Biocatalytic Synthesis of Organosiloxane Copolyimide

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Introduction. Biocatalytic synthesis of polymers[1,2] is of great importance in making functional materials under environmentally benign conditions. Enzyme-mediated synthesis has several advantages which include environmental compatibility, economical synthesis, ease of processability, and stability. Synthesis of polymers using lipase-catalyzed (*Candida antarctica*) polymerization reactions has led to a variety of new materials with interesting properties.[3] We have recently shown that lipase-catalyzed syntheses of siloxane-based organic−inorganic hybrid polyesters and polyamides have great potential as flame-retardant (FR) materials.[4] The thermal and flame-retardant properties of these polymers were further improved by cross-linking techniques using hexamethylenetetramine as a cross-linker.[5] However, the decomposition temperatures (390−400 °C in air atmosphere) of these polymers are lower compared to well-known FR polymers which have a decomposition temperature in the range 500−550 °C,[6] and thus there is a need to improve the thermal stability. Polyimides in general have high thermal stability and as a result have found numerous applications as engineering plastics, high strength composites, thermally stable films, molding compounds, and adhesives. Polyimides are also known for their good oxidative and hydrolytic stability in addition to thermal stability. It is very well-known in the literature that conventional polyimide preparation involves initial formation of a polyamide/polyamic acid, followed by ring closure to form a polyimide.[7] Formation of a stable five-membered ring is the driving force for forming linear rather than cross-linked polymer. In most cases, the intermediate polyamide/polyamic acid is insoluble, and the second step must be carried out by solid-state cyclization reaction at high temperature. Previously reported copolyimides with siloxane moieties showed excellent adhesive and thermal properties compared to other aromatic polyimides.[8] Biocatalytic synthesis of polyimides is a promising new alternative to traditional chemical routes in that it offers a more facile and environmentally friendly approach. In this Communication, we present the biocatalytic synthesis of a siloxane copolyimide using aminopropyl-terminated polydimethylsiloxane and 4,4′-oxydiphthalic anhydride in the presence of lipase as a biocatalyst without using any solvent. To confirm the role of the lipase as a catalyst to driving the reaction to imide formation, the biocatalytically synthesized polyimide was compared with the same polyimide synthesized without the biocatalyst. The synthesis and resulting polymer properties will be discussed.

Experimental Section. a. Materials. Novozyme-435, an immobilized enzyme from Novozymes, Denmark, was used as the biocatalyst. All other chemicals and solvents (Aldrich) were used without further purification. Aminopropyl-terminated polydimethylsiloxane (M_w 900−1000) was purchased from Gelest Inc. 4,4′-Oxydiphthalic anhydride was purchased from Aldrich. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 250 MHz ARX spectrometer equipped with a Silicone Graphics workstation. Gel permeation chromatography (GPC) was used to determine the molecular weights and molecular weight distributions, M_w/M_n, of polymer samples.

b. Polymer Preparation. In a simple procedure (Scheme 1), equimolar amounts of previously dried 4,4′-oxydiphthalic dianhydride (OxyDAH) and aminopropyl-terminated polydimethysiloxane (M_w 900−1000) were placed in a three-neck round-bottom flask. After stirring the monomers for 10 min under a nitrogen atmosphere, 10 wt % of the enzyme Novozyme-435 (immobilized *Candida antarctica* lipase B, protein content 1%) with respect to the weight of the monomers was added. The resulting reaction mixture was stirred at 90 °C under vacuum. After 8 h, the reaction mixture was completely viscous and stopped stirring. The reaction was cooled to room temperature and quenched by adding chloroform and then filtered to remove the enzyme. The solvent was then removed under reduced pressure, and the polymer residue was washed with hexane to remove any unreacted monomers and dried under vacuum to obtain siloximide in 80% yield, which was confirmed by various spectroscopic techniques.

^{1}H NMR ($CDCl_3$): δ = 0.10 (bs, methyl protons of dimethylsiloxane main chain, C-l), 0.64 (t, 2H, C-i), 1.73 (m, 2H, C-h), 3.70 (t, 2H, C-g), 7.40 (dd, 2H, C-e, C-f), 7.47 (d, 2H, C-c and C-d), 7.90 (d, 2H, C-a and C-b). ^{13}C NMR ($CDCl_3$): δ = 0.76, 15.11, 22.32, 40.87, 113.32, 123.80, 125.21, 127.46, 134.78, 160.62, 167.0. M_n (GPC): 75 kDa, PD 1.4.

In the nonenzymatic reaction, the above procedure for enzymatic synthesis was followed except that enzyme was not added. A typical reaction was carried out simply by mixing the amino-terminated PDMS and the corresponding anhydride and heating the reaction mixture at 90 °C under vacuum for 8 h. The polymer siloximide-NE obtained with this simple method without using enzyme was similar to the product obtained enzymatically, except that it seemed to undergo an intermediate step forming polyamic acid. The reaction was monitored by ^{1}H NMR spectroscopy. The details are discussed in the Results and Discussion section.

^{1}H NMR of siloximide-NE ($CDCl_3$): δ = 0.10 (bs, methyl protons of dimethylsiloxane main chain, C-l), 0.64 (t, 2H, C-i), 1.73 (m, 2H, C-h), 3.70 (t, 2H, C-g), 7.40 (dd, 2H, C-g), 7.47 (d, 2H, C-e), 7.90 (d, 2H, C-h). Extra peaks: 7.61−7.64 (m), 8.12−8.17 (d)

Results and Discussion. To date, we have biocatalytically synthesized three types of siloxane-based copolymers, namely, polyesters, polyamides, and polyimides. The synthesis of the copolyamides and polyesters was reported earlier.[3,4] This is the first report of the biocatalytic synthesis of a polyimide. Here copolyimide with OxyDAH monomer and aminopropyl-terminated siloxane was synthesized biocatalytically using Novozyme-435 as the biocatalyst. It is interesting to note that

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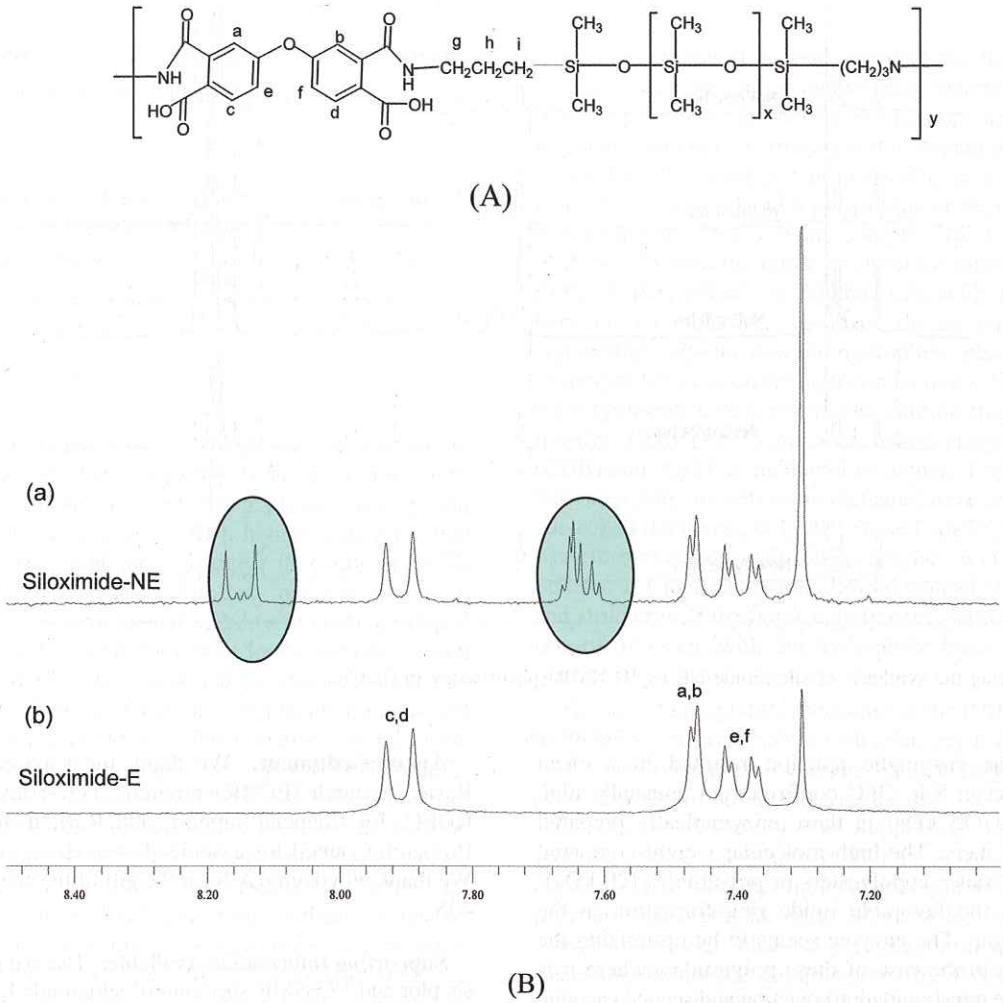
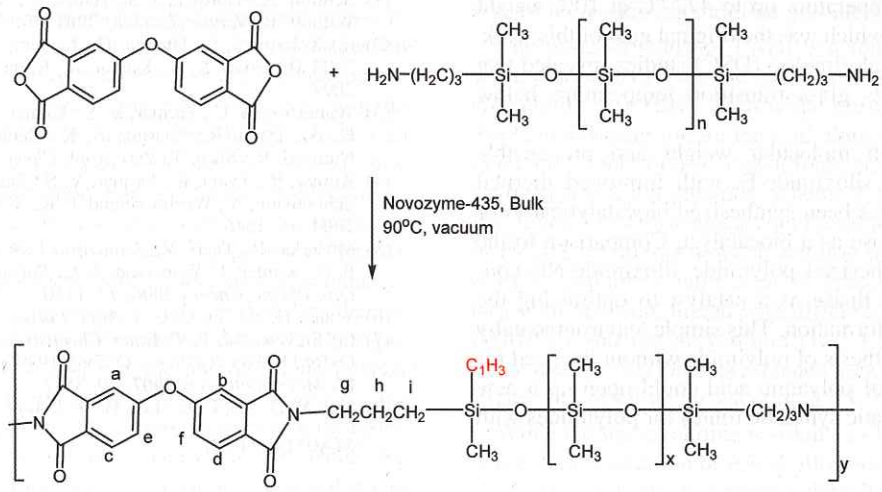


Figure 1. (A) Structure of siloximide-NE in polyamic acid form. (B) Aromatic region of ^{1}H NMR spectra in $CDCl_3$ (a) siloximide-NE and (b) siloximide-E.

Scheme 1. Enzymatic Synthesis of Siloxane Copolyimide, Siloximide-E



in our enzymatic synthetic approach the cyclization takes place in situ and gives rise to a clean linear polyimide product without any further heating, which has been confirmed by NMR spectroscopy. The polyimide preparation using aminopropyl-terminated polydimethylsiloxane and 4,4′-oxydiphthalic anhydride (Scheme 1) without enzyme gave a partially soluble polymer, siloximide-NE. That implies formation of polyamic acid instead of imide directly. However, the enzymatic synthesis gave a soluble polyimide (siloximide-E), and no further purification was necessary. The ^{1}H NMR spectral comparison of the polyimides prepared using enzyme and without enzyme is shown in Figure 1.

The extra peaks at 7.61 and 8.12 ppm in aromatic region (highlighted in Figure 1Ba) confirm the contamination of the product with polyamide/polyamic acid. This demonstrates that lipase (Novozyme-435) is playing a crucial role as a catalyst driving the reaction to imide formation which otherwise is not possible under nonenzymatic conditions. Monitoring of the nonenzymatic reaction (Figure 2) revealed that, even after 24 h of reaction, the product was a mixture of polyimide and amic

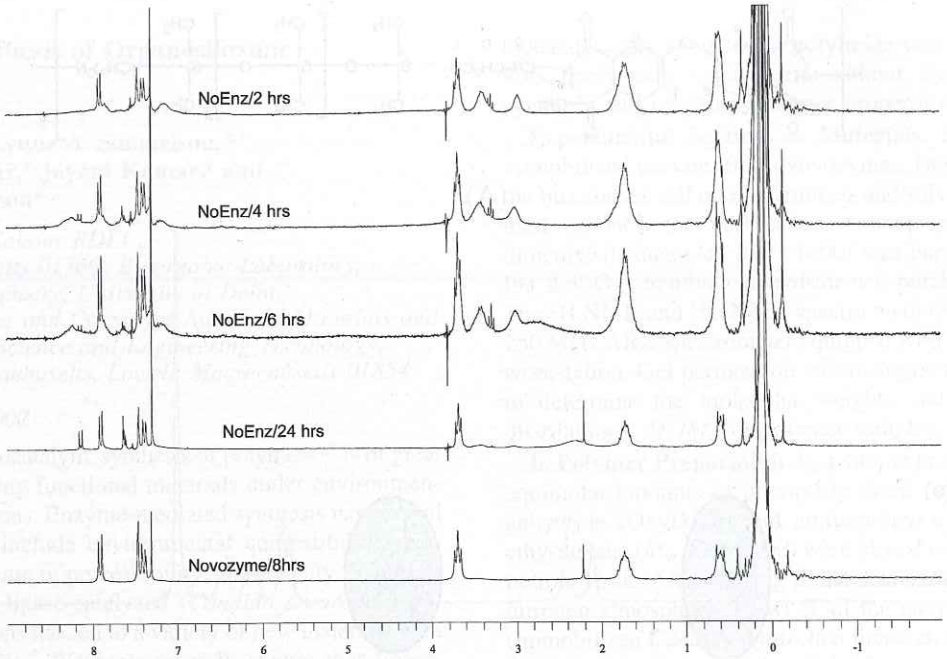


Figure 2. Monitoring the synthesis of siloximide-NE by ^{1}H NMR spectroscopy in $CDCl_3$.

acid, whereas the enzymatic reaction resulted in a clean polyimide product in 8 h. GPC confirmed an unusually high molecular weight (75 kDa) in these enzymatically prepared polysiloxane polymers. The high molecular weight compared to our earlier siloxane−copolyesters or polyamides (20 kDa)[4] could be due to the favorable imide ring formation in the presence of enzyme. The enzyme seems to be optimizing the two-step reaction in the case of these polyimides, where it is first catalyzing the trans(amidation) reaction and second carrying out the imidation with the adjacent COOH groups. The thermogravimetric analysis (TGA) measurements on the siloximide-E (Supporting Information) showed a significantly improved degradation temperature up to 472 °C at 10% weight loss in air atmosphere, which was the original goal of this work. Differential scanning calorimetric (DSC) studies revealed that siloximide-E retains its glass transition temperature below −60 °C.

Conclusion. A high molecular weight and processable siloxane copolyimide, siloximide-E, with improved thermal degradation behavior has been synthesized biocatalytically for the first time using lipase as a biocatalyst. Comparison to the nonenzymatically synthesized polyimide siloximide-NE confirmed the role of the lipase as a catalyst to optimizing the reaction for polyimide formation. This simple, environmentally benign biocatalytic synthesis of polyimide without the need for any intermediate step of polyamic acid could open up a new class of "green" enzymatic synthetic routes for polyimides with improved properties.

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Supporting Information Available: Thermal gravimetric analysis plot and ^{13}C NMR spectrum of siloximide-E. This material is available free of charge via the Internet at http://pubs.acs.org.

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