Reactive & Functional Polymers 87 (2015) 46–52

Contents lists available at ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Synthesis and ion responsiveness of optically active polyacetylenes containing salicylidene Schiff-base moieties

Chunyu Zhang [a], Yu Zhang [b], Hexin Zhang [a], Yanming Hu [a,*], Xuequan Zhang [a], Toshio Masuda [c]

[a] Key Laboratory of Synthetic Rubber, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
[b] Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China
[c] Research Center for Environmentally Friendly Materials Engineering, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran 050-8585, Japan

ARTICLE INFO

Article history:
Received 24 October 2014
Received in revised form 13 January 2015
Accepted 15 January 2015
Available online 22 January 2015

Keywords:
Conjugated polymer
Polyacetylene
Helix
Stimuli-responsive
Polymerization

ABSTRACT

Acetylenic monomers containing salicylidene Schiff-base groups (**1a** and **1b**) as well as Schiff-base and hydroxy groups (**1c**) were synthesized and polymerized with $[(nbd)RhCl]_2/Et_3N$ catalyst to afford the corresponding polymers **2a**–**c** with high molecular weights ($M_n = 2.6–7.2 \times 10^5$) in high yields (75–97%). Polarimetric, circular dichroism (CD), and UV–vis spectroscopic analyses indicated that the polymers formed helical structures with a predominantly one-handed screw sense. The addition of metal ions to salicylidene Schiff-base-containing polymers **2a** and **2b** produced insoluble polymer/metal complexes through ionic cross-linking as a result of salicylaldimine–metal ion complexation. Polymers **2b** and **2c** underwent a helix–coil transition upon the addition of HSO_4^-, whereas these polymers did not exhibit responsiveness to other anions, such as F^-, Cl^-, and Br^-.

1. Introduction

The development of novel artificial helical polymers continues to be a topic of considerable interest and importance in the area of macromolecular science from both fundamental and application-oriented perspectives [1–6]. Over the past decades, tremendous strides have been made in the field of synthetic helical polymer chemistry, and a variety of helical polymers have been successfully synthesized not only to mimic biological helices but also for their potential applications in chiral recognition, asymmetric catalysis, chemical sensors, and so forth [7–10]. Among these polymers, conjugated helical polymers, such as polyisocyanides, polysilanes, and polyacetylenes, are of great interest and are intensively studied because of their unique functions resulting from their helical structures and conjugated main chains.

As a class of typical π-conjugated polymers, polyacetylene and its derivatives exhibit interesting chemical and physical properties [11–13]. Substituted polyacetylenes can form helical structures with a predominantly one-handed screw sense through the introduction of appropriate chiral substituents into the side chain or through the helix-sense-selective polymerization of achiral monomers [14–22]. Polyacetylene derivatives adopt a dynamic helical conformation due to the relatively low energy barriers for helix reversal [3]. These derivatives can undergo helix/random coil transitions and/or helix inversions in response to external stimuli, such as temperature, light, and change of medium conditions, including polarity and pH, which is attractive in a wide variety of fields, including life sciences, pharmacy, and chemical engineering. Although various helical polyacetylenes have been reported, sophisticated studies are still being performed to design and tailor desired polymer properties.

Salicylidene Schiff bases, which are an important and versatile class of ligands, have attracted considerable attention because of their facile preparation via salicylaldehyde–amine condensation, easy modification of their steric and electronic properties, and high binding affinity toward various metal ions [23–25]. Various salicylidene Schiff-base/metal complexes have been synthesized and have found potential applications in optic materials, chemical sensors, biological probes, and efficient catalysts for organic reactions [26–29]. However, compared with the extensively studied low-molecular-weight systems, the synthesis and applications of salicylidene Schiff-base-containing polymers are quite limited. Lu and coworkers prepared “light-controllable” fluorescent polystyrene micelles via salicylaldimine–Zn^{2+} complexation [30]. Theato and coworkers prepared thermo- and light-responsive polyacrylamides that contained different amounts of salicylideneaniline chromophores [31]. Cai and coworkers reported the synthesis of metal-functionalized polymer micelles through Co^{2+}–salicylaldimine coordination [32]. The above-mentioned salicylidene

---

* Corresponding author. Tel.: +86 431 85262305; fax: +86 431 85262274.
E-mail address: ymhu@ciac.ac.cn (Y. Hu).

http://dx.doi.org/10.1016/j.reactfunctpolym.2015.01.003
1381-5148/

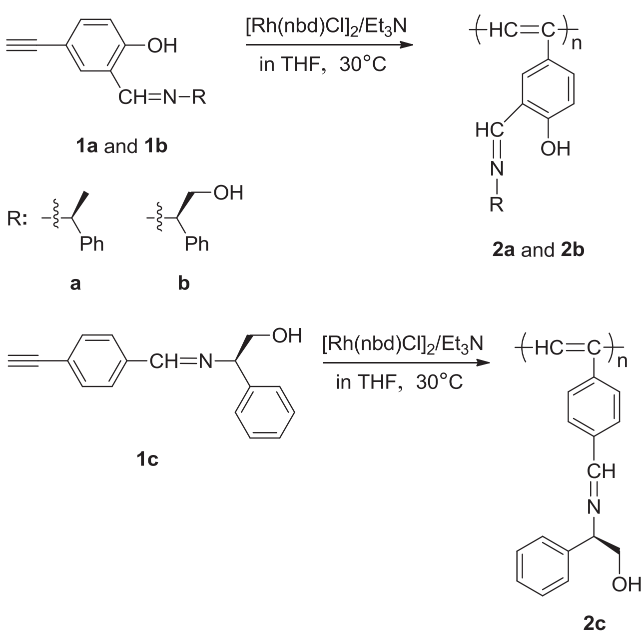
Schiff-base-containing polymers were synthesized through the side-chain modification of polymers via aldehyde–amine condensation. In contrast, the direct polymerization of salicylidene Schiff-base-containing monomers is a simple and straightforward route for the synthesis of well-defined polymers with salicylidene Schiff-base pendant groups. We recently reported that (*S*)- and (*R*)-*N*-(4-ethynylbenzylidene)-1-phenylethanamine, which are Schiff-base-functionalized acetylenic monomers, polymerize with $[(nbd)RhCl]_2/Et_3N$ catalyst to afford helical polyacetylenes [33]. Thus, we can potentially prepare novel functional helical polyacetylenes bearing salicylidene Schiff-base groups through direct polymerization of the corresponding monomers, which could exhibit interesting properties as a result of the combination of the unique characteristics of the salicylidene Schiff base and the higher-order structure of the polyacetylene backbone.

The present study focuses on the synthesis and polymerization of novel acetylenic monomers containing salicylidene Schiff-base moieties (**1a** and **1b**) as well as a monomer containing both Schiff-base and hydroxy groups (**1c**) for comparison (Scheme 1). The secondary structures of the resulting polymers were investigated in detail, and their responsiveness to metal ions and tetra-*n*-butylammonium hydrogen sulfate was examined.

2. Experimental section

2.1. Measurements

^1H and ^{13}C NMR spectra were recorded on a Varian Unity-400 spectrometer. IR spectra were recorded on a BRUKER Vertex-70 spectrophotometer. The number- and weight-averaged molecular weights (M_n and M_w) of the polymers were determined using a gel permeation chromatograph equipped with a Waters 515 HPLC pump and a Waters 2414 differential refractometer using THF as the eluent at a flow rate of 1.0 mL/min and calibrated with polystyrene standards. Elemental analysis of the monomers was performed at the Analytical Center of Dalian University of Technology. Specific rotations ($[\alpha]_D$) were measured using a JASCO DIP-1000 digital polarimeter. CD and UV–vis spectra were recorded on a JASCO J-810 spectropolarimeter.



Scheme 1. Synthesis of poly(phenylacetylene) derivatives **2a–c**.

2.2. Materials

THF, which was used as the polymerization solvent, was distilled over sodium prior to use. Triethylamine was distilled and dried over potassium hydroxide. 4-Bromobenzaldehyde (Aladdin Co.), 5-bromosalicylaldehyde (J & K), (*R*)-1-phenylethanamine (Aldrich), (*R*)-2-phenylglycinol (Aladdin Co.), trimethylsilylacetylene (Acros), bis(triphenylphosphine)palladium(II) dichloride (Aldrich), and $[(nbd)RhCl]_2$ (Aldrich) were used as received. Other solvents, such as methanol, toluene, and $CHCl_3$, were of high purity and were used without further purification. 4-Ethylnylbenzaldehyde and 5-ethynylsalicylaldehyde were synthesized following methods reported in the literature [34,35].

2.3. Monomer synthesis

2.3.1. (R)-4-ethynyl-2-((1-phenylethylimino)methyl)phenol (1a)

A 100-mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar. (*R*)-1-Phenylethanamine (0.61 g, 5 mmol) and 5-ethynylsalicyclaldehyde (0.73 g, 5 mmol) were dissolved in toluene (60 mL). The reaction mixture was heated at reflux temperature for 10 h. The generated water was separated using a Dean–Stark apparatus. Then, toluene in the reaction mixture was removed by evaporation, and the crude product was purified by recrystallization from ethanol to afford bright yellow crystals in 55% yield; $[\alpha]_D = +23°$ ($c = 0.2$ g/dL, $CHCl_3$, room temperature). ^1H NMR (400 MHz, $CDCl_3$): δ 13.8 (s, 1H, OH), 8.31 (s, 1H, $CH{=}N$), 7.42–6.88 (m, 8H, ArH), 4.54 (q, 1H, $N{-}CH$), 2.97 (s, 1H, $HC{\equiv}C$), 1.61 (m, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 ($CH{=}N$), 162.0, 143.5, 136.1, 135.5, 128.9, 127.6, 126.5 118.7, 117.6, 112.3, 83.3, 75.9, 68.4, 24.9. IR (cm^{-1}, $CHCl_3$): 3278, 3107, 2927, 1630 ($CH{=}N$), 1583, 1485, 1396, 1289, 973, 830, 770, 701. Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.78; H, 6.21; N, 5.87.

2.3.2. (R)-4-ethynyl-2-((2-hydroxy-1-phenylethylimino)methyl) phenol (1b)

This monomer was prepared using the same method as for monomer **1a** but with (*R*)-2-phenylglycinol rather than (*R*)-1-phenylethanamine to afford orange crystals in 50% yield; $[\alpha]_D = +9°$ ($c = 0.1$ g/dL, $CHCl_3$, room temperature). ^1H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H, $CH{=}N$), 7.44–6.90 (m, 8H, ArH), 4.47 (t, 1H, $N{-}CH$), 3.91 (m, 2H, CH_2OH), 2.99 (s, 1H, $HC{\equiv}C$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7 ($CH{=}N$), 145.1, 136.8, 132.4, 128.6, 128.3, 127.1, 126.8, 124.3, 83.5, 79.0, 70.0, 25.0. IR (cm^{-1}, $CHCl_3$): 3287, 3061, 2925, 2867, 1633 ($CH{=}N$), 1586, 1487, 1383, 1287, 1068, 893, 830, 760, 700. Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.73; H, 5.65; N, 5.47.

2.3.3. (R)-N-(4-ethynylbenzylidene)-2-phenylglycinol (1c)

This monomer was prepared using the same method as for monomer **1a** but with (*R*)-2-phenylglycinol and 4-ethynylbenzaldehyde rather than (*R*)-1-phenylethanamineand 5-ethynylsalicylaldehyde to afford light yellow crystals in 54% yield; $[\alpha]_D = +125°$ ($c = 0.1$ g/dL, $CHCl_3$, room temperature). ^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H, $CH{=}N$), 7.69–7.29 (m, 9H, ArH), 4.50 (t, 1H, $N{-}CH$), 3.98 (m, 2H, $CH_2{-}O$), 3.22 (s, 1H, $HC{\equiv}C$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 ($CH{=}N$), 140.6, 135.9, 132.4, 129.0, 128.8, 127.7, 126.9, 126.6, 126.3, 124.7, 83.4, 79.4, 67.8, 62.4. IR (cm^{-1}, $CHCl_3$): 3286, 3062, 3029, 2923, 2868, 1641 ($CH{=}N$), 1604, 1493, 1452, 1383, 839, 759, 701. Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.60; H, 5.99; N, 5.55.