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Synthesis of polyesters containing disiloxane subunits: Structural characterization, kinetics, and an examination of the thermal tolerance of Novozym-435

Mark B. Frampton[a,1], Jacqueline P. Séguin[a,1], Drew Marquardt[b], Thad A. Harroun[b], Paul M. Zelisko[a,*]

[a] Department of Chemistry and Centre for Biotechnology, Brock University, St. Catharines, Ontario, Canada
[b] Department of Physics, Brock University, St. Catharines, Ontario, Canada

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ABSTRACT

This paper reports the Novozym-435 mediated polymerization of disiloxane-containing polyester monomers under solvent-free conditions. The thermal tolerance of the immobilized enzyme was examined by conducting polymerization cycles over a temperature range of 35–150 °C. Increasing the temperature up to 100 °C afforded an increase in the apparent second order rate constant. Residual activity was measured using the production of octyl palmitate. The enzyme was shown to retain on average greater than 90% of its residual activity regardless of the polymerization temperature. This prompted a study of the long term thermal tolerance of the biocatalyst in which it was determined that over ten reaction cycles there was a significant decrease in the initial polymerization rate, but no change in the degree of monomer conversion after 24 h. The disiloxane containing polyesters were characterized using nuclear magnetic resonance spectroscopy and Fourier-transform infrared spectroscopy. Differential scanning calorimetry was used to determine the thermal properties of the disiloxane-containing polyesters.

1. Introduction

Silicones and other siloxane-derived materials are of great industrial and economic importance [1]. Low molecular weight cyclic silicones are commonly found in the health care and cosmetics industries where they are typically incorporated into topical applications, the food and beverage industry where they are used as antifoaming agents, and in sealants and coatings where their inherent hydrophobicity is the desired characteristic.

The popularity of siloxanes is a result of their physical and chemical properties, which makes them well suited for a range of applications. Siloxanes, and in particular silicones, are valued for their thermal stability (silicones typically do not degrade until temperatures in excess of 350 °C are obtained), low glass transition temperatures which result from the dynamic nature of the siloxane bond, resistance to oxidation, and low permittivity values [1,2]. The basis for these physical characteristics is derived from the Si—O—Si bond. The angle of the siloxane linkage is rather larger, typically 145°, compared to 109.5° for typical tetrahedral organic systems. It has been postulated that this angle may be flexible enough to actually range from 90° to 180°. The siloxane linkage is highly polarisable as a result of the high ionic nature of the Si—O bond which has been determined to be approximately 51% ionic [3]. The Si—O bond possesses very low rotational bond energy as well as being one of the strongest chemical bonds known with a covalent bond energy of 452 kJ/mol (108 kcal/mol) and ionic bond energy of 1013 kJ/mol (242 kcal/mol) [2].

Many methods have been designed to produce linear, branched, or cross linked silicones. Most commonly used are catalysts based on the platinum complexes developed by Karstedt and Speier, and on alkoxytitanium complexes. Tin carboxylates are commonly used, particularly in the room temperature vulcanization of silicone elastomers. However, the potential toxicity of alkyl tin complexes [4] renders this class of catalyst undesirable especially in the synthesis of biomaterials. Other general cure methods include high temperature vulcanizations, and thermal- or copper-mediated [1,3]-dipolar additions [5,6]. More recent work on the Piers–Rubensztajn reaction has lead to the development of $B(C_6F_5)_3$ as a catalyst for the preparation of star-shaped siloxanes and functionalized silicones from hydrosilanes and alkoxysilanes [7–9].

Polyesters are commercially available in a variety of products such as fibres, fillings, coatings, and textiles and are typically produced under extremes of heat, sometimes in excess of 250 °C, and under reduced pressure [10]. A variety of catalytic methods have been developed for producing polyester materials, typically using

* Corresponding author. Tel.: +1 905 680 5550x4389; fax: +1 905 682 9020.
E-mail address: pzelisko@brocku.ca (P.M. Zelisko).
[1] Tel.: +1 905 680 5550x4389; fax: +1 905 682 9020.

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strong acids over stoichiometric quantities of both diols and diacids. Alternatively, dibutyltin oxide or dibutyltin dilaurate have been employed, but given the aforementioned toxicity concerns, these catalysts may wish to be avoided. While strong acids are ideal for polyester synthesis, they are not always compatible with siloxane polymers due to the possibility for redistribution of the siloxane backbone, or cleavage of the siloxane network [1]. Additionally, the condensation of diols with acyl chlorides, and the ring opening polymerization of lactones have been explored as viable routes to polyester synthesis [11].

Enzymatic methods are becoming increasingly popular in organic, bioorganic, and polymer chemistry. Lipase B from *Candida antarctica* immobilized on a macroporous acrylic resin and sold under the trade name Novozym-435, has been the work horse for synthesizing polymeric materials [12–15] and has been used to synthesize organosilicon amides and esters [16]. Furthermore, an Amberzyme-immobilized cutinase from *Humicola insolens* has garnered some recent attention for its polyester synthase ability [17,18]. This cutinase possessed stricter substrate specificity than N435 showing a preference for C10 and C13 diacids whereas those diacids with chain lengths shorter than C10 were not processed particularly well.

The synthesis of polyesters incorporating siloxanes has been demonstrated although, typically, the siloxane is only a minor component of the final polymer system [13,19–22]. The enzymatic synthesis of polyesters derived exclusively from siloxane-derived monomers has been described [23]. The number of siloxane units of the diol monomer did not affect the polymerization kinetics or the activation energy of the polymerization process [23].

In this paper disiloxane polyesters were synthesized employing N435 catalysis under solvent-free reaction conditions. The disiloxane polyesters were subsequently characterized by nuclear magnetic resonance (NMR) spectroscopy and Fourier-transform infrared (FT-IR) spectroscopy. Differential scanning calorimetry (DSC) was employed to determine the thermal transitions of the monomers and resulting siloxane containing polyesters.

In order for biocatalysis to be viable on an industrial scale cost must be minimized. One method to facilitate this would be to design a catalyst with a high turnover number, or a catalyst that would be amenable to multiple reaction cycles. The residual activity of N435 was examined, after each polymerization, by using a standard enzymatic assay in which the production of octyl palmitate from 1-octanol and palmitic acid was monitored. In conjunction with the residual activity assays, a single batch of N435 was used for multiple 24 h reaction cycles at 100 °C to gain some insight into the thermal tolerance and reusability of N435 as a polymerization catalyst.

2. Experimental

2.1. Materials

Lipase B from *C. antarctica* immobilized on acrylic resin (sold under the trade name Novozym-435, N435; EC.3.1.1.3, 10,000 U/g), activated carbon, 1,1,3,3-tetramethyldisiloxane (TMDS, 97%) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex (Karstedt's catalyst, Pt^0(dvs)) in xylenes were obtained from Sigma–Aldrich (Oakville, Ontario, Canada). 1,3-Bis(3-carboxypropyl)-1,1,3,3-tetramethyldisiloxane (CPr-TMDS) was obtained from Gelest (Morristown, PA, USA). Allyl acetate (98%) was obtained from Alfa Aesar (Ward Hill, MA, USA). Isooctane (2,2,4-trimethylpentane, 99%) was obtained from Caledon Chemicals (Georgetown, Ontario, Canada). Chloroform-*d* ($CDCl_3$, 99.8% deuterated) was a product of Cambridge Isotope Laboratories, Inc. (Andover, MD, USA). Diethyl ether (99%) was acquired from Anachemia Science (Montréal, Québec, Canada). Distilled water was used when necessary. Chemicals were used as received without further modification or purification unless otherwise stated. All of the commercially available reagents were at a minimum pure by NMR (≥95%).

2.2. Methods

2.2.1. Nuclear magnetic resonance spectroscopy (NMR)

All NMR spectra were recorded in $CDCl_3$ on a Bruker Avance AV-300 spectrometer (^{1}H at 300 MHz, ^{13}C at 77 MHz, and ^{29}Si at 59.6 MHz) using the residual signal of $CHCl_3$ as an internal reference for ^{1}H spectra, and the three ^{13}C resonances of $CDCl_3$ as the internal reference for ^{13}C NMR spectra; tetramethylsilane (TMS) was used as an internal standard for ^{29}Si NMR spectra. NMR spectra were analysed using the Bruker Topspin v2.0 software interface.

2.2.2. Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra were recorded on a Mattson research series infrared spectrometer operating in transmittance mode. Samples were prepared as neat, thin films on KBr plates. Each spectrum was comprised of 32–64 scans at 2 cm^{-1} resolution. Analysis of the FTIR data was performed using the Winfirst software platform. Peak assignments were made based on data previously reported in the literature [24].

2.2.3. Differential scanning calorimetry (DSC)

DSC thermograms were acquired on a Shimadzu DSC-60 differential scanning calorimeter. Polymer samples (approximately 10 mg) were transferred into aluminium pans and cooled to −150 °C at a rate of 10 °C/min. Samples were heated at 20 °C/min to 200 °C and subsequently cooled at 10 °C/min to −150 °C. A second heating scan was done at 20 °C/min to 200 °C. DSC data was analysed using the TA60 version 2.11 software platform.

Synthesis of 1,3-*bis*(3-*hydroxypropyl*)-1,1,3,3-*tetramethyldisiloxane* (**4**, 3HP-TMDS, Scheme 1). A round bottomed flask was charged with 1,1,3,3-tetramethyldisiloxane (**2**) and Karstedt's catalyst and stirred for 10 min. Allyl acetate (**1**) was added drop-wise through a septum over 30 min and the reaction mixture was allowed to reflux for 2 h to give 1,3-bis(3-acetoxypropyl)-1,1,3,3-tetramethyldisiloxane (**3**) in 83% isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm): 0.06, 0.11, 0.25 and 0.28 ppm ($\underline{\mathbf{Me_2}}$SiO—), 0.5 ppm (*m*, $CH_2CH_2\underline{\mathbf{CH_2}}$Si, 4H), 1.63 ppm (*m*, $CH_2\underline{\mathbf{CH_2}}CH_2$Si, 4H), 4.01 ppm (*m*, AcO$\underline{\mathbf{CH_2}}CH_2CH_2$Si, 4H), $\underline{\mathbf{CH_3}}$C=O (*s*, 3H); ^{13}C NMR (77.0 MHz, $CDCl_3$, 77.0 ppm): 0.22 ppm (($\underline{\mathbf{CH_3}}$)$_2$SiO—), 14.12 ppm ($CH_2CH_2\underline{\mathbf{CH_2}}$Si), 21.00 ppm ($CH_2\underline{\mathbf{CH_2}}CH_2$Si), 22.59 ppm ($\underline{\mathbf{CH_3}}CO_2R$), 66.94 ppm (AcO$\underline{\mathbf{CH_2}}CH_2CH_2$), 171.16 ppm ($\underline{\mathbf{C}}$=O). De-acylation of bis-acetate **3** was routinely carried out using an 8 fold excess of anhydrous MeOH and 20 mol% K_2CO_3 for 2 h at room temperature to yield diol **4** in nearly 87–95% yield as a clear to straw coloured liquid [25]. ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm): 0.05 ppm (*s*, 12H, $\mathbf{Me_2}$Si), 0.528 ppm (*m*, 4H, $CH_2CH_2\mathbf{CH_2}$Si), 1.646 ppm (*m*, 4H, $CH_2\mathbf{CH_2}CH_2$Si), 2.327 ppm (*t*, 4H, $\mathbf{CH_2}CH_2CH_2$Si, J = 7.5 Hz); ^{13}C NMR (77 MHz, $CDCl_3$, 77.01 ppm): 0.25 ppm ($\mathbf{Me_2}$Si), 18.03 ppm ($CH_2CH_2\mathbf{CH_2}$Si), 19.12 ppm ($CH_2\mathbf{CH_2}CH_2$Si), 37.48 ppm ($\mathbf{CH_2}CH_2CH_2$Si); ^{29}Si NMR (59.6 MHz, $CDCl_3$, TMS): 7.28 ppm; EI-MS: (M^+) 250 *m*/*z*.

Synthesis of 1,3-*bis*(3-*carboxypropyl*)-1,1,3,3-*tetramethyldisiloxane dimethyl ester* (**5**, **CPr-TMDS-DME**). Diester **5** was synthesized using previously published protocols [23]. Briefly, 5.01 g (16.34 mmol) of 1,3-bis(3-carboxypropyl)-1,1,3,3-tetramethyldisiloxane was refluxed in 15 mL of methanol in the presence of 5 mol% *p*-toluene sulfonic acid for 4 h to yield diester **5** as a clear and colourless liquid in 86% yield. ^{1}H NMR