Polymer Bulletin 55, 41–49 (2005)
DOI 10.1007/s00289-005-0415-0

Polymer Bulletin

Preparation and Characterization of Novel Polyimides from 2,6-*bis*[1-(*p*-dimethylaminophenylimino)ethyl] pyridine for the Selective Extraction of some Metals

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Received: 28 March 2005 / Revised version: 8 June 2005 / Accepted: 16 June 2005

Summary

A group of new polyimides has been prepared by solution condensation of 2,6-*bis*[1-(*p*-dimethylaminophenylimino)ethyl] pyridine containing pendant NMe_2 units and various dianhyrides in N-methylpyrrolidone (NMP). The tridentate (N-N'-N) pydim ligands were prepared by Schiff-base condensation of 2,6-diacetylpyridine and 4-dimethylaminoaniline in the presence of formic acid as catalyst. These polymers were investigated for their extraction capabilities for Zn(II), Mn(II), Cu(II), Cd (II) and Ni(II) and at different pH. Under different conditions enhanced selectivity was observed. Up to 98% quantitative recoveries were observed for all metals.

1. Introduction

The selective extraction of noble metals such as Zn, Cd, Mn, Hg, Au, Pd, Ag, Pt, Ir and Co is still an intensively investigated area of research. Noble metal purification is still accomplished by traditional precipitation and complexation procedures that require the large amount of highly toxic mineral acids and complexation agents such sodium or potassium cyanide which have negative impact on environment. In order to circumvent the used of such chemicals liquid-liquid extraction, as well as solid-phase extraction (SPE) techniques applying numerous sorbents, have already been developed. Polymer supported extractants, usually based on PS-DVB or some methacrylates suffer from insufficient selectivity and reduced chemical stability in the extraction media [1-7]. Alternatively, crown ethers on silica [8-11] possessed high selectivity for the metal ions of interest, the use of PS-DVB sorbents impregnated with quanidines [12], poly(amide-ester) based pyridine-2,6-dicarboxylic acids [13], poly(glycidyl mathacrylate) supported oligoamines [14] etc have been described.

Since there is a great interest in pyridine based ligand which is primarily due to their stability under a variety of oxidative and reductive conditions and the fact that pyridine ligands are mild lewis bases and capable of bonding abilities toward metals. Several complexes containing pyridine ligands have appeared in the literature [15].

To the best of our knowledge, however, no paper has dealt with the preparation of polyimide from 2,6-*bis*[1-(*p*-dimethylaminophenylimino)ethyl] pyridine by one-stage polycondensation for solid-phase extraction. We have therefore developed synthetic procedures based on diimines derived from 2,6-diacetylpyridine. This paper reports on the synthesis of 2,6-*bis*(imino)pyridyl with pendant NMe_2 groups at the *p*-position of the phenyl ring that acts as tridentate ligand that could be used to built supromolecular architectures by the self assembling of pydim component with metal ions. The most prominent examples are Cu(II), Cd (II), Mn (II), Zn(II) and Ni(II) complexes due to their ability to form defined supromolecular architectures. The synthesis of polyimides [16-20] starting from these new monomer is reported and the influence of the incorporation of this moiety into the polymer backbone on the sorption capacity of metals has been evaluated.

2. Experimental Section

2.1. Materials.

Reagent grade aromatic dianhydrides such as pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenonetetracarboxylic dianhyride (BPDA), 4,4'-oxydiphthalic anhydride (ODPA) that was sublimed at 250°C under reduced pressure, 3,3',4,4'-biphenyltetracarboxylic dianhydride (BTDA) was used after crystallization in proper solvents (all Aldrich Co.), dimethylaminoaniline and 2,6-diacetylpyridine (Merck). Aqueous standard solutions of $Zn(NO_3)_2$, $Ni(NO_3)_2$,$Mn(NO_3)_2$, $Cu(NO_3)_2$, $Cr(NO_3)$ (in 0.5 M HNO_3), (all Merck, Germany) were used.

2.2. Instrumentation.

Infrared spectra were recorded as KBr pellets in the range 4000 - 400 cm^{-1} on an Ati Unicam Mattson 1000 Fourier Transform Infrared Spectrometer. ^1H NMR spectra (300.133 MHz) and ^{13}C NMR on a Bruker AM 300 WB with δ referenced to residual solvent $CDCl_3$. Microanalyses were performed by the TUBITAK (Ankara). Differential scanning calorimeter (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu DSC-60, DTA-50 and TGA-50 thermal analyzers respectively.

Inherent viscosities ($\eta_{inh} = \ln\eta_r/c$ at polymer concentration of 0.5 g/dL) were measured with an Ubbelohde suspended-level viscometer at 30 °C using NMP as the solvent.

Gel Permeation Chromotagraphy GPC , size exclusion chromotagraphy (SEC) analyses were performed at 30°C using NMP as eluant at a flow rate of 0.5 mL/min. A differential refractometer was used as a detector. The instrument (Agilent 1100 series GPC-SEC system) was calibrated with a mixture of polystyrene standards (polysciences; molecular masses between 200-1200000 Da) using GPC software for the determination of the average molecular masses and the polydispersity of the polymer samples.

SPE experiments were carried out using 1.5 mL PP-Isolute SPE cartridges equipped with PP frits as given in literature [6].

2.3. Procedures.

Synthesis of 2,6-bis[1-(p-dimethylaminophenylimino)ethyl] pyridine (1):

As shown in Scheme 1, the tridentate ligand used in this study is pyridine diimine ligand prepared by the Schiff-base condensation of 2 equiv. of the 4-dimethylaminoaniline with 2,6-diacetylpyridine in the presence of catalytic amount of formic acid. The mixture was stirred under nitrogen atmosphere with reflux and the precipitate formed was collected by filtration and washed with ethyl alcohol and dried in air (m.p.197°C). The compound gave satisfactory microanalysis; displaced the expected ^{1}H and ^{13}C NMR spectra. δ_H (300 MHz, $CDCl_3$) 2.45 (6H,s,H-*d*), 2.94 (12H,s, H-5), 6.76 (4H,d,*J* 9.0, H-*3*), 6.85 (4H,d,*J* 8.9, H-*2*), 7.80 (1H,t,*J* 8.0, H-*a*), 8.29 (2H,d, *J*7.7, H-*b*); δ_C (75.4 MHz, $CDCl_3$) 16.2 (C-*d*), 41.0 (C-*5*), 113.2 (C-*3*), 121.4, 121.8 (C-*b*, C-*2*), 136.6 (C-*a*), 141.0 (C-*4*), 147.7 (C-*1*), 156.0 (C-*c*), 166.5 (C-*e*). Analytically calculated for $C_{25}H_{29}N_5$, (399.54) C: 75.15; H: 7.32; N: 17.53, Found: C: 75.37; H: 7.95; N: 16.99.

Synthesis of polyimides:

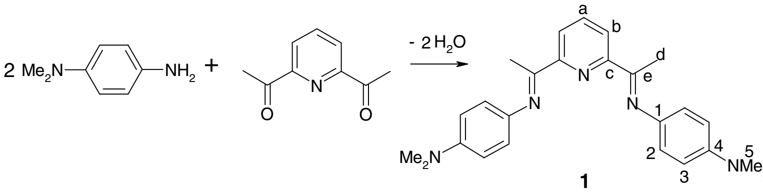
A typical polyimide (**P1a-d)** synthesis was performed as follows: Monomer 2,6-*bis*[1-(*p*-dimethylaminophenylimino)ethyl] pyridine (1.66g, 4.15 mmol) was dissolved in NMP (15 mL) in a 50 mL Schlenk tube equipped with a nitrogen line, overhead stirrer, a xylene filled Dean-Stark trap, and a condenser. PMDA (0.9 g, 4.15 mmol) was added to the amine solution and stirred overnight to give a viscous solution. The mixture was heated to 70°C, xylene (5 mL) was added, and the mixture was refluxed for 3-h. Following the removal of xylene by distillation, the reaction mixture was cooled at room temperature and the product was precipitated by addition of a large excess of methanol. The dark yellow product was isolated and dried at 100°C under vacuum and then at 200-250°C under nitrogen for 2h; Yield, 89%. ^{1}H and ^{13}C NMR spectra. δ_H (300 MHz,d^6 DMSO) 2.38 (s,H-*d*), 6.82 (d,*J* 9.0, H-*3*), 6.78 (d,*J* 8.9, H-*2*), 7.85 (t,*J* 8.0, H-*a*), 8.32 (d, *J*7.7, H-*b*), 9,01 (s, pyromellitic); Analytically calculated for $C_{25}H_{29}N_5$, (399.54) C: 75.15; H: 7.32; N: 17.53, Found: C: 75.37; H: 7.95; N: 16.99.

SPE Experiments

For all experiments he SPE material was first stirred in methanol-water (20:80) for 1h. Columns were slurry packed and conditioned by passing 100 mL of methanol-water solution through the column, followed by 100 mL water flow rate of 3mL/min. For SPE, solutions containing 100 ppm single element standards, respectively, were passed through a sluury-packed filtration column (Isolute^{TM} accessories, 200 mg sorbent). Recoveries were determined under non-competitive conditions by AAS.

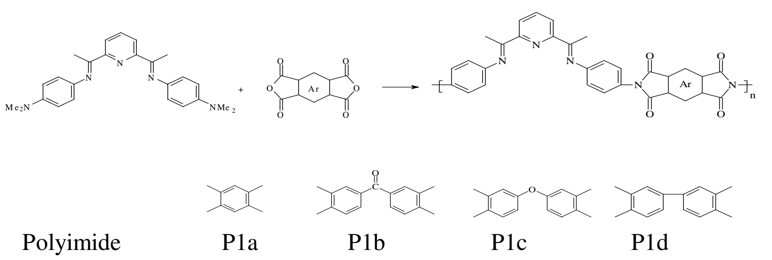
3. Results and Discussion

The starting monomer 2,6-bis[1-(p-dimethylaminophenylimino)ethyl]pyridine, (1) used in the synthesis of polyimides was prepared by the Schiff-base condensation of two equiv. of the desired aniline with 2,6-diacetylpyridine as shown in Scheme 1. In this work, the synthesis of tridentate ligand with promising properties was achieved.



Scheme 1: Synthesis of 2,6-bis[1-(*p*-dimethylaminophenylimino) ethyl] pyridine, **(1)**

Incorporating NMe_2 groups at the p-position of the phenyl ring facilitated not only polyimide synthesis, but also a potent to prepare metal coordinated polymers.
FT-IR, ^{1}H and ^{13} C NMR spectra and elemental analysis were used to confirm the structures of the monomer, 2,6-*bis*[1-(*p*-dimethylamino phenylimino) ethyl] pyridine. The NMR spectra of the monomer was diagnostic. Only a single set of signals were observed for two pendant groups of pydim complexes in both ^{1}H and ^{13}C NMR spectra that indicate the two arms of the ligands are magnetically equivalent in solution and the ligands are tridentate.
Polyimides P1a-d were synthesized by one-stage polycondensation of dianhydrides with 2,6-*bis*[1-(*p*-dimethylaminophenylimino)ethyl] pyridine.



Scheme 2: Polyimide synthesis **(P1a-d)**

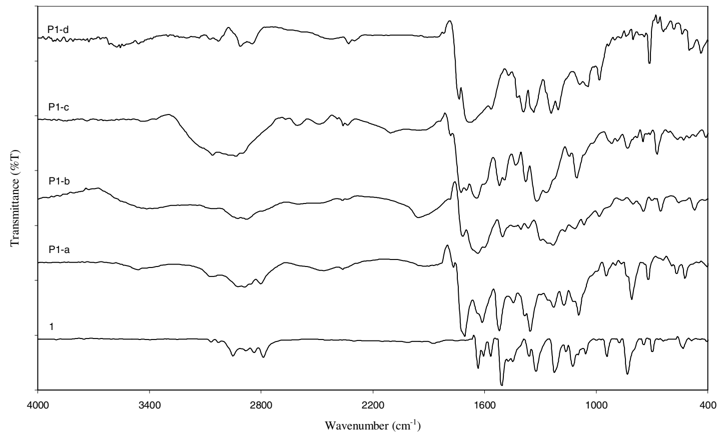


Figure 1. FT-IR Spectrum of polyimides prepared from 2,6-*bis*[1-(*p*-dimethylaminophenylimino)ethyl] pyridine **(P1a-d)** and the monomer

All the polymerizations proceeded in homogeneous solution and the precipitation was prevented in all cases by adjusting the solvent to the monomer ratio. The FT-IR spectra (Figure 1) showed that aliphatic C-H stretching frequencies were appeared between 2850-2890 cm^{-1}, 1720-1730 cm^{-1} sym. imide ν (C=O), 1765-1790 cm^{-1} asym. imide ν (C=O) stretching, C-N imide ring stretching 1360 cm^{-1}, whereas imide ring deformation was appeared at near 1070 cm^{-1} and C-N bending at 730-760 cm^{-1}and the C=N peak in the monomers gave two peaks at 1440-1660 cm^{-1} respectively [21-22].

Polyimides were synthesized in NMP solvent in a one-stage solution polycondensation in which the dimethylamino groups were reacted with a stoichiometric amount of the dianhydride (Scheme 2). The polymers were isolated in almost quantitative yield by precipitation from methanol. The formation of the imide ring was confirmed by FTIR. that was discussed in our previous papers [23-24].

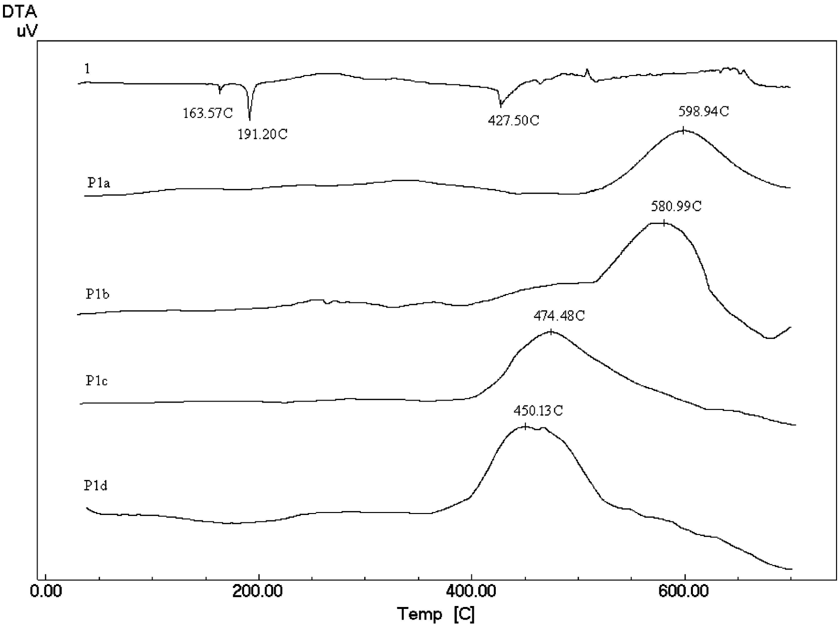


Figure 2. DTA curves of polyimides prepared from 2,6-*bis*[1-(*p*-dimethylaminophenylimino)ethyl] pyridine (P1a-d)

The thermal properties of the polyimides were evaluated by differential scanning calorimetry (DSC), differential thermal analysis (DTA) (Figure2) and thermogravimetry (TG) (Figure3). The thermal behavior data of all the polymers are presented in Table 1. DSC experiments were conducted at a heating rate of 10 °C/min in nitrogen. Rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so T_g's of all the polyimides could easily be read in the subsequent heating DSC traces. The T_g values of polyimides P1a-d were in the 245-391 °C range depending on the structure of the dianhyride component and decreasing with increasing flexibility of the polymer backbones. As expected, the polyimide P1a derived from PMDA exhibited the highest T_g because of the rigid pyromellitimide unit. The thermal stability of the polymers was evaluated by TGA conducted at a heating rate of 10 °C/min. in nitrogen atmosphere. The temperatures of 10% weight loss in nitrogen stayed within 415-524 °C range. P1-d having oxygen group in dianhyride exhibited the lowest T_{10} values than the other polyimides.

The solubility of the polyimides was tested in various organic solvents, and the results are summarized in Table 2. Polymers had excellent solubilities in aprotic polar solvents such as NMP, DMAc, DMF and DMSO. This high solubility might be attributed to the formation of some intermolecular spacing due to the tridentate ligand.

Table 1. Thermal properties of polyimides

Polymer	P1a	P1b	P1c	P1d
TGA Analyisis				
On set	477	418	411	386
End set	644	623	652	630
% 10[a]	524	470	481	415
Char[b]	39	26	21	35
IDT[c]	475	399	425	367
DTA Analyisis[d]				
TDP[e]	599	581	474	450
On set	504	513	406	393
End set	692	644	570	532
Heat (kJ/g)	1,17	6,33	3,30	2,78
DSC Analyisis[f]				
On set	367	277	275	263
End set	432	262	290	227
Transition (mW)	-5.42	-3.50	-6.34	-2.50
Tg (°C)	391	261	288	245

[a]10% weight loss, as assesses by TGA at a heating rate of 10°C/min. in nitrogen.; [b]Char yields, calculated as the percentage of the solid residue after heating from room temperature to 900°C in nitrogen.; [c]IDT (initial decomposition temperature) is the temperature at which an initial loss of mass was observed.; [d]DTA thermo grams of polyimides with a heating rate of 10°C/min in a air atmosphere.; [e]TDP (thermal decomposition peak); [f]DSC termograms of polyimides with a heating rate of 10°C/min in a nitrogen atmosphere.

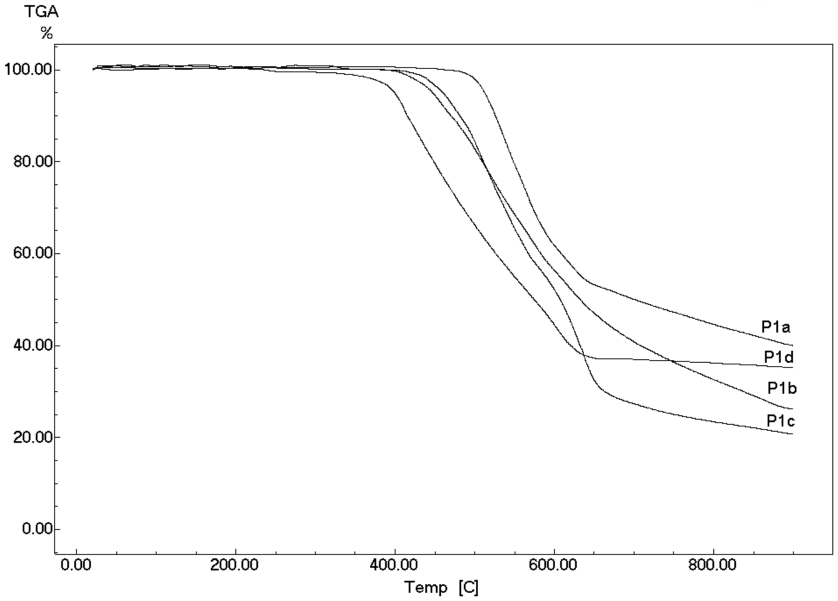


Figure 3. TGA curves of polyimides P1a-d

Table 2. Some Physicochemical properties of synthesized polyimides

Polymer	P1a	P1b	P1c	P1d
Yield (%)	89	78	74	82
d (g/cm^3)[a]	1,15	1,37	1,23	1,25
η (dL/g)[b]	1.28	1.45	1.30	1.39
Solubility[d]				
NMP	+	+	+	+
DMF	±	+	±	±
DMAc	±	±	±	±
Ether	-	-	-	-
THF	-	-	-	-
Hexane	-	-	-	-
DMSO	+	+	±	±

[a]Determined by suspension method at 30°C.; [b]Measured at a concentration of 0,5 dL/g in NMP at 30°C using an Ubbelohde viscometer.; [c]Film was cast on microscope slides via blade technique, all of them are brittle and transparent; [d](Solubility tested at 2% solid concentration; + soluble at room temperature (25°C); ± soluble upon heating; - insoluble at room temperature)

Table 3. Properties of Polyimides, obtained by the one-step method

Diamine	Polyimide Code	$[\eta]$[a]	M_n x 10^{-4}[b]	M_w x 10^{-4}[b]	H.I.
PMDA	P1a	1.28	3.29	4.82	1.46
BPDA	P1b	1.45	50.13	91.73	1.83
BTDA	P1c	1.30	9.24	12.20	1.32
ODPA	P1d	1.39	15.03	23.87	1.58

[a]Measured at a concentration of 0,5 dL/g in NMP at 30°C using an Ubbelohde viscometer;

[b]GPC (10 mg mL^{-1} NMP solution, polystyrene standards)

Table 3 summarizes values of the number average molecular weight (Mn), the weight average molecular weight (Mw) and the polydispersity index of the polymers.

Table 4. Summary of UV experiments performed with polyimides and various metal ions in water at different pH

Metal ion	pH	λmax (nm)
Zn (II)	5	307, 319
Mn (II)	6	307, 310
Cu (II)	6	307, 319
Cd (II)	8	307, 319
Cd (II)	6	307, 319
Ni (II)	6	295, 300
Ni (II)	2	295, 300

Table 5. Extraction capabilities[a] of polymers for selected metal ions at pH=6.0

Polyimide Code[b]	Zn (II)	Mn (II)	Cu(II)	Cd (II)	Ni (II)
P1a	91	92	93	94	91
P1b	96	95	95	95	96
P1c	90	94	95	95	90
P1d	93	91	94	91	92

[a]recovery %, [b]Loading (mg metal/ gram support > 6), Relative standard deviation ± 3 %

SPE Experiments

The polymer supported organic reactions in which the structure of the ligand was not changed during polymerization was directly used for preliminary investigations concerning the complex formation capabilities with various metals.

For this purpose, solutions of metals summarized in Table 4, in the presence of interfering ions , were extracted under different conditions. The loadings that reach the theoretical amount were indicative for the complex formations which explain for the selectivity of the sorbent for certain metal ions. Metals sorbed onto the material (>90%) desorbed by nitric acid (5M). In case loading was stopped before reaching the corresponding point of breakthrough. The data in Table 4 and 5 illustrate the potential of polyimide based sorbent for the extraction of metals which may be used to substitute traditional purification techniques. From the entire set of data, the following extraction order was deduced at given pH: Cr ≈ Mn ≈ Cd ≈Zn ≈ Ni. This is clearly indicates that new sorbents allows the adsorption of metals onto the material under competitive or non-compotetive conditions.

4. Conclusions

Novel monomers, 2,6-*bis*[1-(*p*-dimethylaminophenylimino)ethyl] pyridine, 1, was prepared in high purity . Since the tridentate ligands not only offers suitable sites for metal coordination, but also stable under oxidative conditions and there is a great interest in these type of ligands due to their mild basicity, a series of polyimides was prepared and tested. All polyimides not only showed good thermal properties and high glass-transition temperatures but also the introduction of tridentate units in polyimides backbone results in potent polyimides that could be used further complexation with various metals.

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