Homogeneous Graft Copolymerization of Chitosan with Butyl Acrylate by γ-Irradiation via a 6-*O*-Maleoyl-*N*-phthaloyl-chitosan Intermediate

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ABSTRACT: The graft copolymerization of butyl acrylate (BA) onto chitosan was tried via a new protection-graft-deprotection procedure. About 6-*O*-maleoyl-*N*-phthaloyl-chitosan was synthesized and characterized by Fourier transform infrared spectra analysis (FT-IR) and ^{1}H-NMR. Because the intermediate 6-*O*-maleoyl-*N*-phthaloyl-chitosan was soluble in organic solvents, the graft copolymerization was carried out in a homogeneous system. Grafting was initiated by γ-irradiation. The graft extent was dependent on the irradiation dose and the concentration of BA monomer, and copolymers with grafting above 100% were readily prepared. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 489–493, 2006

Key words: chitosan; 6-*O*-maleoyl-*N*-phthaloyl-chitosan; butyl acrylate; graft copolymerization; γ-ray irradiation

INTRODUCTION

Chitosan is a polycationic polymer with a specific structure and biological properties such as immunological activity,[1] antibacterial,[2,3] or wound healing.[4] Moreover, it is a nontoxic and biodegradable polymer.[5,6] Because of its biocompatibility, biodegradability, and avirulence, chitosan has been used in many areas, such as in biomedical and agriculture. Recently, there has been a growing interest in grafting modification of chitosan for biomedical, industrial, and agriculture applications. Using the γ-ray of ^{60}Co γ-irradiation method, organic substrate can generate substantial free radicals and the process of initiation reaction is simple. So it is used to initiate the polymerization of monomer with vinyl group.

By γ-irradiation, chitosan can be grafted with considerable monomers, which has vinyl group. Graft copolymerization of styrene, vinylacetate, acrylamide, MMA, HEMA, and *N*,*N*-dimethylaminoethylmethacrylate onto chitosan using ^{60}Co γ-irradiation has been reported in the literature.[7–9] But chitosan is insoluble in common solvents and is difficult to discuss the structure–property relationship. The soluble derivatives of chitosan are useful for performing modification reaction in a facile and controlled manner. 6-*O*-maleoyl-*N*-phthaloyl-chitosan has proved to be a derivative with improved solubility in organic solvents, while the phthaloyl group can be deprotected easily to regenerate a free amino group.[10,11] Because of these advantages, it has been utilized as a versatile key intermediate for some regioselective chemical modifications.[12,13]

In this work, we intended to carry out the graft copolymerization of chitosan with butyl acrylate (BA) via 6-*O*-maleoyl-*N*-phthaloyl-chitosan as intermediate. This not only enabled the grafting reaction to be carried out in a homogeneous system but also retained the abundant amino groups in the chitosan-*graft*-PBA copolymers. Butyl acrylate was selected because it is hydrophobic and soft monomer, which when grafted onto the chitosan is expected to increase the hydrophobicity and flexibility of macromolecule.

EXPERIMENTAL

Materials and instruments

Chitosan was obtained from San Huan Ocean Biochemical Co. Ltd. (China). Its degree of deacetylation and the apparent viscosity were determined as 91.2% and 30 MPa s. Dimethylformamide (DMF) was distilled under reduced pressure from calcium hydride and stored over molecular sieves (4 Å). Butyl acrylate (BA) was of chemical grade. Maleic anhydride was of reagent grade and used as received.

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Phthaloylation of chitosan

Chitosan (1 g) was heated with excess phthalic anhydride (2.7 g) in dried DMF at 120–130°C for 5 h to give phthalylchitosan (PHCS), according to the previously reported procedure.[1,4]

Synthesis of 6-*o*-maleoyl-*n*-phthaloyl-chitosan

A mixture of *N*-phthaloyl-chitosan and maleic anhydride in dimethylformamide was stirred for 24 h at 110–130°C under a nitrogen atmosphere. The homogeneous solution was cooled to room temperature and poured to ice-water. The precipitate was collected by filtration, successively washed completely by Soxhlet's extraction with ethanol, and dried to acquire 6-*O*-maleoyl-*N*-phthaloyl-chitosan (PHCSMA).

Preparation of graft copolymers

In a typical grafting reaction, an exact amount of dry 6-*O*-maleoyl-*N*-phthaloyl-chitosan was first dissolved in *N*, *N*-dimethylformamide solution, followed by the addition of monomer (BA). After stirring for 10 min constantly, the mixture was added slowly in water using a 50 cm^3 stoppered bottle. The solution was deoxygenated by slow bubbling of nitrogen gas through the solution for 5 min. The sample bottles were irradiated for a specified time in a ^{60}Co γ-ray source chamber. After completion of the reaction, the contents were collected by filtration. It was extracted completely by Soxhlet's extraction method with ethanol, and dried to acquire 6-*O*-maleoyl-*N*-phthaloyl-chitosan-*g*-PBA. The homopolymer of butyl acrylate was removed from the crude graft copolymer films by exhaustive Soxhlet's extraction method with toluene for 48 h. The graft parameters [grafting percentage (*G*%), grafting efficiency (*E*%), homopolymer percentage (*H*%)] used to characterize the nature of the copolymer are defined and calculated as follows:

$$G\% = \frac{W_g - W_0}{W_0} \times 100$$

$$E\% = \frac{W_g - W_0}{W_2} \times 100$$

$$H\% = \frac{W_H}{W_2 + W_3} \times 100$$

where W_g is weight of graft copolymer, W_0 is weight of 6-*O*-maleoyl-*N*-phthaloyl-chitosan, where W_2 is weight of reacted monomer (BA), W_3 is weight of unreacted monomer (BA), and W_H is weight of homopolymer.

Deprotection of the graft product

A mixture of graft copolymer and hydrazine monohydrate was heated with stirring for 1–2 h at 100–110°C under a nitrogen atmosphere. After cooling, the mixture was poured to water. The residue was resuspended in water, and the white precipitate was filtered. It was washed with ethanol and extracted by Soxhlet's extraction method with toluene and dried to afford chitosan-*g*-PBA, which possesses reactive amino groups.

Measurements

All infrared spectra were obtained from samples in KBr pellets using a Bruker EQUINOX 55 FTIR spectrophotometer. ^{1}H-NMR spectrum was recorded on an AVANCE 300 NMR Spectrometer, using dimethyl sulfoxide and D_2O-containing CF_3COOD as solvent. Elemental analysis was carried out with an Elementar Vario EL-III Elemental analysis instrument. The degree of substitution (DS) was determined from the *C*/*N* value of elemental analysis. X-ray diffractograms were obtained by the powder method with the use of a Philips X'Dert Pro X-ray diffractometer equipped with graphite monochromatized CuKα radiation (l = 0.154178 nm). The scanning range was 5–40° with a scanning rate of 2°/min. The thermal gravimetric analysis (TGA) was conducted on a Shimadzu TGA-50H Thermal Analyzer under N_2 flow. The heating rate was 20°C/min.

RESULTS AND DISCUSSION

Preparation of 6-*o*-maleoyl-*n*-phthaloyl-chitosan

In this work, we tried to graft poly(BA) onto chitosan, and to make grafting occur mainly at hydroxyl groups while amino groups remained free. To achieve this goal, phthaloylchitosan was prepared initially. 6-*O*-maleoyl-*N*-phthaloyl-chitosan, which phthaloyl group could be deprotected easily to regenerate the free amino group, was prepared by reacting phthaloylchitosan with maleic anhydride. It has been utilized as a versatile key intermediate for some regioselective chemical modification of chitosan. On the other hand, the introduction of bulky phthaloyl groups prevented the formation of intra- and interhydrogen bonds of chitosan, and consequently, improved its solubility in organic solvents, such as DMF and DMSO. This made it possible to carry out grafting of BA onto chitosan in homogeneous system, and the more important consequence is to mix chitosan together with BA at the molecular level. Therefore, the *N*-phthaloyl group would be indispensable for both protection and solubilization.

Figure 1 shows that 6-*O*-maleoyl-*N*-phthaloyl-chitosan showed the phthalimido characteristic peaks at

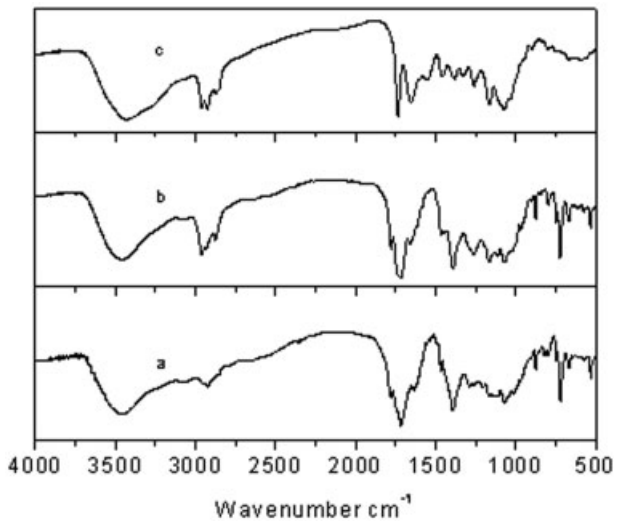

Figure 1 IR spectra of (a) 6-*O*-maleoyl-*N*-phthaloyl-chitosan, (b) 6-*O*-maleoyl-*N*-phthaloyl-chitosan-*g*-PBA, (c) chitosan-*g*-PBA.

1710, 1777, and 720 cm^{-1} and the characteristic peaks of the —CH═CH— group at 1634 and 3063 cm^{-1}. The DS value (degree of substitution) prepared here was found to be about 96.8%, calculated from the elemental analysis data.

Fourier transform infrared analysis

The FTIR spectrum of the chitosan-*graft*-PBA was shown in Figure 1. Compared to the spectrum of the graft copolymer before deprotection, the peaks at 1777, 1710 (carbonyl), and 720 cm^{-1} (phenyl ring) had disappeared, while the peaks at 2800–3000 cm^{-1} (methylene groups) still existed. Moreover, an ester carbonyl stretching band was observed at 1735 cm^{-1}, which belonged to PBA. It proved that the PBA chains were grafted onto chitosan successfully and not removed by hydrazine.

NMR analysis

In Figure 2, ^{1}H-NMR spectrum of 6-*O*-maleoyl-*N*-phthaloyl-chitosan, the signals due to the methylene protons of the CH═CH and phenyl ring were detected at 5.8–6.5 ppm, and 7.4–8.0, respectively, besides the broad peaks of chitosan backbone hydrogens (at 2.8–5.3).

The ^{1}H-NMR spectrum of graft copolymer was shown in Figure 3. The signals due to the methyl and methylene protons of butyl groups were detected at 0.5–1.5 ppm, and 4.0–5.0 ppm, respectively, besides the peaks of chitosan backbone hydrogens (at 2.8–5.0). The peaks at 2.0–2.8 ppm belonged to methylene protons of maleic acid and acrylic acid. What's more, the ^{1}H-NMR data suggested that some incomplete deprotection occurred since there were weak aromatic phthalimido peaks at 7.0–8.0 ppm.

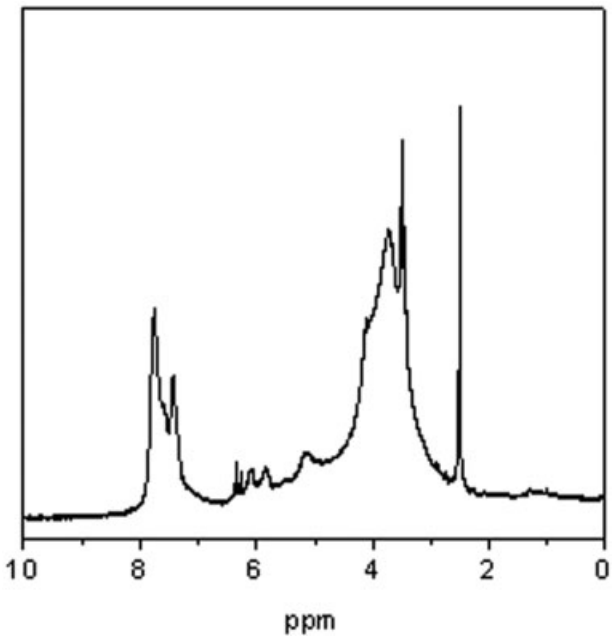

Figure 2 ^{1}H-NMR spectrum of 6-*O*-maleoyl-*N*-phthaloyl-chitosan.

X-ray diffraction analysis

Diffractograms of pure chitosan and 6-*O*-maleoyl-*N*-phthaloyl-chitosan-*g*-PBA are presented in Figure 4. The diffractogram of pure chitosan sample shows the characteristic peak at $2\theta = 11°$ and 20°. Note that the peak $2\theta = 11°$ disappeared and the peak $2\theta = 20°$de-

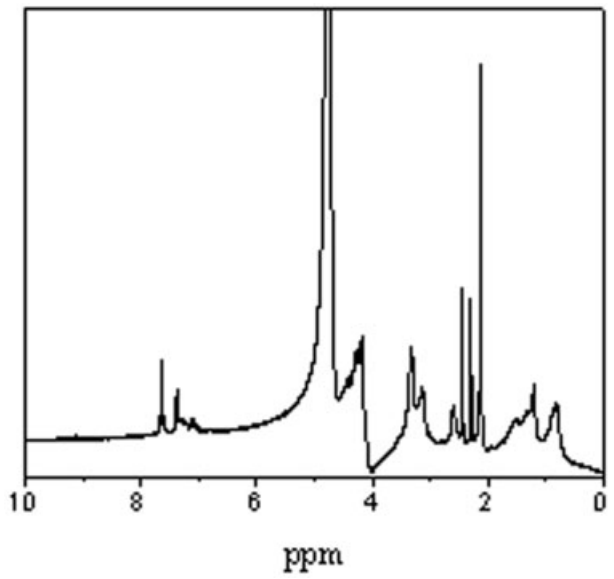

Figure 3 ^{1}H-NMR spectrum of graft copolymer.

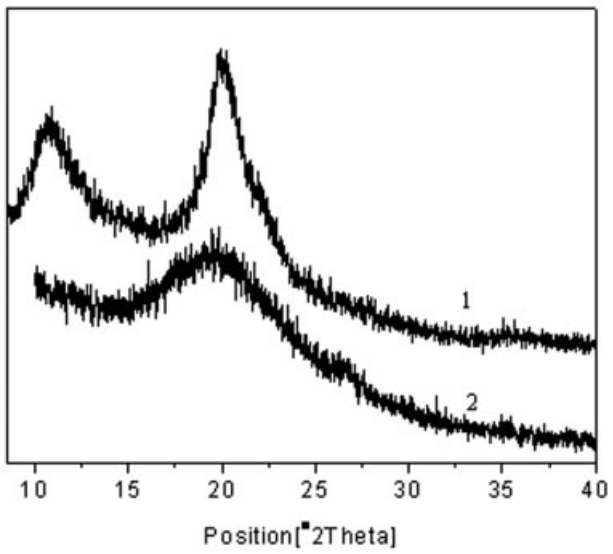

Figure 4 X-ray diffraction patterns. (1) Chitosan and (2) graft copolymer (grafting percentage 298.3%).

creased sharply in 6-*O*-maleoyl-*N*-phthaloyl-chitosan-*g*-PBA. A decrease in crystallinity may be due to the introduction of bulky pendant chains of grafted PBA in chitosan matrix.

TGA analysis

The TGA thermogram 6-*O*-maleoyl-*N*-phthaloyl-chitosan-*g*-PBA is presented in Figure 5. The thermal degradation profile of 6-*O*-maleoyl-*N*-phthaloyl-chitosan-*g*-PBA exhibits two main decomposition stages. The first stage is attributed to the degradation of chitosan. The second stage is the degradation of the whole material.

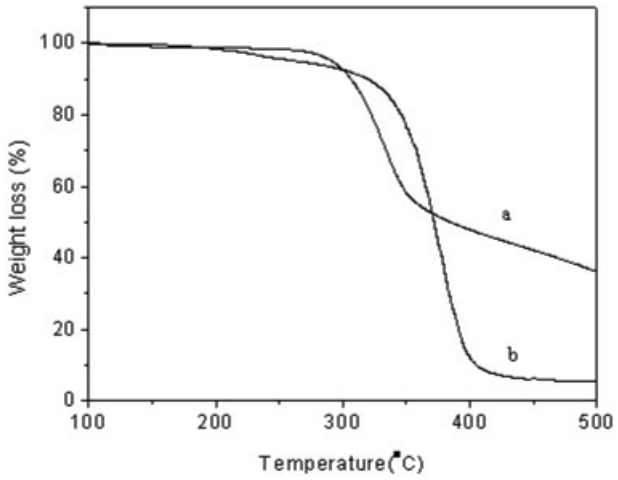

Figure 5 TGA thermograms of (a) chitosan and (b) graft copolymer (grafting percentage 298.3%).

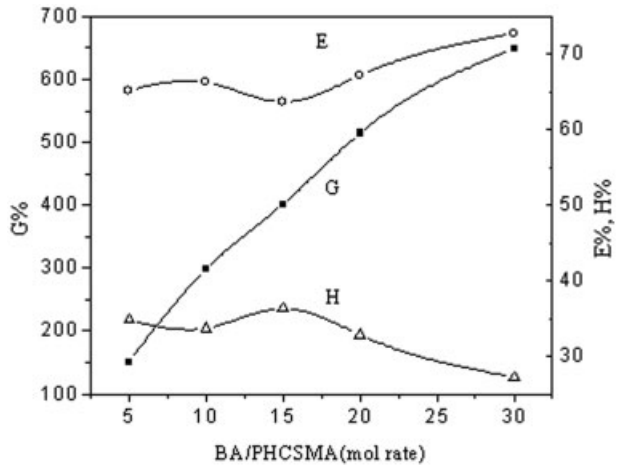

Figure 6 Effect of butyl acrylate concentration. Dose rate: 120.08 Gy/min; dose: 20 KGy; T = 20°C; G: percentage of graft; E: efficiency of graft; H: percentage of homopolymer.

Influence of reaction conditions on graft parameters

Effect of butyl acrylate concentration

The effect of butyl acrylate concentration on graft copolymerization of butyl acrylate (BA) onto 6-*O*-maleoyl-*N*-phthaloyl-chitosan is depicted in Figure 6. With an increase in butyl acrylate concentration, *G*% increases continuously, which is a very general trend in grafting reaction. *E*% gets a rise and *H*% declines. This may be explained as follows: with an increase in monomer concentration, the amount of grafting chains rise; when the concentration of monomer is higher, the radicals generated by the irradiation of γ-ray on grafting chains continuously initiate graft of monomer. Therefore, *E*% increases and *H*% decreases correspondingly.

Effect of dose rate

The intensity dependence of graft parameter was investigated for the irradiation dose rate range of 40–140 Gy/min. The results are depicted in Figure 7. It is found that in the range of 40–120 Gy/min, *G*% and *E*% increase and *H*% decreases. At dose rates higher than 120 Gy/min, *G*% and *E*% decrease and *H*% increases. From 40 to 120 Gy/min, with an increase of dose rate, the number of free radical species increases. The radicals continuously initiate graft of monomer. Therefore, *G*% and *E*% increase and *H*% decreases. At dose rates higher than 120 Gy/min, the number of free radical decreases due to the diminution of reaction time. Under such conditions, *H*% increases and *E*% decreases accordingly.

Effect of total dose

The influence of dose on the graft parameters is investigated and shown in Figure 8. It can be seen that *G*%

and *E*% increase with increasing irradiation dose, which may be due to the increasing concentration of free radicals formed in the polymer substrate. The figure shows that *H*% decreases continuously with the increase of dose. This may be due to the fact that homopolymer is grafted onto the chitosan under the irradiation of γ-ray.

CONCLUSIONS

Chitosan-*g*-PBA copolymers were synthesized through the γ-ray irradiation polymerization using 6-*O*-maleoyl-*N*-phthaloyl-chitosa as intermediate. The graft copolymerization was carried out in homogenous system. The graft extent was dependent on the irradiation dose and the concentration of BA monomer, and copolymers with grafting above 100% were readily prepared. It is a potential method to combine chitosan with the hydrophobic synthetic polymers. Thus the copolymer was expected as an amphoteric nature/synthetic hybrid material to have considerable importance in many fields. Chitosan-*g*-PBA can be expected to have broad application for seed coating, antistaling agent of vegetable and fruit, and so on. Further work on the thermal properties and mechanical properties is in progress on these grafting copolymers.

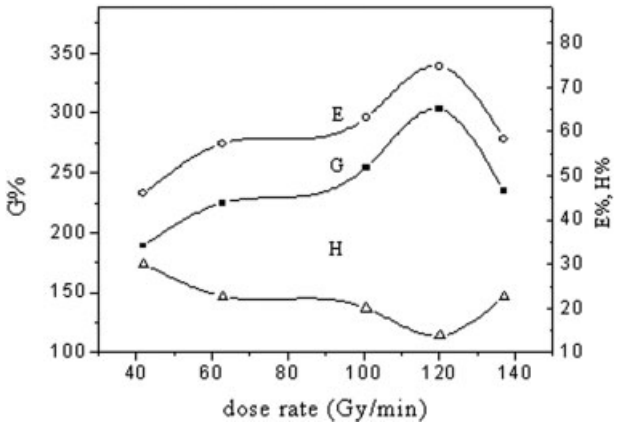

Figure 7 Effect of radiation dose rate. Dose: 20 KGy; *T* = 20°C; *G*: percentage of graft; *E*: efficiency of graft; *H*: percentage of homopolymer.

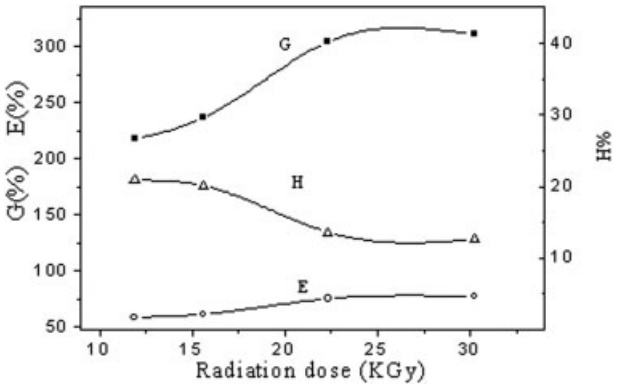

Figure 8 Effect of radiation dose. Dose rate: 120.08 Gy/min; *T* = 20°C; *G*: percentage of graft; *E*: efficiency of graft; *H*: percentage of homopolymer.

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