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A novel and simple procedure to synthesize chitosan-*graft*-polycaprolactone in an ionic liquid

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ABSTRACT

An ionic liquid, 1-ethyl-3-methylimidazolium acetate (EMIMAc), was synthesized and employed as a homogeneous and green reaction media to prepare chitosan-*graft*-polycaprolactone (CS-*g*-PCL) *via* ring-opening polymerization, using stannous octoate ($Sn(Oct)_2$) as a catalyst. The structures and compositions of copolymers could be facilely controlled by the reaction conditions and feed ratios. The grafting content of polycaprolactone (PCL) could reach as high as 630%. The chemical structures of the copolymers were systematically characterized by ^{1}H NMR, Fourier transform infrared spectroscopy (FTIR) and wide-angle X-ray diffraction (WAXD), while thermal properties were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal stability and glass transition temperature (T_g) of the graft copolymers vary regularly with the change of PCL grafting content.

1. Introduction

Chitosan (CS), with a repeating structure unit of β-(1,4)-2-amino-2-deoxy-β-D-glucose, is a fully or partly deacetylated product of chitin, which is abundant natural resource. Recently, chitosan has attracted much attention for its favorable properties such as good biocompatibility, biodegradability, biological activity and non-toxicity. In particular, the unique polycationic nature endows the chitosan with various charming functions, including antibacterial activity and remarkable affinity to proteins and DNA. Therefore, chitosan has been widely used in many fields such as removal of metal ions from waste water (Ravi Kumar, 2000), tissue engineering scaffolds (Duan, Dong, Yuan, & Yao, 2004), packaging (Sébastien, Stéphane, Copinet, & Coma, 2006), cosmetics, drug carriers and wound healing accelerator (Kweon, Song, & Park, 2003). Unfortunately, the application of chitosan suffers greatly from many drawbacks such as insufficient mechanical properties, especially the brittleness, poor solubility (low solubility in aqueous and insolubility in common organic solvents) and processability (nonthermal plasticity), resulting from the strong intramolecular and intermolecular hydrogen bonds between hydroxyl groups and amino groups (Hirase, Higashiyama, Mori, Takahara, & Yamane, 2010; Martino, Pollet, & Avérous, 2011; Qian & Zhang, 2010; Wu, Yu, Mi, Wu, & Shyu, 2004).

Thus, various chitosan based graft copolymers have been developed, such as chitosan-*g*-poly(methylmethacrylate) (Singh, Tripathi, Tiwari, & Sanghi, 2006) chitosan-*g*-polyacrylonitrile (Yuan & Jiang, 2011), chitosan-*g*-poly(vinyl acetate), chitosan-*g*-poly(L-lactic acid) (Jayakumar, Prabaharan, Reis, & Mano, 2005), chitosan-*g*-poly(vinyl alcohol) (Xiao, Gao, & Gao, 2010), and chitosan-*g*-poly(1,4-dioxan-2-one) (Liu, Zhai, Wang, & Wang, 2008). Graft of aliphatic polyester onto chitosan is regarded as the most effective method to extend the applications of chitosan as a functional biomaterial because it can combines the merits of both CS and polyesters. Moreover, the CS can effectively buffer the acidity of degradation products of polyesters due to its basic characteristics. PCL, as promising aliphatic polyester, is fully biodegradable, biocompatible and nontoxic (Liu, Li, Garreau, & Vert, 2000; Williams et al., 2005). Therefore, PCL has been widely used in biomedical area. It has been reported that the grafting with PCL can substantially improve the solubility and mechanical properties of chitosan (Liu, Wang, Shen, & Fang, 2005; Zhou, Huang, Xu, & Fan, 2009).

However, conventional technique to synthesize CS-*g*-PCL copolymers usually carries out in heterogeneous reaction

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mediums and involves large quantity of volatile organic solvents, which seriously pollute our environment. These heterogeneous reactions have many other disadvantages such as time consuming, uneven grafting and wide grafting distributions since the graft reactions tend to take place at the surface of chitosan. An effective alternative to solve these problems is to prepare organic soluble chitosan derivatives as intermediate of the graft reaction, and the most common is phthaloylchitosan (Cai, Jiang, Chen, et al., 2009; Cai, Jiang, Tu, Wang, & Zhu, 2009; Liu et al., 2005). However, this method complicates the preparation procedure and increases the production cost.

Ionic liquids (ILs), as a new generation of green solvents, have attracted increasing attention recently owing to their low vapor pressure and tunable solvability by varying the structure of cations and anions (Klingshirn, Broker, Holbrey, Shaughnessy, & Rogers, 2002; Zhao, Jackson, Song, & Olubajo, 2006). Recently, imidazole based ionic liquids have been reported to successfully dissolve polysaccharide such as chitosan, chitin and cellulose (Liao, Liu, Zhang, & Gong, 2006; Xiao, Chen, Wu, Wu, & Dai, 2011), and were regarded as green solvents to replace the volatile organic solvents traditionally used in processing and synthesis industries. Guo, Wang, Shen, Shu, & Sun (2013) prepared cellulose-*g*-PCL nanomicelles by homogenous ring-opening polymerization in the ionic liquid of 1-N-butyl-3-methylimidazolium chloride. Dong et al. (2008) and Yan et al. (2009) synthesized cellulose-*graft*-poly(L-lactide) copolymers in the ionic liquid of 1-allyl-3-methylimidazolium chloride with $Sn(Oct)_2$ and 4-dimethylaminopyridine as catalyst, respectively. Although many novel cellulose-based hybrid biomaterials have been prepared in ionic liquids (Barthel & Heinze, 2006; Heinze, Schwikal, & Barthel, 2005), up to now, very little information is available on the modification of chitosan or chitin in ionic liquid, except the acetylation of α-chitin (Mine, Izawa, Kaneko, & Kadokawa, 2009), to the best of our knowledge. In this work, PCL was grafted onto the unmodified CS in the ionic liquid of EMIMAc for the first time. The main working objective is to gain CS-*g*-PCL with high grafting content in a short time in the homogeneous media of ionic liquid. The structures of the copolymer were systematically investigated by FTIR, ^{1}H NMR, DSC, and WAXD.

2. Materials and methods

2.1. Materials

Chitosan (degree of deacetylation = 85%, determined by ^{1}H NMR analysis, M_w = 52 kDa) was supplied by Golden-shell Biochemical Co. Ltd. (Zhejiang, China) and dried in vacuum at 60 °C for 12 h before use. Stannous octoate and ε-caprolactone (ε-CL) were purchased from Alfa Aesar (USA), and ε-CL was distilled under reduced pressure from calcium hydride before use. 1-Ethyl-3-methylimidazolium bromine was obtained from Chengjie Chemical Reagent Co. Ltd. (Shanghai, China). Lead (II) acetate trihydrate was bought from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the other chemicals and solvents were analytical grade and used as received without further purification.

2.2. Preparation of EMIMAc

1-Ethyl-3-methylimidazolium bromine (0.2 mol) and lead (II) acetate trihydrate (0.1 mol) were dissolved in 30 mL of distilled water and 70 mL of distilled water, respectively. After they were completely dissolved, 1-ethyl-3-methylimidazolium bromine solution was poured into lead (II) acetate trihydrate solution under vigorous mechanical stirring. The reaction was carried out at 35 °C for 48 h under nitrogen atmosphere. Then the reaction system was refrigerated at 3 °C for 12 h and the precipitates were filtered off. The filtrates were distilled under reduced pressure to remove the water. The obtained EMIMAc (moisture content < 0.02%; bromide content < 0.004%) was light yellow viscous liquid and the yield was 93%.

2.3. Synthesis of CS-g-PCL in EMIMAc

CS-*g*-PCL was synthesized in EMIMAc according to the following procedure. In a dry 100 mL of three-neck flask, which was evacuated and purged with nitrogen for three times, 8 g of EMIMAc and 0.4 g of CS were introduced under nitrogen atmosphere. Then the temperature was raised to 100 °C and the reaction system was gradually reduced to 5–15 Pa, and maintained for 6 h to get a homogenous solution. Subsequently, the system was cooled to room temperature and a predetermined amount of ε-CL and 0.5 wt% of $Sn(Oct)_2$ (with respect to ε-CL) were added. After that, the exhausting-refilling process was repeated for 3 times. Then the reaction was carried out at 100 °C for predetermined time under nitrogen atmosphere. After that, the product was purified by reprecipitation in ethanol and filtered. The EMIMAc, unreacted ε-CL monomer and PCL homopolymer were removed by Soxhlet extraction with acetone for 24 h. The dried CS-*g*-PCL powder was obtained under vacuum oven at 60 °C for 12 h. The whole synthesis procedure of CS-g-PCL is shown in Scheme 1.

2.4. Characterization

2.4.1. Element analysis

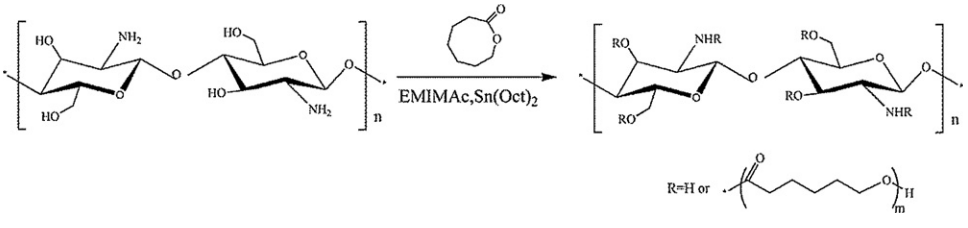
The contents of carbon, hydrogen and nitrogen were measured with a FLASH EA1112 element analyzer (EA). Since the absolute content of nitrogen was constant, the grafting content can be calculated according to the following equation:

$$\frac{N_{CS}}{1+x} = N_{CS\text{-g-PCL}}$$

where N_{CS} and $N_{CS\text{-g-PCL}}$ are the contents of the nitrogen element in chitosan and CS-*g*-PCL, respectively; and x is the weight percentage of PCL relative to chitosan.

2.4.2. FTIR spectroscopy

FTIR spectra of neat chitosan and all the CS-*g*-PCL powder were recorded with a Nicolet 6700 FT-IR spectrometer from 650 to 4000 cm^{-1} at room temperature. The sample was scanned 32 times and the resolution ratio was 4 cm^{-1}.



Scheme 1. Synthesis scheme of CS-g-PCL.

Table 1
Results of the graft copolymerization under different conditions.

Sample	Solvent	CL/CS (mol/mol)	*t* (h)	Yield[a] (g)	PCL-H[b] (g)	Grafting content[c] (%)	Grafting efficiency[d] (%)
0	DMSO	10	5	0.45	0.05	8	38
1	EMIMAc	5	5	0.52	0.09	56	63
2	EMIMAc	10	5	0.50	0.10	86	65
3	EMIMAc	20	2	0.53	0.06	68	76
4	EMIMAc	20	5	0.54	0.07	140	80
5	EMIMAc	20	10	0.94	0.16	199	76
6	EMIMAc	20	20	1.89	0.34	317	77
7	EMIMAc	50	5	1.36	0.42	160	58
8	EMIMAc	50	10	2.50	0.97	311	54
9	EMIMAc	50	20	3.86	1.62	630	54

[a] The weight of samples recovered.

[b] The weight of PCL homopolymer removed by acetone extraction.

[c] Grafting content (%) = 100 × ($W_{\text{graft copolymer}} - W_{\text{chitosan of graft copolymer}}$)/$W_{\text{chitosan of graft copolymer}}$ (determined by EA).

[d] Grafting efficiency (%) = 100 × $W_{\text{graft copolymer}}$ × PCL content (%)/($W_{\text{graft copolymer}}$ × PCL content (%) + PCL-H), where $W_{\text{graft copolymer}}$ = Yield − PCL-H; PCL content (%) = Grafting content (%)/(100 + Grafting content (%)).

2.4.3. NMR

^{1}H NMR spectra were performed using a Bruker DMX-400 NMR spectrometer using $CDCl_3$ as solvent for PCL, and D_2O/CF_3COOD (95:5, v/v) for the rest samples.

2.4.4. Differential scanning calorimetry (DSC)

DSC analysis was carried out with a TA Q2000 differential scanning calorimeter (TA Instruments) under nitrogen atmosphere (50 mL min^{-1}). The samples were first heated to 180 °C and maintained for 5 min to eliminate the thermal histories. Then they were cooled to −80 °C at a rate of 20 °C min^{-1} and held there for 10 min. After that, the samples were reheated to 180 °C with the same rate. Both of the cooling and reheating scans were recorded for analysis.

2.4.5. Wide-angle X-ray diffraction (WAXD) analysis

The WAXD measurements were determined with a Ragaku Model D/max-2B X-ray diffractometer (Japan) with a Cu/kα radiation (40 kV, 20 mA), and the experimental data were collected from 3° to 60° at a scanning rate 2° min^{-1}.

2.4.6. Thermogravimetric analysis (TGA)

TGA was conducted with a Perkin-Elmer TGA-7 under nitrogen atmosphere at a rate of 20 °C min^{-1}.

3. Results and discussion

3.1. Synthesis of CS-g-PCL

The CS-*g*-PCL copolymer was synthesized by grafting the PCL onto chitosan through ring-opening polymerization of ε-CL in EMIMAc with $Sn(Oct)_2$ as the catalyst (Scheme 1). Since ethanol is good solvent for EMIMAc but poor solvent for graft polymers, the polymers can be directly recovered from alcohol coagulants. The results of the graft copolymerization under various reaction conditions are summarized in Table 1.

DMSO was a common solvent employed to swell chitosan for chitosan modification (Cai, Jiang, Chen, et al., 2009; Cai, Jiang, Tu, et al., 2009). However, the grafting content of PCL was as low as 8% (Table 1) when DMSO was used as the solvent, suggesting that heterogenous reaction is not beneficial to the graft copolymerization. In contrast, the grafting content of PCL was much higher in EMIMAc due to the homogenous nature. Therefore, it can be concluded that the homogenous graft copolymerization of ε-CL in ionic liquid of EMIMAc is much more efficient than that in common solvent of DMSO.

The effect of feed ratios and reaction times on the grafting content is shown in Table 1. It can be found from samples 1, 2, 4, 7 that the grafting content of PCL increases evidently with the increasing feed ratio of CL/CS. This trend can be explained as that probability of collision and reaction between ε-CL monomers and D-glucosamine (GlcN) units increases when more ε-CL is introduced. In contrast, the grafting efficiency of the copolymers increased with the increasing feed ratio of CL/CS and achieved a maximum value when feed ratio of CL/CS is 20, then decreased with further increasing feed ratio of CL/CS. Another conspicuous tendency among samples 3–6 and 7–9 was that the grafting content of PCL also increases substantially with increasing reaction time. When the feed ratio of CL/CS was 50 and the reaction time was 20 h, the grafting content of PCL can achieve as high as 630%, which was greatly higher than the values reported by most literatures (Liu, Chen, & Fang, 2006; Liu et al., 2005; Zhou et al., 2009). The high grafting content of PCL is attributed to the fact that chitosan dissolves well in EMIMAc and the grafting copolymerization takes place in homogeneous condition. Due to the highly insoluble nature of chitosan, the traditional technique to modify chitosan always needs to synthesize chitosan precursor to enhance the solubility and thus involves large quantity of organic solvent which seriously pollute the environment. As contrast, the present strategy is a much more simple and highly efficient procedure to prepare chitosan graft copolymers with high grafting content.

3.2. FTIR analysis of CS-g-PCL

Fig. 1 displays the FTIR spectra of chitosan, PCL and CS-*g*-PCL copolymers with various grafting contents. As shown in the FTIR

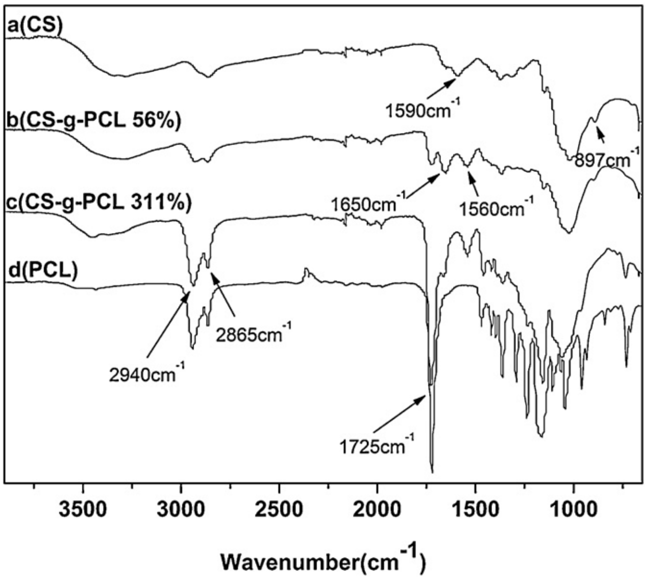


Fig. 1. FTIR spectra of chitosan (a), sample 1 (b), sample 8 (c), and PCL (d).

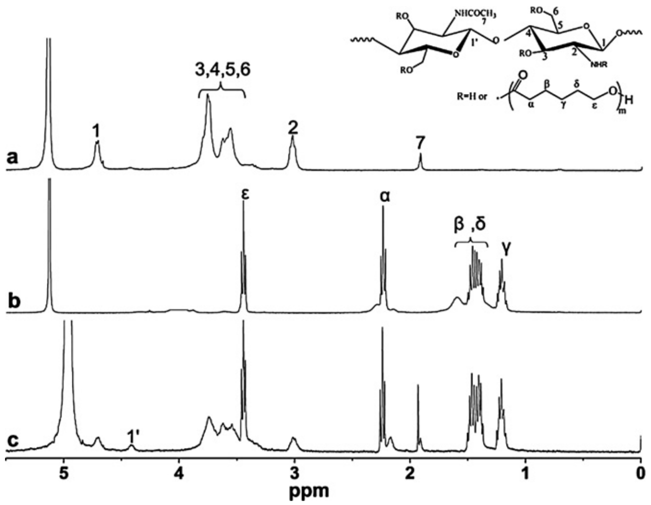


Fig. 2. ^{1}H NMR spectra of chitosan (a), PCL (b) and sample 1 (c).

spectrum of native CS (Fig. 1a), the characteristic peak at 897 cm^{-1} is assigned to the C—O stretching of glycoside linkage, the peak at 1160 cm^{-1} is attributed to the asymmetric C—O stretching of C—O—C bridge and the peak at 1590 cm^{-1} belongs to the N—H deformations of amino group. The peaks at 1650 cm^{-1} and 1380 cm^{-1} are associated with the C═O stretching and the C—H bending of amide group, indicating the incomplete deacetylation of the chitosan. The characteristic peaks of PCL can be detected in the spectra of CS-*g*-PCL (Fig. 1b and c). The strong peak at 1725 cm^{-1} is assigned to the stretching vibration of C═O on PCL ester group, while the peaks at 2865 cm^{-1} and 2940 cm^{-1} are arising from the stretching vibration of C—H of —CH$_2$ group on PCL. Hence, the presence of PCL side chains in the modified chitosan can be confirmed.

Furthermore, it can be found from Fig. 1 that the peak at 1725 cm^{-1}, attributing to ester carbonyl, became stronger with the increase of grafting content of PCL in the copolymer. At the same time, the intensity of the peak at 1650 cm^{-1} (amide I) increases and a new peak at 1560 cm^{-1} (amide I) appears after grafting, implying that PCL has been grafted to CS backbone at the amino groups. It is well known that the hydrophilic groups on chitosan such as hydroxyl and amino groups exhibit broad peaks in the range of 3000–3500 cm^{-1} due to their strong hydrogen interactions. The intensity of these peaks decreases obviously after the graft copolymerization, indicating the reduction of number of hydroxyl and amino groups in the chitosan derivative.

3.3. ^{1}H NMR spectra of CS-g-PCL

The ^{1}H NMR spectra of CS, PCL and CS-*g*-PCL are shown in Fig. 2. The characteristic signals of chitosan protons were observed at 4.72 ppm for H-1, 3.02 ppm for H-2, 1.92 ppm for H-7 and 3.3–3.8 ppm for H-3, -4, -5, -6 in Fig. 2a. As indicated in Fig. 2b, the signals occurring at 1.20, 2.23, 3.48 and 1.4–1.6 ppm are assigned to H-γ, H-α, H-ε, H-β, -δ of PCL, respectively. Obviously, the spectrum of the graft copolymer (Fig. 2c) demonstrates all the proton signals of chitosan and PCL. Thus, the structure of PCL-*g*-CS can be verified. Moreover, the intensity of signals at 4.45 ppm attributed to H-1′ increases, while the signal at 4.72 ppm arising from H-1 decreases after copolymerization. It suggests that PCL was grafted onto the CS skeleton through —NH$_2$. The variation of the intensity of the peaks at 3.5–3.8 ppm implied that the graft reaction also occurs on the —OH. Thus, the grafting of CS by PCL takes place at random along the CS backbones and produces a random copolymer. The simultaneous grafting of PCL on reactive groups of —NH$_2$ and —OH suggests that graft copolymerization is highly effective, which is ascribed to the homogeneous reaction nature.

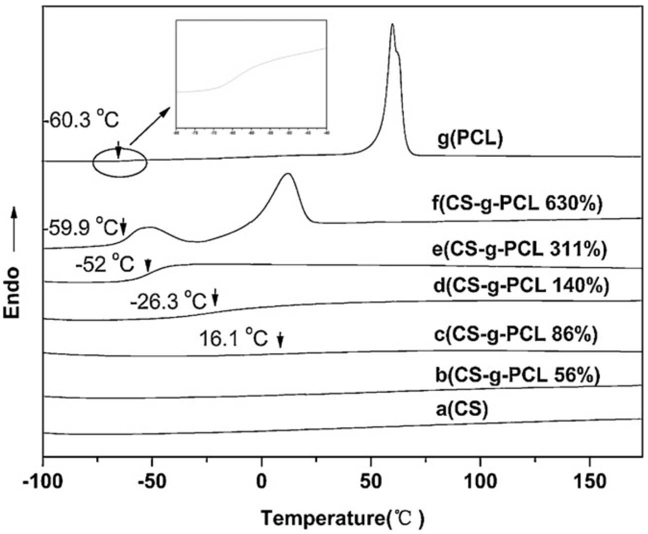


Fig. 3. DSC thermograms of chitosan (a), sample 1 (b), sample 2 (c), sample 4 (d), sample 8 (e), sample 9 (f) and PCL (g) in the second heating run.

3.4. Differential scanning calorimetry

The DSC thermograms of chitosan, PCL and CS-*g*-PCL are presented in Fig. 3. It is well regarded that, owing to the strong inter/intramolecular hydrogen bonds between —OH and —NH$_2$, the melting point of chitosan is much higher than its decomposition temperature. Thus, chitosan cannot melt and lacks thermoplasticity. It is regarded that the variation in heat capacity, arising from the change in specific volume near T_g, is too small to be detected by DSC. As a result, no obvious glass transition attributing to CS can be observed in Fig. 3. In contrast, the molecular chains of PCL are much more flexible and the glass transition is more prominent. The T_g of copolymer is almost invisible for CS-*g*-PCL with low grafting content. However, with increasing grafting content of PCL, the T_g of copolymer gradually becomes evident and decreases steadily from 16.1 °C to −59.9 °C to gradually approach to the T_g of pure PCL. Interestingly, there is an evident endothermic peak for CS-*g*-PCL with highest grafting content, arising from the melting of PCL side chains. It indicates that when the side chain length of PCL increases to some extent, some fascinating thermal behaviors transformation would happen. Nevertheless, the endothermic peak appeared at a much lower temperature region (11.9 °C, lower than room temperature) as compared to pure PCL, suggesting very poor crystal structure of PCL side chains in CS-*g*-PCL. It may be original from the fact that the chain length of PCL side chains is not long enough. Furthermore, the crystallization of PCL side chains has been greatly restrained by CS main chains.

3.5. Wide-angle X-ray diffraction

WAXD was performed to study the crystal structure and the corresponding results are given in Fig. 4. As far as chitosan is regarded, whose crystal form was rhombic (Dung, Milas, Rinaudo, & Desbrieres, 1994), the peak at *ca* 11° was assigned to crystal form I, while the strong peak at *ca* 20° was ascribed to crystal form II (Zhang, Ping, Zhang, & Shen, 2003). Upon grafted by PCL, the peak at *ca* 11° disappeared and the peak at *ca* 20° became widened and weaken. It indicates that the degree of crystallinity of chitosan in the copolymer is reduced upon graft copolymerization. These results can be explained as that the PCL side chains disturbed the regularity

Table 2
The data of thermogravimetric analysis of chitosan and CS-*g*-PCL copolymers.

	Chitosan	Sample 1	Sample 2	Sample 4	Sample 8	Sample 9	PCL
$T_{\max}$ (°C)	318.78	267.78	274.34	306.32	327.52	328.94	330.89
Residue at 700 °C (%)	38.84	37.18	31.99	22.46	11.75	5.67	0.36

of packing between chitosan chains, decreasing its crystallizability as well as the ability to form hydrogen bonds. However, characteristic peaks arising from PCL are undetectable for the graft copolymers, even for the sample with highest grafting content. It may be arising from the fact that the crystallizability of PCL side chains is very poor. Furthermore, the testing temperature for WAXD experiment was carried out at room temperature, which is higher than the melting point of graft copolymers, thus no crystals were formed at room temperature.

3.6. Thermogravimetric analysis

The TGA thermograms of chitosan and CS-*g*-PCL copolymers are presented in Fig. 5. It can be found that native chitosan go through a two-stage degradation. Similar results have been reported by Feng and Dong (2006). The first stage located at 20–170 °C with a slight weight loss about 5% is due to the vaporization of water and elimination of unstable fragments. The second one, the primary stage, starts at 170 °C, corresponds to the degradation of chitosan main chains. The basic data of thermogravimetric analysis are listed in Table 2. Chitosan has the highest weight residue at 700 °C (38.8%), while the PCL homopolymer has the lowest weight residue. The weight residue decreases significantly with increasing graft content of PCL and approaches to that of PCL. The residue is as low as 5.67% when the grafting content of PCL is 630%. This result can be reasonable interpreted as that the PCL chains dominate the decomposition process when the grafting content of PCL is high enough.

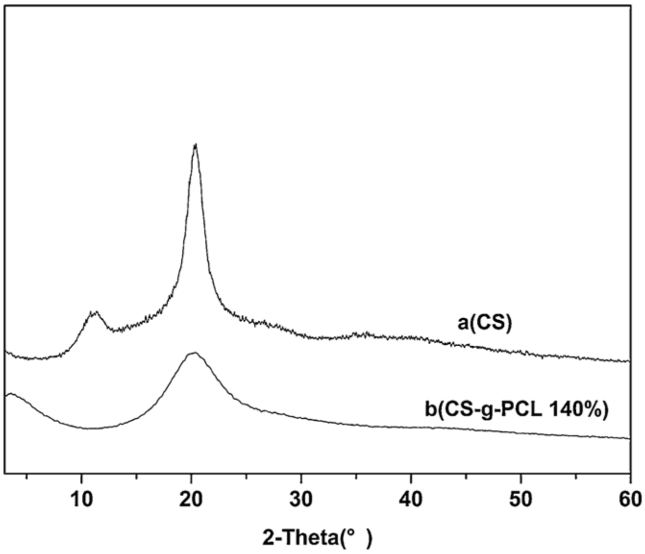


Fig. 4. WAXD patterns of chitosan (a) and sample 4 (b).

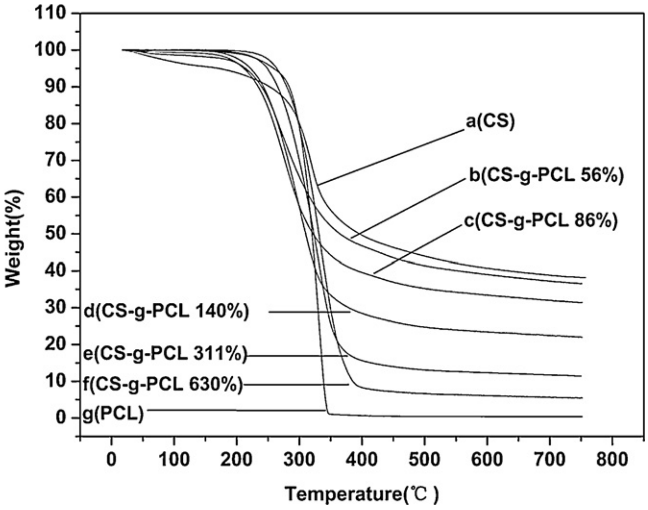


Fig. 5. TG thermograms of chitosan (a), sample 1 (b), sample 2 (c), sample 4 (d), sample 8 (e), sample 9 (f) and PCL (g).

Furthermore, the maximal decomposition temperature ($T_{\max}$) increases steadily and gradually approaches to that of PCL with the increase of grafting content because PCL becomes the main composition of copolymer. It consists well with the results for chitosan-*graft*-poly(*p*-dioxanone) (Wang et al., 2009). The $T_{\max}$ of sample 1, sample 2 and sample 4 is lower than that of chitosan while the $T_{\max}$ of sample 8 and sample 9 is higher than that of chitosan. This result can be explained by the fact that the introduction of PCL partially destroys the hydrogen bonds of chitosan (Wu et al., 2005) when the grafting content is low, causing a depressed thermal stability. With further increase in the grafting content of PCL, PCL becomes the main composition of copolymer, and the thermal stability is close to that of PCL homopolymer.

4. Conclusions

In conclusions, a novel, convenient, and efficient procedure to prepare CS-*g*-PCL was proposed in this contribution by ring-opening polymerization of ε-caprolactone, using EMIMAc as a homogenous reaction media and stannous octoate as the catalyst. It is much more effective to realize the graft copolymerization in EMIMAc than in conventional solvent of DMSO. Both of the —OH and —NH_2 participates in the reaction and the grafting contents of PCL surprisingly achieve as high as 630%. With increasing grafting content of PCL, the T_g of copolymer gradually becomes evident and decreases steadily to approach to the T_g of pure PCL. The melting behavior of grafted side PCL segment emerges when the grafting content approaches a certain extent. In summary, this article provides a novel, convenient, and efficient method to synthesize CS-*g*-PCL. The obtained graft copolymers are expected to have the advantageous properties of two polymers and are promising to have some applications in many fields, such as tissue engineering or drug and gene delivery.

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