Synthesis, Characterization, and Degradation Investigation of Water-Soluble β-Cyclodextrin-Based Epoxy Resins

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ABSTRACT: A series of β -cyclodextrin-based epoxy resins were synthesized with different epoxy equivalent weights. Their chemical structures were characterized with Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance Spectroscopy (NMR) examination. These epoxy resins were cured using L-arginine as a curing agent, and the degradation behavior of the cured

INTRODUCTION

Cyclodextrins (CDs), derived from enzymatic degradation of starch, are cyclic oligosaccharides composed of glucose units that are joined by α -1,4-glucosidic linkages. The most commonly used CD subtypes are α -CD, β -CD, and γ -CD, which consist of 6, 7, and 8 glucose units, respectively.^{1–4} These doughnut-shaped molecules have unique property to form inclusion compounds with a variety of guest molecules, ensuring their wide applications in the enantiomer separation and drug delivery system.^{5–8}

Like starch, CDs have a property that they are stable in basic media and hydrolyzable in acid media with the product of acidic hydrolysis being small saccharides like glucose.^{9,10} However, different from starch, CDs constituted a nonreducing oligosaccharide, which may keep stable in the absence of oxidants. For theses two reasons, CDs can be used as a precursor for preparing degradable epoxy resins.

Epoxy resins have been widely used as matrix of composite materials, surface coating, adhesives, and microelectronics.^{11–16} However, because the lack of thermal and basic/acidic degradability, it has made a heavy burden on our environment.¹⁷ In particular, in the use of composite materials, the epoxy resin has to be discarded together with reinforcement

resins was evaluated under different acidic buffer solutions at 37°C. The degradable behavior of such epoxy resins suggested potential applications as environment friendly materials. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1675–1683, 2012

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fiber after its service, which strengthened the impact on the environment. For this reason, it is a natural requirement to prepare degradable epoxy resins.

One way to prepare degradable epoxy resin was to use degradable precursors. Park developed a degradable epoxy resin from castor oil.¹⁸ Jin prepared another from epoxidized soybean oil and diglycidylether of bisphenol A.¹⁹ It was noticed that the degradation of oligosaccharide was more easily than abovementioned precursors, so it would be worthy to try a preparation of epoxy resin with oligosaccharides.

The goal of this study was to synthesize degradable epoxy resins using nonreducing oligosaccharide (β -CD). The chemical structure of β -CD is shown in Figure 1. The chemical structures have been characterized. The degradation behavior of the cured polymers was investigated. In view of their future biological application, L-arginine was particularly selected as a curing agent of the epoxy resins.

EXPERIMENTAL SECTION

Materials

β-CD, sodium hydride (NaH), and sodium hydroxide (NaOH) were purchased from Sinopharm Chemical Reagent Beijing. Allyl glycidyl ether (AGE) and *m*-chloroperoxybenzoic acid (mCPBA) were obtained from Aladdin reagent Shanghai. Anhydrous MgSO₄, *N*,*N*-dimethylformamide (DMF), cyclohexane, chloroform (CHCl₃), and ethanol absolute were supplied by Beijing Modern Eastern Finechemical. Before use, DMF and cyclohexane were dried over calcium hydride for 2 days and distilled before usage. β-CD

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Figure 1 Chemical structure of β -CD.

was dried at 90°C under vacuum to constant weight, and NaH was washed with dry cyclohexane.

Synthesis

Synthesis of heptakis [2,3-di-O-(3-allyloxy-2-hydroxy-propyl)]-β-CD (allyloxy-β-CD I)

Into a 100-mL flask equipped with a stirrer, thermometer, reflux condenser, and a pressure equalized dropping funnel, was charged 10.5 g of NaOH aqueous solution (20 wt %) and β -CD (2.838 g, 0.0025 mol). The mixture was stirred at 75°C to allow β -CD dissolved completely and subsequently cooled to 45°C. AGE (8.988 g, 0.0787 mol) was added gradually over 30 min, and then the mixture was stirred at 45°C for another 12 h to complete the reaction.

After the system was cooled to room temperature, it was diluted with 50 mL ethanol and was adjusted to neutral by introducing a solution of hydrochloride acid in ethanol. Subsequently, the mixture was distilled in a rotary vacuum evaporator to remove ethanol and water. The remaining product was diluted with another 50 mL of ethanol, and the precipitated sodium chloride was removed by filtration. The dissolved components were distilled to remove the low boiling point liquid leaving a light-yellowish, viscous transparent liquid, which was denoted as allyloxy- β -CD I. The reactions are shown in Scheme 1.

Synthesis of heptakis [2,3,6-tri-O-(3-allyloxy-2hydroxypropyl)]-β-CD (allyloxy-β-CD II)

To a suspension of NaH (3.6 g of NaH 70%, 0.105 mol) in DMF (30 mL) was added a solution of β -CD (2.838 g, 0.0025 mol) in DMF (20 mL) dropwise over a period of 1 h at 80°C. The mixture was stirred for additional 1 h and subsequently cooled to 50°C. AGE (8.988 g, 0.0787 mol) was added dropwise over a pe-

riod of 1 h, and the solution was stirred for additional 12 h for the reaction of substitution to occur.

After the reaction was completed, methanol (5 mL) was added dropwise to react with excess NaH. DMF and excess AGE were removed by evaporation under diminished pressure. The residue was diluted with 50 mL ethanol and was adjusted to neutral using a solution of hydrochloride acid in ethanol. Subsequently, the mixture was distilled in a rotary vacuum evaporator to remove ethanol and water. The remaining product was diluted with 50 mL of fresh ethanol, and the precipitated sodium chloride was removed by filtration. The dissolved components were distilled to remove the low boiling point liquid leaving a light-yellowish, viscous transparent liquid, which was denoted as allyloxy- β -CD II. The reactions are shown in Scheme 1.

Synthesis of β -CD-based epoxy resins (epoxy- β -CD)

Into a 250-mL flask, a homogeneous solution of mCPBA (12 g of mCPBA 75%, 0.05 mol) in 50 mL of CHCl₃ was loaded, into which a solution of allyloxy- β -CD I (6.832 g, 0.0025 mol) or allyloxy- β -CD II (5.886 g, 0.0017 mol) in 30 mL of CHCl₃ was introduced. The mixture was stirred at 30°C for 12 h during which white metachlorobenzoic acid was precipitated as a by-product of the reaction between mCPBA and allyloxy- β -CD. To maintain the system at a low viscosity, fresh CHCl₃ (up to 20 mL) was added during the subsequent reflux operation for 2 h.

After completion of the reaction, the mixture was distilled in rotary evaporator to remove $CHCl_3$. Water of 50 mL was introduced to dissolve the remaining product, and the precipitated metachlorobenzoic acid and excess mCPBA were removed by filtration. The dissolved components were distilled to remove water resulting in a colorless, viscous transparent liquid, which was denoted as epoxy- β -CD I or epoxy- β -CD II. The reactions are shown in Scheme 1.

Preparation of cured epoxy resins samples

The epoxy- β -CD was heated to 80° C under vacuum to remove air bubbles and moisture. Subsequently the epoxy- β -CD and L-arginine was mixed at 80° C with a stoichiometric amount, that is, 1 mol of —NH in L-arginine for 1 mol of epoxy in β -CD-based epoxy resins. The mixture was cured at 80° C for 2 h, 100° C for 2 h, and finally postcured at 120° C for 1 h.

Characterization

FTIR spectra were recorded on a Nexus 670 infrared spectrometer.

¹H and ¹³C nuclear magnetic resonance (¹H NMR and ¹³C NMR) characterization was carried out by



Scheme 1 Synthesis of β -CD-based epoxy resin.

Bruker AV600 NMR spectrometer using D_2O as a solvent and tetramethylsilane as an internal standard.

Differential Scanning Calorimetry (DSC) experiments were performed on a Thermal Analysis (TA) instruments Q100 differential scanning calorimeter under a N_2 atmosphere at a ramp rate of 10.0°C min⁻¹ for both heating and cooling.

Peel test was measured with the Instron 1121 tensile tester. Specimens were made by adhering two identical Polyethylene terephthalate (PET) membranes by the mixtures of epoxy- β -CD and L-arginine, with an interlayer of about 50-pm thick. After cured reaction, the final specimens were cut to the size of 15-mm wide and 100-mm long. A tension stress (peel force) is measured when the both layers are peeled off from each other at a speed of 100 mm min^{-1} using a peeling tape.

Degradation behavior

The degradation behaviors of the β -CD-based epoxy resin cured products in buffer solution (Tris–HCl



NaOH/H₂O

NaH/DMF

Scheme 2 Deprotonation of β -CD in NaOH/H₂O and NaH/DMF.

buffer, pH 2, 4, and 6 and phosphate buffer, pH 7.4) were measured. The samples $(40 \times 10 \times 2.0 \text{ mm}^3)$ were incubated in buffer solutions at 37°C with stirring. At the times of 6, 12, 18, 24, 30, 36, 42, and 48 h, the sample was washed in deionized water and dried in an oven to constant weight. A relative weight loss percentage (*W*%) after immersion of the samples was calculated from the following equation:

$$W\% = [(W_0 - W_t)/W_0] \times 100\%$$

where W_0 and W_t stand for initial and final weight after a specific immersion time, respectively.

RESULTS AND DISCUSSION

Synthesis and characterization

The allyloxy- β -CD was synthesized via ring-opening reaction between β -CD and AGE. It involved a nucleophilic substitution of β -CD on epoxy groups of AGE. β -CD reacted first with NaH or NaOH to form an oxygen anion, and then the active oxygen anion attacked the CH₂— of epoxy groups resulted in a $-O-CH_2$ — linkage. β -CD-based epoxy resins were prepared by the oxidation reaction between allyloxy- β -CD and mCPBA in CHCl₃.

In this work, two different reaction media (NaH/ DMF and NaOH/H₂O) were used for preparing the β -CD-based epoxy resins, as shown in Scheme 1. It could be seen that, β -CD had three kinds of hydroxyl groups in its D-glucose units, that is, C_6 —OH, C_2 —OH, and C_3 —OH with different reactivities: C_2 —OH was the most acidic, C_6 —OH the most basic, and C_3 —OH the medium [25]. In the NaOH/H₂O system, C_2 —OH and C_3 —OH would be deprotonated forming oxyanions, and their reactivity was higher than that of nondeprotonated C_6 —OH due to the fact that the steric hindrance was lowered by the enlarged distance between the oxyanions caused by electrostatic repulsion (shown in Scheme 2). In the NaH/DMF system, all C_6 —OH, C_2 —OH, and C_3 —OH could be deprotonated, so the C_6 —OH would have the highest reactivity for steric considerations.

The preparation in NaOH/H₂O system is easier than in NaH/DMF system and no organic solvent was used, for this reason this system is preferred for the preparation of low-substituted β -CD epoxy resin (epoxy- β -CD I), whereas NaH/DMF system should be used for the preparation of high-substituted β -CD epoxy resin (epoxy- β -CD II).

It was found that the AGE loading had serious effect on the water solubility of the product. The higher the AGE loading, the larger the water solubility. In the NaOH system, an AGE loading of at least 14 folds that of β -CD should be used to ensure a good water solubility of the product.

In the NaOH/H₂O system, the hydrolysis of AGE is inevitable, as shown in Scheme 3. However, the hydrolysis by-product, α -allyl glycerol ether, possessed a lower boiling point than the main-product, therefore could be removed by distillation.



Scheme 3 Hydrolysis reaction of AGE in NaOH/H₂O.

The degree of completion of the reaction was monitored by FTIR (Fig. 2). The epoxy groups on AGE reacted with hydroxyls of β -CD led to β -CD substituted by 3-allyloxy-2-hydroxypropyl, as a result the peak at 911 cm⁻¹ for epoxy groups was no longer showed up on trace a of Figure 2, and -C=Cfeature (1646 cm⁻¹) appeared. The β -CD-based epoxy resins were obtained after oxidation reaction. In the Trace b, the disappearance of peak at 1646 cm⁻¹ (-C=C) with the appearance of epoxy feature at 911 cm⁻¹ suggested the oxidation reaction was complete. The two traces in Figure 2 demonstrated qualitatively the successive preparation of β -CD-based epoxy resins.

The ¹H NMR spectrum c in Figure 3 was for epoxy-β-CD I. The allyloxy-β-CD I gave rise to identical spectrum as c between the chemical shifts 3.5 and 5.0 ppm, with differentiations in the range from 2.0 to 3.5 ppm and from 5.0 to 7.0 ppm shown in spectrum a and spectrum b, respectively, in Figure 3. For allyloxy- β -CD I, the features at 5.903 and 5.202-5.297 ppm in spectrum b were assigned to the protons on the double bonds ($-CH-CH_2$). After oxidative reaction with mCPBA, those features disappeared and new features at 2.717, 2.896, and 3.282 ppm in spectrum c standing for epoxy groups $(C_{11}-H \text{ and } C_{12}-H_2)$ appeared. During the oxidation reaction, the proton of C_1 on β -CD was not affected, for this reason, the ratio of the integral area for C_1 —*H* over that of C_{11} —*H* at 3.282 ppm could be used to estimate the number of epoxy groups formed. Taken Figure 4 as an example, the ratio of



Figure 3 ¹H NMR spectra of allyloxy- β -CD I and epoxy- β -CD I.

 C_{11} — H/C_1 —H was 2.13, this meant that 2.13 epoxy groups was attached per glucose unit. There were three possible reactive sites, C_2 —OH, C_3 —OH, and C_6 —OH on the glucose unit, however, the reactivities of the OH groups were not uniform. The sites C_2 —OH and C_3 —OH were much more reactive, because the OH groups on the two sites were deprotonated in the NaOH aqueous solution. The contribution from C_6 —OH was much smaller. All the possibilities were further showed by ¹³C NMR spectrum in Figure 4.

The chemical shifts of various carbons in Figure 4 are presented in Table I. For C_2 —OH and C_3 —OH, there were two possibilities: attached and not attached with epoxy groups. When attached, the structure is described by structural formula b in Figure 4. If not, the feature for C_2 and C_3 were not



Figure 2 FTIR spectra of allyloxy-β-CD and epoxy-β-CD.





Assignment	C ₁	C ₂	C ₃	C_4	C ₅	C ₆	
ppm Assignment ppm	102.7 C ₇ 72.1	70.5 C ₈ 68.9	81.5 C ₉ 71.7	81.2 C ₁₀ 62.7	77.9 C ₁₁ 51.6	60.1 C ₁₂ 44.9	

discerned and featured as C_{14} (as shown in structural formula a in Fig. 4). Despite their higher reactivity, the steric hindrance may prohibit from their complete reaction. Similarly, the reaction on C_6 —OH also had two possible ways, one was attached with an epoxy group, the feature C_6 was transformed to C_{13} ; and the other was to keep the OH groups intact with the chemical shift unchanged.

When the preparation was carried out in NaH/ DMF system, the product (allyloxy- β -CD II) was quite different from that in NaOH/H₂O system, as shown in the ¹H NMR spectrum (Fig. 5). The oxidation was similar, as evidence by the disappearance of the feature for double bonds (CH—CH₂; 5.910 and 5.192–5.298 ppm) and the appearance of those for epoxy groups (2.643, 2.809, and 3.166 ppm). The number of epoxy groups was also estimated by the ratio of integral area of C₁₁—H (3.166 ppm) over that of C₁—H, and a value of 2.91 was obtained. This value was a little smaller than the theoretical value of 3, and the reason was explained using ¹³C NMR spectrum below.

The ¹³C NMR spectrum for epoxy- β -CD II is shown in Figure 6, with the chemical shifts of various carbons listed in Table II.

If the C_6 —OH had not been substituted, a feature should have been observed at 60.1 ppm. The absence



Figure 5 1 H NMR spectra of allyloxy- β -CD II and epoxy- β -CD II.



Figure 6 13 C NMR spectrum of epoxy- β -CD II.

of that feature indicated the complete reaction at C₆. As a result, the C₂—OH and C₃—OH were partially substituted. The carbon atoms linked with intact hydroxy groups resulted in a feature at 73.4 ppm (denoted as C_{13}).

Characterization of cured epoxy-β-CD

Figure 7 depicts the FTIR spectra of epoxy- β -CD II (Trace a) and cured epoxy- β -CD II (Trace b). The cured product was obtained via the cured reaction between epoxy- β -CD II and L-arginine. In Figure 7(b), the disappearance of the peak at 911 cm⁻¹ suggested the cured reaction was almost complete. Different from epoxy groups in commercial Diglycidyl Ether of Bisphenol A (DGEBA) epoxy resins, epoxy groups in epoxy- β -CD possessed the more flexible segmental motion ability, which can improve the probability of collision between epoxy groups and amino groups in cured agent, so the curing reaction could almost be completed.

DSC thermograms of epoxy- β -CD were given in Figure 8. DSC curves of uncured products showed that the melting point of epoxy- β -CD I and epoxy- β -CD II were about 13.1°C and 17.3°C, respectively. DSC curves of all cured products had two distinct

TABLE II Chemical Shift (ppm) and Assignment of ¹³C NMR of Epoxy-β-CD II

I - J I							
Assignment	C1	C ₂	C ₃	C_4	C_5	C ₆	
ppm Assignment ppm	102.3 C ₇ 72.7	70.8 C ₈ 69.4	81.6 C ₉ 71.8	81.4 C ₁₀ 63.7	77.6 C ₁₁ 50.9	68.4 C ₁₂ 44.2	



Figure 7 FTIR spectra of epoxy- β -CD II and cured epoxy- β -CD II.

 $T_{\rm g}$ transitions ($T_{\rm g}$ 1 and $T_{\rm g}$ 2 values are listed in Table III), the lower of which indicated the motion of the AGE and L-arginine segments and the higher $T_{\rm g}$ indicated the motion of the β -CD macrorings, whose motion requires a relatively higher energy.

Figure 9 depicts the evolution of the peel force versus elongation at a speed of 100 mm min⁻¹. The peel curves exhibited three characteristic zones. An increase in the peel force was observed at the beginning, followed by a "steady-state" evolution, and then the peel force decreased. As given in Figure 9, the peel force of cured epoxy- β -CD I was higher than that of cured epoxy- β -CD II, which was attributed to the enhanced polarity and content of β -CD. First, the β -CD in epoxy- β -CD I because of multiple



Figure 8 DSC thermograms of epoxy-β-CD: (a) cured epoxy-β-CD II, (c) cured epoxy-β-CD I, (b) cured 50/50 w/w mixture of I and II, (d) epoxy-β-CD I, and (e) epoxy-β-CD II.



Figure 9 Peel force versus elongation curves for cured epoxy- β -CD: (a) cured epoxy- β -CD II, (c) cured epoxy- β -CD I and (b) cured 50/50 w/w mixture of I and II.

intact primary hydroxyl (C_6 —OH). Second, β -CD itself constituted a hollow structure, which was more readily to absorb polar species like PET membrane than nonpolar species. With a higher β -CD content, the absorb force became stronger.

Degradation behavior

The epoxy resins prepared from NaH/DMF and NaOH/H₂O systems were cured using L-arginine as curing agent. The cured resins were incubated in acidic buffer solutions for different lengths of time and their degradation behavior at 37° C was presented in Figure 10. The pH value of the solution was marked at the left-up corner of each figure, where the weight losses of three samples were compared: curve a presented the sample from NaH/DMF system, curve c from NaOH/H₂O system, and b stood for a 50/50 w/w mixture of above two.

It was clear that the higher the acidity of the solution (the lower the pH value), the faster the degradation rate. This provided an explanation of the degradation mechanism. β -CD could be hydrolyzed in acidic media and caused break of the α -1,4-glucosidic linkages resulted in small saccharides.

At given pH value, the sample from NaOH/H₂O system gave rise to the highest degradation rate, and that from NaH/DMF the lowest. This was attributed to their different β -CD contents. The sample from

TABLE III $T_{g}1$ and $T_{g}2$ Values of Cured Products

Sample	$T_{\rm g}1~(^{\circ}{\rm C})$	$T_{\rm g}2~(^{\circ}{\rm C})$
Cured epoxy-β-CD II (a)	-31	62
50/50 w/w mixture of I and II	-27	65
Cured epoxy-β-CD I (b)	-23	73

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Figure 10 Relative weight loss percentage against immersion time for cured epoxy-β-CD under variation of pH.

NaOH/H₂O system which possessed less epoxy groups and thus more β -CD content, for this reason, it displayed a higher degradation rate.

Also for the low content of epoxy groups, the sample from $NaOH/H_2O$ system had a lower degree of crosslinking, and thus was more easily swollen by the acidic media. This constituted another reason for its faster degradation.

 β -CD itself constituted a hollow structure, which was more readily to absorb polar species than non-polar species. As a result, the acidity of the liquid in the cavity would be lager than outside, and this also promoted the break of the bonds between glucose units.

CONCLUSIONS

A series of β -CD-base epoxy resins were synthesized having different epoxy equivalent weights. The structures of the resins and its precursors were confirmed by FTIR and NMR spectra. With the introduction of β -CD moieties into the skeleton, the

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resulting epoxy polymer cured with L-arginine exhibited excellent degradation behavior. This pronounced properties made it potential for environment friendly materials.

References

- Frank, V. D. M.; Tina, V.; Cornelus, F. V. N.; Wim, E. H. Biomacromolecules 2009, 10, 3157.
- Wolfram, S.; Joel, J.; Katrin, G.; Thomas, S.; Daniel, H.; Haruyo, S.; Kyoko, K.; Steven, M. S.; Takeshi, T. Chem Rev 1998, 98, 1787.
- 3. Jozsef, S. Chem Rev 1998, 98, 1743.
- 4. Hans, J. S.; Frank, H.; Volker, R. Chem Rev 1998, 98, 1755.
- 5. Kaneto, U.; Fumitoshi, H.; Tetsumi, I. Chem Rev 1998, 98, 2045.
- Paola, F.; Marco, L.; Elisabetta, M.; Gian, F. P. J Am Chem Soc 2004, 126, 4343.
- Ulf, S.; Christoph, S.; Carmen, A. L.; Asteria, L.; Francisco, O. E.; Angel, C.; Jose, B. M. Int J Pharm 2006, 312, 66.
- Liu, Y. Y.; Fan, X. D.; Hu, H.; Tang, Z. H. Macromol Biosci 2004, 4, 729.
- Fernando, O. C.; Cyril, R.; Brian, C.; Torben, E. P.; Mikael, B. J Am Chem Soc 2005, 127, 3238.
- Fernando, O. C.; Jeannette, B.; Line, S. L.; Mikael, B. J Org Chem 2005, 70, 7217.

- Francis, B.; Thomas, S.; Sadhana, R.; Thuaud, N.; Ramaswamy, R.; Jose, S.; Rao, V. L. J Polym Sci Part B: Polym Phys 2007, 45, 2481.
- Li, G.; Li, P.; Zhang, C.; Yu, Y.; Liu, H.; Zhang, S.; Jia, X. L. Yang, X. P.Xue, Z.; Ryu, S. Compos Sci Technol 2008, 68, 987.
- Mustapha, E. G.; Abderrahim, E. B.; Salah, E. H.; Mohamed, R.; Ahmed, E. H. Polym Degrad Stabil 2009, 94, 2101.
- 14. Xu, K.; Chen, M. C.; Zhang, K.; Hu, J. W. Polymer 2004, 45, 1133.
- 15. Espinosa, M. A.; Galià, M.; Cádiz, V. Polymer 2004, 45, 6103.
- 16. Pan, G.; Du, Z.; Zhang, C.; Li, C.; Yang, X.; Li, H. Polymer 2007, 48, 3686.
- 17. Lukaszczyk, J.; Jaszcz, K. Macromol Chem Phys 2002, 203, 301.
- Park, S. J.; Jin, F. L.; Lee, J. R. Macromol Chem Phys 2004, 205, 2048.
- Jin, F. L.; Park, S. J. Mater Sci Eng A—Struct Mater Prop Microstruct Process 2008, 478, 402.
- 20. Abdul, R. K.; Peter, F.; Keith, J. S.; Valerian, T. D. Chem Rev 1998, 98, 1977.