



# Amphiphilic Polyethylene-*b*-poly(L-lysine) Block Copolymer: Synthesis, Self-assembly, and Responsivity

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## General Procedures

All manipulations involving air- and moisture- sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with standard vacuum-line, Schlenk, or glovebox techniques.

## Materials

Dichloromethane and chloroform were distilled from CaH<sub>2</sub> under nitrogen, and toluene and hexane from Na/K alloy. Ethylene (99.99%) was purified by passing through Agilent moisture and oxygen traps. Amine-imine nickel complex [Ar-N=C(Me)-(Me)<sub>2</sub>C-NH-Ar]NiBr<sub>2</sub> (Ar = 2,6-diisopropylphenyl) was synthesized according to our previously reported method. MMAO (7 wt. % Al in heptane) was purchased from Akzo-Nobel and used as received. ZnEt<sub>2</sub> was purchased from Aldrich and used as received.  $\epsilon$ -Benzoyloxycarbonyl-L-lysine-N-carboxyanhydride (Z-Lys-NCA) was purchased from Acros and was recrystallized from hexane/ethyl acetate mixture solvent three times to afford pure polymerization-grade NCA monomer. All solvents and other reagents if not specified were directly purchased and used as received.

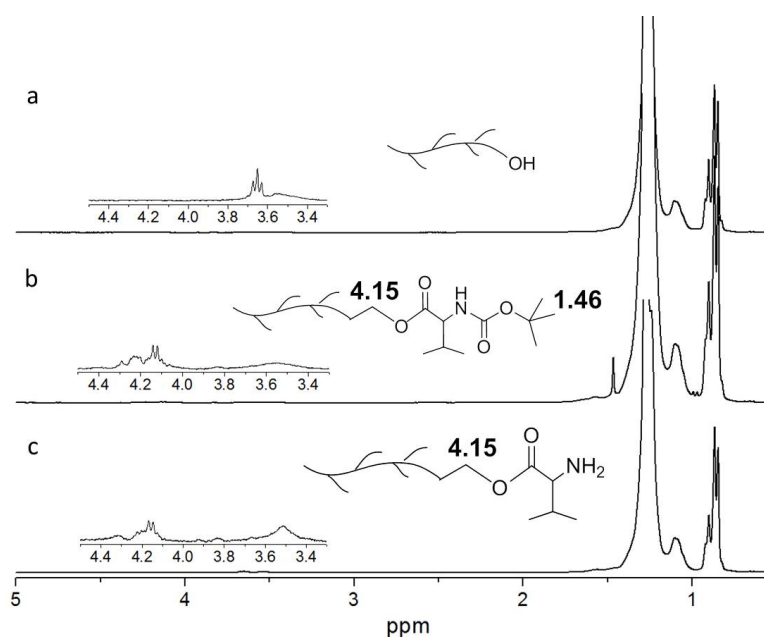
## Synthesis of PE-OH

In a typical procedure, a round-bottom Schlenk flask with stirring bar was heated 3 h to 150 °C under vacuum and then cooled to room temperature. The flask was pressurized to 1 atm of ethylene and vented three times. The 200 equiv. MMAO solution as a cocatalyst was introduced into the glass reactor under 0.2 atm of ethylene. The system was maintained by continuously stirring for 5 min, and then toluene and 2 mL solution of amine-imine nickel complex (100  $\mu$ mol) in CH<sub>2</sub>Cl<sub>2</sub> were syringed into the well-stirred solution in order, and the total reaction volume was kept at 60 mL. The ethylene pressure was kept a constant value of 0.2 atm throughout the reaction. The reaction temperature of 20 °C was maintained in polymerization experiment. After 15 minutes, the ethylene feed was stopped, and the reaction flask was charged with N<sub>2</sub> and vented for three times. Then ZnEt<sub>2</sub> solution (Zn/Ni=300) was charged into reaction system, and the system was maintained by continuously stirring for 3 h at room temperature. Dry O<sub>2</sub> was introduced into solution, and oxidative workup was performed at 100 °C for 2 h. Finally, the reaction solution was poured into acidic methanol (95:5 methanol/HCl). The resulting precipitated polymers were collected and treated by filtration, washing with methanol several times, and drying in vacuum at 40 °C to a constant weight. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 3.65 (t, 2H); 1.4-0.5 (PE).

## Synthesis of PE-COOCH(*i*Pr)NH<sub>2</sub>

A dried flask containing 0.5 g PE-OH and 0.05 g *N*-*tert*-butoxycarbonyl-L-valine (BOC-L-valine) dissolved in 40 mL toluene was treated with a solution of 0.05 g DCC for 72 h at room temperature. Then, the dicyclohexylurea was removed by filtration. The polymer solution in the toluene was precipitated when poured into an excess of cold ethanol. The resulting precipitated polymer (PE-COOCH(*i*Pr)NH-BOC) (0.46 g) was collected and purified by filtration, washing with ethanol several times, and drying in vacuum at 40 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 4.15 (t, 2H); 1.46 (s, 9H); 1.4-0.5 (PE and  $\text{CH}(\text{CH}_3)_2$ ).

The obtained PE-COOCH(*i*Pr)NH-BOC was dissolved in 30 mL toluene. The solution was treated with 15 mL trifluoroacetic acid (TFA) for 2 h. TFA was then removed in vacuum, the residue was dissolved in 30 mL toluene and saturated aqueous  $\text{NaHCO}_3$  and water. The polymer was precipitated when its toluene solution was poured into an excess of ethanol. The resulting precipitated polymer (PE-COOCH(*i*Pr)NH $_2$ ) (0.41 g) was collected and purified by filtration, washing with ethanol several times, and drying in vacuum at 40 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm) 4.14 (t, 2H); 1.4-0.5 (PE and  $\text{CH}(\text{CH}_3)_2$ ).



**Figure S1.**  $^1\text{H}$  NMR spectra of (a) PE<sub>607</sub>-OH, (b) PE<sub>607</sub>-Val-Boc, and (c) PE<sub>607</sub>-NH $_2$ .

**Table S1.** DLS characterizations of PE<sub>607</sub>-*b*-PLL<sub>275</sub> polymeric micelles self-assembled in water at different pH values (Figure 6B).

Entry	pH	Average $R_h$ (nm)	PDI	Peak value of $R_h$ (nm)
1	1.5	$97 \pm 1$	0.140	102
2	6.2	$117 \pm 2$	0.112	115