}, and, k_{trM}, the inhibition rate constants (L mol^{-1} s^{-1}).

5. Termination of free radicals:
   Collisions between free radicals and/or oligomeric free radicals could result in their termination:

$$R_t^* + R_t^* \xrightarrow{\overline{k_t}} \text{Polymer} \qquad (13)$$

where $\overline{k_t}$ is the average termination rate constant (L mol^{-1} s^{-1}).

From the above kinetic reactions, the rate equations can be expressed as follows: First, the disappearance rate of the initiator is obtained by the combination of eqs. (2) and (3):

$$\frac{-d[I]}{dt} = k_{de}[CS][I] + k_d[I] \qquad (14)$$

From eqs. (4)–(6), the production rate of degraded chitosan chain CS is

$$\frac{d[CS]}{dt} = \overline{k_{dC}}[C\!-\!O\!-\!C][R_t^*] \qquad (15)$$

$$[C-O-C] = [C-O-C]_0 - [CS]$$

where $[C\!-\!O\!-\!C] = [C\!-\!O\!-\!C]_0 - [CS]$ and $[C\!-\!O\!-\!C]_0$ is the initial concentration of the glycosidic $C\!-\!O\!-\!C$ unit (mol/L); $[C\!-\!O\!-\!C]$, the concentration of the $C\!-\!O\!-\!C$ unit (mol/L); $\overline{k_{dC}}$ the average degra-

dation rate constant (L mol^{-1} s^{-1}). The rate of change of total free radicals can be expressed as

$$\frac{d[R_t^*]}{dt} = 2k_d f[I] - \overline{k_t}[R_t^*]^2 - \overline{k_{tr}}[R_t^*][CS] \qquad (16)$$

where f is the efficiency of the free radicals, and $\overline{k_{tr}}$ the average inhibition rate constant (L mol^{-1} s^{-1}). If a quasi-steady-state approximation is assumed, eq. (16) then is equal to zero:

$$2k_d f[I] - \overline{k_t}[R_t^*]^2 - \overline{k_{tr}}[R_t^*][CS] = 0 \qquad (17)$$

The concentration of total free radicals thus can be obtained by solving the above equation:

$$[R_t^*] = \frac{-\overline{k_{tr}}[CS] + \sqrt{(\overline{k_{tr}}[CS])^2 + 8\overline{k_t}k_d f[I]}}{2\overline{k_t}} \qquad (18)$$

By using a Runge–Kutta method to solve the simultaneous equations, eqs. (14), (15), and (18), the theoretical concentrations of different species, the initiator $[I]$, the total free radicals $[R_t^*]$, and the degraded chitosan chain $[CS]$ could be calculated at different reaction times. All the parameters needed to solve the equations were taken from the literature[8–11] and are listed in Table II. The results show that both $[I]$ and $[R_t^*]$ decreased with the reaction time, while $[CS]$ increased, as shown in Figures 3–5.

Figure 3 indicates that the addition of chitosan would decrease the concentration of the "effective"

TABLE II
Parameters Needed to Solve the Rate Equations

KPS concentration $[I]_0$ (mol/L H$_2$O)	0.004
Molecular weight of chitosan repeating unit including glycosidic oxygen (g/mol)	183
k_d (1/s)	9.23×10^{-6}
f	0.9
$\overline{k_t}$ (L mol^{-1} s^{-1})	2.69×10^7
$\overline{k_{tr}}$ (L mol^{-1} s^{-1})	50
k_{de} (L mol^{-1} s^{-1})	1
$\overline{k_{dC}}$ (L mol^{-1} s^{-1})	650

$\overline{k_{tr}}$, k_{de}, and $\overline{k_{dC}}$ are adjustable parameters.
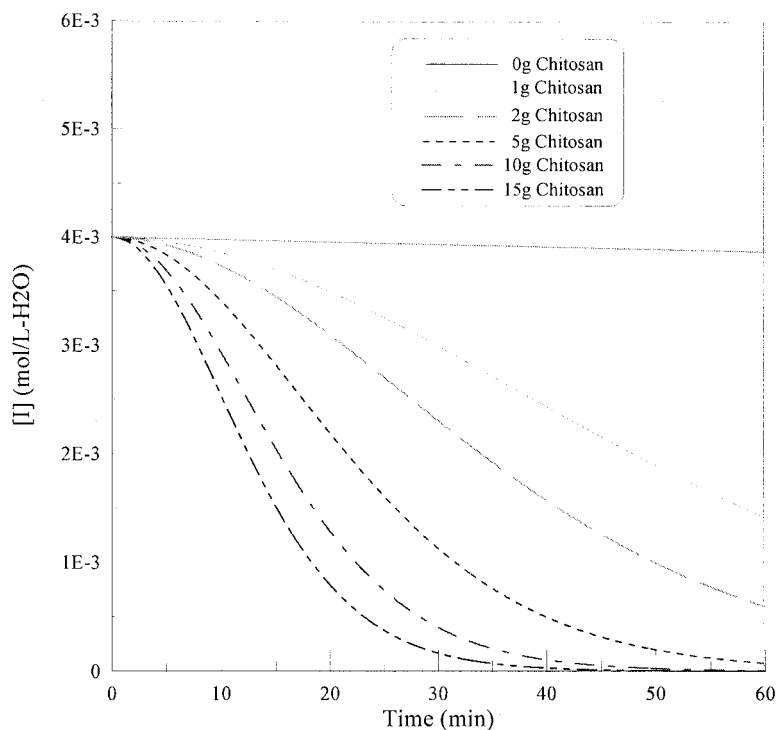
Figure 3 Calculated concentration of initiator with reaction time at different amounts of chitosan addition.

KPS initiator. This is due to the electrostatic immobilization of the persulfate ion by the cationic chitosan chains. Therefore, increasing the amount of chitosan would accelerate the decreasing rate of the effective KPS initiator. Also, the addition of chitosan decreased the total free-radical concentration as shown in Figure 4, because of the electrostatic immobilization of the persulfate ion and also the inhibition of free radicals by the degraded chitosan chains. Therefore, in the two-stage reaction system, the total free-radical con-
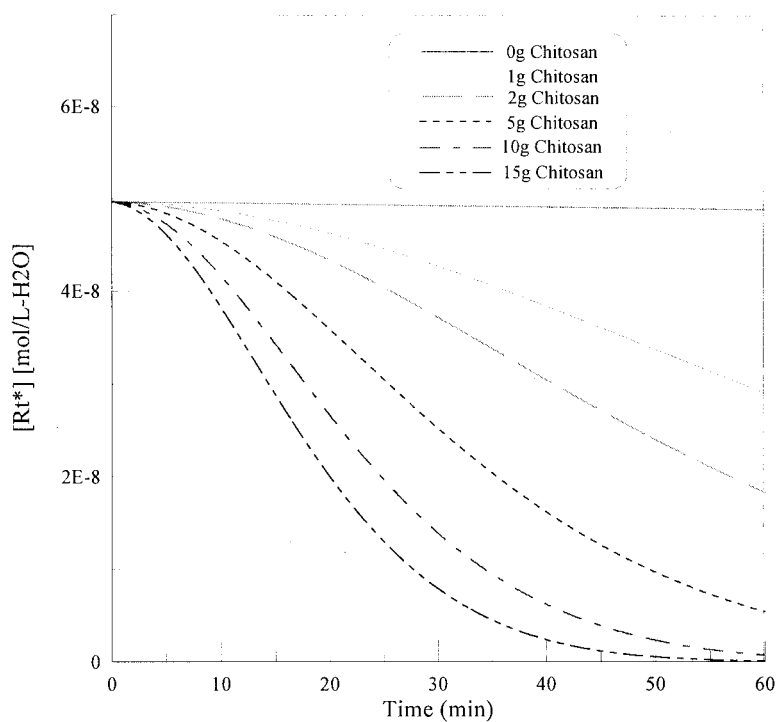

Figure 4 Calculated concentration of total free radicals with reaction time at different amounts of chitosan addition.
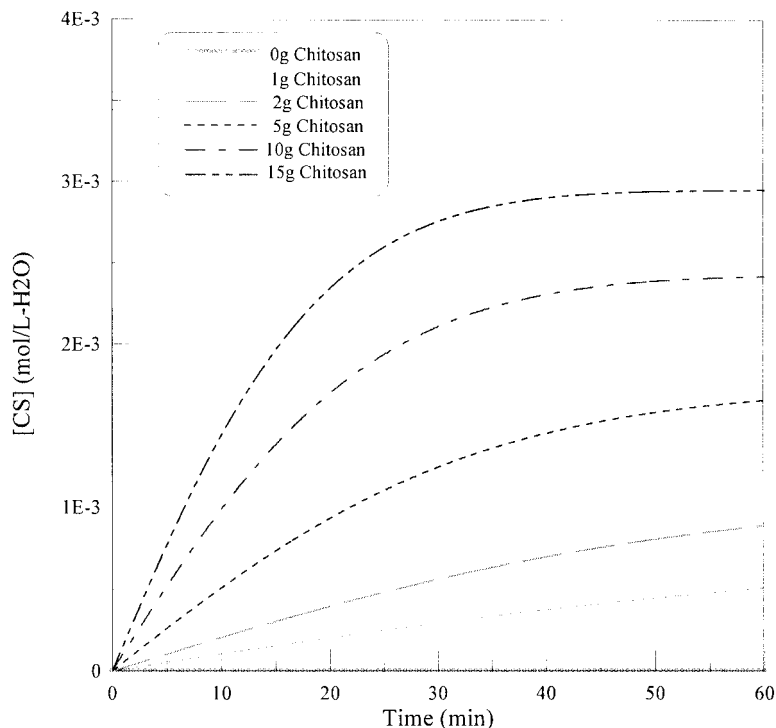
Figure 5 Calculated concentration of degraded chitosan chain with reaction time at different amounts of chitosan addition.

centration was already decreased in the predegradation stage; consequently, the polymerization rate would be smaller once the monomer was added to the system. This agrees with the results shown in Figure 2. With 15 g of chitosan addition, it was even experimentally observed that there was no polymerization at all if chitosan was already predegraded for 1 h. This was predicted in Figure 4: that there was no free radical present in the system after 1 h of degradation. Now that the total free-radical concentration was decreased and the chitosan could serve as a surfactant, the molecular weight of PMMA was expected to increase when chitosan was added. Indeed, the number-average molecular weight of PMMA, extracted from the latex particles, was increased from 86,900 for the system without chitosan to 127,900 for the two-stage reaction system with the addition of 15 g chitosan.[7]

From the above results, it is known that the concentrations of chitosan and the total free radicals would have an effect on the polymerization rate. In emulsion polymerization, the polymerization rate (R_p) is usually expressed as the following equation:

$$R_p = \frac{-d[M]}{dt} = \overline{k_p}[M]_P \frac{\overline{n}N_P}{N_A} \qquad (19)$$

In the equation, $\overline{k_p}$ is the average rate of propagation ($cm^3\ mol^{-1}\ s^{-1}$); $[M]_P$, the monomer concentration inside the polymer particles (mol/cm^3); $\overline{n}$, the average number of free radicals in the polymer particles; N_p, the number of polymer particles (particles/cm^3); and N_A,

the Avogadro number. From this equation, the polymerization rate is proportional to the number of polymer particles, N_p, which, in turn, is related to the concentration of the surfactant and the rate of free-radical production. In this system, chitosan could serve the role of the surfactant, and the concentration of the effective surfactant was assumed to be proportional to the concentration of the chitosan repeating unit, CSU. Therefore, it was assumed that N_p is proportional to the ath power of the total free-radical concentration and the bth power of the chitosan repeating unit concentration, that is,

$$R_p \propto N_P \propto [R_t^*]^a [CSU]^b \qquad (20)$$

To determine the dependence order a, a two-stage reaction system with 15-g chitosan addition was chosen where the CSU concentration was kept constant. The initial polymerization rate R_p at different predegradation times was calculated from the initial slope of the conversion curves in Figure 2. The corresponding total free-radical concentration $[R_t^*]$ at different predegradation times was obtained from the theoretical curve in Figure 4. When R_p was plotted against $[R_t^*]$ in a logarithmic scale, a linear plot with a slope of 0.83 was observed as shown in Figure 6. It indicates that the dependence order, a, was equal to 0.83. Again, with the same system, the initial R_p was now plotted with the concentration of the effective KPS initiator shown in Figure 3. Another linear plot with a slope of 0.48 was found (Fig. 7). This order is between the literature values of the emulsion polymerization with and without the surfactant, 0.4 and 0.5, respectively.[9-11]
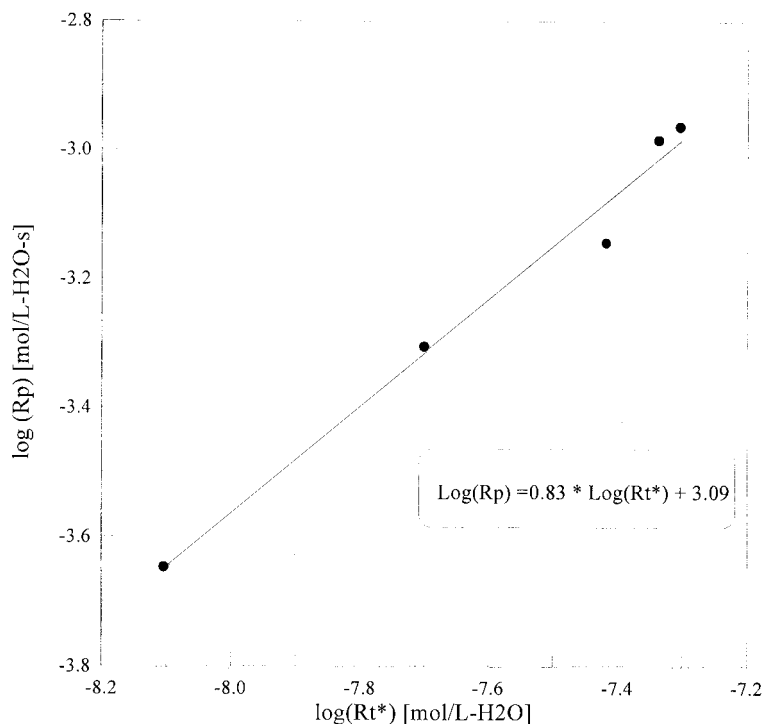
Figure 6 Linear dependence of log R_p on log $[R_t{}^*]$ in the two-stage reaction system.

To determine the dependence order b, a one-stage reaction system with different amounts of chitosan addition was chosen. The initial R_p was calculated from Figure 1 and then divided by the 0.83-power of the theoretical $[R_t{}^*]$ at beginning of the reaction from Figure 4. The calculated value, $R_p/[R_t{}^*]^{0.83}$, was then plotted against the chitosan repeating unit concentration, $[CSU]$. As shown in Figure 8, a linear plot was again observed with a 0.82-order dependence. In the literature,[11] the reported dependence order of the initial polymerization rate on the surfactant concentration is in the range of 0.4–1.2. The experimental value
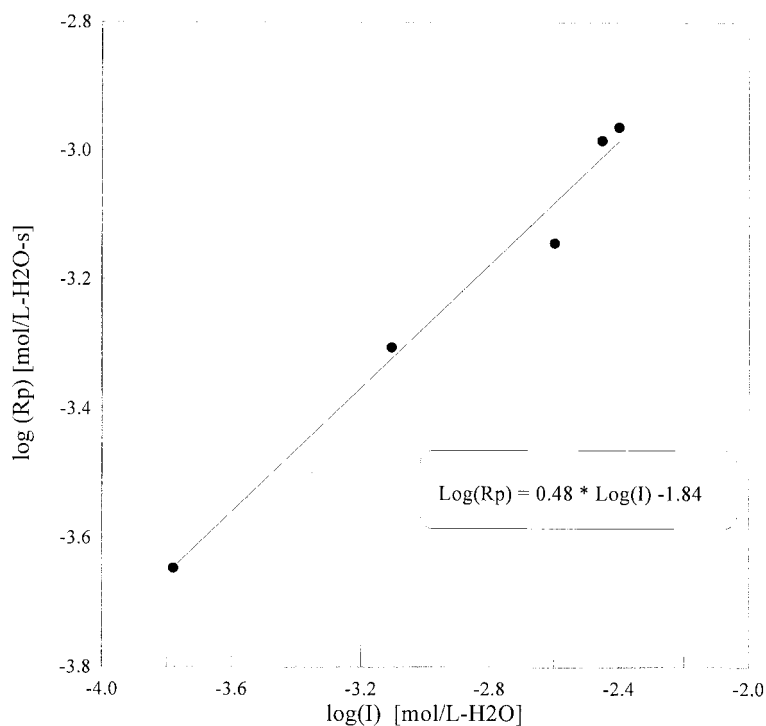

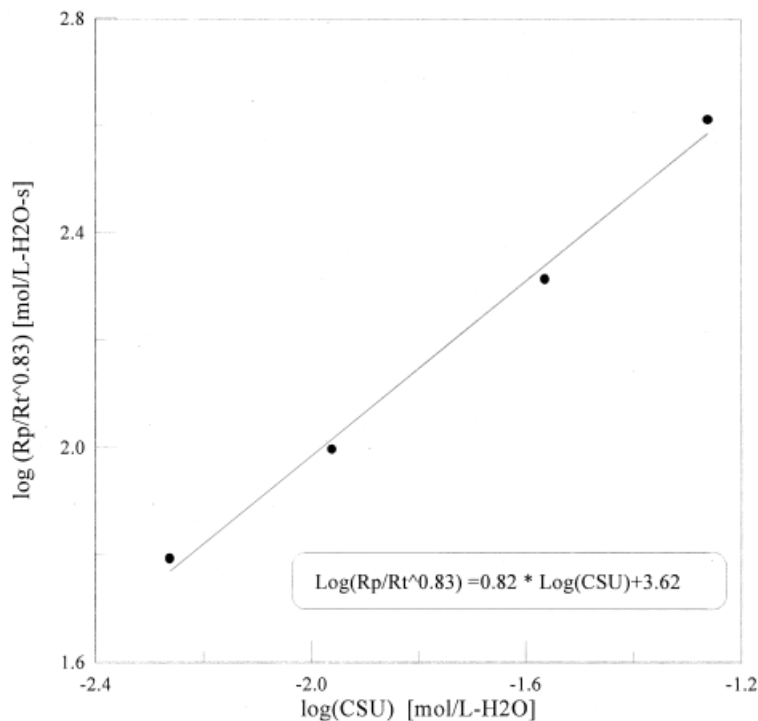**Figure 7** Linear dependence of log R_p on log $[I]$ in the two-stage reaction system.

Figure 8 Linear dependence of $\log(R_p/[R_t*]^{0.83})$ on $\log[CSU]$ in the one-stage reaction system.

thus falls in this range. From the above results, the polymerization rate varies with the 0.83- and 0.82-power of the total free-radical concentration and chitosan repeating unit concentration, respectively:

$$R_p \propto N_P \propto [R_t^*]^{0.83}[CSU]^{0.82} \qquad (21)$$

CONCLUSIONS

The emulsion polymerization of MMA in the presence of chitosan was studied. A potassium persulfate initiator was used; however, it not only initiated the polymerization but also degraded the chitosan molecules. Several conclusions are listed below:

1. A reaction mechanism was proposed and the theoretical concentration of the initiator, the total free radicals, and the degraded chitosan chain were all calculated. The results show that the total free-radical concentration was decreased and the decreasing rate was increased with the amount of chitosan addition.
2. If chitosan served mainly as a surfactant, the addition of chitosan would increase the polymer particle number and, consequently, the polymerization rate. It provides the electrosteric stabilization of the latex particles.
3. However, if chitosan was degraded by KPS free radicals prior to polymerization of the monomer, the degraded chitosan chain could deactivate KPS and inhibit the free radicals. Therefore, the following polymerization was slower than that without

any predegradation of chitosan. Once chitosan underwent degradation for too long, for example, 1 h, no polymerization could be observed.
4. The experimental results show that the polymerization rate varied with 0.83- and 0.82-order of the total free-radical concentration and chitosan repeating unit concentration, respectively.

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