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# Expanding the scope of organocatalysis for alternating copolymerization of dihydrocoumarin and styrene oxide

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## ABSTRACT

Metal-free copolymerization of 3,4-dihydrocoumarin and styrene oxide catalyzed by several organobases has been investigated. The products were shown to have strict alternating sequence distributions regardless of catalyst used. Compared with previously employed *t*-BuP<sub>4</sub> superbase, phosphazene bases (PBs) with lower basicity (i.e. *t*-BuP<sub>2</sub> and *t*-BuP<sub>1</sub>) afforded higher monomer conversions, higher molar masses, and significantly lower proportions of macrocycles in the products. Proton exchange between the mildly basic PBs and the hydroxy species was considered responsible for such improvements, which reduced chain-end nucleophilicity and thus suppressed side reactions. The use of *N*-heterocyclic bases, i.e. TBD and DBU, also resulted in products comprising linear and cyclic alternating copolymers. However, the molar masses of the two populations were not distinctly different as observed in the cases of PBs. Alternating copolymerization catalyzed by TBD or DBU also occurred in the absence of a hydroxy compound, and the products were shown to be predominantly macrocycles. Unlike initiator/chain-end activation by non-nucleophilic PBs, a mechanism involving nucleophilic monomer activation and zwitterionic chain growth was therefore suggested for such bases.

## 1. Introduction

Styrene oxide (SO) is one of the most largely produced and inexpensive commercial epoxide monomers. Because of the steric hindrance caused by direct connection of phenyl on the oxirane ring and the electron-withdrawing effect of phenyl reducing the nucleophilicity of the alkoxide chain end, traditional anionic ring-opening polymerization of SO based on alkali metal counterions usually leads to much lower degrees of polymerization as compared with smaller epoxides (e.g. ethylene oxide or propylene oxide), even if high temperatures and long reaction times were applied [1–4]. Advancement of organometallic ROP catalysis in the last two decades has led to the achievement of high-molar-mass and, in many cases, stereoregular poly(styrene oxide) (PSO) [5–9]. In addition to homopolymers and block copolymers [2–4], alternating copolymers of SO and non-homopolymerizable compounds, in particular, carbon dioxide [10–14], carbonyl sulfide [15,16], and cyclic anhydrides [17–19], have drawn even more attention due to the challenge, significance and attraction of alternating copolymerization [20,21], the (bio)renewable features of the comonomers, and the desirable properties of the resultant alternating polyesters or polycarbonates associated with pendent phenyls such as high thermal stability and glass transition temperature ( $T_g$ ) [11,17,22].

Organocatalytic polymerization has blossomed unprecedentedly in the last 15 years with a rich diversity of organic molecules accumulating in polymer chemists' arsenal for choosing an appropriate catalyst for each specific type of monomer or polymerization reaction [23–25]. In many cases, organocatalysts have shown special strength and efficacy for reaching high polymerization rates and

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controlled macromolecular characteristics. For instance, a bulky, highly basic and non-nucleophilic phosphazene superbase (*t*-BuP<sub>4</sub>) has been used to promote the ROP of SO and afforded high-molar-mass products in a reasonable scale of reaction time [26]. More importantly, the organocatalytic ROP proceeded in a living manner allowing for controlled molar masses with low dispersities as well as facile achievement of end-group functionalities and PSO-based macromolecular structures [26–28].

Epoxide-based alternating copolymerizations through organocatalysis have also been investigated [29–34], though to a much lower extent than organocatalytic polymerizations of other types. Yet SO has scarcely been involved in such studies. Very recently, we have shown that copolymerization of 3,4-dihydrocoumarin (DHC) and SO catalyzed by *t*-BuP<sub>4</sub> resulted in copolymers with perfect alternating monomeric sequence distributions [34]. P(DHC-*alt*-SO) exhibited a higher  $T_g$  than the alternating copolymers derived from other epoxide monomers. Owing to the *in situ* activation-initiation mechanism of phosphazene catalysis, non-linear P(DHC-*alt*-SO)s could be readily synthesized by the use of multihydroxy initiators. However, the alternating ring-opening copolymerization (ROAP) of DHC and SO generally suffered from low monomer conversions, low molar masses and bimodal molar mass distributions of the products, which were considered as the consequences of competitive side reactions such as intramolecular transesterification (backbiting) engendered by the super-basicity of *t*-BuP<sub>4</sub>.

It has been demonstrated that *t*-BuP<sub>4</sub> triggers extremely fast ROP of cyclic esters but brings about extensive macromolecular transesterification reactions [35–37]. On the other hand, phosphazene bases (PBs) with lower basicity are able to ensure that ROP proceeds mildly and more selectively so that controlled molar masses and low dispersities of polyesters can be achieved [38–41]. Cyclic guanidine and amidine type bases such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), whose conjugate acids also feature lower  $pK_a$  values than that of *t*-BuP<sub>4</sub>, can also afford well-defined polyesters provided with proper catalyst-monomer suitability and reaction conditions [23,24,42–46], though more complicated polymerization mechanisms involving monomer/chain-end dual activation and zwitterionic chain growth are proposed for such *N*-heterocyclic bases. In this study, we have attempted to use these relatively mild bases, instead of *t*-BuP<sub>4</sub>, for the copolymerization of DHC and SO in order to expand the scope of organocatalysis and to further reveal the structure-property relationships of organocatalysts for this ROAP reaction.

## 2. Experimental section

### 2.1. Chemicals

SO (Aladdin, 99%) and DHC (Aladdin, 99%) were dried over calcium hydride (CaH<sub>2</sub>) overnight and vacuum-distilled. Then SO was stirred with sodium hydride (NaH) for 4 h and distilled again under vacuum. Tetrahydrofuran (THF) and toluene (Guangzhou Chemical Reagent, 99%) were successively dried over molecular sieve (4 Å), CaH<sub>2</sub>, and *n*-BuLi. TBD (TCI, 98%), DBU (Aladdin, 98%), and 1,4-benzenedimethanol (BDM; Aladdin, 99%) were dried twice by azeotropic distillation of THF before use. Acetic acid (AcOH; Aladdin, 99%) and *tert*-butylimino-tris(dimethylamino)phosphorane (*t*-BuP<sub>1</sub>; Aldrich, 97%) was used as received. 1-*tert*-Butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ<sup>5</sup>,4λ<sup>5</sup>-catenadi(phosphazene) (*t*-BuP<sub>2</sub>; 2.0 M solution in THF, Aldrich) was used after evaporation of THF.

### 2.2. Instrumentation

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at room temperature (RT) on a Bruker AV600 NMR spectrometer using CDCl<sub>3</sub> as the solvent and tetramethylsilane as the internal standard, and were used to calculate the monomer conversion using integrals of the characteristic signals from the monomer and polymer. Size exclusion chromatography (SEC) coupled with RI and UV detectors was conducted in THF at 35 °C using two identical PLgel columns (5 μm, MIXED-C) at a flow rate of 1.0 mL min<sup>-1</sup>. Calibration was done with a series of narrowly dispersed polystyrene standards to obtain apparent number-average molar mass ( $M_{n,SEC}$ ) and molar mass distribution ( $D_M$ ) of the (co)polymers. Matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) measurements were carried out on a Bruker Autoflex III Smartbeam MALDI-TOF mass spectrometer (Bruker, Germany). Copolymers were dissolved in THF (10 mg mL<sup>-1</sup>) and mixed with a THF solution of sodium trifluoroacetate (10 mg mL<sup>-1</sup>) in a volume ratio of 5:1. This solution was subsequently mixed with a THF solution of matrix (2,5-dihydroxybenzoic acid, 20 mg mL<sup>-1</sup>) in a volume ratio of 1:10. The final solution (0.4 μL) was spotted on the target plate and dried in air. The reflective positive ion mode was used to acquire the mass spectra of the samples. Calibration was done externally with poly(methyl methacrylate) standards using the nearest neighboring positions.

### 2.3. Copolymerization

*Poly(3,4-dihydrocoumarin-*alt*-styrene oxide)*, *P(DHC-*alt*-SO)*. A typical procedure for DHCSO2 (Table 1) is as follows. BDM (0.0138 g, 0.10 mmol) was charged in a reaction flask and dried by azeotropic distillation of THF twice. Then DHC (2.66 mL, 21.0 mmol) and SO (2.28 mL, 20.0 mmol) were added in a glovebox. The mixture was carefully shaken to ensure complete mixing and dissolving, followed by addition of *t*-BuP<sub>1</sub> (47.0 μL, 0.20 mmol). Then the flask was sealed by a stopcock, taken out of the glovebox, docked back on the Schlenk line, immersed in an oil bath preheated at 80 °C, and magnetically stirred. Aliquots were withdrawn (ca. 0.05 mL each) in an argon flow at different time intervals for NMR and SEC analysis. After 96 h, the flask was cooled down to RT. Then 1 mL of AcOH was injected into the reaction mixture in an argon flow. A small amount of the solution was withdrawn for NMR and SEC analysis. The rest was diluted with toluene and poured into cold methanol (–20 °C) to precipitate the

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