JOURNAL OF CHEMICAL RESEARCH 2009 FEBRUARY, 101–103 **RESEARCH PAPER** 101

Synthesis of new bipyridine-containing polystyrene derived from 1,10-phenanthroline

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This report describes the synthesis of two new bipyridine-containing polystyrene compounds from 1,10-phenanthroline by four steps.

Keywords: 1,10-phenanthroline, bipyridine-containing polystyrene, metal containing polymer

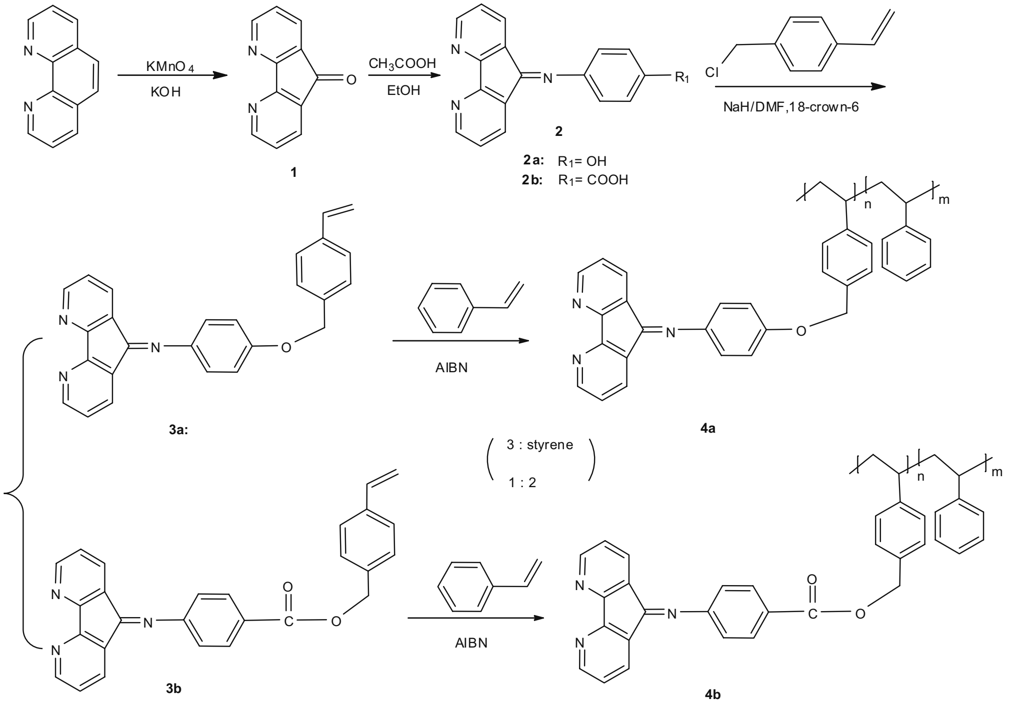
In recent years, functional polystyrene has received special attention and has been investigated extensively for polymer-supported catalysts,[1] supramolecular polymers,[2] and polymeric receptors.[3] In the meantime, the synthesis of metal containing polymers has attracted considerable attention due to their many applications in the fields of catalysis,[4] conducting and photoresponsive materials[5] and supramolecular chemistry.[6] Bipyridyl compounds such as 2,2'-bipyridine, 1,10-phenanthroline, and their derivatives are also strong bidentate chelating[7] and bridging agents[8] which have been widely explored due to their easy accessibility, easy modification and relative air stability.[9] Therefore, some bipyridine-containing ligands were synthesised and used for preparation of metal containing polymers(MCPs).[10]

Here we report on the synthesis of two new bipyridine-containing polystyrene compounds starting from 1,10-phenanthroline as shown in Scheme 1, which will be explored in the area of catalytic and fluorescent metal–organic coordination polymers in a further study. The ratio of monomer **3**/styrene was 1/2 in the reaction of monomer **3** with styrene. The products **4a** and **4b** are solid, separated and purified easily from styrene. Furthermore, ^{1}H NMR spectra show that there is no unsaturated double bond ($ArCH{=}CH_2$) in the product, which indicates that there is no compound **3** in the solid material. So, in the unit of **4a** and **4b**, m/n = should be 2/1.

Experimental

All reagents and solvents were purchased commercially as AC grade and were used without further purification unless noted. Ethanol and DMF were dried over 4 Å activated molecular sieves prior to use. Melting points were determined in open capillaries and uncorrected. Mass spectra were made with LC-MSD-Trap-SL. Elemental analyses were obtained Elementar Vario EL III, and a calculated result was based on the 2:1 ratio. ^{1}H NMR spectra were obtained with a Varian XL300 spectrometer. The IR spectra were determined as potassium bromide pellets on a Bruker Equinox55 FT-IR spectrophotometer. TGA and DSC were carried out on a Netzsch STA 409 PG/PC and on a DS822 under air atmosphere, respectively. GPC analysis was conducted with a Shimadzu LC-6A.

Synthesis of 4,5-diazafluoren-9-one **(dafo) 1**: Light yellow needle obtained by oxidation of 1,10-phenanthroline with $KMnO_4$ in a KOH solution following a literature method.[11] M.p. 215–216 °C MS: *m/z* = 182.23. ^{1}H NMR ($CDCl_3$, 300 MHz, relative to TMS): δ8.81 (dd, 2H, J_1 = 5.1, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.01 (dd, 2H, J_1 = 5.1, J_2 = 1.5 Hz, pyridyl H *para* to N), 7.36 (t, 2H, J_1 = 7.6, J_2 = 5.1 Hz, pyridyl H *ortho* to N).



Scheme 1

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Synthesis of ligand **2**: A mixture of compound **1** (455 mg, 2.5 mmol), glacial acetic acid (0.25 mL, 2.5 mmol), ethanol (20 mL) and aniline derivatives (3 mmol) were heated under reflux for 15 h, and then the desired precipitate was filtered, washed with ethanol three times and then dried in vacuum oven at 50 °C.

9-(4-Hydroxyanilino)-4,5-diazafluorene **2a** (607 mg, 89%): M.p.>300 °C. MS: *m/z* = 272.85. Elemental analysis Calcd for $C_{17}H_{11}N_3O$: C, 74.71; H, 4.06; N, 15.38. Found: C, 74.65; H, 4.00; N, 15.42%. ^1H NMR ($CDCl_3$, 300 MHz, relative to TMS): δ9.53 (s, 1H, –OH), 8.79 (dd, 1H, J_1 = 4.9, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.67 (dd, 1H, J_1 = 4.9, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.27 (dd, 1H, J_1 = 7.6, J_2 = 1.5 Hz, pyridyl H *para* to N), 7.54 (t, 1H, J_1 = 7.6, J_2 = 4.9 Hz, pyridyl H *ortho* to N), 7.27 (t, 1H, J_1 = 7.6, J_2 = 4.9 Hz, pyridyl H *ortho* to N), 7.13 (dd, 1H, J_1 = 7.6, J_2 = 1.5 Hz, pyridyl H *para* to N), 6.90 (m, 4H, ArH). IR (KBr): 3144, 3038, 1638, 1646, 1592, 1561, 1401 cm^{-1}.

9-(4-Carboxyanilino)-4,5-diazafluorene **2b** (640 mg, 85%): M.p.>300 °C. MS: *m/z* = 300.99. Elemental analysis: Calcd for $C_{18}H_{11}N_3O_2$: C, 71.75; H, 3.68; N, 13.95. Found: C, 71.70; H, 3.63; N, 13.89%. ^1H NMR ($CDCl_3$, 300 MHz, relative to TMS): δ12.93 (s, 1H, –COOH), 8.82 (dd, 1H, J_1 = 4.9, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.68 (dd, 1H, J_1 = 4.9, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.29 (dd, 1H, J_1 = 7.7, J_2 = 1.5 Hz, pyridyl H *para* to N), 8.02 (d, 2H, J = 8.6 Hz, ArH), 7.56 (t, 1H, J_1 = 7.7, J_2 = 4.9 Hz, pyridyl H *ortho* to N), 7.24 (t, 1H, J_1 = 7.7, J_2 = 4.9 Hz, pyridyl H *ortho* to N), 7.17 (d, 2H, J = 8.6 Hz, ArH), 6.83 (dd, 1H, J_1 = 7.7, J_2 = 1.5 Hz, pyridyl H *para* to N). IR (KBr): 3094, 3032, 1702, 1643, 1646, 1598, 1398 cm^{-1}.

Synthesis of monomer 3: To an ice cooled solution of ligand **2** (2 mmol) in dry DMF (30 mL) was added NaH (120 mg, 3 mmol, 1.5 equiv., as 60% purity in oil) and 18–crown-6 (catalytic amount), then the mixture was stirred at this temperature for 30 min. 4-Vinylbenzylchloride (0.3 mL, 2.2 mmol) was then added dropwise at this temperature and the solution was allowed to warm to room temperature. After stirring for 24 h, the resulting mixture was poured carefully into water (100 mL). The product was extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and concentrated. Flash column chromatography (SiO_2, ethyl acetate/petroleum ether (60–90) 1/2) afforded monomer **3**.

9-[4-(4'-Vinylbenzyloxy)anilino]-4,5-diazafluorene **3a** (670 mg, 86%): M.p. 230–232 °C. MS: *m/z* = 389.10. Elemental analysis Calcd for $C_{26}H_{19}N_3O$: C, 80.18; H, 4.92; N, 10.79. Found: C, 80.24; H, 4.88; N, 10.80%. ^1H NMR ($CDCl_3$, 300 MHz, relative to TMS): δ8.80 (dd, 1H, J_1 = 4.8, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.65 (dd, 1H, J_1 = 4.8, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.26 (dd, 1H, J_1 = 7.6, J_2 = 1.5 Hz, pyridyl H *para* to N), 7.58 (t, 1H, J_1 = 7.6, J_2 = 4.8 Hz, pyridyl H *ortho* to N), 7.25 (t, 1H, J_1 = 7.6, J_2 = 4.8 Hz, pyridyl H *ortho* to N), 7.10 (m, 3H, ArH and pyridyl H *para* to N), 6.89 (m, 6H, ArH), 6.70 (dd, 1H, J_1 = 17.1, J_2 = 10.6 Hz, =CH), 5.80 (d, 1H, J = 17.1 Hz, =CH_2), 5.32 (d, 1H, J = 10.6 Hz, =CH_2), 5.01 (s, 2H, O–CH_2). IR (KBr): 3033, 1669, 1616, 1593, 1565, 1404 cm^{-1}.

9-[4-(4'-Vinylbenzylbenzoate)anilino]-4,5-diazafluorene **3b** (750 mg, 90%): M.p.: 235–237 °C. MS: *m/z* = 417.10. Elemental analysis Calcd for $C_{27}H_{19}N_3O$: C, 77.68; H, 4.59; N, 10.07. Found: C, 77.70; H, 4.55; N, 10.10%. ^1H NMR ($CDCl_3$, 300 MHz, relative to TMS): δ8.83 (dd, 1H, J_1 = 4.8, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.66 (dd, 1H, J_1 = 4.8, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.26 (dd, 1H, J_1 = 7.6, J_2 = 1.5 Hz, pyridyl H *para* to N), 7.96 (d, 2H, J = 8.5 Hz, ArH), 7.58 (t, 1H, J_1 = 7.6, J_2 = 4.8 Hz, pyridyl H *ortho* to N), 7.28 (t, 1H, J_1 = 7.6, J_2 = 4.8 Hz, pyridyl H *ortho* to N), 7.15 (d, 2H, J = 8.5 Hz, ArH), 7.07 (d, 2H, J = 7.3 Hz, ArH), 6.93 (d, 2H, J = 7.3 Hz, ArH), 6.83 (dd, 1H, J_1 = 7.6, J_2 = 1.5 Hz, pyridyl H *para* to N), 6.65 (dd, 1H, J_1 = 17.1, J_2 = 10.6 Hz, =CH), 5.83 (d, 1H, J = 17.1 Hz, =CH_2), 5.30 (d, 1H, J = 10.6 Hz, =CH_2), 5.10 (s, 2H, O-CH_2). IR (KBr): 3036, 1673, 1641, 1592, 1560, 1400 cm^{-1}.

Table 1 Solubility in various solvents

Polymer	THF	ethanol	$CHCl_3$	DMF	Toluene	DMSO
4a	+ +	-	+ +	+ +	+	+ -
4b	+ +	-	+ +	+ +	+	+ -

+ + : absolutely soluble at 25 °C, + : mainly soluble at 25 °C and absolutely soluble at 50 °C.
+ -: insoluble at 25 °C and mainly soluble at 50 °C, -: insoluble at 25 °C and 50 °C.

Synthesis of bipyridine-containing polymer **4**: To a THF solution of monomer **3** (1.2 mmol in 3 mL) was added AIBN (0.028 g, 0.18 mmol) and styrene (255 mg, 2.4 mmol). The solution was purged with argon thoroughly. Polymerisation was carried out for 48 h at 75 °C. After cooling to room temperature the polymer was first precipitated by addition to methanol followed by hexane. The precipitate was filtered and dried in vacuum at 50 °C to give the polymer **4**.

4a (635 mg, 88%): Elemental analysis: Calcd for polymer **4a** $(C_{26}H_{19}N_3O)_n(C_8H_8)_m$ (m/n = 2/1): C, 84.42; N, 7.04; H, 5.86. Found: C, 84.50; H, 5.96; N, 6.83%. The concentration of the bipyridine was 1.63 mmol/g [6.83/(3 × 14.00) × 100]. ^1H NMR ($CDCl_3$, 300 MHz, relative to TMS): δ8.89 (d, 1H, J_1 = 5.1, pyridyl H *ortho* to N), 8.68 (d, 1H, J_1 = 5.0, pyridyl H *ortho* to N), 8.28 (d, 1H, J_1 = 7.6, pyridyl H *para* to N), 7.40–6.45 (m, broad signal due to the polymer resonance), 5.12 (s, 2H, O–CH_2), 1.85–1.21 (m, broad signal due to the polymer resonance). IR (KBr): 3042, 2928, 1632, 1606, 1596, 1551, 1402 cm^{-1}.

4b (650 mg, 86%): Elemental analysis: Calcd for polymer **4b** $(C_{27}H_{19}N_3O)_n(C_8H_8)_m$ (m/n = 2/1): C, 82.56; H, 5.60; N, 6.72. Found: C, 82.55; H, 5.83; N, 6.50%. The concentration of the bipyridine was 1.55 mmol/g [6.50/(3 × 14.00) × 100]. ^1H NMR ($CDCl_3$, 300 MHz, relative to TMS): δ8.86 (d, 1H, J_1 = 5.0, pyridyl H *ortho* to N), 8.60 (d, 1H, J_1 = 5.0, pyridyl H *ortho* to N), 8.23 (d, 1H, J_1 = 7.6, pyridyl H *para* to N), 7.93 (d, 2H, J = 8.4 Hz, Ar), 7.45–6.45 (m, broad signal due to the polymer resonance), 5.10 (s, 2H, O–CH_2), 1.86–1.20 (m, broad signal due to the polymer resonance). IR (KBr): 3048, 2923, 1672, 1636, 1592, 1399 cm^{-1}.

Properties of bipyridine-containing polymer **4**

The polystyrenes were characterised by IR, ^1H NMR and elemental analysis. The properties of bipyridine-containing polymer **4** were listed in Tables 1 and 2, and the TGA and DSC curves of the desired bipyridine-containing polymers were shown in Figs 1 and 2, respectively. GPC results showed that the new polymers had narrow molecular weight distributions. The thermal degradation of **4a** and

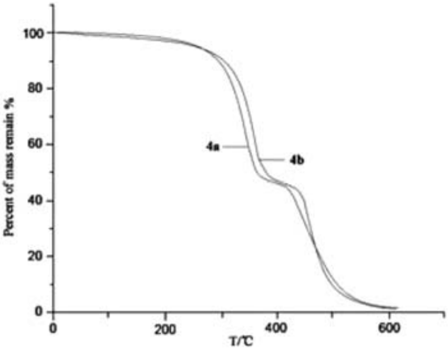

Fig. 1 TGA curves of polymer **4**.

Table 2 GPC and thermal analysis of the bipyridine-containing polystyrenes

Polymer	GPC^a			Thermal analysis	
	M_n(g/mol)	M_W(g/mol)	M_w/M_n	T_d/°C^b	T_g/°C^c
4a	6853	8402	1.23	322	175
4b	7035	9005	1.28	340	183

^{a}As calibrated against linear polystyrene strands with low polydispersity index. The eluent for samples was THF. M_w: Weight average molecular weight; M_n: Number average molecular weight.
^{b}T_d was determined by TGA at a heating rate of 20 °C min^{-1}.
^{c}T_g was conducted by DSC at a heating rate of 10 °C min^{-1}.

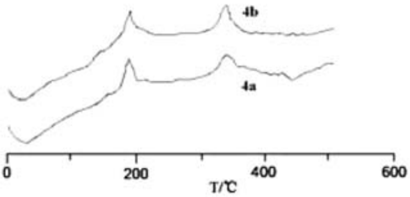

Fig. 2 DSC curves of polymer **4**.

4b started at above 300 °C, which indicated that **4a** and **4b** have good thermally stability. The TGA curves of polymer **4** presented two weight loss stages, which can be assigned to the loss of ligand **2** and the polystrene decomposition. Meanwhile, in Fig. 2, further two broad exothermic peaks were observed in the DSC curves at about 350 °C due to the rupture of polymer molecular chains already considered in the curves of TGA.

Received 27 October 2008; accepted 4 December 2008
Paper 08/0265 doi: 10.3184/030823409X401853

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