Synthesis of Polysiloxane–Polyester Copolymer by Lipase-Catalyzed Polycondensation

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ABSTRACT: Polysiloxane–polyester copolymers have been synthesized for the first time by direct polycondensation of a series of diacids (butanedioic, hexanedioic, and octanedioic acid) and α,ω-bis(3-hydroxypropyl) polydimethylsiloxanes catalyzed with Novozyme-435 in high yields (>90%) without the cleavage of Si—O bonds. The effects of monomer chain length, reaction temperature, and water removal method on the number–average molecular weight (M_n) of the resulted copolymers were investigated. Thermogravimetric and differential scanning calorimetry analyses indicated that the produced copolymer was more thermally stable than poly(1,8-octyladipate) and the T_g was lowered to −111°C. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1901–1907, 2008

Key words: polysiloxanes; polycondensation; enzymes

INTRODUCTION

Polydimethylsiloxane (PDMS) has been extensively studied for its unique properties, such as excellent thermal, oxidative and UV stability, low glass transition temperature (T_g), strong hydrophobicity, and low surface energy.[1–7] The introduction of PDMS will bring improved clarity, surface smoothness, nonsticking properties, hydrophobicity, and thermal stability to the resulting copolymers.[8–10] PDMS-containing copolymers with improved characteristics have been widely used in thermoplastic elastomers, water repellents, lubricants, surfactants, and so on.[11–14]

The said polysiloxane–polyester copolymer is a kind of novel multiblock copolymer containing PDMS connected with ester units. Generally, esters are synthesized by condensation catalyzed with acid, base, or organometallic catalysts.[15,16] The use of a chemical catalyst usually requires harsh reaction conditions such as high temperature (>190°C) and makes the side reactions more uncontrollable.[17–21] These reaction conditions may destroy Si—O bonds.[22] So, the synthesis of polysiloxane–polyester copolymer is still a great challenge. Previous studies indicate that polyesters could be synthesized by lipase-catalyzed polycondensation of diacid and diol monomers.[23–32] Tanaka et al. studied the lipase-catalyzed synthesis of organic silane.[33–35] Polymers containing organosilicones, different from the polysiloxane-polyester copolymer herein, were also prepared by enzyme-catalysis.[36,37] Gross and coworkers[38] have reported the esterification of α,β-ethylglucoside and 1,3-bis(3-carboxypropyl) tetramethyldisiloxane with Novozyme-435. These results suggest that polycondensation under mild conditions with lipase as the catalyst may be used to synthesize polysiloxane–polyester copolymer without Si—O bond cleavage. And to the best of our knowledge, synthesis of polysiloxane–polyester copolymer by lipase-catalyzed polycondensation has not been reported.

In this article, we present the synthesis of polysiloxane–polyester copolymers by polycondensation of a series of diacids and α,ω-bis(3-hydroxypropyl) PDMS with Novozyme-435, and the thermal properties analyses of the copolymers.

EXPERIMENTAL

Materials

1,1,3,3-tetramethyldisiloxane (TMDS), octamethylcyclotetrasiloxane (D_4), and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) were purchased from Chenguang Second Chemical Factory and purified by fractionation. Diacids (butanedioic, hexanedioic, and octanedioic acid) were purchased from Beijing Chemical Reagents Company and used as received. Other chemicals were purchased from Beijing Chemical Works. Allyl alcohol was dried with anhydrous magnesium sulfate. Hexane was distilled from deep purple solution of sodium benzophenone. Chloroform was used as received. Novozyme-435 was a product of Novozymes (Denmark).[39]

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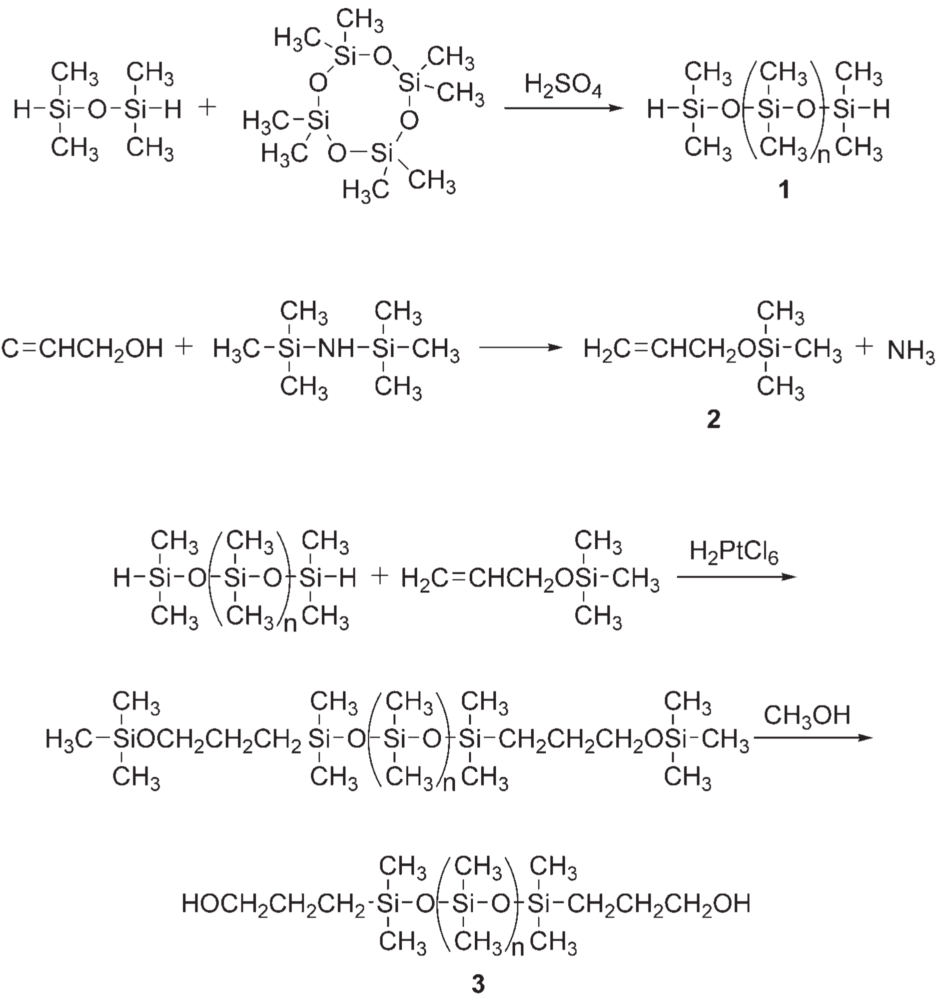


1a, 3a: n=4

1b, 3b: n=8

Scheme 1 The synthesis route of monomer.

Measurements

^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra were recorded in $CDCl_3$ solutions with a Bruker WM 300 spectrometer. The chemical shifts in parts per million (ppm) were referenced relative to tetramethylsilane (TMS). Parameters of ^{29}Si-NMR: number of scans is larger than 500, pulse sequence is zgdc, and time interval between successive accumulations is 2 s.

The molecular weights of the polymer samples were determined by gel permeation chromatography (GPC) with Waters 515 HPLC pump, Waters 2410 refractive-index detector, and Waters Styragel columns (HT4). Toluene was used as the eluent at a flow rate of 1.0 mL/min at 40°C. Monodispersive polystyrene standard samples were employed for molecular weight calibration. The degree of polymerization (DP) of the copolymer was calculated from the number–average molecular weight (M_n).

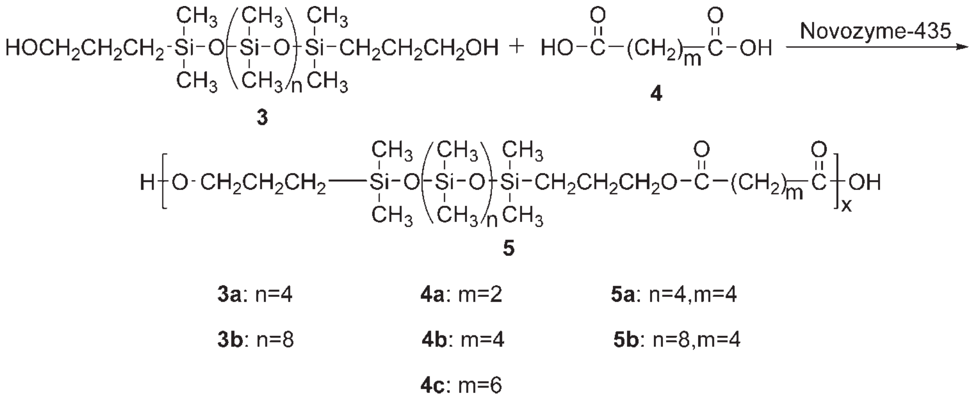
Thermogravimetric (TG) analyses were carried out on a Perkin-Elmer Pyris 1 instrument at a heating rate of 10°C/min under flowing nitrogen. Differential scanning calorimetry (DSC) experiments were performed on a Mettler Toledo 822e instrument under nitrogen at a heating rate of 10°C/min.

Synthesis of monomers

The synthesis route of α,ω-bis(3-hydroxypropyl) polydimethylsiloxane is shown in Scheme 1.

Synthesis of α,ω-dihydrogen polydimethylsiloxane (**1a** and **1b**)

To stirred TMDS (0.25 mol) and D_4 (0.25 mol for **1a**, 0.5 mol for **1b**) was added 98% sulfuric acid (2.5 mL for **1a**, 5 mL for **1b**) and stirred at room temperature.



Scheme 2 The lipase-catalyzed polycondensation.

After 6 h, water (10 mL for **1a**, 25 mL for **1b**) was added and stirred for about 12 h. Raw product was rinsed by water until it became neutral and dried with anhydrous magnesium sulfate. After filtration, the filtrate was vacuumed at 80°C and gave pure product.

1a (yield 82%). ^{1}H—NMR (δ, ppm): 4.71 (m, Si*H*), 0.19 [d, OSi(CH_3)$_2$H], 0.08 [m, OSi(CH_3)$_2$O]. ^{29}Si-NMR (δ, ppm): −5.8 (*Si*H), −18.8 [O*Si*(CH$_3$)$_2$OSi(CH$_3$)$_2$H], −20.8 [OSi(CH$_3$)$_2$O*Si*(CH$_3$)$_2$OSi(CH$_3$)$_2$O].

The ^{1}H- and ^{29}Si-NMR spectra of **1b** (yield 88%) are similar to those of **1a**.

Synthesis of (allyloxy) trimethylsilane (**2**)

HMDS (1.5 mol) was added dropwise to stirred allyl alcohol (2.5 mol) under 50°C. After the addition completed, the mixture was then stirred for 4 h at 50°C. Fractionation was employed to give pure product (yield 81%).

^{29}Si-NMR (δ, ppm): 20.1 [s, O*Si*(CH$_3$)$_3$].

Synthesis of α,ω-bis(3-hydroxypropyl) polydimethylsiloxane (**3a** and **3b**)[40–42]

Compound **1** (0.2 mol) was slowly added at 90°C to compound **2** (0.5 mol) containing a catalytic amount of H_2PtCl_6. After the addition completed, the mixture was then stirred for 10 h at 120°C. The mixture was treated with activated charcoal to remove colored impurities and the catalyst, and then filtered. The filtrate was mixed with 600 mL methanol and vigorously stirred for 6 h at ambient temperature. Rotary evaporation was employed to give product **3**.

3a (yield 88%). ^{1}H NMR (δ, ppm): 3.59 (m, CH_2OH), 1.91 (s, O*H*), 1.59 (CH_2CH$_2$OH), 0.53 (m, SiCH_2), 0.04–0.16 (m, SiCH_3). ^{13}C NMR (δ, ppm): 66.1 (CH$_2$OH), 27.2 (CH$_2$CH$_2$OH), 14.7 (SiCH$_2$), 0.8-2.5 (SiCH$_3$). ^{29}Si-NMR (δ, ppm): 7.9 (*Si*CH$_2$), −21.3 [O*Si*(CH$_3$)$_2$OSi(CH$_3$)$_2$ CH$_2$], −21.9 [OSi(CH$_3$)$_2$O*Si*(CH$_3$)$_2$OSi(CH$_3$)$_2$O].

The ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra of **3b** (yield 86%) are similar to those of **3a**.

General procedure for lipase-catalyzed polycondensation

Scheme 2 shows the reaction of the lipase-catalyzed polycondensation.

Water removal by vacuum

To a 50 mL round-bottom flask equipped with a magnetic stirrer was charged compound **3** (5 mmol), diacid **4** (5 mmol), and Novozyme-435 beads (10% w/w relative to monomers, dried at room temperature/5 mmHg/24 h). The reactions were performed at constant temperatures in bulk. After the first 6 h of the reaction, vacuum was exerted to remove water. Product samples were taken at selected time intervals (15 min, 30 min, 2 h, 4 h, 8 h, 12 h, 24 h, 36 h, and 48 h) and analyzed by GPC. The polymerization was terminated after 48 h by adding excess chloroform, and the enzyme was removed by filtration. The solvent was then evaporated by rotary evaporator to obtain the product (yield $> 90\%$).

Water removal by Dean-Stark trap

To a 100 mL round-bottom flask equipped with a magnetic stirrer and Dean-Stark trap was charged **3a** (10 mmol), **4b** (10 mmol), 70 mL hexane, and Novozyme-435 beads (10% w/w relative to monomers, dried at room temperature/5 mmHg/24 h). The reaction was then continued at reflux temperature. The produced water was removed azeotropically from the Dean-Stark trap. The polymerization was terminated after 48 h by adding excess chloroform, and the enzyme was removed by filtration. The solvent was then evaporated by rotary evaporator to obtain the product (yield, 91%).

RESULTS AND DISCUSSION

The studied monomers include three diacids (butanedioic, hexanedioic, and octanedioic acid) and two

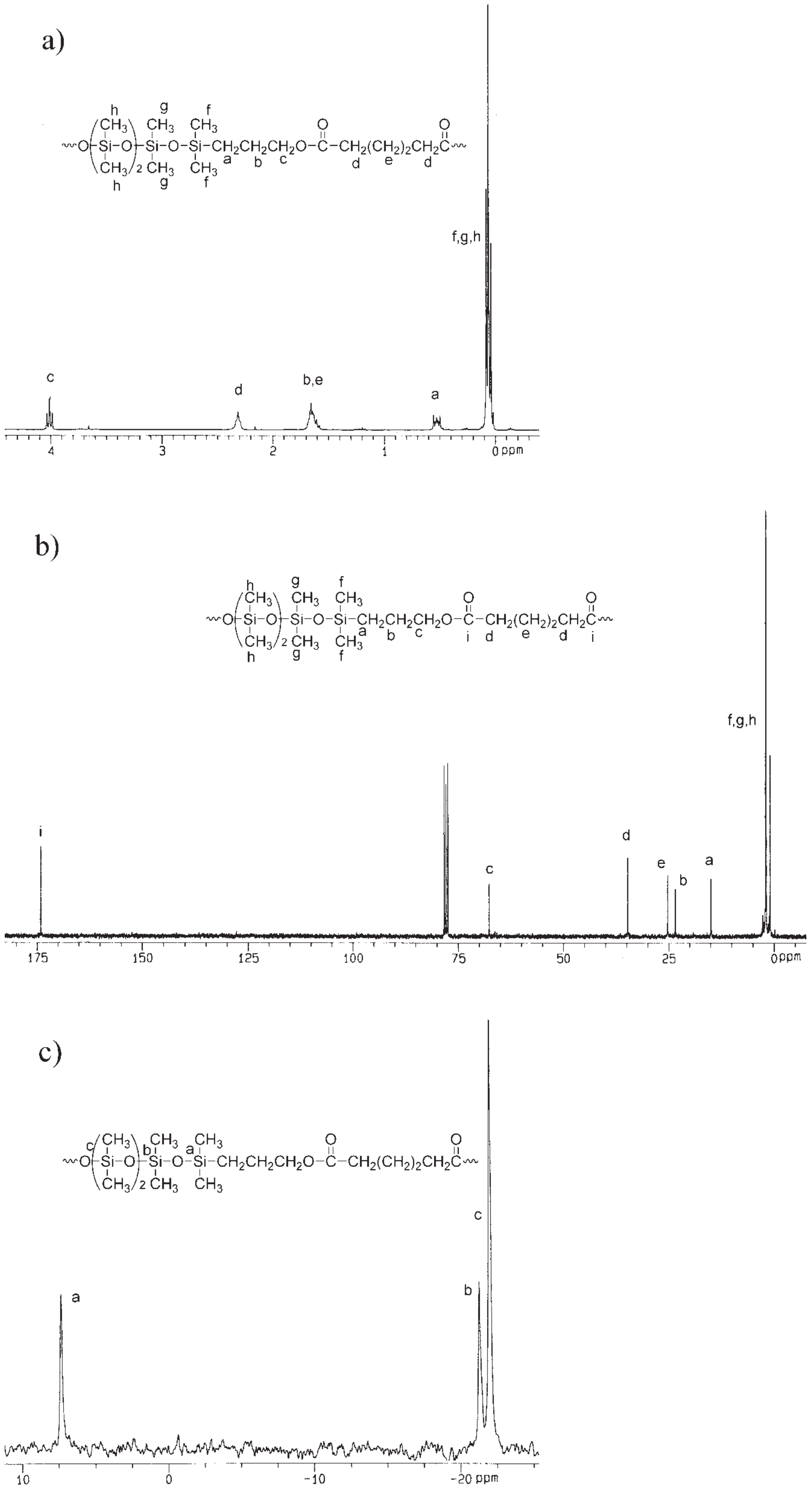


Figure 1 (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{29}Si-NMR spectra of the polysiloxane–polyester copolymer synthesized form **3a** and **4b** in bulk under vacuum (90°C, 1% w/w catalyst/monomer).

α,ω-bis(3-hydroxypropyl) polydimethylsiloxanes with different siloxane chain lengths (**3a** and **3b**). The synthesis route of the monomers is shown in Scheme 1. Allyl alcohol was protected by HMDS and hydrosilated with α,ω-dihydrogen polydimethylsiloxane from TMDS and D_4, and then alcoholysis was used to get α,ω-bis(3-hydroxypropyl) polydimethylsiloxane. Polycondensations (Scheme 2) were carried out under vacuum (in bulk) or with a Dean-Stark trap (in hexane) to remove water. Different reaction temperatures (50, 70, and 90°C) were also examined. The progress of polymerization was monitored by GPC. The polymer dispersities (PDIs) of the copolymers were 1.4–2.1, and independent of the reactants and reaction conditions. Nuclear Magnetic Resonance (NMR) was used to characterize the structures of products. TG and DSC analyses were employed to study the thermal stabilities of the copolymers.

The structure of polysiloxane–polyester copolymer was confirmed by ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra (Fig. 1). Three signals of ^{29}Si appeared at the same positions, respectively, in Figure 1(c) as the ^{29}Si-NMR spectrum of **3a**, which indicated that decomposition or redistribution of polysiloxane did not occur. So, polysiloxane–polyester copolymer was successfully prepared by lipase-catalyzed polycondensation.

Effect of monomer chain length on degree of polymerization

The Novozyme-435 catalyzed polycondensations of **3a** with diacids (butanedioic, hexanedioic, and octanedioic acid) were carried out in solvent-free systems. Polymer samples were taken from the reactions at 15 min, 30 min, 2 h, 4 h, 8 h, 12 h, 24 h, 36 h, and 48 h, respectively. The results are shown in Figure 2. The DP of the products enhanced with the increase of reaction time. It is noted that, with the increase of the chain length of diacid, the DP of product increased (**4c** > **4b** > **4a**), though the difference was not large. This is due to the fact that the diacid with longer methylene chain is more hydrophobic. It is consistent with previous studies.[28–30,43]

Figure 3 shows the DP of copolymer as a function of time when α,ω-bis(3-hydroxypropyl) polydimethylsiloxane chain length was different. Reactions of **4b** with **3a** or **3b** were carried out at 90°C in bulk. Figure 3 indicates that, during the initial 2 h of the reaction, **3a** showed higher reactivity than **3b**. It's due to the compound **3a**, as it is smaller molecule than **3b** and moves more freely than **3b**. After that, more rapid polymerization of **3b** was observed. At 48 h, the reaction product of **3b** and **4b** gave much higher DP than that of **3a** and **4b**. This may be reasoned by the hydrophobicity of the monomers. More hydrophobic monomer (**3b**) can facilitate the polycondensation and produce longer chain product. Similar phenomenon was also observed in the lipase-catalyzed polycondensation of diacids and diols.[28–30,43]

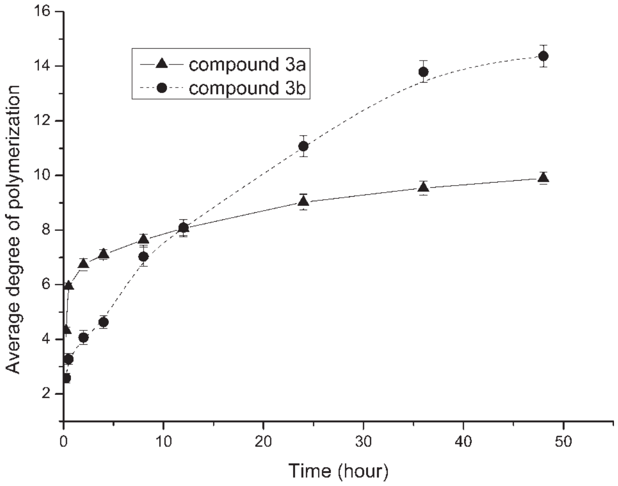


Figure 3 Effect of α,ω-bis(3-hydroxypropyl) polydimethylsiloxane on DP (compound **3**/hexanedioic acid, in bulk with vacuum, 90°C, 1% w/w catalyst/monomer).

Effect of reaction temperature on number–average molecular weight (M_n)

Temperature has great effect on the activity and stability of a biocatalyst and the thermodynamic equilibrium of a reaction as well. The polycondensations of

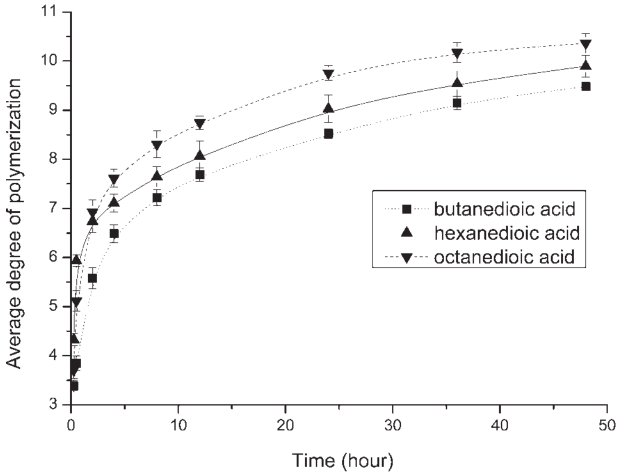


Figure 2 Effect of diacid on DP (diacid/**3a**, in bulk with vacuum, 90°C, 1% w/w catalyst/monomer).

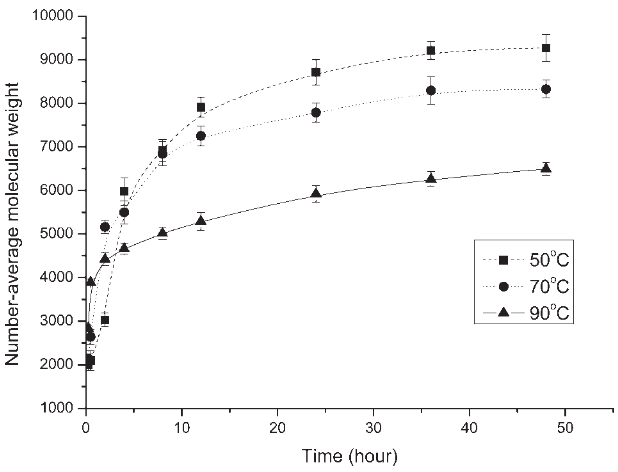


Figure 4 Effect of reaction temperature on M_n (**3a**/**4b**, in bulk with vacuum, 1% w/w catalyst/monomer).

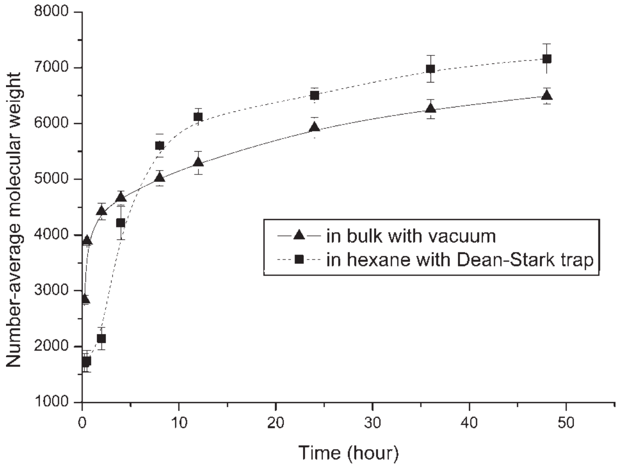


Figure 5 Effect of water removal method on M_n (**3a**/**4b**, 90°C, 1% w/w catalyst/monomer).

4b and **3a** were performed at different temperatures (50, 70, and 90°C) and the polymerization below 50°C was not carried out because of the high viscosity of the reaction system. As shown in Figure 4, at the beginning of the reactions, high temperature was helpful to speed polycondensation reaction (90°C > 70°C > 50°C). This is due to the higher activity of the reactants at higher temperature. However, as reaction proceeded, lower temperature was preferred to give high M_n product (50°C > 70°C > 90°C). It can be attributed to the denaturation of the enzyme and increased water activity (a_w) at high temperature. As mentioned in some previous studies, 50°C is the optimum temperature for the nonaqueous esterification reactions catalyzed by Novozyme-435,[44,45] which matches well with the result herein. The equilibrium of polycondensation is influenced by the water formed during the reaction as a byproduct. Park et al.[46] studied the effect of temperature on a_w in the reaction of Novozyme-435 catalyzed esterification and observed higher a_w at elevated temperature. So, low reaction temperature facilitates esterification. Therefore, enzyme catalyzed reaction at the lowest temperature (50°C) gave the highest M_n (9300 g/mol). There are some other works that got different results.[29,31] We think it is because of the difference of the reaction systems.

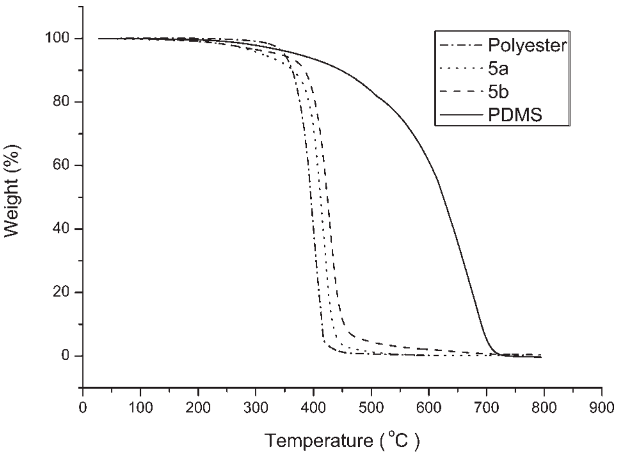


Figure 6 The TG curves of poly(1,8-octyladipate), **5a, 5b**, and **PDMS**.

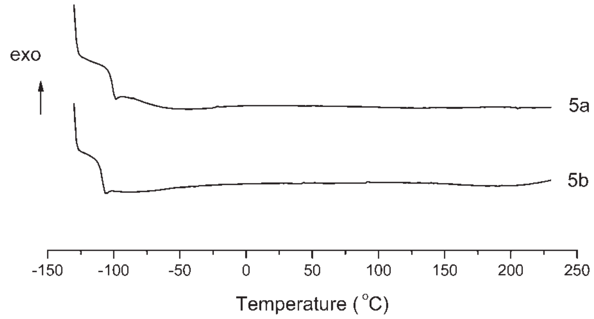


Figure 7 The DSC curves of **5a** and **5b**.

Effect of water removal method on number–average molecular weight (M_n)

In polycondensation, the removal of generated water is very important to drive the formation of long chain product. Two methods, Vacuum and Dean-Stark trap, were employed for removing water. As shown in Figure 5, initially, the reaction in bulk under vacuum showed an advantage over that in hexane with the Dean-Stark trap in polymer forming, which is due to the higher concentration of reactants in bulk than that in solvent. After that, polymerization in hexane was faster than that in bulk and gave higher M_n product. This is because water is easier to remove by Dean-Stark trap and chains move more free in hexane than in bulk.

Thermal analysis of the copolymer

Thermal properties of polysiloxane–polyester copolymer were investigated by TG and DSC (Figs. 6 and 7) and the results are shown in Table I. The thermal stabilities of **5a** and **5b** are discussed and compared with those of poly(1,8-octyladipate) and PDMS by three parameters: the onset temperature of thermal degradation (T_{onset}), the midweight loss temperature ($T_{0.5}$), and the peak temperature of derivative ther-

TABLE I
Thermal Properties of Poly(1,8-octyladipate), 5a, 5b, and PDMS

Sample	T_{onset} (°C)	T_p (°C)	$T_{0.5}$ (°C)	T_g (°C)
Poly(1,8-octyladipate)[a]	371	400	396	–
5a	388	421	412	−103
5b	399	428	424	−111
PDMS	556	684	625	−123

[a] Melting range: 69.1–71.0°C.

mogravimetry curve (T_p). The results show that the existence of polysiloxane enhanced the thermal stability of the produced copolymer, and it was more significant as the siloxane chain length increased. DSC measurements indicated that the produced polysiloxane–polyester copolymers had very low T_g which tended to decrease as the siloxane chain length increased.

CONCLUSIONS

With Novozyme-435 as the catalyst, polysiloxane–polyester copolymer was successfully synthesized by polycondensation of α,ω-bis(3-hydroxypropyl) polydimethylsiloxane and diacid in solvent or solvent-free system without polysiloxane destroyed. The yields of the produced copolymers were higher than 90%. The DP of the copolymers increased when the monomers with longer chains. And a lower temperature (50°C) was preferred for obtaining high M_n copolymers. Higher M_n product was obtained by polycondensation in hexane with Dean-Stark trap to remove water than that in bulk with vacuum. TG analysis showed that polysiloxane–polyester copolymer was more thermally stable than poly(1,8-octyladipate), and the longer the siloxane chain was the more thermally stable the copolymer was. The produced copolymers also had low T_g.

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