Synthesis and properties of iridium polymer complexes based on novel bipyridyl ligands

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A novel monomer, *viz.*, bipyridyl-containing dicarboxylic acid, was synthesized from 6-pyridyl-3,4-pyridine dicarboxylic acid anhydride and 5-aminoisophthalic acid. Novel polymer macroligands, *viz.*, copolyamides containing 5, 15, 30, and 45% of the bipyridyl side groups, were obtained based on this monomer by low-temperature polycondensation. Metal polymer complexes (MPC) with different $Ir(ppy)_2$ content were synthesized by the reaction of the polymer ligand with the binuclear complex [$Ir(ppy)_2Cll_2$ (ppy is 2-phenylpyridine) and their properties were studied.

Key words: 2-pyridylquinoline, oxidation, decarboxylation, bipyridyl-containing monomers, copolyamides, iridium, metal polymer complexes, luminescence.

The capability of nitrogen-containing heterocycles, such as 1,10-phenanthroline, 2,2'-biguinoline, and 2,2'-bipyridyl, to form complex compounds with metal ions is widely used in many fields of chemistry and technology.1-3The complexes containing the above-mentioned ligands find application in analytical chemistry and catalyst systems, as well as working laser materials. In recent years, a novel investigation step of transition metal complexes with nitrogen-containing ligands came on, which is a step of extensive investigation of their photophysical, spectralluminescent, and electrochemical properties.^{4–7} Of special interest are macromolecular ligands with nitrogencontaining heterocyclic moieties in the polymer backbone or side groups, which combine interesting physical properties with processibility and high performance. Among a number of transition metal polymer complexes, the metal polymer complexes (MPC) based on iridium provoke intense interest of investigators.⁸ At the same time, the articles dedicated to the synthesis of polymers with ligand groups, in particular, bipyridyl groups, are few.⁹ This is obviously due to the difficulties occuring during the synthesis of reactive bipyridyl derivatives, which can act as monomers upon polymerization or polycondensation or can be used for chemical modification of macromolecular compounds. The aim of the present work is to develop the synthetic procedure for a novel available bifunctional bipyridyl-containing monomers, to prepare polymers with

side bipyridyl groups and iridium polymer complexes based on them, and to study their properties.

Results and Discussion

To prepare macromolecular ligands with side bipyridyl groups, low-temperature polycondensation was used, which allows preparation of high-molecular-weight polymers having good stress-strain properties and high thermal stability. At the first step, it was necessary to obtain the reactive bifuncitonal monomer for polycondensation that contains the bipyridyl group. This problem was solved by oxidation of 2-(2-pyridyl)cinchonic acid. The general synthetic scheme is given below.

According to Scheme 1, 2-(2-pyridyl)quinoline-4carboxylic acid (1) synthesized from isatin and 2-acetylpyridine by the Pfitzinger reaction⁶ was oxidized with potassium permanganate in the alkaline medium. Under these conditions, the benzene ring of quinoline fragment¹⁰ undergoes oxidation to form 6-(2-pyridyl)pyridine-2,3,4-tricarboxylic acid (2). The carboxyl group in the 2 position is readly removed upon decarboxylation¹¹ in a AcOH—Ac₂O mixture, cyclization involving the carboxyl groups in the 3 and 4 positions occuring simultaneously with decarboxylation to form 6-(2-pyridyl)pyridine-3,4-dicarboxylic acid anhydride (3). The bifunctional monomer for polymerization was synthesized by the reaction of compound **3** with

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5-aminoisophthalic acid. This reaction proceeds in two steps: at the first step, the amido acid forms, which is transformed without isolation to the imide by heating in a Ac_2O-Py mixture to yield 5-[6-(2-pyridyl)-5-aza-phthalimido]isophthalic acid (4). At the second step, the reaction of 4 with thionyl chloride affords 5-[6-(2-pyridyl)-5-azaphthalimido]isophthalic acid dichloride (5).

Based on dichloride 5 and 4,4'-diaminodiphenyl ether (6), copolyamides 8a-d containing 5, 15, 30, and 45 mol.% of the units with side bipyridyl groups were synthesized by low-temperature polycondensation (Scheme 2). As a comonomer, terephthaloyl-[bis(3-methoxy-4-oxy-benzoic)] acid dichloride (7) was chosen, since, on its basis, polyamides with a high inherent viscosity can be obtained,¹² whose films possess good thermal stability and required mechanical characteristics.

The metal polymer complexes of iridium can be obtained conveniently by the reaction of macromolecular ligands with the binuclear bridged complex **9** (see Ref. 5).

By the reaction in the chain of copolyamides **8a–d** with complex **9**, the metal polymer complexes **10a–d** were obtained (Scheme 3).

Copolymer	Copolymer composition (%)			Properties of films					
	n	р	q	$[\eta]/dLg^{-1}$	<i>E</i> /GPa	σ _y /MPa	σ_b/MPa	ε _b (%)	$T_{\rm g}/^{\circ}{\rm C}$
8a	5			2.8	4.18	140	205	35	221
10a		1.25	3.75	3.0	4.22	**	139	4.8	221
8b	15			2.2	4.12	136	174	29	224
10b		5.55	9.45	2.4	4.04	135	180	31	238
8c	30			1.8	3.94	140	165	21	230
10c		11.4	18.6	2.0	3.95	**	124	8.3	264
8d	45			1.4	3.88	138	157	19	237
10d		14.4	30.6	1.7	3.82	**	112	5.0	316

Table 1. Composition, inherent viscosity (η) , and mechanical and thermal characteristics of the films of *co*-PAs with different concentrations of the units with side bipyridyl groups and MPCs based thereon

* *E* is Young's modulus, σ_y is a yield point, ε_b is the ultimate deformation of a film, σ_b is the ultimate strength of a film before destruction, T_g is a glass transition point. ** The σ_y values cannot be determined due to low strain-to-destruction values of the material.

Scheme 2



8: n = 5 (a), 15 (b), 30 (c), 45 mol.% (d)



The compositions of the metal polymer complexes synthesized were established by elemental analysis and ¹H NMR spectroscopy. The studies performed allowed us to determine the portion of units containing the complex fragments. As for the most of macromolecular reactions, the complex formation does not result in the complete conversion of any of the polymer ligands synthesized. The degree of modification is about 60–75% depending on the content of side bipyridyl units (Table 1). Thus, the metal polymer complexes 10a-d are tercopolymers where, along with the units containing the complex fragments, there are units with side bipyridyl groups underwent no complex formation.

All synthesized polymers 8a-d and the iridium polymer complexes 10a-d based on them possess high intrinsic viscousity (see Table 1) and we succeeded in the preparation of stable transparent films from solutions of these polymers in *N*-methyl-2-pyrrolidone.

The mechanical test results (see Table 1) evidence that the concentration ratio of the m and n type units have

Scheme 3

8a-d $\xrightarrow{[Ir(ppy)_2CI]_2} A_p C_q B_m$ 10a-d



10: p+q = 5 (**a**), 15 (**b**), 30 (**c**), 45 mol.% (**d**)

a noticeable effect on the properties of the copolyamide (*co*-PA) films (see Scheme 2). As the content of units with side bipyridyl groups in the macrochains grows, the Young's modulus values of films decrease steadily. Upon

the increase in the concentration of these units from 5 to 45%, the *E* value decreases from 4.18 to 3.82 GPa.

The observed decrease in the film rigidity reflects changes in the characteristics of intermolecular bonding system in the copolymer as the concentration of side groups in the macrochains grows. It is known¹³ that the structures of the polyamide films are characterized by the presence of the extensive system of intermolecular hydrogen bonding, which results in high Young's moduli of such materials. The introduction of bulky side bipyridyl groups to the chain decreases the concentration of these bonds. When analyzing the intermolecular interactions in the co-PAs under study, one should keep in mind a possible formation of additional hydrogen bonds involving the nitrogen atoms of the bipyridyl groups in the systems with such side fragments. However, when estimating the role of these groups in the hydrogen bond formation, one should take into account the fact that the nitrogen atom of the side chain can interact with both adjacent macrochains and the same main chain. Since upon introduction of the bipyridyl groups to the macrochain, the Young's moduli of films decrease, one can assume that in the co-PAs under consideration, there occur interactions of the second type, which result in a successive decrease in the concentration of intermolecular bonds in the polymer.

The same trend of the successive decrease in the *co*-PA film rigidity with introducing the side groups to the material is observed also when analyzing the change in the yield stress of the material: σ_y drops successively (see Table 1).

Finally, the growth in the concentration of the units containing bipyridyl groups leads to a gradual decrease in the ultimate strain of the film (ε_b) and, consequently, in the strength (σ_b). For example, upon the increase in the concentration of these units from 5 to 45%, the deformability drops almost two-fold. However, strong ($\sigma_b > 100$ MPa) and sufficiently elastic films ($\varepsilon_b \ge 19\%$) were obtained for all *co*-PAs synthesized in the present work.

The MPC formation does not result in a noticeable change in the modulus values of the films compared to the starting co-PAs (see Table 1). At the same time, for the most of the compositions under study, the complex formation leads to a considerable decrease in the ultimate deformations of the films (to 5-8%). An exception to this case is the composition containing 15% of the units with side bipyridyl groups. For the films of such composition, the complex formation proceeds virtually without decrease in the elasticity (see Table 1). This makes it possible to compare the stress-strain curve shape of the films of co-PA and the complex based on it (Fig. 1). The complex formation results in no change in the character of the deformation processes in the material. As judged by the stressstrain curve shapes and the results of visual observations of the behaviour of the samples during the test, the strain process in both materials occurs according to the mecha-



Fig. 1. Strain curves of the films of *co*-PA 8b (1) and MPC 10b (2).

nism of stress-induced elastic deformation without necking and any other manifestations of local strain.

As noted above, the experimental results suggest that the introduction of bulky Ir(ppy)₂ groups to the polymer chains does not provoke in a noticeable change in the modulus values of the films. This fact seems to be rather unexpected. Indeed, these groups, especially if their concentration is high (30-45%), must impede the formation of a regular system of intermolecular interactions in the material, which, in turn, must provoke the decrease in the *E* values of the complex films compared to those for the corresponding co-PAs. The absence of such effect in the experiments performed suggests that, as a result of the complex formation in the films, the formation of new intermolecular bonds takes place, which compensates the effect of "loosening" of the material structure due to the presence of the bulky Ir(ppy)₂ groups. As such alternative type of intermolecular interactions, one can propose the known interaction mechanism of the aromatic fragments of these groups with different aromatic groups of adjacent chains.14

As the studies on the relaxation transitions in the *co*-PA and MPC films showed (see Table 1), the glass transition points of *co*-PAs displace successively to the high-temperature region with increasing the content of the units with side bipyridyl groups in the polymer chains. The same tendency is observed when analyzing the behavior of the MPC films, a more intensive growth in T_g compared to the films of the starting *co*-PAs being observed for these films. With increasing the concentration of complexes, the segmental mobility defrost, which is necessary for the transformation of the sample from the glassy state to the high-elasticity one, is made difficult. As a result, the glass transition temperature increases, which was observed in the studies performed.

The luminescence spectra of the metal polymer complexes in DMF are shown in Fig. 2. In a solution, a broad



Fig. 2. Dependence of the luminescence intensity (I) of solutions of MPCs in DMF on the composition of the copolymer: 10a (I), 10b (2), 10c (3), and 10d (4).

luminescence band of the MPC with the Ir^I ions from 575 to 750 nm was observed in the red region of the visible spectrum with the intensity maximum at 630 nm. On going from solutions of the polymers under study to the self-supporting films (Fig. 3), we observed a shift of the luminescence spectral bands to the short-wave region by 20-30 nm.

The results obtained agree well with the published data¹⁵ for the solutions of low-molecular-weight iridium complexes with the bipyridyl derivatives in MeCN, which luminesce in the region of 620 nm.

The analysis of the spectra obtained (see Fig. 2) allows one to conclude that the dependence of the luminescence intensity of the MPC with the Ir^{I} ion on the copolymer composition is of extreme nature with the intensity maximum at 15 mol.% of the metal-bonding fragments. This can be explained by the fact that, in the range to 15 mol.%



Fig. 3. The effect of the ligand : $Ir(ppy)_2$ ratio (mol.%) in copolymer **10b** on the luminescence intensity in the films: 1 : 1 (*I*), 1 : 0.5 (*2*), and 1 : 0.25 (*3*).

of the monomeric metal-bonding units, there occurs an increase in the luminescence in a solution according to the mass action law due to a more effective complex formation. With further increase in the local concentration of the MPC with the Ir^{I} ion above 15 mol.% in a solution of individual macromolecules, concentration quenching of luminescence is beginning to manifest itself.¹⁶

For the copolymers with the optimum quantity of the metal-bonding units, we varied the content of the Ir^{I} ions (see Fig. 3). The analysis of the luminescence spectra showed that a decrease in the $[Ir^{I}]$: [bipyridyl] ratio from 1 to 0.25 results in virtually the same decrease in the intensity of the luminescence band of the MPC, which confirms the drawn conclusion on the absence of concentration quenching for the chosen optimum ratio between the ligand and unreactive monomer units.

Experimental

Purification of the starting compounds and solvents. 5-Aminoisophthalic acid, isatin, 2-acetylpyridine, potassium permanganate, *N*-methyl-2-pyrrolidone, propylene oxide, Et₂O, (Aldrich) underwent no additional purification. Thionyl chloride, AcOH, and Ac₂O were purified by simple distillation with taking the corresponding fraction: 75.5 °C (thionyl chloride), 117–118 °C (AcOH), and 138–140 °C (Ac₂O). DMF was dried over calcium hydride and distilled *in vacuo* (b.p. 76 °C at 40 Torr), Py was dried over potassium hydroxide and distilled (b.p. 114–115 °C), and 4,4 ´-diaminodiphenyl ether was purified by vacuum distillation (m.p. 190–191 °C).

Synthesis of the starting compounds and polymers. 2-(2-Pyr-idyl)quinoline-4-carboxylic acid 1 was synthesized by the Pfitz-inger reaction from isatin and 2-acetylpyridine according to the previously described procedure.⁶

Terephthaloyl-[bis(3-methoxy-4-oxybenzoic)] acid dichloride 6 was prepared according to the published procedure.¹²

The synthesis of *tetrakis*(2-phenylpyridine- C^2 , N')(μ -dichloro)diiridium) (**9**) was performed according to a known procedure.⁵

Synthesis of 6-(2-pyridyl)pyridine-2,3,4-tricarboxylic acid (2). To a solution of compound 1 (10 g, 0.04 mol) in 15% aqueous solution of KOH (20 mL), a solution of potassium permanganate (39 g, 0.247 mol) in water (800 mL) was added with stirring. The mixture was refluxed for 40 min, cooled to room temperature, and manganese dioxide that formed was filtered off. Sulfuric acid was added to the filtrate until a weak-acid reaction and the solution was concentrated until potassium sulfate began to crystallize out, the K₂SO₄ precipitate was filtered off after cooling. Sulfuric acid was added to the filtrate until a weak-acid reaction. potassium 2-pyridyl-4,5,6-pyridine tricarboxylate being precipitated. The precipitate was boiled in EtOH, filtered off, dried, dissolved in water, and acidified with a solution of hydrochloric acid to pH 3. The precipitate that formed was filtered off, washed with a small amount of water, dried at 50 °C in vacuo. The yield was 7.5 g (71%), m.p. 250 °C. ¹H NMR (DMSO-d₆), δ: 7.61 (dd, 1 H, H(4), J = 9.5 Hz, J = 2 Hz); 8.10 (t, 1 H, H(3), J = 9.5 Hz); 8.50 (d, 1 H, H(5), J = 9.5 Hz); 8.78 (d, 1 H, H(2), J = 8 Hz); 8.82 (s, 1 H, H(1)).

Synthesis of 6-(2-pyridyl)pyridine-3,4-dicarboxylic acid anhydride (3). Acid 2 (4.5 g, 0.018 mol) was refluxed for 5 h in a mixture of AcOH (180 mL) and Ac₂O (18 mL), then 3/4 of the solvent mixture was removed. The crystals that formed were filtered off, washed with Et₂O, and dried at 50 °C *in vacuo*. The yield was 2.9 g (73%), m.p. 190 °C. ¹H NMR (DMSO-d₆), 8: 7.55 (dd, 1 H, H(4), J=9.5 Hz, J=2 Hz); 8.02 (t, 1 H, H(3), J=9.5 Hz); 8.45 (d, 1 H, H(5), J=9.5 Hz); 8.55 (s, 1 H, H(6)); 8.76 (d, 1 H, H(2), J= 8 Hz); 9.08 (s, 1 H, H(1)).

Synthesis of 5-[6-(2-pyridyl)-5-azaphthalimido]isophthalic cid (4). To a solution of 5-aminoisophthalic acid (1.6 g, 0.009 mol) in DMF (35 mL) cooled to 0 °C, compound 3 (2 g, 0.009 mol) was added. The solution was stirred for 5 h at room temperature. Ac₂O (1.1 mL) and Py (0.27 mL) were added to the resulted suspension. The mixture was refluxed for 5 h and, after cooling to room temperature, poured to water. The resulted precipitate was filtered off, washed with water, dried at 50 °C *in vacuo* and recrystallized from a DMF–water (1 : 1) mixture. The yield was 3g (83%). ¹H NMR (DMSO-d₆), &: 7.62 (dd, 1 H, H(4), J=9.5 Hz, J = 2 Hz); &.08 (t, 1 H, H(3), J = 9.5 Hz); &.33 (s, 2 H, H(7), H(11)); &.53 (d, 1 H, H(5), J = 9.5 Hz); &.55 (t, 1 H, H(9), J= 2 Hz); &.79 (s, 1 H, H(6)); &.83 (d, 1 H, H(2), J= 8 Hz); 9.36 (s, 1 H, H(1)), 13.57 (br.s, 2 H, H(8), H(10)).

Synthesis of 5-[6-(2-pyridyl)-5-azaphthalimido]isophthaloyl dichloride (5). A solution of compound 4 (1 g, 0.003 mol) in thionyl chloride (50 mL) was refluxed for 5 h. After termination of heating, thionyl chloride (40 mL) was removed. The precipitate that formed was filtered off and dried at room temperature. The yield was 1 g (91%). Found (%): C, 56.32; H, 2.19; Cl, 16.59; N, 9.80. $C_{20}H_{19}Cl_2N_3O_4$. Calculated (%): C, 56.36; H, 2.13; Cl, 16.64; N, 9.86; O, 15.02.

Synthesis of copolymers. To a solution of 4,4'-diaminodiphenyl ether (0.1 g, $5 \cdot 10^{-4}$ mol) in *N*-methyl-2-pyrrolidone (3 mL) cooled to -15 °C, compound 5 (0.0324 g, $8 \cdot 10^{-5}$ mol) and terephthaloyl-[bis(3-methoxy-4-oxybenzoic)] acid dichloride (0.217 g, $4.3 \cdot 10^{-4}$ mol) were added. The suspension was stirred for 40 min at -15 °C, the cooling bath was removed, and propylene oxide (0.1 mL) was added. After complete dissolution of dichlorides, the mixture was stirred for 4–5 h at room temperature.

The procedure is given for copolymer **8b** containing 15% of the bipyridyl units. Copolymers **8a**, **8c**, and **8d** containing 5, 30, and 45% of the bipyridyl units, respectively, were synthesized according to the analogous procedure.

Copolymer 8a. Found (%): C, 70.55; H, 3.81; N, 4.55. $C_{3560}H_{2565}N_{215}O_{880}$. Calculated (%): C, 70.61; H, 3.83; N, 4.51; O, 21.05. ¹H NMR (DMSO-d₆), δ : 3.9 (s, 5.7 H, MeO); 7.0–8.4 (m, 17.9 H, Ar); 10.35 (s, 2 H, NH).

Copolymer 8b. Found (%): C, 68.49; H, 4.02; N, 5.68. $C_{3540}H_{2495}N_{245}O_{840}$. Calculated (%): C, 68.69; H, 4.03; N, 5.54; O, 21.74. ¹H NMR (DMSO-d₆), δ : 3.9 (s, 5.1 H, MeO); 7.0–8.4 (m, 21 H, Ar); 10.35 (s, 2 H, NH).

Copolymer 8c. Found (%): C, 68.75; H, 3.92; N, 6.72. $C_{3480}H_{2390}N_{290}O_{780}$. Calculated (%): C, 68.81; H, 3.94; N, 6.68; O, 20.57. ¹H NMR (DMSO-d₆), δ : 3,9 (s, 4.2 H, MeO); 7.0–8.4 (m, 25.3 H, Ar); 10.35 (s, 2 H, NH).

Copolymer 8d. Found (%): C, 68.89; H, 3.89; N, 7.85. $C_{3420}H_{2285}N_{469}O_{720}$. Calculated (%): C, 68.93; H, 3.84; N, 7.88; O, 19.35. ¹H NMR (DMSO-d₆), δ : 3.9 (s, 3.3 H, MeO); 7.0–8.4 (m, 31.9 H, Ar); 10.35 (s, 2 H, NH).

The calculations were performed for copolymers $8\mathbf{a} - \mathbf{d}$ with (m+n) = 100.

From the resulted solutions of polymers, films were cast on glass supports and dried at 200 °C until a constant weight. The film thickness was $6-25 \ \mu m$.

Synthesis of iridum polymer complexes. To a solution of compound **8b** (0.0588 g, $9.5 \cdot 10^{-5}$ mol) in *N*-methyl-2-pyrrolidone (2 mL), compound **9** (0.0063 g, $0.7 \cdot 10^{-5}$ mol) was added. The mixture was heated with stirring under argon for 10 h at 110 °C and, after cooling, poured to EtOH. The sedimented polymer was purified by extraction in EtOH for 24 h, dried *in vacuo*, and dissolved in *N*-methyl-2-pyrrolidone. Films were cast on glass supports, dried at 200 °C until a constant weight. The film thickness is 6–25 µm.

The procedure is given for MPC **10b** containing 15% of the bipyridyl units. Metal polymer complexes **10a**, **10c**, and **10d** containing 5, 30, and 45% of the bipyridyl units, respectively, were synthesized according to the analogous procedure.

Complex 10a. Found (%): C, 68.61; H, 4.10; N, 4.86; Cl, 0.07. $C_{3690}H_{2075}N_{225}O_{880}Cl_5Ir_5$. Calculated (%): C, 68.4; H, 3.2; N, 4.9; O, 22.0; Cl, 0.27; Ir, 1.5. ¹H NMR (DMSO-d₆), δ : 3.9 (s, 5.7 H, MeO); 7.05–8.4 (m, 19.5 H, Ar); 10.35 (s, 2 H, NH).

Complex 10b. Found (%): C, 67.2; H, 3.95; N, 5.52; Cl, 0.50. $C_{3870}H_{2225}N_{275}O_{840}Cl_{15}Ir_{15}$. Calculated (%): C, 66.9; H, 3.2; N, 5.5; O, 19.4; Cl, 0.8; Ir, 4.2. ¹H NMR (DMSO-d₆), δ : 3.9 (s, 5.1 H, MeO); 7.05–8.4 (m, 22.8 H, Ar); 10.35 (s, 2 H, NH).

Complex 10c. Found (%): C, 65.05; H, 3.91; N, 6.67; Cl, 0.96. C₄₁₄₀H₂₄₅₀N₃₅₀O₇₈₀Cl₃₀Ir₃₀. Calculated (%): C, 65.1; H, 3.2; N, 6.4; O, 16.3; Cl, 1.4; Ir, 7.6. ¹H NMR (DMSO-d₆), δ : 3.9 (s, 4.2 H, MeO); 7.05–8.4 (m, 29.4 H, Ar); 10.35 (s, 2 H, NH).

Complex 10d. Found (%): C, 64.8; H, 3.65; N, 7.3; Cl, 1.43. $C_{4410}H_{2675}N_{425}O_{720}Cl_{45}Ir_{45}$. Calculated (%): C, 63.5; H, 3.2; N, 7.1; O, 13.8; Cl, 1.9; Ir, 10.4. ¹H NMR (DMSO-d₆), δ : 3.9 (s, 3.3 H, MeO); 7.05–8.4 (m, 40.7 H, Ar); 10.35 (s, 2 H, NH).

The calculations were performed for copolymers 10a-d with (m+p+q) = 100 for the case when the complex formation proceeds by 100%.

¹H NMR spectra for 1% solutions were recorded on a Bruker Avance-400 (400 MHz) spectrometer using Me_4Si as the internal standard.

Luminescence spectra were recorded on a LS-100 (PTI®) spectrofluorometer. The slit width of excitation and recording monochromators was 1 mm at the reciprocal linear dispersion of 4 nm mm⁻¹. Photoluminescence was excited by the wavelength of 370 nm based on the absorption band of the MPC formed with the Ir^I ions.

The inherent viscosities $[\eta]$ of polymers were determined on a Ubbelohde instrument (solutions in DMF) at 20 °C.

The uniaxial tensile tests of the films were performed using an UTS 10 (UTStestsysteme, Germany) universal mechanical test device. During testing, the Young's modulus *E*, the yield point σ_y (as the intersection point of the tangents to the initial linear section of the stress-strain curve and to the section of development of stress-induced elastic deformation), strength σ_b and ultimate deformation ϵ_b . The above-mentioned characteristics were obtained by averaging of the test results for seven samples.

The glass transition temperatures of the films under study were determined by the dynamic mechanical analysis on a DMA 242 C (NETZSCH) device. The measurements were performed on a frequency of 1 Hz at the strain amplitude of 10 μ m at the heating rate of 10 deg min⁻¹. The basic dimensions of the samples are 1.5×10 mm. The glass transition points T_g were determined by the position of the maximum on the temperature dependences of the mechanical loss tangent.

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