

# Rapid Synthesis and Characterization of Chitosan-g-Poly(D,L-lactide) Copolymers with Hydroxyethyl Chitosan as a Macroinitiator Under Microwave Irradiation

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Received 14 July 2011; accepted 9 September 2011

DOI 10.1002/app.35603

Published online in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Hydroxyethyl chitosan (HECS) was first prepared by the reaction of 2-chloroethanol with chitosan (CS). Then, CS-g-poly(D,L-lactide) (PDLLA) copolymers were synthesized through the ring-opening polymerization of D,L-lactide with CS and HECS as the macroinitiators, respectively, under microwave irradiation. The optimal synthesis conditions obtained by an orthogonal experiment were as follows: microwave power = 10 W, temperature = 130°C, irradiation time = 15 min, and catalyst concentration = 0.05 mol %. The reactivity of CS was improved by hydroxyethylation, which contributed to a higher percentage of grafting. Compared with the conventional thermal polymerization, the microwave polymerization method showed a significantly higher polymerization rate and

improved efficiency. An enhanced percentage of grafting ranging from 236.25 to 317.50%, and an average degree of polymerization of PDLLA side chains ranging from 13.25 to 24.17 were achieved under microwave irradiation when the value of  $n_{D,L-lactide}/n_{minoglucoside}$  units was increased from 20 : 1 to 40 : 1. The higher percentage of grafting facilitated decreases in the crystallinity and thermal stability of the copolymers, which were attributed to the weakening intramolecular and intermolecular hydrogen bonds of CS. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** biodegradable; graft copolymers; polyesters; polysaccharides; synthesis

## INTRODUCTION

Chitosan (CS) and its derivatives have been investigated extensively in biomedical fields such as drug-delivery vehicles, surgical materials, wound healing, and scaffold materials because of their nontoxicity, biocompatibility, biodegradability, low immunogenicity, and chemical modification.<sup>1–4</sup> However, the extended applications of CS are often limited by its poor processability and insolubility in water, which

is due to its rigid crystalline nature.<sup>5</sup> An effective solution for decreasing the intramolecular and intermolecular hydrogen bonds is to graft-copolymerize CS with another synthetic polymer,<sup>6</sup> such as polylactide (PLA).<sup>7</sup> As one of the biodegradable polyesters, PLA has been widely used in sustained drug-delivery systems, implants for orthopedic devices, surgical repair materials, and tissue engineering scaffold materials for its excellent mechanical properties and processability, biodegradability, biocompatibility, and nontoxicity.<sup>8,9</sup>

Many researchers have investigated the preparation of CS-g-PLA copolymers via the conventional thermal polymerization method.<sup>10–15</sup> However, the percentage of grafting and the average degree of polymerization of PLA side chains were not so desirable because of the existence of both intramolecular and intermolecular hydrogen bonds and the rigid crystalline nature of CS. Furthermore, for a thermal polymerization system, a long reaction time and a high reaction temperature are usually necessary; this may lead to the degradation of PLA side chains. Hereby, it was necessary to investigate a new technique for CS-g-PLA preparation under a mild reaction temperature and a short reaction time with lower cost.

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Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 30500128, 30900296.

Contract grant sponsor: Key Program of National Science and Technology Department of China (863 Program); contract grant number: 2007AA091603.

Contract grant sponsor: Guangdong Provincial Natural Science Foundation of China; contract grant number: 10151063201000033.

Contract grant sponsor: Sci-Tech Innovation Foundation of the 211 Project for Biomaterials and Tissue Engineering, Jinan University of China; contract grant number: 50621030.

Recently, the use of microwave irradiation in polymer science has received increasing interest because of its remarkable enhancement in the rates of some reactions over conventional thermal polymerization.<sup>16,17</sup> Microwave energy could be absorbed directly throughout the entire reaction mixture; this causes it to heat up evenly and rapidly. The copolymers of CS with vinyl monomers have been synthesized successfully under microwave irradiation.<sup>18–20</sup> Singh et al.<sup>18</sup> reported that acrylonitrile could be grafted onto CS with a grafting percentage of 170% in 1.5 min with microwave irradiation, compared to a maximum grafting percentage of 105% in 1 h by conventional thermal polymerization.

Few results have been reported on the synthesis of CS-g-PLA copolymer under microwave irradiation. In this study, microwave irradiation was used to replace conventional thermal polymerization to synthesize the graft copolymer. Meanwhile, hydroxyethyl chitosan (HECS) was synthesized to weaken the intramolecular and intermolecular hydrogen bonds and to enhance the reaction activity of CS. The effects of the irradiation power, temperature, irradiation time, catalyst concentration, and feed ratio on the grafting percentage, chemical structure, and physical properties of HECS-g-poly(D,L-lactide) (PDLLA) were investigated.

## EXPERIMENTAL

### Materials

D,L-lactide was provided by Glaco, Ltd. (Beijing, China). CS (number-average molecular weight = 300,000, degree of deacetylation = 90%) was purchased from Haidebei Marline Bioengineering Co., Ltd. (Jinan, China). Stannous octoate [Sn(Oct)<sub>2</sub>] was provided by Sigma-Aldrich. All chemicals used were analytical grade.

### Synthesis of HECS

HECS was prepared by the reaction of alkaliified CS with 2-chloroethanol in isopropyl alcohol. The degree of substitution of the hydroxyethyl group in the aminoglucoside unit of HECS was 1.44, as obtained by elemental analysis.

### Synthesis of the HECS-g-PDLLA copolymers

The microwave-assisted synthesis of the HECS-g-PDLLA copolymers was carried out in a CEM-Discover single-mode microwave oven. Briefly, a mixture of D,L-lactide and HECS ( $n_{\text{D,L-lactide}}/n_{\text{aminoglucoside}} = 20 : 1$ – $40 : 1$ ) and a certain amount of Sn(Oct)<sub>2</sub> solution in *n*-hexane were added to the CEM vial with a Snap-On cap. The reaction mixture was kept *in vacuo* (<1 mmHg) for 30 min to remove the solvent and moisture before it

**TABLE I**  
**Design of the Orthogonal Table L<sub>9</sub> (3<sup>4</sup>)<sup>a</sup>**

Factor	Level 1	Level 2	Level 3
A: Power (W)	5	10	15
B: Time (min)	10	15	20
C: Temperature (°C)	120	130	140
D: Catalyst ratio (mol %) <sup>b</sup>	0.05	0.10	0.15

<sup>a</sup>  $n_{\text{D,L-lactide}}/n_{\text{aminoglucoside}} = 20 : 1$ .

<sup>b</sup> Relative to D,L-lactide.

was exposed to microwave irradiation under the desired irradiation power and time. The crude products were washed twice with ethyl acetate and were subsequently extracted in a Soxhlet extractor with acetone for 48 h. The purified product was dried *in vacuo* at 40°C for 24 h. A CS-g-PDLLA copolymer prepared under the same conditions was used as the control.

The effects of the synthesis conditions, that is, microwave power, irradiation time, temperature, and concentration of the catalyst, on the grafting percentage of the HECS-g-PDLLA copolymers were investigated through orthogonal experimental design (Table I).

The thermal polymerization of HECS-g-PDLLA was performed at 130°C for 24 h, and other procedures were the same as those of the microwave-assisted synthesis.

### Characterization

All Fourier transform infrared (FTIR) spectra were obtained with a Bruker EQUINOX55 FTIR spectrophotometer (Germany). <sup>1</sup>H-NMR spectra were recorded on a Varian NOVA 500 spectrometer with tetramethylsilane as the internal reference; hexadeuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>), CF<sub>3</sub>COOD-D<sub>2</sub>O, and D<sub>2</sub>O as solvents for the graft copolymers, and HECS and CS measurement, respectively. Elemental analyses were performed with a 2400 series II CHNS/O elemental analyzer (PerkinElmer). The crystal structures of the CS, HECS, and the grafting copolymers were determined in a Rigaku D/max-3A diffractometer (Japan) with a Cu K $\alpha$  ray line at a scan rate of 8°/min. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses was carried out with a Netzsch TG 209 system (Germany) under a nitrogen atmosphere. The samples were heated from room temperature to 500°C at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Microwave-assisted synthesis of the HECS-g-PDLLA copolymers

#### Range analysis

The range analysis was done to clarify the significance levels of different factors on the grafting

**TABLE II**  
Orthogonal Test Design and Results

No.	A	B	C	D	Grafting percentage (%) <sup>a</sup>
1	5	10	120	0.05	202.45
2	5	15	130	0.10	217.34
3	5	20	140	0.15	205.71
4	10	10	130	0.15	229.37
5	10	15	140	0.05	227.93
6	10	20	120	0.10	210.82
7	15	10	140	0.10	196.79
8	15	15	120	0.15	192.94
9	15	20	130	0.05	203.16
$K_1$	208.50	209.54	202.07	211.18	
$K_2$	222.71	212.74	216.62	208.32	
$K_3$	197.63	206.56	210.14	209.34	
$R$	25.08	6.17	14.55	2.86	

A, power (W); B, time (min); C, temperature (°C); D, catalyst ratio (mol %).

<sup>a</sup> Grafting percentage = [Graft copolymer (g) – HECS (g)] ÷ HECS (g) × 100%.

percentage of the obtained HECS-g-PDLLA copolymers. It is believed that the most significant factors could be disclosed on the basis of the result of range analysis. Table II summarizes the statistics analysis of the effects of different factors on the grafting percentage of the copolymers. The  $K$  value for each level of a parameter was the average of three values, and the average value for each factor ( $R$ ) was the difference between the maximal and minimal values of the three levels. On the basis of the results of range analysis, the significance sequence of all of the investigated influencing factors was lined, and the order of significance levels was as follows:  $A > C > B > D$ , and the optimum synthesis condition was  $A_2C_2B_2D_1$ . In other words, the optimal conditions for the microwave-assisted grafting copolymerization was as follows: microwave power = 10 W, temperature = 130°C, irradiation time = 15 min, and catalyst concentration = 0.05%.

Therefore, we concluded that microwave power played a key role in this copolymerization. When the microwave power was increased from 5 to 15 W,

the grafting percentage of the copolymer increased accordingly in the beginning but decreased on further exposure. A maximum value of 222.71 was obtained at 10 W. This indicated that a higher microwave power was in favor of grafting copolymerization, but an excessive microwave power might have induced the degradation of the PDLLA side chains, which led to a lower grafting percentage. Similarly, an adequate temperature was in favor of the increase in the grafting percentage. Grafting percentages of 202.07, 216.62, and 210.14 were obtained at corresponding temperatures of 120, 130, and 140°C, respectively. The decrease of the grafting percentage at 140°C should have been due to the degradation of the PDLLA side chains at high temperature. Microwave irradiation time was another influence factor on the grafting copolymerization. With an increase in the irradiation time from 10 to 15 min, the grafting percentage of the copolymer increased from 209.54 to 212.74. However, when the irradiation time was further prolonged to 20 min, the grafting percentage decreased to 206.56 instead. It seemed that appropriately extending the irradiation time was beneficial to the grafting copolymerization, whereas overirradiation caused the thermal degradation of the PDLLA side chains as well.

The effect of catalyst concentration on the grafting copolymerization was also studied, as shown in Table II. The results show that the grafting percentage of the copolymer was less dependent on the Sn(Oct)<sub>2</sub> content. It is well known that alcohol/amino compounds act as initiators of the Sn(Oct)<sub>2</sub>-catalyzed ring-opening polymerization provide proper control of the molecular weights independent of the catalyst content.<sup>21,22</sup>

#### Effect of the hydroxyethylation of CS on the microwave-assisted grafting copolymerization

To decrease the intramolecular and intermolecular hydrogen bonds and enhance the reaction activity of CS, HECS was obtained by the reaction of 2-chloroethanol with CS; this was used for the preparation

**TABLE III**  
Elemental Analysis Results of CS, HECS, and the Graft Copolymers

Sample	$n_{D,L-lactide}/n_{aminoglucoside}$ unit	C (wt %)	N (wt %)	$n_C/n_N^a$
CS	—	40.75	7.69	6.18
HECS	—	41.81	5.38	9.06
HECS-g-PDLLA (thermal polymerization)	20 : 1	44.23	1.86	27.78
	40 : 1	45.72	1.44	37.02
HECS-g-PDLLA (microwave polymerization)	20 : 1	46.38	1.11	48.81
	40 : 1	48.15	0.69	81.57
CS-g-PDLLA (microwave polymerization)	20 : 1	43.82	2.36	21.66
	40 : 1	45.06	1.69	31.14

<sup>a</sup> The value of  $n_C/n_N = C$  (wt %) × 14/[N (wt %) × 12].

TABLE IV  
Graft Copolymerization of D,L-Lactide onto CS and HECS<sup>a</sup>

Sample	HECS-g-PDLLA				CS-g-PDLLA	
	Thermal polymerizaion		Microwave polymerization		Microwave polymerization	
$n_{D,L\text{-lactide}}/n_{\text{aminoglucoside unit}}$	20 : 1	40 : 1	20 : 1	40 : 1	20 : 1	40 : 1
Time	24 h	24 h	15 min	15 min	15 min	15 min
Grafting percentage (%) <sup>b</sup>	183.12	225.54	236.25	317.50	165.83	208.52
Polymerization degree of side chains <sup>c</sup>	6.24	9.32	13.25	24.17	5.16	8.32

<sup>a</sup> Temperature = 130°C; catalyst ratio (mol %) = 0.05.

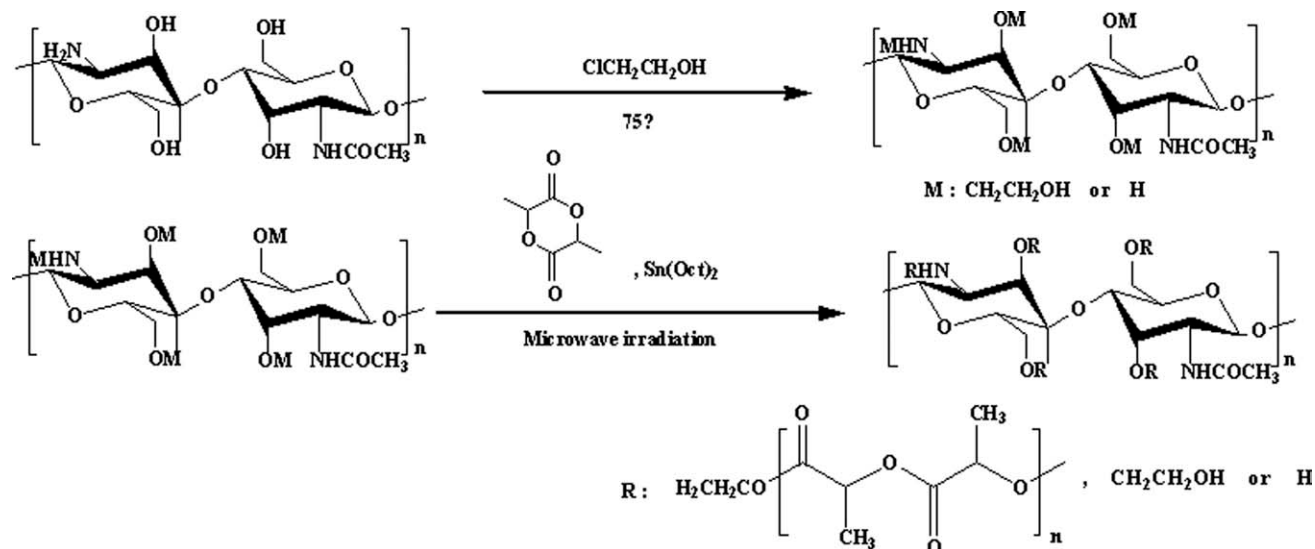
<sup>b</sup> Grafting percentage = [Graft copolymer (g) - HECS (g)] ÷ HECS (g) × 100%.

<sup>c</sup> Average polymerization degree of PDLLA = [( $n_C/n_N$ )<sub>copolymer</sub> - ( $n_C/n_N$ )<sub>CS</sub>]/3 or [( $n_C/n_N$ )<sub>copolymer</sub> - ( $n_C/n_N$ )<sub>HECS</sub>]/3.

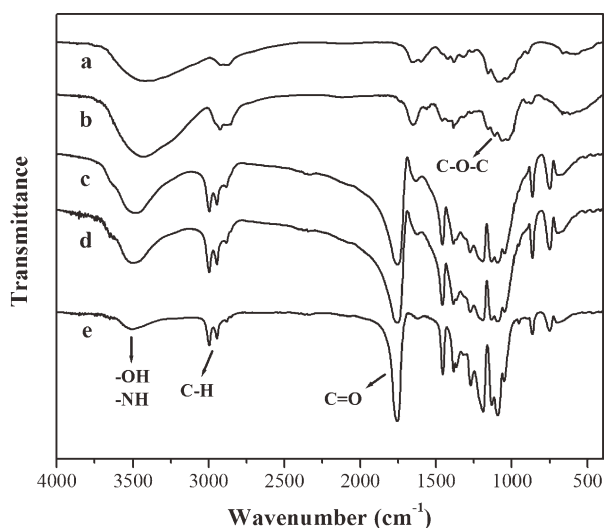
of HECS-g-PDLLA copolymers under microwave irradiation. Elemental analysis was used to determine the degree of substitution of the hydroxyethyl groups and the average polymerization degree of the PDLLA side chains on CS and HECS chains. The weight percentages of C and N for CS, HECS, and the graft copolymers were obtained by elemental analysis, as shown in Table III. The grafting copolymerization from HECS and CS was compared in terms of the grafting percentage and average polymerization degree of the side chains in the copolymers (Table IV). With increasing ratio of  $n_{D,L\text{-lactide}}$  to  $n_{\text{aminoglucoside unit}}$  from 20 : 1 to 40 : 1, the grafting percentage and average degree of polymerization of PDLLA in HECS-g-PDLLA increased from 236.25 to 317.50% and from 13.25 to 24.17, respectively; these values were much higher than those of CS-g-PDLLA, that is, from 165.83 to 208.52% and 5.16 to 8.32, respectively. We suggest that the reaction activity of CS improved after hydroxyethylation, maybe because of the weakened intramolecular and intermolecular hydrogen bonds in CS.

Effect of the microwave irradiation on the grafting copolymerization

Microwave-assisted ring-opening polymerization has been proven to be more rapid and efficient than conventional thermal polymerization.<sup>23–25</sup> In this study, we investigated the grafting percentage and polymerization degree of the side chains in HECS-g-PDLLA by using different grafting copolymerization methods, that is, microwave-assisted polymerization and conventional thermal polymerization. By increasing  $n_{D,L\text{-lactide}}/n_{\text{aminoglucoside unit}}$  from 20 : 1 to 40 : 1, only grafting percentages from 183.12 to 225.54% and polymerization degrees of PDLLA side chains from 6.24 to 9.32 of the copolymer were obtained with conventional thermal polymerization for 24 h; these values were much lower than those of the copolymer obtained under microwave irradiation for 15 min, as shown in Table III. This indicates that microwave irradiation could effectively improve the reaction activity of HECS and the grafting percentage of HECS-g-PDLLA and greatly shorten the polymerization time as well.



Scheme 1 Synthesis of HECS and the HECS-g-PDLLA copolymer.

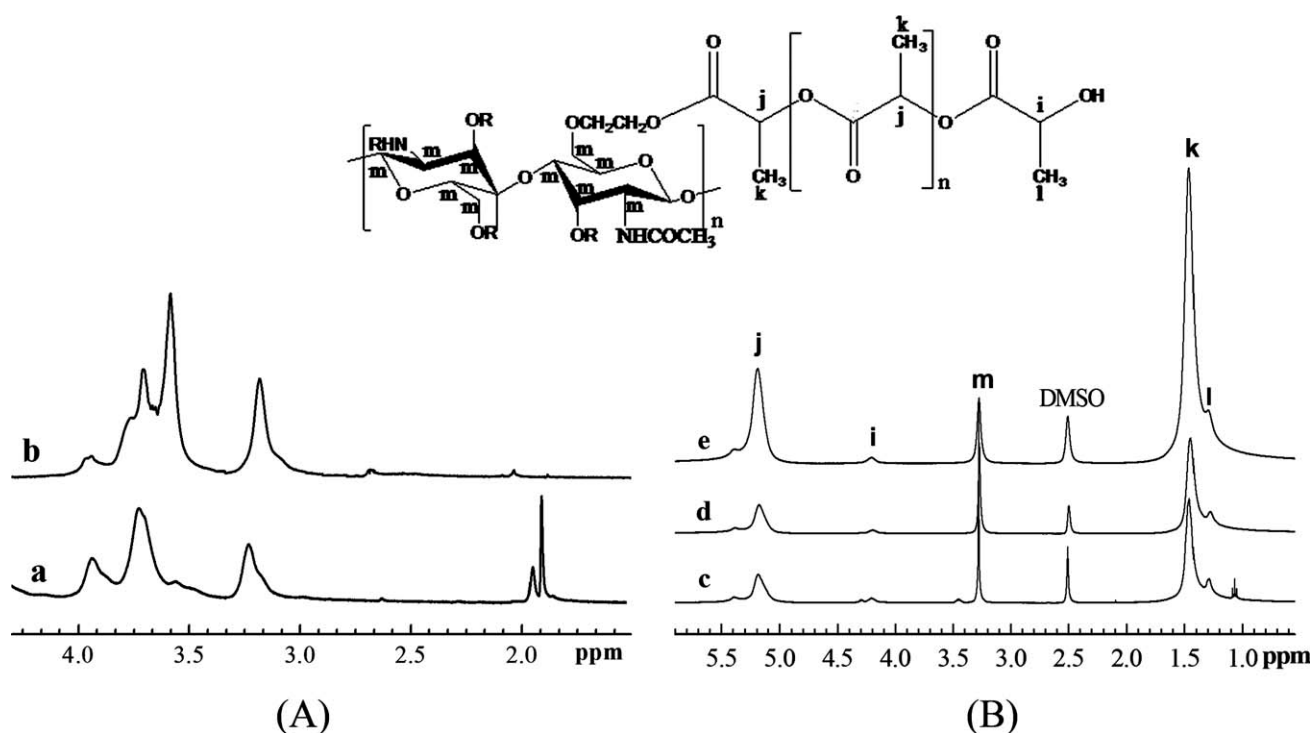


**Figure 1** FTIR spectra of (a) CS, (b) HECS, and graft copolymers with various feed molar ratios ( $n_{D,L-lactide}/n_{aminoglucoside}$  unit): (c) 20 : 1, (d) 30 : 1, and (e) 40 : 1.

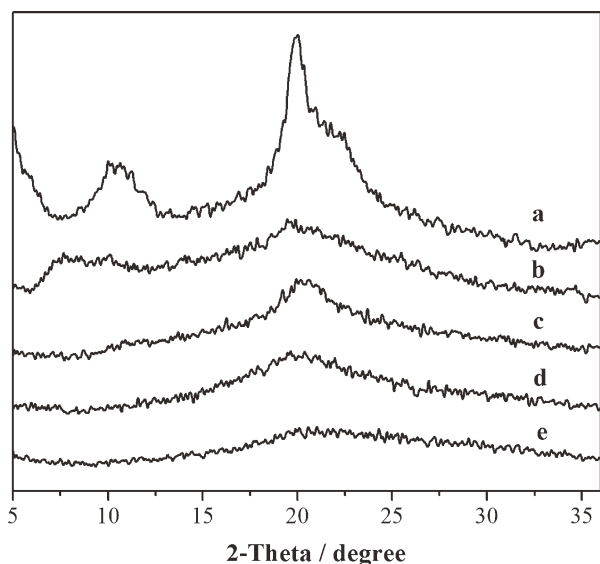
### Structure of the HECS-g-PDLLA copolymers

The synthesis of the HECS-g-PLLA copolymer was carried out, as shown in Scheme 1. There were four types of reactive groups on the HECS molecular chain that could be used for graft modification, that is, the primary hydroxyl groups introduced from hydroxyethylation, C<sub>6</sub> primary hydroxyl groups, C<sub>3</sub> secondary hydroxyl groups, and free amino groups on the deacetylated unit.

The FTIR spectra of CS, HECS, and HECS-g-PDLLA copolymers are shown in Figure 1. Compared to the spectrum of CS, the FTIR spectrum of HECS showed a new absorption peak around 1108 cm<sup>-1</sup>, which was assigned to the symmetric C—O—C stretching vibration absorption. The absorption peak around 1560 cm<sup>-1</sup> corresponded to the amino group that was weakened, whereas the absorption peak around 2930 cm<sup>-1</sup> presenting for methylene was increased after hydroxyethylation. The results indicate that 2-chloroethanol successfully reacted with the hydroxyl and amino groups of CS. In comparison to the FTIR spectrum of HECS, a new absorption peak appeared at 1758 cm<sup>-1</sup> on the spectra of the copolymers; this peak was assigned to the stretching vibration absorption of carbonyl groups on the PDLLA side chains. These peaks of 1093, 1131, and 1186 cm<sup>-1</sup> observed in the copolymers were assigned to the symmetric C—O—C stretching modes of the ester groups. This result suggested that the D,L-lactide was grafted to HECS under microwave irradiation.<sup>7</sup> With increasing  $n_{D,L-lactide}/n_{aminoglucoside}$  unit of HECS, the intensity of the new peak at 1758 cm<sup>-1</sup> became stronger, whereas the absorption peak at about 3500 cm<sup>-1</sup> attributed to the hydroxyl groups, the amino groups, and the amide of HECS was significantly weakened. This indicated that more D,L-lactide groups were conjugated to HECS.



**Figure 2** <sup>1</sup>H-NMR spectra of (a) CS, (b) HECS, and graft copolymers with various feed molar ratios ( $n_{D,L-lactide}/n_{aminoglucoside}$  unit): (c) 20 : 1, (d) 30 : 1, and (e) 40 : 1.



**Figure 3** X-ray spectra of (a) CS, (b) HECS, and graft copolymers with various feed molar ratios ( $n_{D,L-lactide}/n_{aminoglucoside}$  unit): (c) 20 : 1, (d) 30 : 1, and (e) 40 : 1.

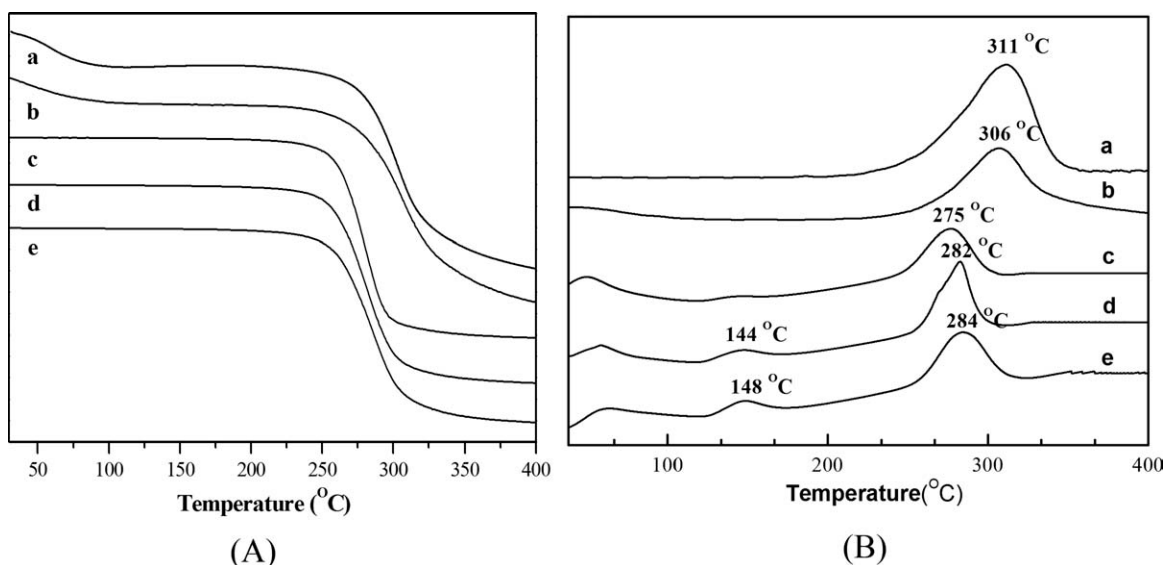
The  $^1\text{H-NMR}$  spectra of CS, HECS, and HECS-*g*-PDLLA copolymers are compared in Figure 2(A,B). CS showed multiplets at  $\delta$  values of 3.1–4.0 (H-2, H-3, H-4, H-5, and H-6); these corresponded to the ring methine protons. The singlet at  $\delta = 1.9$  was due to the survival of the *N*-acetylglucosamine units of chitin.<sup>7,15</sup> Compared to that of CS, the  $^1\text{H-NMR}$  spectrum of HECS showed that the signal at  $\delta = 3.6$  was assigned to the methylene protons. In the  $^1\text{H-NMR}$  spectra of the graft copolymers, the single absorption peak at  $\delta = 2.5$  was assigned to the solvent  $\text{DMSO-}d_6$ . The signals at  $\delta = 1.5$  and 5.2 were from the methyl protons and methine protons,

respectively, of the PDLLA side chains. Two weak peaks at  $\delta = 1.3$  and 4.3 corresponding to the terminal methyl protons and methine protons of the PDLLA side chains were observed, too.<sup>7</sup> The interesting thing here is that the original signals of CS almost disappeared, except for the multiplets at  $\delta = 3.2$ –3.5; this may have been due to the absorption of methine or methylene protons in HECS. The results were in fair accordance with those reported in literature.<sup>7</sup>

The average polymerization degree of the PDLLA side chains could be calculated from the ratio of the two integral intensities ( $\delta = 5.18$  and 4.32). With increasing  $n_{D,L-lactide}/n_{aminoglucoside}$  unit ratio of HECS from 20 : 1 to 30 : 1 and 40 : 1, the average polymerization degree of the PDLLA side chains rose from 14.54 to 20.58 and 26.48. It seemed that the composition of the grafting copolymer could be controlled by a change in the value of  $n_{D,L-lactide}/n_{aminoglucoside}$  unit, and a higher concentration of the *D,L*-lactide would lead to a higher average polymerization degree of the PDLLA side chains.

#### Properties of the HECS-*g*-PDLLA copolymers

X-ray diffraction profiles of CS, HECS, and the HECS-*g*-PDLLA copolymers are shown in Figure 3. CS is a partially crystalline polymer because of its regular chain and its strong intramolecular and intermolecular hydrogen bonds. CS showed two diffraction peaks around  $2\theta = 10$  and  $20^\circ$ ; these were assigned to crystal forms I and crystal forms II, respectively.<sup>15</sup> It could be seen that both of the diffraction peaks were weakened after hydroxyethylation. It was possible that the ability for forming



**Figure 4** TG and DTG thermograms of (a) CS, (b) HECS, and graft copolymers with various feed molar ratios ( $n_{D,L-lactide}/n_{aminoglucoside}$  unit): (c) 20 : 1, (d) 30 : 1, and (e) 40 : 1.

hydrogen bonds of CS was decreased after hydroxyethylation, and a lower crystallinity of CS was obtained. It was notable that the peak at  $2\theta = 10^\circ$  completely disappeared and the intensity of the peak at  $2\theta = 20^\circ$  decreased with the grafting of D,L-lactide onto HECS. Furthermore, the intensity of the peak at  $2\theta = 20^\circ$  decreased with increasing  $n_{\text{D,L-lactide}}/n_{\text{aminoglucoside unit}}$  of HECS. At  $n_{\text{D,L-lactide}}/n_{\text{aminoglucoside unit}} = 40$ , an amorphous grafting copolymer was obtained. This implied that the grafting of D,L-lactide onto CS further destroyed the crystallinity of CS.

The effects of the hydroxyethylation and grafting copolymerization of CS on its thermal stability properties were examined by thermogravimetric analysis and DTG analysis. From Figure 4(A,B), it can be seen that both CS and HECS showed a two-stage degradation pattern in thermogravimetric analysis and DTG thermograms. The first stage was attributed to the thermal evaporation of bound water, whereas the second one was ascribed to the thermal degradation of the polysaccharide. However, the onset thermal degradation temperature of HECS was lower than that of the original CS because of the weakened hydrogen bonds after hydroxyethylation.

Similar to CS and HECS, the grafting copolymers showed a two-stage degradation pattern in the DTG thermograms at low  $n_{\text{D,L-lactide}}/n_{\text{aminoglucoside unit}}$  and a three-stage degradation pattern at high  $n_{\text{D,L-lactide}}/n_{\text{aminoglucoside unit}}$ , respectively. The weight loss in the second stage should have been due to the thermal degradation of PLA side chains. Furthermore, the maximum thermal degradation temperature of the copolymers was lower than those of CS (311°C) and HECS (306°C); this indicated that after the grafting of D,L-lactide, the copolymer was thermally unstable. The results suggest that the introduction of flexible PDLLA chains into polysaccharide not only destroyed the crystalline structure of HECS but also reduced the hydrogen bonds caused by —OH and —NH groups in the HECS chain.<sup>14</sup> Figure 4(B) also shows that the maximum thermal degradation temperature of the copolymers increased slightly from 275 to 284°C. This was most probably because the hydrogen bonds among HECS were formed again through the covalently grafted PDLLA chains.

## CONCLUSIONS

HECS-g-PDLLA copolymers were successfully synthesized by the bulk ring-opening- grafting copolymerization of D,L-lactide onto HECS with Sn(Oct)<sub>2</sub> as a catalyst under microwave irradiation. In comparison to conventional thermal polymerization, microwave irradiation effectively improved the polymerization rate and grafting percentage of HECS-g-PDLLA with a noticeably shorter polymerization

time. The grafting copolymerization was significantly influenced by the microwave power, temperature, irradiation time, and  $n_{\text{D,L-lactide}}/n_{\text{aminoglucoside unit}}$  feeding ratios. The grafting percentage of the copolymer could be adjusted by control of the ratio of  $n_{\text{D,L-lactide}}$  to  $n_{\text{aminoglucoside unit}}$ . A higher feeding ratio enhanced the grafting percentage. When hydroxyethyl groups and PDLLA chains were incorporated into the polymer, the intramolecular and intermolecular hydrogen bonds of CS were weakened. Furthermore, the crystallinity of CS decreased with increasing grafting percentage of the copolymer; this could be advantageous for improving the solubility and processing property of CS.

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