

Synthesis, Characterization, and Coordination Behavior of Copoly(styrene-maleimide) Functionalized with Terpyridine

Gholam Ali Koohmareh, Morteza Sharifi

Department of Chemistry, Faculty of Science, University of Isfahan, Isfahan 81746-73441, Iran

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ABSTRACT: A maleimide functionalized terpyridine, 4'(4-maleimidophenyl)-2, 2' : 6', 2''-terpyridine, was synthesized and copolymerized with styrene via radical polymerization. The synthesized monomer was characterized by CHN elemental analysis, FT-IR, ¹H NMR, and Mass spectrometry. The structure of polymer was also confirmed by FT-IR and UV-Vis spectroscopy. The resulting polymer was soluble in chloroform and polar aprotic solvents, and showed an inherent viscosity of 1.5 dL/g in *N,N*-dimethyl formamide at 25°C. The polymer solution in CHCl₃/methanol showed a metal-ligand charge-transfer band of 586 nm upon addition

of Fe(II) ion, exhibiting that coordination between terpyridine units and Fe(II) had occurred. The thermal stability of polymer before and after complexation with Fe(II) was examined by thermogravimetric analysis. For polymer before complexation, the weight loss started at 180°C whereas for complexed polymer it started at 260°C, which demonstrates good thermal stability of complexed polymer. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 179–183, 2010

Key words: polystyrene; synthesis; thermal properties; metal-polymer complexes

INTRODUCTION

Hybrid materials are formed by integrating organic and inorganic units into the same molecular backbone leading to a wide variety of advanced properties and applications.¹ This increase in complexity can cause new properties not foreseen for the single moiety.² To make hybrid materials, one approach is the synthesis of macromolecules containing metal-ligand complexes in the side chain.³ These complexes give interesting properties such as luminescence, electro and photochemistry, catalysis, charge, magnetism, and thermochromism.⁴ Because of their high-binding affinity for transition metal ions, 2, 2'-bipyridine and 2, 2' : 6', 2''-terpyridine ligands are of particular interest to introduce metal binding sites into polymers.^{5–10} Macromolecules bearing terpyridine units in the side chain were the first terpyridine containing polymers that were synthesized by polymerizing monomer functionalized terpyridine either by free radical polymerization or any other condensation methods.^{11–17} Here, a maleimide functionalized terpyridine, 4'(4-maleimidophenyl)-2, 2' : 6', 2''-terpyridine, was synthesized and copolymerized with styrene via radical polymerization. The physical properties and coordination behavior of this polymer were investigated.

Correspondence to: G. A. Koohmareh (g.a.koohmareh@sci.ui.ac.ir).

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EXPERIMENTAL

Materials

Acetyl pyridine, 4-nitrobenzaldehyde, and styrene, pyridine, methanol, maleic anhydride, and *N*-methyl-2-pyrrolidone (NMP) were purchased from Aldrich or Merck chemical companies. Ethanol and concentrated hydrochloric acid (36%) were bought from commercial sources and used as received. *N*-[2-(pyrid-2'-yl)-2-oxoethyl]pyridinium iodide (Krönke salt) was prepared in our laboratory, according to the standard procedure.¹⁸

Instrumentation

The FT-IR spectrums were recorded using Nicolet Impact 410 FT-IR spectrophotometer in potassium bromide pellets. The elemental analysis was carried out by a Thermoquest CHNS-Ovelemental analyzer. Thermogravimetric analysis (TGA) was performed using a Mettler TG5 in nitrogen atmosphere at a heating rate of 10°C/min. The UV-Visible absorption spectrums were recorded using a Carry 2501-pc spectrophotometer.

Synthesis of 3-(4-nitrophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (1)

To an ice-cold solution of KOH (0.309 g, 5.5 mmol) in methanol (11 mL) and H₂O (2 mL), 4-nitrobenzaldehyde (0.871 g, 5.5 mmol) and freshly distilled 2-

acetylpyridine (0.62 mL, 5.5 mmol) was added. The mixture was stirred for 1 h in an ice-bath and then the temperature raised up to room temperature for 30 min. The precipitated solid was filtered off and washed with cold methanol. The crude product was recrystallized from EtOH. Yield: 85%. UV (EtOH): 319 nm. IR (KBr, cm^{-1}): 1679 (C=O), 1517 (NO_2), 1352 (NO_2). m/z : 254.06 (25%), 255.06 (16.7%).

Synthesis of 4'(4-nitrophenyl)-2, 2' : 6', 2''-terpyridine (2)

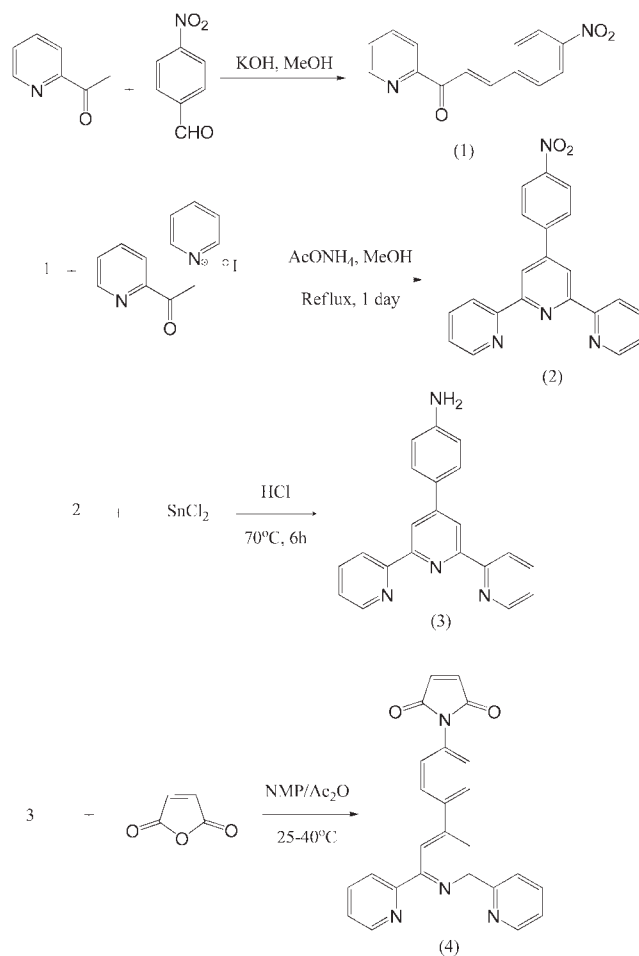
A mixture of 1 (1.34 g, 5 mmol), ammonium acetate (2.314 g, 30 mmol), Krönke salt (1.63 g, 5 mmol), and dry methanol (50 mL) was refluxed for 18 h. The mixture was then cooled, and the brownish solid was filtered off and washed with cold methanol. The crude product was recrystallized from ethanol. Yield: 92%. UV (EtOH): 285, 243 nm. IR (film, cm^{-1}): 1529, 1351, 1505. m/z : 354.11 (26%), 355.12 (17%).

Synthesis of 4'(4-aminophenyl)-2, 2' : 6', 2''-terpyridine (3)

A mixture of 2 (0.605 g, 1.7 mmol) and Tin(II) chloride dihydrate (1.536 g, 6.8 mmol) in concentrated hydrochloric acid (9 mL) was heated at 70°C for 5 h. Then, the solution was cooled and poured into NaOH solution (10 mL, 10%). The mixture was stirred for 30 min and the pH of the solution adjusted to 8 and stirring was continued for 1 h. The solid was filtered and recrystallized with a mixture of MeOH/ CHCl_3 and dried under vacuum oven at 70°C. Yield: (84%). Mp: 250°C. UV (EtOH): 285, 243, 313 nm. FT-IR (KBr, cm^{-1}): 3338, 1584. m/z : 324.3, 244.21.

Synthesis of 4'(4-maleimidophenyl)-2, 2' : 6', 2''-terpyridine (4)

Under nitrogen atmosphere, a solution of maleic anhydride (0.098 g, 1 mmol) and 3 (0.324 g, 1 mmol) in dry NMP (4 mL) was stirred for 12 h at 25°C. The acetic anhydride (4 mL) was then added to the reaction mixture and stirred for 12 h at 40°C. After cooling the solution, it was poured into water and filtered off. The product was washed with methanol several times, and recrystallized from ethanol and dried in a vacuum oven at 50°C for 24 h. Yield 75%. Mp: 278°C. UV: 334 nm. FT-IR (KBr, cm^{-1}): 1717, 1585, 1381. $^1\text{H-NMR}$ (DMSO- d_6 , δ): 7.2–8 ppm (CH, arom), 5.2 ppm (CH, maleimide). CHNS analysis C: 74.27% (calc.74.25), H: 3.95% (calc.3.99), N: 13.82% (calc.13.85), O: 7.91% (calc.7.91), m/z 404.13 (M^+ , 100), 405.13 (15.7%).



Scheme 1 Synthesis of maleimide functionalized terpyridine.

Synthesis of terpyridine functionalized copoly(styrene-maleimide)

A mixture of 4 (0.0848 g, 0.21 mmol), styrene (0.5 mL, 4.35 mmol) and azobis isobutyronitrile, AIBN (6 mg, 0.04 mmol) in dry 1,2-dichloroethane (5 mL) was heated in a closed flask at 80°C for 4 days. The viscous content was then poured into methanol (25 mL). The precipitated polymer was removed by filtration, washed with MeOH and dried over P_2O_5 to obtain a light yellowish brown (440 mg, 76%). Amount of terpyridine units in the polystyrene backbone: 5%. η_{inh} : 1.57. FT-IR (KBr, cm^{-1}): 3024, 1600, 1450, and 1400.

RESULTS AND DISCUSSIONS

4'(4-aminophenyl)-2, 2' : 6', 2''-terpyridine was synthesized in three steps by modified, previously reported, procedures,^{19–22} starting from acetyl pyridine and 4-nitro benzaldehyde to synthesize related enone compound, which was then treated with the known organic salt, Kröhnke reagent, to form the nitro compound (2). The current nitro terpyridine was then

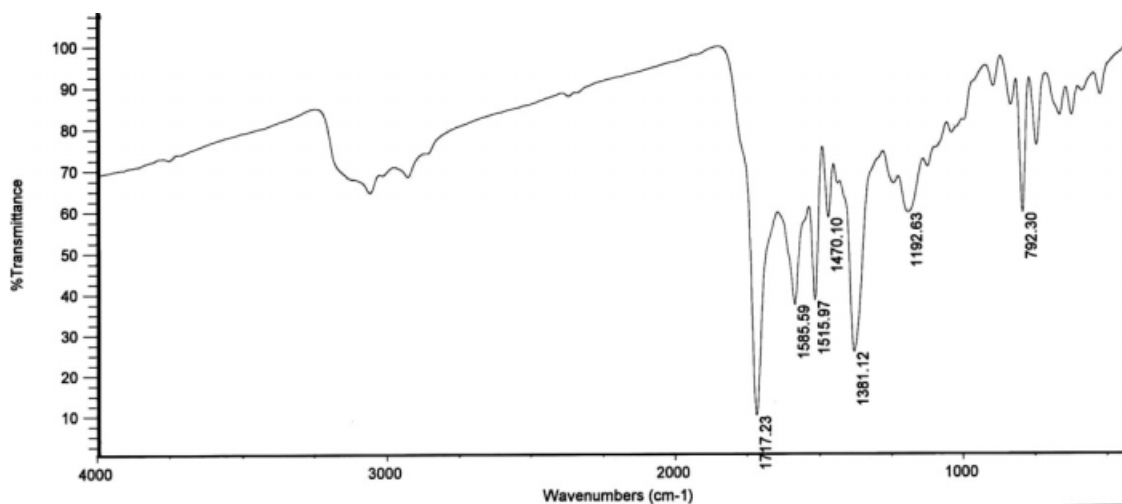


Figure 1 FT-IR spectrum of synthesized monomer.

reduced to amino compound using a known reducing reagent, SnCl₂/HCl with 84% yield (Scheme 1).

The amino terpyridine compound was reacted with maleic anhydride in NMP in the presence of acetic anhydride to obtain maleimide functionalized terpyridine in 70% yield (Scheme 1). The synthesized monomer was characterized with FT-IR, ¹H NMR, MASS, and CHNS elemental analysis. In the FT-IR spectra, the peaks related to amino group and OH band of acid disappeared, and a new sharp peak at 1717 cm⁻¹ was observed (Fig. 1).

In Mass spectrum, the peaks at 404.60 and 405.95 for (M+1), confirm formation of this monomer (Fig. 2). The ¹H NMR spectrum shows broad peaks

at $\delta = 8.1$ – 7.2 ppm for aromatic protons and a peak at $\delta = 5.2$ ppm for the maleimide protons. Polymerization was carried out in a low polar solvent, 1, 2-dichloroethane with high solubility and AIBN as initiator at 80°C for 4 days (Scheme 2). This method results in a good polymer chain growth without a need for any further purification of the polymer because of its good work up.

The presence of some peaks at the range of 200–300 nm in UV-Vis spectrums of the synthesized polymer confirms terpyridine group (Fig. 3). Also, its FT-IR shows the C–H bond for polystyrene methylenes at 3024 cm⁻¹ and the known 1600 cm⁻¹ peak for terpyridine substructure. The solubility

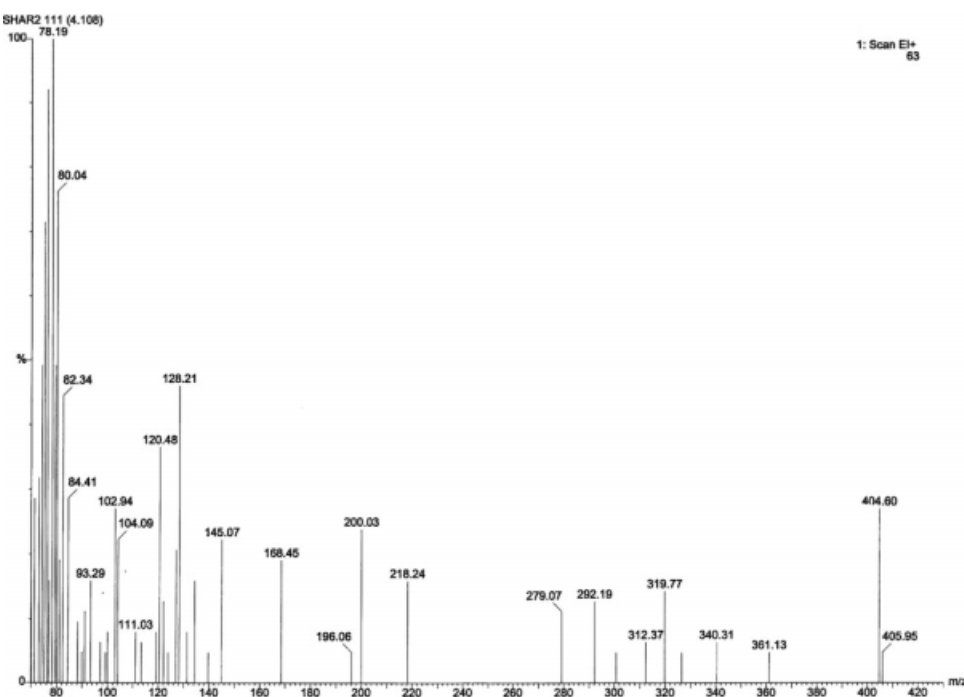
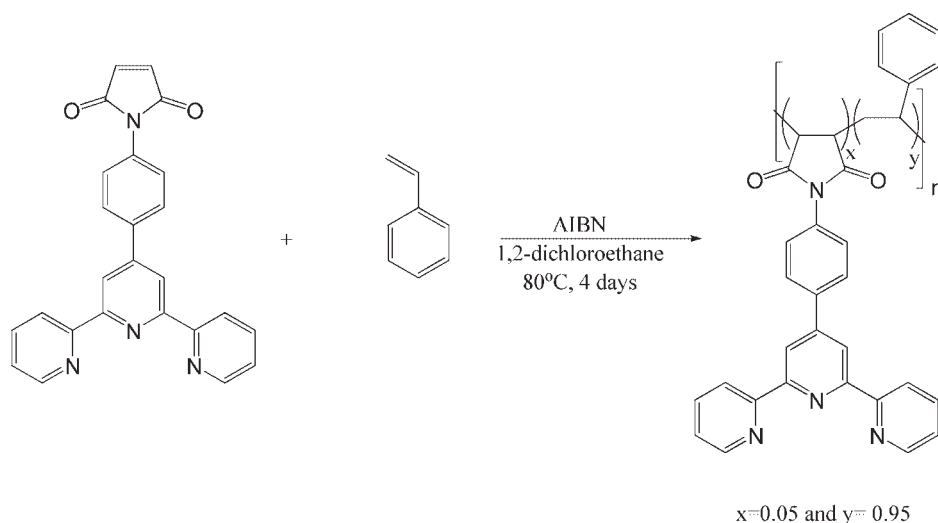


Figure 2 Mass spectrum of synthesized monomer.



Scheme 2 Synthesis of copoly(styrene-maleimide) functionalized with terpyridine.

behavior of the synthesized polymer was examined, and the results demonstrate that the polymer is soluble in chloroform (CHCl_3), NMP, dimethyl sulfoxide (DMSO), *N,N*-dimethyl formamide (DMF), and *N,N*-dimethyl acetamide (DMAc).

The viscosity of the formed polymer was determined with a Canon-Fenske viscosimeter in DMF at 25°C with concentration of 0.25 g/dL and shows a good polymer chain growth compared with that of similar existing polymers with MW as high as 5000 g/mol.

UV-Vis measurement and Fe titration of polymer solution in $\text{CHCl}_3/\text{MeOH}$ demonstrate the formation of terpyridine linkage on the side chain of polymer backbone (Fig. 3). With this measurement, we observed that by adding Fe(II), the polymer shows some peaks of metal-ligand charge-transfer band at 586 nm and results in higher absorptions. After add-

ing 50 mol % Fe(II) solution, a constant value for absorbance is observed, which proves that maximum complexation between terpyridine units and Fe(II) had resulted (Fig. 3, inset). This information reveals a crosslinking between the polymer chains in dilute solution that had occurred. The complexed polymer was prepared under a similar condition and the addition of NH_4PF_6 methanolic solution results in precipitated polymer.

TGA of the coordinated and uncoordinated shows that cross coordination does not affect the nature of the polymer backbone but gives a good result in the thermal stability of polystyrene. TGA thermogram of synthesized polymer before titration with Fe(II) showed the weight loss starts at 180°C and when it is coordinated with Fe(II) and crosslinking is done, the weight loss starts at 260°C , which is shown in the more thermal stability for crosslinked polymer (Fig. 4).

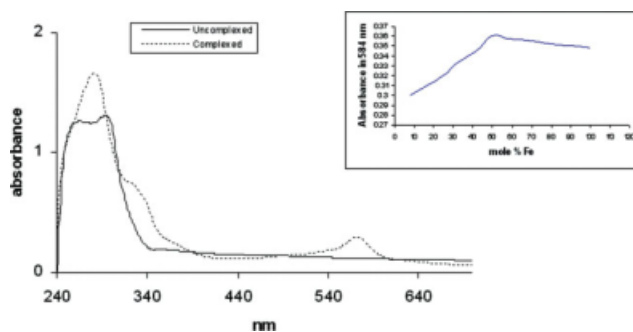


Figure 3 UV-VIS spectrum of uncomplexed and complexed polymer with Fe(II) and Fe titration curve of the uncomplexed polymer.

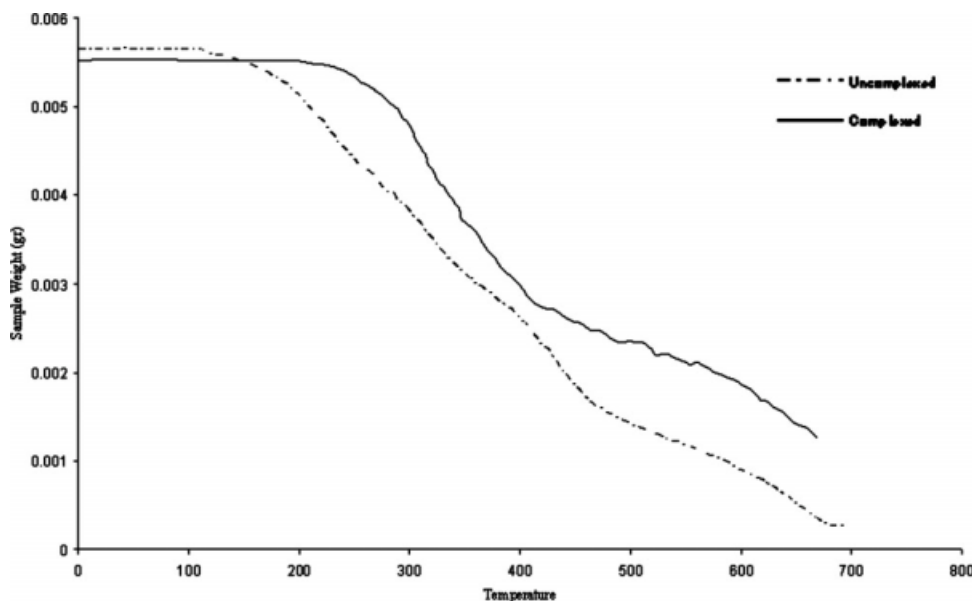


Figure 4 TGA thermogram of synthesized polymer before and after treating with Fe(II).

CONCLUSION

The radical copolymerization of styrene and maleimide functionalized terpyridine as a new ligand with high coordination effect leads to copolymers with side chains terpyridines attached at the backbone of polystyrene. Incorporating the complexes into the polymer could be explained using UV-Vis spectroscopy. This suggests a remarkable stability of the metal-complex containing polystyrene. The vacant ligands offer the possibility of polymer analogous functionalization and grafting procedures. Therefore, polymer crosslinked by coordinative bonds may be formed, offering a wide range of potential variations and novel interesting properties. Investigations on functionalization and electrochemistry of the presented systems are in progress.

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