



A facile route to obtain an acidic hydrogel containing lactate moieties



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ABSTRACT

The idea to develop hydrophilic lactic acid-based polyelectrolyte was presented. A facile route was utilized to prepare smart hydrogels that contained lactate units and carboxylic groups. The hydrogels were obtained through the radical cross-linking reaction between an unsaturated lactate-contained macromonomer and acrylic acid (AA)/itaconic acid (IA) monomer pair. The structure and performances of the hydrogels were characterized with thermogravimetric analysis, dynamic thermal analysis, scanning electron microscopy, swelling tests and adsorption measurements. The equilibrium swelling ratios of the hydrogels in acidic (pH 3.6) and basic (pH 11.5) media reached 25.3 and 62.3 respectively. The pH-sensitive swelling behaviors of the hydrogel confirmed that the hydrogels contained carboxylic groups and they were hydrophilic. The metal ions including calcium, copper, lead and cerium ions were bound into the hydrogels, which also confirmed the existence of the carboxyl groups. Moreover, the swelling ratio and adsorption capacity of the gel prepared from monomer pair were significantly higher than those obtained in absence of IA, which suggested that the properties of the hydrogels could be controllable by simply adjusting the ratio of AA/IA. In addition, the weight loss percentage of the hydrogel was around 37% after two-week in vitro degradation, which indicated the hydrogel contained lactate units.

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1. Introduction

There is an interesting phenomenon in developing lactic acid-based polymers. Lactic acid (LA) is the starting material to prepare LA-based polymers [1,2]. LA is a water-soluble carboxylic acid, but the reported homopolymer and copolymers of LA are all hydrophobic and neutral [3–5]. Can we obtain hydrophilic LA-based polymers? Can polyelectrolyte be synthesized from LA?

Generally, LA forms polymers through ester-bond connection. The labile lactate groups make LA-based polymers degradable [6,7]. The lactate sequences on the backbone of the polymers are quite long, which is the major reason why they are hydrophobic. On the other hand, the properties of the carboxyl groups of LA have completely disappeared after the polymerization of LA. Therefore, to retain or incorporate hydrophilic components and ionizable groups is one possible strategy to obtain hydrophilic LA-based polyelectrolyte.

Polyethylene glycol (PEG) is a water-soluble, flexible, non-toxic and biocompatible polymer [8]. It is often adopted to enhance the hydrophilicity of PLA [9]. Most of the obtained polymers are block copolymers of PLA and PEG. No carboxylic group is remained as well. Recently, we have prepared a water-soluble LA-based diacid (LEM) by using LA and PEG as raw materials. Then, LEM is applied

to generate a kind of hydrogel contained lactate units and PVA [10]. However, the amount of carboxylic groups remained in the hydrogel are limited.

There are two well-known facts which are useful for developing hydrophilic LA-based polymers. Firstly, biodegradable hydrogel is a kind of material which suitable for biomedical, pharmaceutical, environmental and other applications [11–13]. Moreover, the structure and properties of hydrogels are able to be manipulated by means of varying the polymer composition and controlling the cross-linking process [14]. Secondly, the outstanding characteristics of LA-based polymers are their renewable, non-toxic, biocompatible and biodegradable nature [15,16]. Obviously, the water-soluble property of lactic acid can be applied to prepare intelligent hydrogel, and it is a meaningful issue.

Actually, LEM is a macromonomer that contains carbon–carbon double bonds (C=C). It can form polymer and reserve numerous carboxylic groups by taking advantage of the reactivity of C=C. An unsaturated starch-based macromonomer has been chemically cross-linked with vinyl monomer to produce a gel bearing highly acidic groups in our lab [17]. Accordingly, radical cross-linking reaction between LEM and vinyl monomer pair is adopted to reach our goal. The experimental results are described as following, which indicates our idea is facile and practicable. To the best of our knowledge, no similar report has been found so far.

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2. Experimental part

2.1. Materials

Lactate-based macromonomer (LEM, number average molecular weight is ca. 7100) was prepared in our lab through the esterification between maleic anhydride and a diol derived from lactic acid (LA) and poly(ethylene glycol) (PEG) [10]. Potassium persulphate ($K_2S_2O_8$, Shanghai Chemical Agents Ltd. Co., China) was purified by recrystallizing from distilled water. Acrylic acid (AA) was purified by soaking with activated carbon. Itaconic acid (IA) and other agents were all purchased domestically and used as received as analytical grade reagents.

2.2. Synthesis of anionic lactate-based hydrogel

Lactate-based hydrogel was generated by free radical cross-linking reaction between LEM and AA/IA monomer pair. They were represented as LEMA, which was obtained in absence of IA, and LEMAI afterward. Briefly, the predetermined amount of LEM, AA and IA were dissolved in distilled water. The ratio of AA/LEM was fixed as 0.4:1 (wt/wt), and the ratio of IA/AA was changed as 0, 0.2, 0.5, 1 and 2 (wt/wt). Then, 0.02 g $K_2S_2O_8$ was added into the aqueous solution and mixed homogeneously. The mixture was kept at 60 °C for 4 h. A light yellow gel was formed. The crude gel was soaked with distilled water, and the solution was replaced with refresh water repeatedly to thoroughly remove the remained monomers and homopolymer of AA.

2.3. Characterizations

LEMA and LEMAI were powered, mixed with dry KBr and compressed into disks respectively. Fourier transform infrared spectra (FTIR) of the samples were recorded using a Nexus 470 FTIR spectrometer. Thermogravimetric analyses (TGA) of LEMAI were carried out with a TA instruments SDT 2960 simultaneous DSC-TGA analyzer. TGA was conducted over the temperature range from 25 to 800 °C with a programmed temperature increment of 10 °C/min under N_2 atmosphere. The Au-coated cross-sections of the gels were examined with a Hitachi S-3500 N scanning electron microscope (SEM). The glass transition temperatures (T_g) of the gels were determined using a Q800 dynamic mechanical thermal analysis (DMTA) instrument, which was performed over the temperature range from 90 to 90 °C with heating speed of 5 °C/min at 1 Hz.

2.4. Properties of anionic lactate-based hydrogel

The dried LEMAI pieces were weighed and successively placed in vials that contained 5 mL NaAc–HAc (pH 3.6), Na_2HPO_4 –NaOH (pH 11.5) and NaAc–HAc (pH 3.6) buffer solutions, and maintained at 37 °C for 24 h respectively. The samples were removed. After the surface liquid had been blotted up with filter paper, the samples were weighed. The swelling ratios (SR) of the gels were calculated as $SR = W_{wet}/W_{dry}$, where W_{wet} and W_{dry} were the weight of swollen and dry gels respectively. An average of triplicate measurements was taken.

One gram gel pieces were placed in 10 mL aqueous solution containing Pb^{2+} , Cu^{2+} or Ce^{2+} and were kept at 37 °C respectively. At predetermined intervals, 0.2 mL solution was sampled to analyze the concentration of metal ions with Shimadzu UV2450 UV–Visible spectrophotometer at 576, 725 and 253 nm respectively. The maximum adsorption wavelengths of the ions were measured by scanning their solutions. The adsorption capacities Q (mg/g) of the samples were calculated according to the formula

$Q = (C_0 - C)V/W_0$, where C_0 and C ($\mu\text{g/mL}$) were the initial and equilibrium concentration of the metal ion in the solution respectively, V was the volume (mL) of solution, and W_0 was the initial dry weight of the gel samples (g). The linear relationships between concentration (C) and absorbency (A) of metal ions were measured by UV spectrophotometry. The equations for lead, copper and cerium ions were $A = 1.5818C + 0.0283$ ($R^2 = 0.9981$), $A = 0.271C + 0.0012$ ($R^2 = 0.9998$, EDTA as chelator), and $A = 14.099C + 0.0296$ ($R^2 = 0.9992$) respectively.

The gels were weighed, placed in cuvettes that contained 10 mL phosphate-buffer saline (PBS, 0.1 M, pH 7.4), and maintained at 37 °C for 4 days. The samples were removed, rinsed with distilled water, dried at 60 °C and weighed. The weight loss percentages (WLP) were calculated as $WLP (\%) = (W_0 - W)/W_0 \times 100$, where W_0 and W were the initial dry mass of samples and their dry mass after degradation respectively. An average of triplicate measurements was taken.

3. Results and discussion

It is known that hydrogels are polymer networks which are capable of absorbing large amount of water and they are usually produced from hydrophilic polymers [18]. In view of LEM is a water-soluble unsaturated macromonomer, it may be a good candidate for preparing hydrogel. It is found that the gel is easily obtained through the radical cross-linking reaction between LEM and AA/IA monomer pair (Scheme 1). Moreover, a great amount of carboxyl groups are incorporated onto the backbone of the formed hydrogels. IA is an alpha-substituted acrylic acid, its first and second dissociation constants (PKa) are 3.84 and 5.55 respectively [19]. The PKa of polyacrylic acid is 4.7 [20]. Accordingly, IA is easier to be deprotonated than AA. On the other hand, AA is more easily to perform radical polymerization compared to IA. Thus, IA is utilized as a secondary cross-linker to provide the products more acidic groups.

Both the FTIR spectra of LEMA and LEMAI are similar to that of their precursor LEM (Fig. 1). The characteristic absorption bands of the hydroxyl groups appear around 3441 and 1356 cm^{-1} . It is found that the characteristic absorption peak of carbonyl group appears at 1735 cm^{-1} on the spectra of the samples. The characteristic peaks that appeared at 2882 and 1468 cm^{-1} are attributed to C–H, methyl or methylene groups. The stretching vibration of C–O bonds of the samples appears around 1106 cm^{-1} . FTIR analysis results suggest that the structures of lactate-based gels are as shown in scheme 1. The chemically cross-linked LEMA and LEMAI show higher thermal resistance than their precursor, LEM (Fig. 2). It is found that the remained fraction at 600 °C of LEM, LEMAI and LEMA are 0%, 9.0% and 18.5% respectively. The thermal stability is evidently enhanced, which also confirms that the hydrogel is obtained as expected. As AA is more active than IA, the cross-linking degree of LEMA is probably higher than that of LEMAI prepared under the same reaction condition. Consequently, the thermal stability of LEMA is higher than that of LEMAI.

The glass transition temperatures (T_g) of LEMA and LEMAI are 2.2 and 24.0 °C (Fig. 3) respectively. The T_g value of LEM obtained from differential scanning calorimetry is around –41 °C [10]. Though T_g values of the hydrogels and their precursor are measured by using different methods, it is still can be concluded that the T_g values of LEMA and LEMAI are higher than that of LEM. This result is consistent with the principle that T_g of cross-linked polymer is higher than that of linear one, and suggests the hydrogel is produced as designed. Interestingly, the T_g value of LEMA will be 48.0 °C after soaking in the saturated calcium chloride aqueous solution for 24 h. This phenomenon may be attributed to the anion-cation interaction [21] between the carboxyl groups of LEM and calcium ions.

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