**ESI** for "Nucleophilic Polyaddition in Water Based on Chemo-Selective Reaction of Cyclic Carbonate with Amine" by Bungo Ochiai, Yuriko Satoh, and Takeshi Endo

## Materials

1,6-Hexamethylenediamine (HDA, Tokyo Kasei Kogyo Co., Tokyo, Japan), 4,4'-methylene-biscyclohexylamine (HMDA, Tokyo Kasei Kogyo Co., Tokyo, Japan), *n*-butylamine (Tokyo Kasei Kogyo Co., Tokyo, Japan) were used as received. 2,2-(4-(1,3-Dioxolane-2-one-4yl)methoxyphenyl)-propane (BisAC),[15] 1,4-bis(1,3-dioxolane-2-one-4yl)methoxybutane (C4C),[15] and 4-phenoxymethyl-1,3-dioxolane-2-one[19] were prepared as reported. Water was distilled under nitrogen atmosphere prior to use.

## Measurements

$^1$H Nuclear magnetic resonance (NMR) spectra were measured on a JEOL JNM-LA-270 instrument using tetramethylsilane as an internal standard (270 MHz). Size exclusion chromatography (SEC) measurements were performed on a Tosoh HLC-8120 GPC instrument equipped with four consecutive polystyrene gel column [Tosoh TSK-gel (bead size); α-M (13 μm), α-4000 (10 μm), α-3000 (7 μm), and α-2500 (7 μm)] using *N,N*-dimethyl formamide (DMF) containing 50 mM lithium bromide and 50 mM phosphoric acid as an eluent at 40 ˚C. Polystyrene standards were used for calibration.

## Typical experimental procedure

To a test tube containing a magnetic stir bar, BisAC (214 mg, 500 μmol), HDA (58.1 mg, 500 μmol), and water (1.0 mL) were added under nitrogen atmosphere. After the tube was cooled by liquid nitrogen, the tube was degassed and sealed off. The polyaddition was conducted at the desired temperature for 24 or 48h. Then, the tube was opened, and DMF was added until the mixture became homogeneous. The

resulting solution was poured into an excess amount of saturated aqueous NaCl solution. The precipitate was collected by centrifugation, and dried under reduced pressure to obtain poly(hydroxyurethane).

The yields of the polymer were determined as follows. In some cases (i.e., unsuccessful polymerizations), the insoluble parts contain the residual HMDA and the hydrolyzed products from BisAC (HDA and the hydrolyzed product from C4C are soluble in saturated NaCl solution). The weights of these contaminants, calculated from $^{1}$H NMR analysis, are reduced from the weights of the insoluble parts. No contaminants were detectable in the polymers quantitatively obtained.