Macromolecular Ligands Carrying Side Bipyridyl-Containing Groups and Their Metal–Polymer Complexes with Iridium

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Abstract—A series of copolyamides carrying side bipyridyl-containing groups and their metal-polymer complexes with iridium were synthesized. The stress-strain, thermal, molecular-weight, and luminescent characteristics of these compounds were examined. All the polymers synthesized exhibit high performance in the stress-strain characteristics and high thermal stability.

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Metal-containing polymers, or metal-polymer complexes (MPCs), have become an area of increased interest in recent years due to their potential for diversified technical applications. The presence of transition metals in the polymer chain of metal complexes offers a broad range of possibilities for combining their chemical, electrical, magnetic, optical, and redox properties with those of organic substances. This gave an impetus to rapid progress in studying the functional properties of MPCs and provided motivation for searching new application fields for them. By now, a large number of soluble, semiconducting [1], photovoltaic [2], and luminescent [3, 4] metal-polymer complexes have been synthesized and examined. They have found several high-technological applications, e.g., as active layers of LEDs, polymer solar cells, and chemical sensors. Since recently, polymers containing Ir(III) complexes have attracted considerable attention owing to the great potentialities of these materials for optoelectronic applications [5].

EXPERIMENTAL

Isatin, 2-acetylpyridine, 2-phenylpyridine, \( \text{IrCl}_3 \cdot 3\text{H}_2\text{O} \), vanillic acid, terephthalic acid, 5-aminoisophthalic acid, N-methylpyrrrolidone (NMP), and propylene oxide were commercial products and used without further purification. Other reagents and solvents were purified before use: 4,4'-diaminodiphenylmethane (DADPM) by vacuum distillation, mp 89–91°C; m-phenylenediamine (MPDA), by vacuum distillation, mp 64–66°C; \( p \)-phenylenediamine (PPDA), by vacuum distillation, mp 143–145°C; 1,4-bis(4-aminophenoxybenzene) (BAPB), by recrystallization from ethanol, mp 173°C; thionyl chloride, by distillation, mp 78°C; \( N,N \)-dimethylformamide (DMF), by drying over calcium hydride, followed by vacuum distillation, mp 153°C; acetic anhydride, by simple distillation, mp 140°C; pyridine, by drying over granulated caustic potash, followed by simple distillation, mp 115°C; ethanol, by simple distillation, mp 78°C; and toluene, by simple distillation, mp 110–111°C.*

For synthesis of 5-[5-(2-pyridyl)-4-azaphthalimido] isophthaloyl dichloride (5) we used the procedure described in [6], and for synthesis of terephthaloylbis(3-methoxy-4-oxobenzoyl) dichloride, the procedure from [7]. A binuclear iridium complex with 2-phenylpyridine \( [\text{Ir(ppy)}_2\text{Cl}]_2 \) was synthesized by the technique described in [8].
All the polymers were synthesized by the following general method. Diamine (0.001 mol) and NMP (6 ml) were introduced into a 25-ml round-bottomed flask equipped with a stirrer. The resulting mixture was stirred until complete dissolution of diamine and cooled to –15°C in an ice-salt bath, after which 0.00103 mol of dichloroanhydride was added into the cooled solution. The resulting suspension was stirred at the indicated temperature for 30 min, after which 3 drops of propylene oxide were added, and stirring was continued for 5 h at room temperature.

In the case when more than one diamine or dichloroanhydride were added, these compounds were introduced at 15-min intervals into the cooled solution.

The polymer solution was filtered, cast onto a glass substrate, and dried.

Metal-Polymer Complexes. The \([\text{Ir}_2(\text{ppy})_4\text{Cl}_2]\) complex was added to a polymer solution in NMP at the molar ratio of 1.3:1.0. The resulting mixture was heated to 110°C with stirring for 10 h, after which the polymer was precipitated into ethanol and extracted in a Soxhlet apparatus for 10 h. The resulting polymer was dried, dissolved in NMP, and cast into films.

The \(^1\)H NMR spectra of 1% solutions were recorded on an Avance-400 (Bruker, FRG) spectrometer operating at \(^1\)H resonance frequency of 400 MHz, with Me₄Si as internal standard.*

The luminescence spectra were measured on an LS-100 (PTI®, Canada) spectrofluorimeter. The choice of the excitation wavelength of 380 nm was based on the luminescence excitation spectra of the MPC. The spectral width of the slit of the excitation and emission monochromators was 4 nm; FEU 800 multiplication was used.

The films were mechanically tested in the uniaxial stretching mode using a UTS 10 universal testing machine (UTS Testsysteme, FRG). We determined the modulus of elasticity \(E\), yield strength \(\sigma_y\) (the point of intersection of the tangents to the initial linear portion of the stress–strain curve and to the portion corresponding to development of forced elastic deformation), tensile strength \(\sigma_t\), and elongation at break \(\varepsilon_b\). These characteristics were obtained by averaging the testing results for seven samples.

The glass transition temperatures of the films were determined by the dynamic mechanical analysis technique on a DMA 242 C (NETZSCH) instrument. The measurements were conducted at the frequency of 1 Hz with the deformation amplitude of 10 at the heating rate of 10 deg min⁻¹. The basic dimensions of the samples were 1.5×10 mm. The glass transition temperature \(T_g\) was taken to be the maximum of the loss tangent–temperature curve.

The phase transition temperatures were also determined with the use of a DSC 204 F1 Phoenix (NETZSCH) differential scanning calorimeter. The target curve was recorded during the second heating run at the heating rate 10 deg min⁻¹.

The thermal stability was determined thermogravimetrically on a TG 209 F1 Iris (NETZSCH) instrument, also at the heating rate of 10 deg min⁻¹.

Elemental analysis was carried out using a CHNOS elemental analyzer (Vario El III, Elementar Analysensysteme GmbH, Hanau, FRG).

The polymers were synthesized by low-temperature polycondensation which technique gives polymer solutions with good viscosity characteristics, capable of forming mechanically strong self-supporting films. In this technique, the first phase consists in synthesizing a bifunctional monomer containing a ligand moiety to be incorporated into the main or side chain of the polymer. As objects of our study served polymers carrying side bipyridyl-containing moieties, which are known [9, 10] to offer a number of advantages, in particular, enhanced flexibility of the polymer chain and its associated improved solubility. Considering the above-said, we synthesized a reactive bipyridyl-containing bifunctional monomer for low-temperature polycondensation reactions, 5-[5-(2-pyridyl)-4-azaphthalimido]isophthaloyl dichloride (5), whose preparation procedure is based on isatin chemistry. The synthesis route of this compound is presented schematically below (Scheme 1).

In the first stage, the Pfützinger reaction between isatin and 2-acetylpyridine gave 2-(2-pyridyl)-quinoline-4-carboxylic acid (1) [4], which was oxidized with potassium permanganate in an alkaline medium into 6-pyridyl-pyridine-2,3,4-tricarboxylic acid (2) in the second stage. Under these conditions, the benzene ring in the quinoline cycle is oxidized giving two vicinal carboxy groups. The third stage consisted in decarboxylation of 6-pyridyl-pyridine-2,3,4-tricarboxylic acid in position 6 into 6-pyridyl-3,4-pyridinedicarboxylic anhydride (3). A 9 : 1 acetic acid-acetic anhydride mixture served as decarboxylating agent, which afforded fairly mild reaction conditions and, thereby, selective decarboxylation. Another benefit of this approach is formation of an anhydride cycle simultaneously with decarboxylation. In the fourth stage, the reaction of...