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Synthesis and chemosensory properties of terpyridine-containing diblock polycarbazole through RAFT polymerization

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ABSTRACT

This paper describes the synthesis of a terpyridine-containing diblock copolymer, poly(N-vinylcarbazole)-*block*-poly[4′-((4-vinylphenyl) phenyl)-2,2′:6′,2″- terpyridine] (poly(VK_{15}-*b*-TPY_4)), using the macro-chain transfer agent VK macro-CTA, and employing two-step reverse addition-fragmentation transfer (RAFT) polymerization. We examined the effect of terpyridine units on sensory characteristics of fluorescent chemosensors. VK macro-CTA and diblock copolymer poly(VK_{15}-*b*-TPY_4) both exhibited moderate thermal stability, with thermal decomposition temperatures of 5% weight losses at approximately 307 °C and 378 °C, respectively, suggesting that the enhancement of thermal stability was attributed to the incorporation of terpyridine segments into the block copolymer. Poly(VK_{15}-*b*-TPY_4) exhibited higher sensitivities to Ni^{2+} and Mn^{2+} ions, with Stern–Volmer constants (K_{sv}) of 2.58×10^5 M^{-1} and 2.57×10^5 M^{-1}, respectively. Adding a Zn^{2+} ion not only caused partial fluorescence enhancement (3.2-fold quantum efficiency) but also induced a bathochromic shift of emission peak by approximately 56 nm (from 429 nm to 485 nm), indicating that the Zn^{2+}-terpyridine complex reduced the twist and vibration of the C–C polymer backbone and enhanced the charge transfer from donors to acceptors because of the more planar and rigid structure. Our results suggest that poly(VK_{15}-*b*-TPY_4) is a promising material for chemosensory applications.

1. Introduction

The growth of chemosensors for sensing various analytes by applying color or fluorescence intensity has increased and chemosensors have attracted particular attention for various environmental applications during the past decade because of their high analyte sensitivity and ease of measurement [1–3]. Fluorescent chemosensors based on conjugated polymers have been developed for measuring pH and detecting metal ions and biological species. These detection properties arise because the fluorescence properties of the chemosensor depend on coupling between the receptors on the polymer and detected analytes [4,5]. A chemosensor comprises a receptor (the recognition site) and a fluorophore group (the signal source). The signal translates the recognition event into the fluorophore group [6–8]. Polymer-based optical sensors offer several crucial advantages over low molecular-weight molecules, including transformation and amplification of the fluorescent signal [9]. The high sensitivity is mainly acquired by the highly conjugated polymer chain through which the signal is transformed and amplified. Fluorescent pyridine-based derivatives such as 1,10-phenanthroline [10,11], 2,2′-bipyridine [12–15], and 2,2′:6′,2″-terpyridine [16–19] have high binding affinities toward many metal ions in low oxidation states because of dπ—pπ* bonding modes.

In recent years, the use of controlled/living radical polymerization (CLRP) methods (e.g., atom transfer radical polymerization (ATRP) [20–22], nitroxide-mediated radical polymerization (NMP) [23], and reversible addition-fragmentation chain transfer (RAFT) polymerization [24–26]) has increased extensively in the preparation of block polymers, because using these methods yields advantages such as a simple experimental setup, a wide range of functional monomers, and complex macromolecular architectures with well-defined end groups of narrow polydispersity in the CLRP methods [27,28]. RAFT polymerization is a well-established CLRP method that exhibits numerous appealing characteristics for controlling the synthesis of a wide variety of macromolecular architectures and for maintaining molecular weight control, narrow molecular weight distributions, and functionality [29]. The absence of catalysts and the ease of scaling up make RAFT one of the most versatile CLRP techniques. To our best knowledge, only a few studies on the synthesis of the fluorescent chemosensor polymers using RAFT methods have been done. Zhao et al. [30] employed the RAFT technique to prepare thermo- and pH-responsive fluorescent polymers (PCN51 and PCN250). Their results verified that PCN250 shows absorbance enhancement or decrease at different pH values. However, the fluorescence intensity of this copolymer demonstrates enhancement with a rise in temperature if pH values are in the range of 4–10. In

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addition, fluorescence suppression of PCN250 was observed with high proton concentration. Tian et al. [31] synthesized a polymer chemosensor (PNa) containing a naphthalimide signal moiety and piperazinyl ring recognition moiety for detecting protons through RAFT polymerization. PNa and its corresponding monomer (Na) showed both fluorescence enhancement in a low proton concentration and fluorescence suppression in a high proton concentration, which can be observed by both the naked eyes and optical responses.

In our previous study [32], we examined the effect of microwave heating on the polymerization kinetics of a 4-acetoxystyrene-based macro-chain transfer agent (macro-CTA) and investigated the effects of azobenzene on the E/Z photoisomerization, as well as the self-assembly behavior of a diblock copolymer in a THF/H_2O solution by using RAFT polymerization. In this study, we employed a two-step RAFT polymerization technique to synthesize a macro-CTA, VK macro-CTA, and a novel terpyridine-based block polymer, poly(VK_{15}-*b*-TPY_4). We examined the effect of a terpyridine unit on the optoelectronic properties of polymers and on the sensory characteristics of fluorescent chemosensors. Poly(VK_{15}-*b*-TPY_4) takes advantage of luminescence properties of the carbazole-based polymer chain and metal ion-coordinating ability of the terpyridine unit to yield a highly effective transition-metal chemosensor. In the present system, we found that poly(VK_{15}-*b*-TPY_4) exhibiting a pendant terpyridine unit shows highly selective response to specific metal cations (Mn^{2+} and Ni^{2+}). Moreover, adding a Zn^{2+} ion not only caused partial fluorescence enhancement but also induced a broad red-shifted emission peak in the range of 400–650 nm, indicating that the Zn^{2+}–TPY complex reduced the twist and vibration of the C–C polymer backbone and enhanced the charge transfer from donors to acceptors because of the higher planarization and rigidity of structure compared with the pristine poly(VK_{15}-*b*-TPY_4). Our results suggest that poly(VK_{15}-*b*-TPY_4) has potential applications in chemosensors.

2. Experimental

2.1. Materials

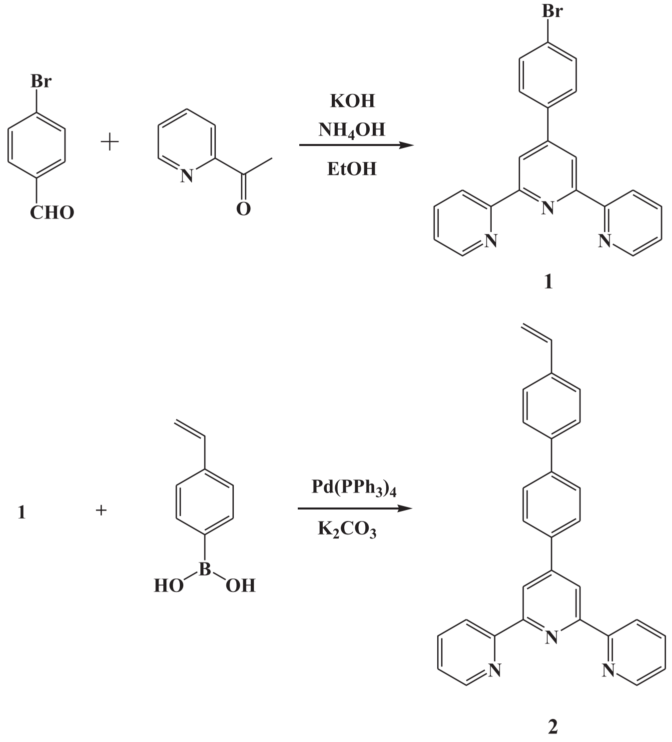
Synthetic routes for the target terpyridine-based monomer (2) are shown in Scheme 1. The target intermediate, 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine (1), was synthesized following the processes reported previously [33–35]. Synthetic routes for the target macro-CTAs (VK macro-CTAs) and diblock copolymer (poly(VK_{15}-*b*-TPY_4)) are shown in Scheme 2. The polymers were synthesized following the procedures reported in the supporting information. 9-Vinylcarbazole (Sigma-Aldrich, 98%) and 2,2′-azoisobutyronitrile (AIBN, 98%, Sigma-Aldrich) were recrystallized from methanol twice. All organic solvents and reagents were purchased from Acros, Alfa, and Aldrich Chemical Co. and used without further purification. *S*-(Thiobenzoyl)thioglycolic acid (CTA, 99%, Sigma-Aldrich) and other chemical reagents were used as received unless otherwise noted. Toluene (Acros, 99.5%) and tetrahydrofuran (THF, >99.9%, Sigma-Aldrich) were dried with appropriate drying agents, calcium hydride or sodium, then distilled under reduced pressure and stored over 4 Å molecular sieves before use.

2.2. Measurements

^1H NMR (400 MHz) spectra were recorded on a Bruker AMX-400 FT-NMR, and chemical shifts were reported in ppm using tetramethylsilane (TMS) as an internal standard. Elemental analysis was carried out on a Heraeus CHN–O rapid elemental analyzer. Number-average molecular weight (M_n) and polydispersity index (PDI) of polymers were measured with a gel permeation chromatograph (GPC), model CR4A from Shimadzu, using tetrahydrofuran (THF) as an eluent and the rate of elution was 1.0 ml min^{-1}. Polystyrene standard (1000–136000 g mol^{-1}) was used for calibration. Thermal analysis was performed using a differential scanning calorimeter (Perkin Elmer DSC 7) at a scanning rate of 20 K/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 20 K/min using a Perkin Elmer TGA-7 thermal analyzer. UV/visible absorption spectra were measured using a Jasco V-670 spectrophotometer and photoluminescence (PL) spectra were obtained using an OBB Quattro II fluorescence spectrophotometer. Fluorescence quantum yields of compounds in chloroform using 9,10-diphenylanthracene ($\lambda_{ex} = 350$ nm) as the standard were estimated at room temperature by the dilution method (1×10^{-7} M, assuming a quantum efficiency of unity). Cyclic voltammograms were recorded with a voltammetric analyzer (model CV-50 W from BAS) at room temperature under nitrogen atmosphere with a scanning rate of 100 mV/s. The measuring cell comprised polymer-coated ITO as the working electrode, Ag/AgCl electrode as the reference electrode, and platinum wire electrode as the auxiliary electrode. The electrodes were immersed in acetonitrile containing 0.1 M tetrabutylammonium perchlorate ($(n\text{-Bu})_4NClO_4$) as electrolyte. The energy levels were calculated using the ferrocene (FOC) value of −4.8 eV with respect to vacuum level, which is defined as zero. All the computational calculations were performed at B3LYP/6-31G* level using density functional theory (DFT) with Gaussian 09 program [36]. The DFT calculations on the model compounds based on VKTPY and VKTPY-Zn^{2+} were performed using default-spin.

2.3. Fluorescent titration of polymer

Fluorescent titration experiments were carried out in THF solution. The chloride salts of Li^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Al^{3+}, Ba^{2+}, Ag^+, Pb^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} (5.0×10^{-5} M) were dissolved in distilled water. Titration was done by adding the metal ion solution to a test tube with polymer solution. The final concentration of polymer was 1.0×10^{-6} M. Titration of the metal ions was terminated until no



Scheme 1. Synthetic routes of terpyridine-based monomer (2).