Supporting Information

Combining Chemoenzymatic Monomer Transformation with ATRP: A facile "one-pot" approach to functional polymers

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Experimental Section

1. Materials

Ethyl 2-bromoisobutyrate (EBiB, J&K Chemical, 98%), copper bromide (CuBr, J&K Chemical, 98%), 4,4'-Dinonyl-2,2'-dipyridyl (dNbpy, J&K Chemical, 98%), 4-Nitrophenyl acetate (4-NPA, J&K Chemical, 97%), triethylamine (TEA, J&K Chemical, 99.5%) and immobilized *Candida Antarctica* lipase B (Novozym 435, Beijing Cliscent Science and Technology Co., LTD) were used as purchased. Methanol, ethanol, hexanol, benzyl alcohol, polyethylene glycol methyl ether (Mn~350), *iso*-propanol and *tert*-butanol were all purchased from J&K Chemical and used directly without further purification. 2,2,2-Trifluoethyl methacrylate (TFEMA,

J&K Chemical, 98%) was passed through a basic aluminum oxide column prior to use.

2. Instrumental Analysis

Gel permeation chromatography (GPC) analyses of polymers were performed using tetrahydrofuran (THF) as the eluent. The GPC system was a Shimadzu LC-20AD pump system comprising an auto injector, a MZ-Gel SDplus 10.0 μm guard column (50 × 8.0 mm, 10^2 Å) followed by three MZ-Gel SDplus 10.0 μm bead-size columns (10^5, 10^3, and 10^2 Å) and a differential refractive index (dRI) detector. The system was calibrated with narrow molecular weight distribution polystyrene standards ranging from 200 to 10^6g mol^{-1}.

^{1}H NMR spectra were obtained using a JEOL JNM-ECA400 (400MHz) spectrometer for all samples. UV–vis absorption spectra were recorded on a Perkin-Elmer LAMBDA 35 UV/vis system.

3. Method

3.1. "One-pot" chemoenzymatic ATRP process

A typical "one-pot" chemoenzymatic ATRP procedure is as follows. To schlenk tube A were charged TFEMA (1.0 g, 6.0 mmol), hexanol (0.61g, 6.0 mmol), TEA (0.60 g, 6.0 mmol), EBiB (14.6 mg, 0.075 mmol) and toluene (6.0 mL). The resulting solution was then degassed through three freeze-pump-thaw cycles. In the mean time, CuBr (5.4 mg, 0.038 mmol), dNbpy (46.0 mg, 0.11 mmol) and Novozym 435 (0.5 g) were added into another schlenk tube B equipped with a magnetic stir bar followed by evacuated and backfilled with nitrogen for three times. Then the thawed solution in

tube A was cannulated into tube B under nitrogen atmosphere. The final reaction mixture was put into an oil bath maintained at 45 ^{o}C. Samples were withdrawn periodically for ^{1}H NMR and GPC analyses for conversion and molecular weight determination, respectively. At the end of the polymerization, the mixture was centrifuged to remove immobilized enzyme, then passed through a short neutral alumina column prior to further purification. The purified polymer was obtained via precipitation from THF to methanol for three times, and then dried under vacuum for further characterization. All polymers in current report are obtained with the same approach.

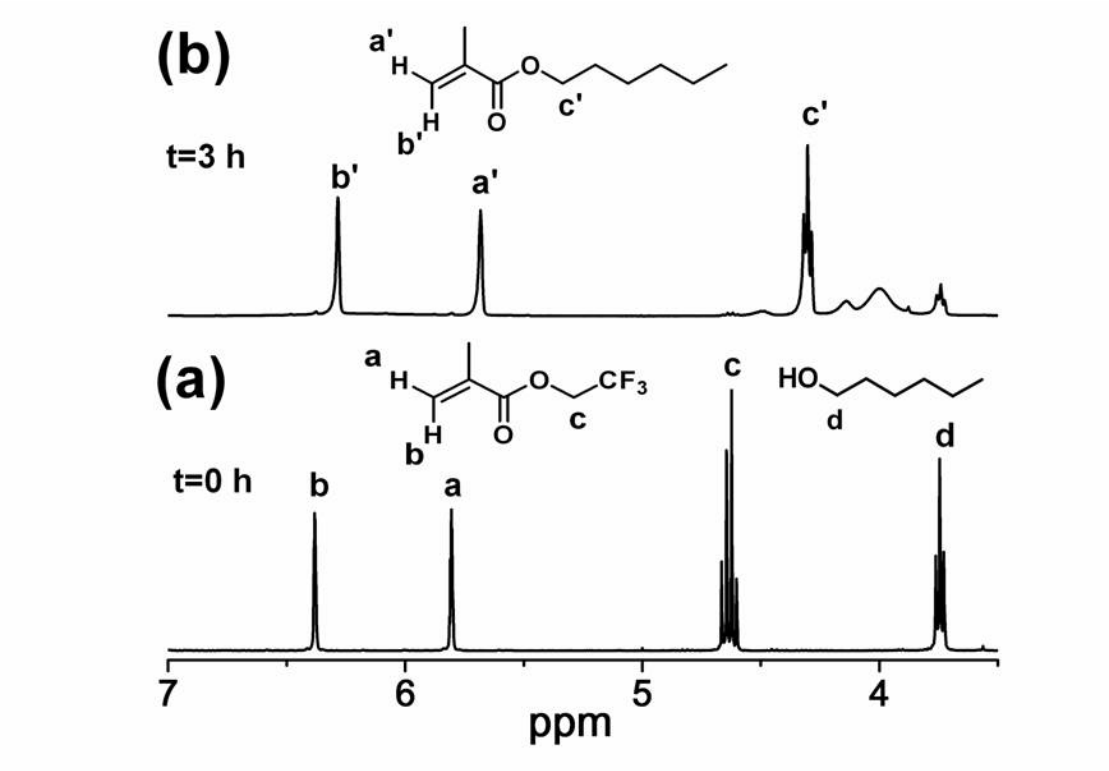
3.2.Enzyme activity test

The Novozym 435 after polymerization was collected by centrifugation and washed using toluene to remove copper salts until the washing liquor turned from light green to colorless. Subsequently the enzyme was dried under vacuum until constant weight for next activity test using 4-NPA as substrate. The typical procedure is as follow.

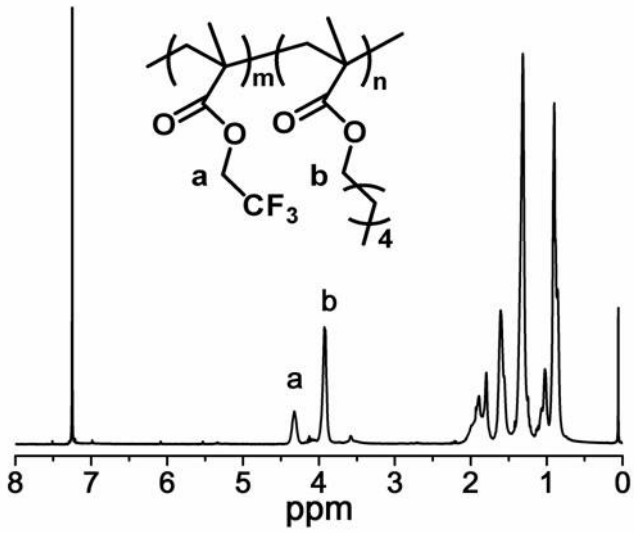
A toluene solution (1.0 mL) containing 4-NPA (20.0 mg, 0.11 mmol) and methanol (7.0 mg, 0.22 mmol) was added into a 1.5 mL vial containing 6.0 mg recycled Novozym 435. The assay reactions were carried out at 35 ^{o}C (450 rpm). Samples were withdrawn periodically for enzyme activity analysis. The produced 4-nitrophenol (4-NP) in the reaction was determined by UV/Vis at the λ_{max} (304 nm). The enzyme activity was defined as the the formation rate of 4-NP catalyzed by enzyme. The activity of pristine enzyme was tested with the same fashion and defined

as a control (100%) to calculate the retained activity of enzyme samples after polymerization.

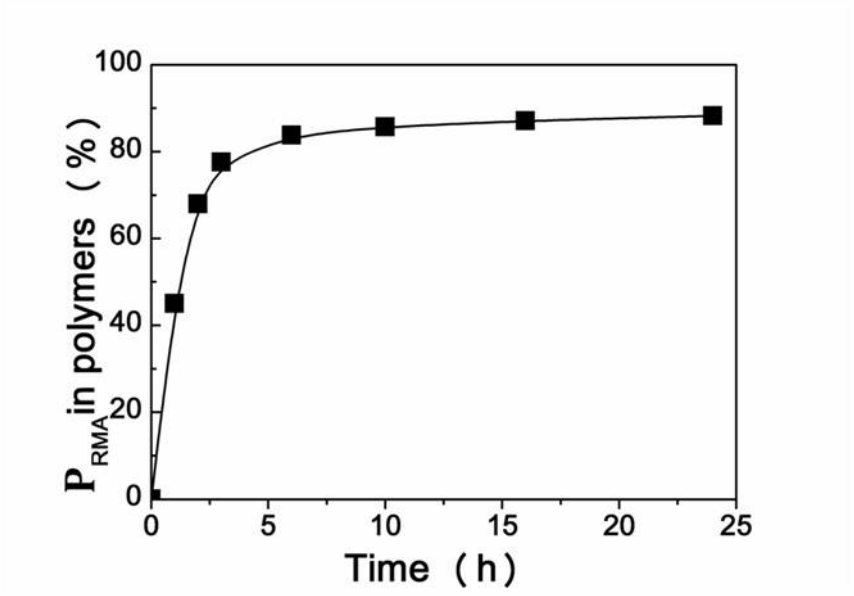
Supporting Data



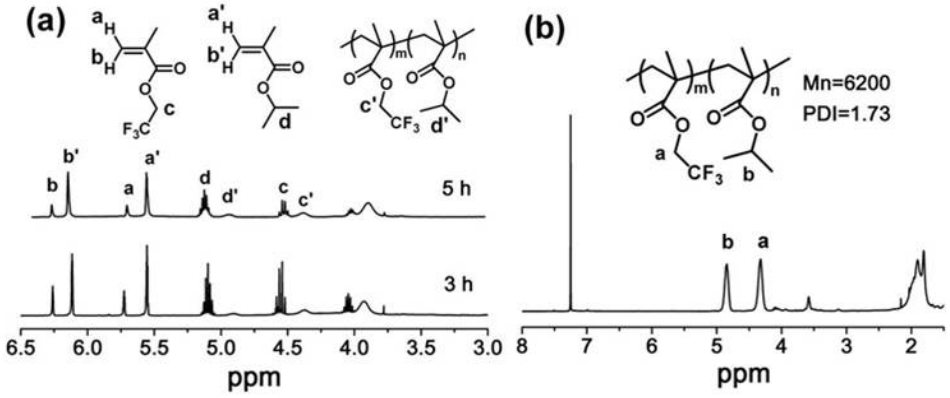
SFig. 1. The ^{1}H NMR analyses ($CDCl_3$) of the chemoenzymatic-ATRP process at 0 h (a) and 3 h (b).



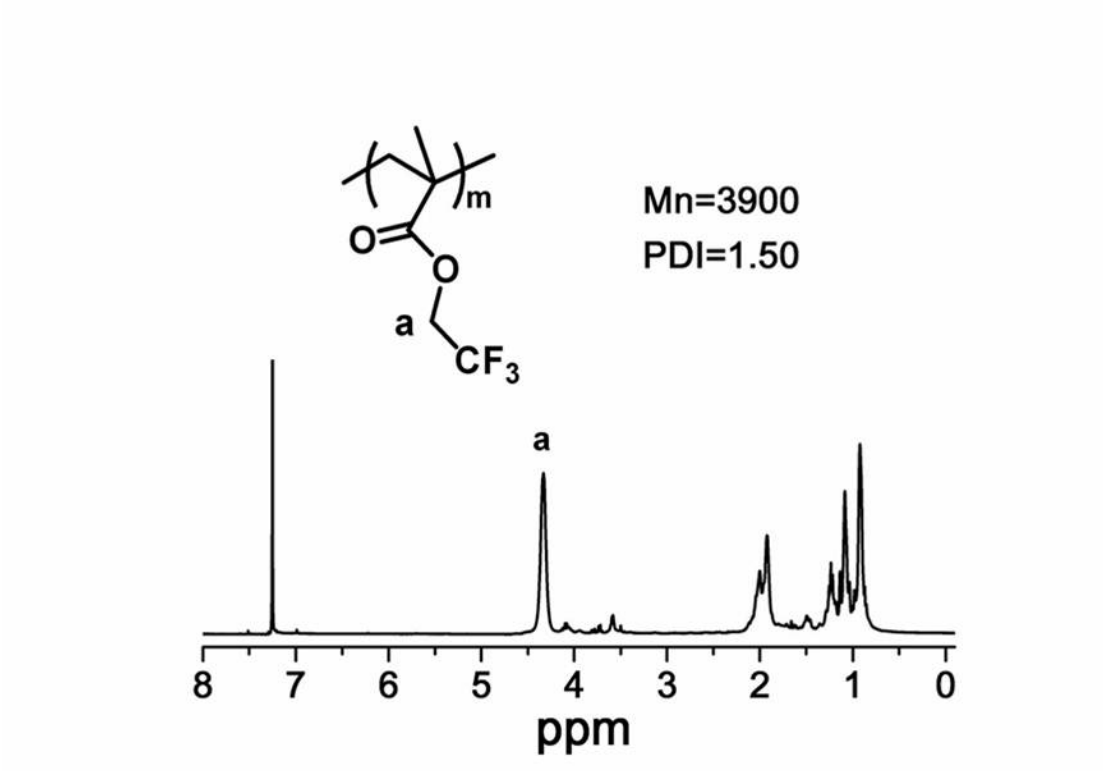
SFig. 2. The ^{1}H NMR spectra ($CDCl_3$) of polymer after purification at 3 h.



SFig. 3. The proportion of HMA in poly(TFEMA)-*co*-poly(HMA) *versus* reaction time during the "one-pot" chemoenzymatic-ATRP process.



SFig. 4. "One-pot" chemoenzymatic ATRP for copolymers via *in-situ* transesterification of TFEMA and *iso*-propanol: Transesterification conversion and monomer conversion *versus* polymerization time (a); The ^{1}H NMR spectrum ($CDCl_3$) of purified poly(TFEMA)-*co*-poly(*i*PMA) (b).



SFig. 5. The ^{1}H NMR spectra ($CDCl_3$) of polymer by the "one-pot" chemoenzymatic-ATRP of TFEMA and *tert*-butanol.