Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

A Multicomponent Polymerization System: Click-Chemoenzymatic-ATRP in One-pot for Polymer Synthesis

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Experimental Section

1. Materials

Ethyl 2-bromoisobutyrate (EBiB, J&K Chemical, 98%), sodium azide (NaN_3, Acros Organics, 99%), 6-chloro-1-hexanol (Aladdin, 95%), sodium iodide (Aladdin, 99.5%), 1-ethynyl-1-cyclohexanol (ECH, J&K Chemical, 99%), phenylacetylene (Aladdin, 97%), 1-hexyne (Aladdin, 97%), copper bromide (CuBr, 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), mesitylene (J&K Chemical, 98%) were used as purchased. 2,2,2-Trifluoethyl methacrylate (TFEMA, J&K Chemical, 98%) was passed through a basic aluminum oxide column prior to use. Methanol, acetone, diethyl ether, dichloromethane and toluene were all purchased from J&K Chemical and used directly without further purification.

4'-(4-(Octadecyloxy)phenyl)-2,2':6',2''-terpyridine (tpy) was synthesized as previous literature.[1]

2. Instrumental Analysis

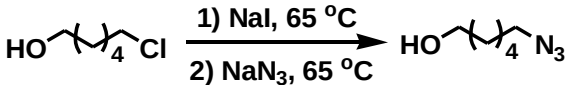
Gel permeation chromatography (GPC) analyses of polymers were performed using N, N-dimethyl formamide (DMF) as the eluent. The GPC system was a Shimadzu LC-20AD pump system comprising an auto injector, a MZ-Gel SDplus 10.0 μm guard column(50 × 8.0 mm, 10^2 Å) followed by a MZ-Gel SDplus 5.0 μm bead-size column (50 – 10^6 Å, linear) and a Shimadzu RID-10A refractive index detector. The system was calibrated with narrow molecular weight distribution

polystyrene standards ranging from 200 to 10^6 g mol^{-1}.

^{1}H NMR and ^{13}C NMR spectra were obtained using a JEOL JNM-ECA400 (400MHz) spectrometer for all samples. The ESI-MS data were collected using a MicroTOF-QII Bruker. The FT-IR spectra were obtained in a transmission mode on a Perkin-Elmer Spectrum 100 spectrometer (Waltham, MA, USA).

3. Method

3.1. Preparation of 6-azide hexane (6-AzOH).



6-Chloro-1-hexanol (6.83 g, 0.05 mol) was dissolved in acetone and NaI (8.99 g, 0.06 mol) was added. The solution was refluxed at 65 °C overnight. Then NaN_3 (4.88 g, 0.075 mol) was added into the reaction system and water was added until homogeneous phase. After refluxed for 6 h, the acetone was evaporated under vacuum and the remaining mixture was redissolved in ethyl acetate following by washing with water for 3 times to remove inorganic sodium salts. Then the organic phase was collected and dried by anhydrous magnesium sulfate ($MgSO_4$). The product was obtained by removing the solvent.

^{1}H NMR (400 MHz, $CDCl_3$)/ppm: 3.58 (t, J = 6.6 Hz, 2H, CH_2OH), 3.23 (t, J = 6.9 Hz, 2H, CH_2N_3), 1.56 (m, 4H, C$H_2$$CH_2OH, CH_2$$CH_2N_3$), 1.35 (m, 4H, C$H_2CH_2$$CH_2CH_2N_3$, 4-H). ^{13}C NMR (100 MHz, CDCl3)/ppm: 62.82, 51.46, 32.61, 28.88, 26.60, 25.40.

IR(ν/cm^{-1}): 3368, 2936, 2862, 2095, 1455, 1349, 1256, 1054, 907, 814, 729.

ESI-MS: M+Na^+ expected (observed): 166.0951 (166.0946).

3.2. 'One-pot' click-chemoenzymatic-ATRP process

A typical 'one-pot' click-chemoenzymatic-ATRP procedure is as follows. To schlenk tube **A** were charged TFEMA (1.200 g, 7.14 mmol), 6-AzOH (1.022 g, 7.14 mmol), ECH (0.975 g, 7.85 mmol), EBiB (7.0 mg, 0.036 mmol), TEA (0.722 g, 7.14 mmol) and toluene (8.0 mL), anisole (15 mg). Mesitylene (0.15 mL) was added as internal standard for calculating conversion using ^{1}H NMR. The resulting solution was then degassed through three freeze-pump-thaw cycles. In the mean time, CuBr (2.5 mg, 0.017 mmol), tpy (31.0 mg, 0.054 mmol) and Novozym 435 (0.600 g) were added into 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 a 45 ^{o}C oil bath. Samples were withdrawn periodically for ^{1}H NMR and GPC analyses for conversion and molecular weight determination, respectively. After stopping the polymerization, the reaction 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 petroleum ether for three times followed by ultrasonic washed with diethyl ether for three times, and then dried under vacuum for further characterization. All polymers in current report were obtained with the same approach.

3.3 Enzyme activity test

The pristine Novozym 435 (0.600 g) was added into 8 mL toluene and then sealed in a schlenk tube with a magnetic stir bar. The tube was put into an oil bath

maintained at 45 ^{o}C for 24 hours. Then the enzyme was separated by centrifugation and dried under vacuum until constant weight.

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.

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 (every 3 minutes) 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.

3.4 Model experiment of CALB selectivity.

TFEMA (1.200 g, 7.14 mmol), 6-AzOH (1.022 g, 7.14 mmol), ECH (0.975 g, 7.85 mmol) were mixed together in 8 mL of toluene and sealed in a schlenk tube in the presence of 0.6 g Novozym 435. Mesitylene (0.15 mL) was added as internal standard. The tube was put into an oil bath maintaining at 45 ^{o}C. Samples were withdrawn periodically for ^{1}H NMR characterization.

In comparison, 1-ethynyl-1-cyclohexanol methacrylate (ECHMA) was

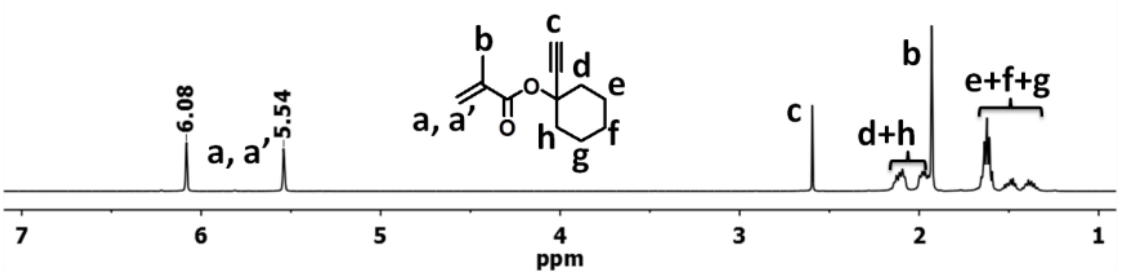
synthesized. ECH and TEA (1:1 in molar ratio) were dissolved in dichloromethane. Methacryloyl chloride was added dropwise into the solution under 0 ^{o}C and then the reaction was stirring for 3 h at room temperature. After the reaction completed, ECHMA was separated as a colorless oil via silica gel column chromatography (1:8 ethyl acetate: petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$)/ppm: 6.08 and 5.54 (2s, 2H, CH_2=C), 2.59 (HC≡C), 2.16-1.95 (m, 4H, CH_2C(C ≡ CH)CH_2), 1.93 (s, 3H, CH_3), 1.62 (m, 4H, $CCH_2CH_2CH_2CH_2$), 1.56-1.31 (m, 2H, $CCH_2CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, CDCl3)/ppm: 165.54, 137.10, 125.38, 83.85, 75.01, 74.17, 36.95, 25.17, 22.40, 18.35.

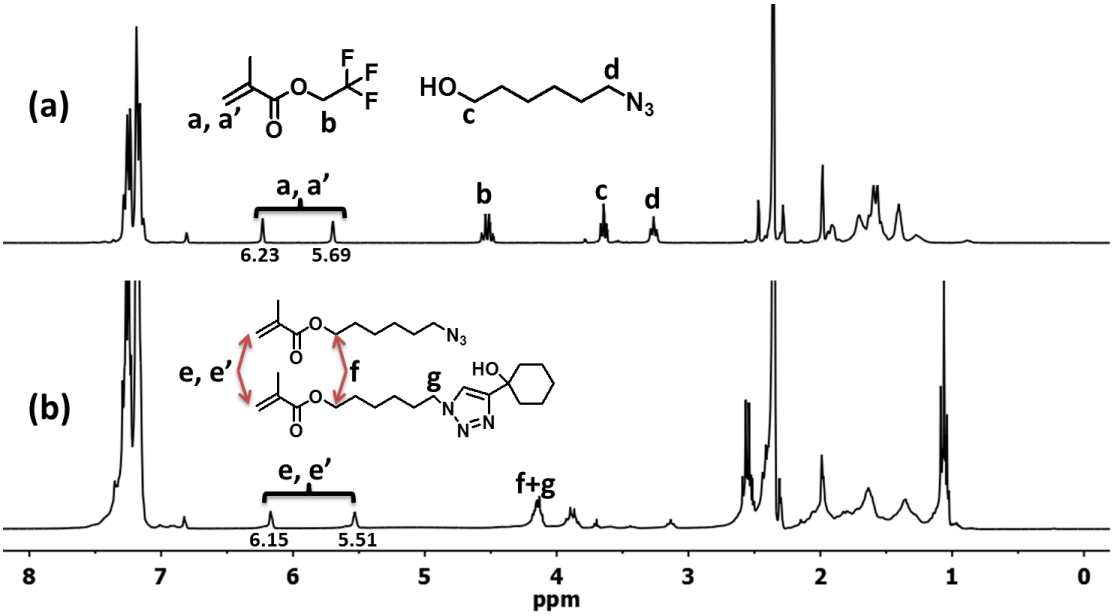
IR(ν/cm^{-1}): 3307, 2941, 2864, 1718, 1637, 1450, 1378, 1325, 1301, 1161, 1139, 1105, 1023, 903, 813, 724, 669.

ESI-MS: M+Na^{+} expected (observed): 215.1043 (215.1043).

Supporting Data



SFig. 1. ^{1}H NMR spectrum of ECHMA.



SFig. 2. ^{1}H NMR analyses of the one-pot MCP process at (a) 0 h and (b) 3 h (in $CDCl_3$).

Reference

1. C. Fu, C. Zhu, S. Wang, H. Liu, Y. Zhang, H. Guo, L. Tao and Y. Wei, *Polym. Chem.*, 2012, **DOI**: 10.1039/C2PY20875J..