

Incorporation of terpyridine into the side chain of copolymers to create multi-functional materials

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Abstract

Polymer architectures containing metal–ligands in their side chain represent a diverse approach to generating multi-functional materials. The ability to define a versatile synthetic platform will enable many chemistries and architectures to be studied. This report describes our latest efforts to prepare these unique polymers by either a direct polymerization of functionalized monomers or a post-polymerization attachment. Random and block copolymers have been successfully prepared. Subsequent functionalization with metal ions leads to a variety of properties including metal induced gelation and solvchromic sensors.

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1. Introduction

Hybrid materials are formed by integrating organic and inorganic components into the same molecular backbone leading to a wide variety of advanced properties and applications [1]. This increase in structural complexity can give rise to new properties not foreseen from the single constituting moieties [2]. One such approach is the synthesis of macromolecules containing metal–ligand complexes [3–13]. These complexes impart properties such as luminescence, electro- and photo-chemistry, catalysis, charge, magnetism, and thermochromism [14]. Polymers containing poly pyridyl metal–ligands in their side chain have included polyoxazolines that gelled in the presence of transition metal ions and were thermal reversibility [15–17] and copolymers based on 4'-vinyl-2,2':6',2''-terpyridinyl [18–21].

The preparation of polymeric systems containing terpyridine (terpy) in the side chain has been limited mainly due to limited emission properties from transition metal complexes [22,23]. Interestingly, terpy binds a range of lanthanide ions resulting in excellent luminescence which we have studied [24]. As a result there has been increased

interest in such polymeric materials, a little more than two years ago our lab and Schubert's reported methylmethacrylate (MMA) polymers containing terpy in the side chain [22,23]. These initial reports only covered random copolymers until our recent work on block–random copolymers which localized the metal ligand to one segment of a block copolymer for the first time [25]. The ability to generate block copolymer architectures with metal–ligands confined to one block will have important applications in the field of supramolecular polymer science.

Access to block copolymers required the application of controlled or living polymerization techniques which are compatible with many functional groups. Our approach has focused on living controlled radical polymerization (CRP) methods including atom transfer radical polymerization (ATRP), nitroxide mediated radical polymerization (NMP), and reversible addition-fragmentation chain transfer polymerization (RAFT). In addition to these synthetic methods, a direct approach that involves the polymerization of vinyl functionalized terpy as well as an indirect approach which focuses on the polymerization of active ester monomers and subsequent conversion to incorporate terpy after polymerization was studied. For this indirect method, the *N*-methacryloxysuccinimide (OSu) ester was selected since these esters provide an excellent way to attach functionality after polymerization. In addition, to the best of our knowledge, the controlled polymerization of OSu

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monomer has only been reported twice for the copolymerization of acrylate based polymers [26,27]. Our work extends the use of this monomer to random copolymers with methyl methacrylate (MMA), *n*-butyl methacrylate (*n*BMA), poly ethylene glycol methacrylate (PEGMA), and styrene (S) as well as very well defined block copolymers with monomodal size exclusion chromatography (SEC) curves and narrow PDI [24].

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), *n*-butyl methacrylate (*n*BMA) and styrene (S) were vacuum-distilled and stored in an air free flask in the freezer. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and stored in the freezer. Poly(ethylene glycol) methyl ether methacrylate macromonomer (PEGMA); ($M_n=480$) was obtained from Aldrich and purified by passing through a neutral alumina. 4'-Chloro-2,2':6',2''-terpyridine was purchased from Lancaster and all other chemicals were used as received from Aldrich. Reagent grade DMF was for GPC. All other solvents were used as received. CuBr (98%) was obtained from Fischer Scientifics, PMDETA (99%), ethyl 2-bromoisobutyrate (2-EiBBr, 98%), and anisole (99.7%) were obtained from Aldrich and used without further purification. PMMA macroinitiator and terpyridine amine were synthesized following the procedure as reported earlier [23–25]. Following ATRP synthesis, polymers were checked for the presence of residual copper by elemental analysis and no copper was detected. This is important considering the complexation studies that were performed.

2.2. Measurements

^1H NMR spectra were obtained at 300 MHz with a Bruker DPX-300 NMR spectrometer in CDCl_3 . The mole percent incorporation of terpyridine into the copolymer was calculated by normalizing the integration values of the OCH_2 from the terpyridine functions, and OCH_3 , from MMA. Gel permeation chromatography (GPC) was performed in dimethylformamide (DMF) or tetrahydrofuran (THF) at room temperature using a PL LC 1120 pump, a Waters R403 differential refractometer, and three PLgel columns (105, 104, and 103 Å) and calibrated with narrow molecular weight poly (methyl methacrylate) standards. UV–vis spectra were obtained using a Perkin–Elmer Lambda 2 series spectrophotometer with PECSS software. Fluorescence spectra were obtained using a Perkin–Elmer LS 55 luminescence spectrometer. IR spectra were obtained using a Bio-Rad FTS 3000 Excalibur Series.

2.3. Synthesis

2.3.1. Synthesis of poly(styrene-*ran*-sty_{terpy}) copolymer

A mixture of the alkoxyamine initiator (5.0 mg, 0.0151 mmol), styrene (608 mg, 5.82 mmol), and sty_{terpy} (300 mg, 0.65 mmol) were degassed by three freeze/thaw cycles, sealed under Nitrogen, and heated at 125 °C under nitrogen for 10 h 25 min. The viscous reaction mixture was then dissolved in dichloromethane (10 ml) and precipitated (2×) into methanol (400 ml). The white precipitate was collected and dried under vacuum at 100 °C to give the desired copolymer as a white precipitate (0.69 g, 66% yield), $M_n=32.1$ k, PD=1.33. ^1H NMR (300 MHz, CDCl_3), δ 8.60–8.62 ppm (dd, broad), 8.10 ppm (s, broad), 8.00–8.08 ppm (m, broad), 7.87 ppm (m, broad), 6.8–7.6 ppm (m, broad), 6.1–6.8 ppm (m, broad), 4.0–4.4 ppm (m, broad), 3.2–3.6 ppm (m, broad). Elemental analysis, Calculated based on 10 mol% sty_{terpy}: Calculated: C% (86.34), H% (7.12), N% (3.99), Found: C% (86.23), H% (7.37), N% (4.03).

2.3.2. Synthesis of poly(styrene-*b*-(styrene-*ran*-sty_{terpy})) copolymer

A mixture of the alkoxyamine initiator, sty_{terpy} (10 mg, 0.0307 mmol), styrene (1.531 g, 14.651 mmol), and acetic anhydride (0.626 mg, 0.00613 mmol) were degassed by three freeze/thaw cycles, sealed under nitrogen, and heated at 125 °C under nitrogen for 7 h. The colorless solid was dissolved in dichloromethane (15 ml) and precipitated (2×) in methanol (400 ml). The white precipitate was dried under vacuum to give the desired polystyrene macroinitiator (1.166 g, 76%), $M_n=44,350$, PDI=1.13. The polystyrene, 6, Starting block (271.8 mg, 0.00613 mmol), sty_{terpy} (272.4 mg, 0.59 mmol) were dissolved in styrene (0.513 g, 2.452 mmol). The mixture was degassed by three freeze/thaw cycles, sealed under nitrogen and heated at 125 °C for 16 h 30 min. the solidified reaction mixture was dissolved in dichloromethane and precipitated (2×) in methanol (500 ml). The white precipitate was dried under vacuum at 100 °C to give the desired copolymer (590 mg, 56% yield) $M_n=67,200$, PDI=1.4. ^1H NMR (300 MHz, CDCl_3), δ 8.603 ppm (s, broad), 8.091 ppm (s, broad), 7.793 ppm (s, broad), 7.040 ppm (s, broad), 6.8–6.0 ppm (m, broad), 4.162 (s, broad), 3.470 ppm (s, broad), 2.41–1.00 ppm (m, broad). Elemental analysis, calculated based on 7.5 mol% sty_{terpy}: calculated: C% (87.47), H% (7.23), N% (3.19), Found: C% (87.14), H% (7.37), N% (3.19).

2.3.3. General procedure for copolymerization of OSu

Table 1 summarizes experimental conditions, molecular weights and MWDs for these random copolymers. In a typical experiment, a dry vial equipped with a stir bar was charged with CuBr (4.3 mg, 0.033 mmol) under a flowing stream of nitrogen. To this, specified amounts of PMDETA (8.5 mg, 0.049 mmol), 2-EiBBr (8.6 mg, 0.044 mmol), and anisole (0.3 ml) were added. After this, MMA (85 mg,

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