



Synthesis of amphiphilic block copolyamines via click reaction



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ABSTRACT

Amine functional polymers have been used in many applications owing to their interesting properties, but are unstable under ambient conditions. Here we report the synthesis of four diblock polyamines using a reversible addition–fragmentation chain-transfer (RAFT) polymerization followed by click chemistry. Four amphiphilic block copolyamines **P1–P4** were synthesized and fully characterized using different spectroscopic and physicochemical techniques. Self-assembly of the polymers shows porous films and spherical particles under different conditions. The polymers were used for the liquid–liquid extraction and solid–liquid extraction of pollutants such as metal nanoparticles, organic dyes and heavy metal ions from water. All polymers showed good extraction efficiency towards nanoparticles and anionic dyes. Such stable and processable polyamines can be explored for potential applications in many areas.

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1. Introduction

The reversible addition–fragmentation chain transfer (RAFT) polymerization is widely used for the synthesis of block copolymers with a specific architecture and a narrow distribution of molecular weights [1–4]. Owing to the presence of hydrophobic and hydrophilic blocks, amphiphilic block copolymers display interesting organizations and properties in solid state and in solution [5]. In addition, amphiphilic polymers have attracted much attention in material science and biomedical applications [6–9]. Polyamines or aminogels are used to extract heavy metal ions, nanoparticles and anionic metal species through electrostatic interactions [10–17]. Polymers such as polyethylenimine (PEI) and polyallylamines with large number of primary and secondary amino groups exhibit good extraction ability for heavy metals [18–20].

Water contamination has been a severe problem around the globe and many countries develop innovative solutions to obtain potable water supply at affordable cost. In addition to heavy metal ions, volatile organic compounds, organic dyes, microorganisms and other industrial pollutants, emerging toxic contaminants such as metal nanoparticles, which are tiny and reactive, warrant development of new materials for water purification. Recently, we have reported the synthesis and characterization of polyamines through functional group modifications on the polymer backbone and used them for removing nanoparticles from water [21].

In general, polymers with amine functionalities are challenging to prepare owing to poor stability, high reactivity, low solubility in common solvents and processing difficulties under ambient conditions. Additionally, free amine groups are prone to oxidation by atmospheric oxygen, triggering degradation of the active amine species. Introduction of amine

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protecting groups during synthesis introduces additional synthetic steps that need to be mitigated in order to increase the reaction yield. Also, the pH dependence of amines make the synthetic conditions rather selective.

Here, we report a strategy to obtain diblock polyamines using a combination of RAFT and click reactions. This simple strategy is versatile and can be used for a convenient synthesis of amphiphilic block polymers. 1,2,3-Triazole group, a versatile functional heterocycle unit formed via click chemistry is known for its coordination with anionic, neutral and cationic guest molecules [22,23]. The concept and the structures of target polymers, PES-*b*-PS (**5**), PAPTPA-*b*-PS (**P-1**), PAPTOA-*b*-PS (**P-2**), PAPTXA-*b*-PS (**P-3**), and PAPTPP-*b*-PS (**P-4**) are shown in Fig. 1. The target molecules are designed to incorporate amine functionalities from anilines and pyridines linked to the polymer backbone by flexible spacer alkyl or aryl chains. Presence of the hydrophobic styrene block is crucial towards increasing the solubility in common organic solvents, air-stability and self-organization polymers under ambient conditions and the spacer alkyl chains provide flexibility to the amine groups to coordinate to metals and organic dyes. The synthesized amphiphilic polymers were used to extract metal nanoparticles, metal ions and organic dyes from aqueous solutions.

2. Experimental

2.1. Materials

Styrene (99%), 4-bromostyrene (98%), silver nitrate (AgNO₃), sodium citrate tribasic, hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O), azobisisobutyronitrile (AIBN), diisopropylethylamine (DIPEA), bromotris(triphenylphosphine) copper(I) (CuBr(PPh₃)₃), cyanomethyl dodecyl trithiocarbonate, tetrabutylammonium fluoride (TBAF, 1.0 M in THF) and sodium borohydride (NaBH₄) were purchased from commercial sources and used without further purification. Chloroform (CHCl₃), tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) were used for dissolving block copolymers. Polyvinylpyrrolidone (PVP) capped water soluble Au and Ag nanoparticles were prepared according to reported procedure [24]. Deionised water was used for preparing stock solutions of nanoparticles.

2.2. Measurements

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance AV300 (300 MHz) NMR instrument with CDCl₃ solvent. FT-IR analyses were performed using Bruker ALPHA FT-IR spectrophotometer by preparing KBr pellets with polymers. Gel permeation chromatography (GPC) was used to determine the average molecular weight of polymers on Waters e2695 alliance system equipped with Waters 2414 refractive index detector using THF as the eluent at a flow rate of 0.3 mL/min at 30 °C. Polystyrene was used as standard for calibration. Thermal degradation studies (TGA) were studied with a SDT 2960 TA Instrument. Samples were heated from 25 to 800 °C at a heating rate of 10 °C/min under N₂ atmosphere. Differential scanning calorimetry (DSC) measurements were done using a Mettler Toledo DSC1 STARE System at 10 °C/min under nitrogen atmosphere. Surface morphology of the dropcasted film was studied using JEOL JSM-6701F field emission scanning electron microscope (FESEM). The size and surface charges of nanoparticles were determined using transmission electron microscope (TEM, JEOL JEM-3011), dynamic light scattering (DLS) and Malvern Zetasizer Nano-ZS analyser. The quantitative determinants of extraction efficiency of nanoparticles were carried out using a UV-Vis spectrophotometer (Shimadzu-1601 PC spectrophotometer) and the concentrations of metal ions were quantitatively measured with Dual-view Optima 5300 DV Inductively coupled plasma-optical emission spectroscopy (ICP-OES) system.

2.2.1. General procedure for click reaction

A solution of the prepolymer **5** (1.0 eq., based on (trimethylsilyl)ethynylstyrene units) in THF (20 mL) was treated with azide derivatives (1.0 eq.), CuBr(PPh₃)₃ (0.01 eq.) and DIPEA (0.5 mL, excess) and the mixture was allowed to stir at room temperature for 24 h. After removing the solvent under reduced pressure, the crude product was precipitated from excess of methanol. The solid was filtered, washed repeatedly with methanol and dried under high vacuum at 40 °C for 16 h.

2.2.2. Synthesis of poly[(trimethylsilyl)ethynylstyrene] **2**

To a solution of (trimethylsilyl)ethynylstyrene **1** (2.0 g, 9.98 mmol) in dry THF (5 mL) was added RAFT reagent cyanomethyl dodecyl trithiocarbonate (0.03 g, 0.099 mmol), AIBN (0.01 g, 0.06 mmol), and the mixture was degassed by repeated freeze–pump–thaw cycles, sealed under vacuum and heated at 70 °C for 12 h. The viscous reaction mixture was dissolved in THF (5 mL) and precipitated from excess methanol to give polymer **2** as a white powder (1.6 g, 80%, Mn = 8600 g/mol, PDI = 1.5); ¹H NMR (300 MHz, CDCl₃): δ 7.25–6.95 (m, Ar–H), 6.75–6.22 (m, Ar–H), 1.95–1.25 (m, –CH₂–CH–), 0.37–0.25 (s, Si(CH₃)₃); IR (KBr, cm⁻¹): 3023 (Ar–H), 2925 (C–H), 2140 (–C≡CH), 1610 (–C=C–).

2.2.3. Synthesis of poly[styrene-*b*-(trimethylsilyl)ethynylstyrene] **4**

A mixture of styrene **3** (2.5 g, 24.9 mmol, 5 eq.) and poly[(trimethylsilyl)ethynylstyrene] **2** (1.0 g, 4.9 mmol, 1 eq.) in dry THF (5 mL) was added AIBN (0.01 g, 0.01 eq.) and the mixture was degassed by repeated freeze–pump–thaw cycles, sealed under vacuum and heated at 70 °C for 6 h. The viscous reaction mixture was dissolved in THF (5 mL) and precipitated from excess methanol to give polymer **4** as a white powder (2.9 g, 82%, Mn = 44400 g/mol, PDI = 1.4); ¹H NMR (300 MHz, CDCl₃): δ

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