

New Soluble Functional Polymers by Free-Radical Copolymerization of Methacrylates and Bipyridine Ruthenium Complexes

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Received 3 June 2003; accepted 15 August 2003

ABSTRACT: The luminescent complex [4-(3-hydroxypropyl)-4'-methyl-2,2'-bipyridine]-bis(2,2'-bipyridine)-ruthenium(II)-bis(hexafluoroantimonate) and its methacrylate derivative were successfully synthesized and fully characterized by two-dimensional ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR techniques [correlation spectroscopy (COSY) and heteronuclear multiple-quantum coherence experiment (HMQC)], as well as matrix-assisted laser desorption ionization time-of-flight mass spectrometry. The respective labeled methyl methacrylate-ruthenium(polypyridyl) copolymers were obtained by free-radical copolymerization with methyl methacrylate and were characterized utilizing NMR, IR, and UV-visible spectroscopy and gel permeation chromatography. © 2003 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 41: 3954–3964, 2003

Keywords: free-radical polymerization; poly(methyl methacrylate); copolymer; tris(2,2'-bipyridine)ruthenium(II) complexes; luminescence

INTRODUCTION

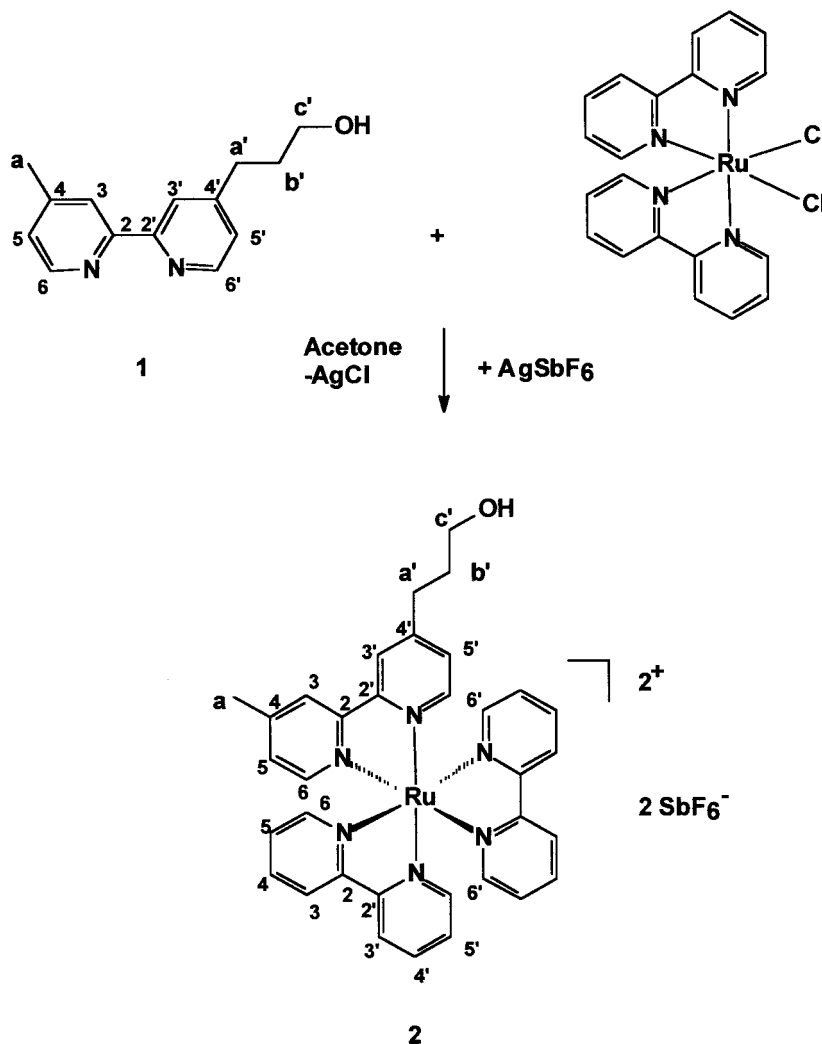
New functional materials with certain properties, good processability, and straightforward synthesis are of central interest in coating, device, and display technology. The covalent labeling of well-known polymers with luminescent systems represents a special topic in these fields. Metal containing systems are particularly important. The construction of “smart” ligands and modified metal–ligand complexes (MLCs) that introduce new suitable functionalities allows the application of a wide range of polymerization reactions and thus opens the way to new functional materials.^{1–4} The design of metal containing macromolecules encompasses three main variable components:

the metal complex itself, its ligand set, and the polymer backbone. Straightforward synthesis over a wide range of tunable materials properties is accessible utilizing free-radical polymerization of acrylates.^{5–7}

The large but still growing family of red emitting ruthenium(II)polypyridyl complexes is currently under intensive investigation for their unique photophysical, photochemical, and molecular sensing properties. A number of diverse and exciting applications for these complexes are currently being investigated, such as electron and energy transfer for binary optical memories, solid-state light-emitting devices (LEDs), or luminescence lifetime-based anion sensors.^{8–15} Complexes with ligands containing functionalized spacer groups, such as 4-(3-hydroxypropyl)-4'-methyl-2,2'-bipyridine (compound **1**, Scheme 1), are of particular interest.¹⁶ The MLCs bearing a modified bipyridine (bpy) ligand with a flexible spacer in the 4-position offer a wide spectrum of

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 41, 3954–3964 (2003)
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Scheme 1. The synthesis of the hydroxyl-functionalized ruthenium(II)tris-bipyridine complex **2**.

binding reactions, whereas the substitution position allows an unhindered metal complexation reaction and mobility of the complex bound to macromolecules. Thus, these designed materials have the advantage of preventing aggregation of the MLCs as observed in polymer blends while still maintaining the characteristics of the polymer backbone and ensuring easy processing of the materials in spin coating or ink-jet printing.^{8,17}

In the present study we describe the synthesis, characterization, and derivatization of a luminescent ruthenium(II) complex family that is based on a mixed ligand system. These new materials were synthesized utilizing free-radical copolymerization of a methacrylate (MA)-derivatized MLC with methyl MA (MMA). They were characterized in detail utilizing NMR, IR, and UV-visible (UV-

vis) spectroscopy, as well as gel permeation chromatography (GPC; see, e.g., Mascio and Scali¹⁸).

EXPERIMENTAL

Instruments and Measurements

Elemental analyses were performed on a Carlo Erba Instruments EA1108 CHNS/O elemental analyzer. NMR spectra were recorded on a Varian Gemini 300 spectrometer at 298 K. The ¹H-¹³C heteronuclear multiple-quantum coherence experiment (HMQC) spectra were recorded on a Varian Inova 500 spectrometer with an indirect probe. The chemical shifts are given in parts per million relative to tetramethylsilane (TMS) or to

solvent signals for proton and carbon spectra. The frequencies and standards were 250.13 MHz for ^1H NMR and 62.90 MHz for $^{13}\text{C}\{^1\text{H}\}$ NMR. All NMR spectra were calibrated relative to partially deuterated solvent peaks, which are reported relative to TMS. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Voyager-DE™ PRO Biospectrometry™ workstation (Applied Biosystems) TOF mass spectrometer using the linear mode for operation. The spectra were obtained in the positive ion mode, and ionization was performed with a 337 nm pulsed nitrogen laser. Data were processed using the Data Explorer™ software package (Applied Biosystems). Gas chromatography with MS (GC-MS) was performed using a Shimadzu GC-MS-QP5000. The mass values that were found are reported as a mass/charge ratio (m/z). The UV-vis spectroscopy was performed on a PerkinElmer Lambda 45 apparatus utilizing a 1 cm cuvette. IR spectra were recorded on a PerkinElmer 1600 Fourier transform IR (FTIR) spectrometer. GPC was carried out on Bio-Beads S-X1 columns (CH_2Cl_2 ; preparative GPC) and on a Waters GPC instrument equipped with a Waters model 510 pump, a model 410 refractive index (RI) detector, and a model 486 UV detector [dimethylformamide (DMF), 10 mm NH_4PF_6 , 50 °C, 0.5 mL/min flow rate, Waters Styragel HT 4, Polymer Laboratories; poly(methyl methacrylate) (PMMA) calibration]. Differential scanning calorimetry (DSC) investigations were performed on a PerkinElmer Pyris-1 DSC system with a heating rate of 40 K/min (glass-transition temperature, T_g).

Materials

All manipulations were performed under an atmosphere of dry argon by employing the usual Schlenk techniques. The solvents were dried according to common methods, distilled, and stored under argon. Compound **1**¹⁹ was described previously, and we synthesized it in a modified procedure. *cis*-(Bpy)₂RuCl₂ · 2H₂O^{20,21} and the respective hydroxypropyl-ligand modified polypyridyl ruthenium(II) complex (**2**)^{22,23} were synthesized according to literature methods. 2,2'-Bpy, 2-bromoethoxy-*tert*-butyl-dimethyl-silane, *n*-butyllithium, triethylamine, methacryloyl chloride, MMA, diisopropylamine, and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Aldrich.

Preparation of Precursors, Monomers, and Copolymers

Compound 1

A solution of diisopropylamine (1.69 mL, 11.94 mmol) in tetrahydrofuran (THF, 10 mL) was cooled to −78 °C and slowly treated with a solution of *n*-butyllithium in *n*-hexane (1.6 M, 8.5 mL, 13.6 mmol). The resulting pale yellow solution of lithium diisopropylamide (LDA) was stirred for 20 min, and then 4,4'-dimethyl-2,2'-bpy (2.0 g, 10.85 mmol) in THF (100 mL) was added over 10 min. When adding the solution of 4,4'-dimethyl-2,2'-bpy to the LDA solution, a dark orange-red solution was obtained. The mixture was stirred for 1 h at −78 °C, and then 2-bromoethoxy-*tert*-butyl-dimethyl-silane (2.86 g, 11.94 mmol) in THF (20 mL) was added within 10 min. The reaction mixture was allowed to warm to room temperature overnight. The reaction was quenched by the slow addition of 5 mL of water. The solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 , washed with water (3×), and dried over Mg_2SO_4 . The crude product was stirred overnight in HCl (1 M) and then neutralized to pH 7 with NaOH (1 M). The resulting solution was extracted with chloroform (5 × 20 mL) and dried over Mg_2SO_4 . After removal of the solvent, compound **1** was isolated as a yellow oil that was purified by column chromatography (ethyl acetate, neutral aluminum oxide column, 30 cm length, 5 cm diameter) with a yield of 1.16 g (47%).

IR (cm^{-1}): 3327, 3054 (OH), 3008, 2934, 2865 (CH), 1594, 1553 (C=C and C=N). ^1H NMR (CDCl_3 , δ): 1.49 [t, $J(\text{HH}) = 4.9$ Hz, OH], 2.02–1.98 (m, 2H, b'), 2.44 (s, 3H, a), 2.81 [t, $J(\text{HH}) = 8.09$ Hz, 2H, a'], 3.70 [dt, $J(\text{HH}) = 6.6$ Hz, $J(\text{HH}) = 4.9$ Hz, 2H, c'], 7.19–7.12 (m, 2H, 5,5'), 8.25–8.23 (m, 2H, 3,3'), 8.57–8.52 (m, 2H, 6,6'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 21.2 (Ca), 31.6 (Cb'), 33.1 (Ca'), 61.8 (Cc'), 121.3 (C3'), 122.1 (C3), 123.9 (C5'), 124.7 (C5'), 148.2 (C4), 148.9, 149.1 (C6,6'), 151.9 (C4'), 156.0 (C2'), 156.2 (C2). GC-MS m/z (ethyl acetate): 228 (M^+); MALDI-TOF-MS (dithranol) m/z : 229.34 ($\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}^+$).

1-bis(2,2'-Bpy)-Ru(II)-bis(hexafluoroantimonate) Complex (2)

A suspension of *cis*-(bpy)₂RuCl₂ · 2H₂O precursor (426 mg, 0.88 mmol) and AgSbF₆ (604.7 mg, 1.76 mmol) in acetone was stirred for 48 h, followed by filtration of the AgCl that was formed.

Compound **1** (200 mg, 0.88 mmol) was added to the filtrate and the mixture was refluxed for 24 h. The solvent was removed under reduced pressure. The crude product was dissolved in CH_2Cl_2 (5 mL) and precipitated with diethyl ether. The precipitate was stirred overnight and then filtered. To remove silver impurities, the complex was again purified by column chromatography (acetone, neutral aluminum oxide column, 4 cm length, 2 cm diameter). The solvent was removed under reduced pressure and the resulting dark orange powder was washed with *n*-hexane. The yield of **2** was 405 mg (56%).

IR (cm^{-1}): 3107, 3081 (OH), 3008, 2926, 2871 (CH), 1615, 1604 (C=C and C=N), 1465, 1445, 1423, 1033 (OH), 770, 731, 658. ^1H NMR (CD_3CN , δ , for assignments see refs. 23, 24): 1.62–1.69 (m, 2H, b'), 2.27 (s, 3H, a), 2.50 (OH), 2.63–2.68 (m, 2H, a'), 3.32–3.38 (m, 2H, c'), 6.99–7.09 (m, 2H, 5,5'), 7.15–7.22 (m, 4H, 5,5'-bpy), 7.31–7.36 (m, 2H, 6,6'), 7.47–7.58 (m, 4H, 6,6'-bpy), 7.81–7.91 (m, 4H, 4,4'-bpy), 8.17–8.19 (m, 2H, 3,3'), 8.28–8.35 (m, 4H, 3,3'-bpy). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , δ , for assignments see refs. 23, 24): 21.1 (Ca), 32.2 (Cb'), 33.6 (Ca'), 61.4 (Cc'), 125.1, 125.2 (C3,3'), 125.9 (C, C3,3'-bpy), 128.4, 128.5 (C5,5'-bpy), 129.1 (C4,4'), 151.3, 151.6 (C4,4'-bpy), 151.6, 151.8 (C5,5'), 152.4, 152.6 (C6,6'), 155.4 (C6,6'-bpy), 154.7, 157.5 (C2,2'), 157.9, 158.0 (C2,2'-bpy). MALDI-TOF-MS m/z (dithranol): 877.38 ($\text{C}_{34}\text{H}_{32}\text{N}_6\text{ORuSbF}_6^+$). ELEM. ANAL. Calcd for $\text{C}_{34}\text{H}_{32}\text{N}_6\text{ORuSb}_2\text{F}_{12}$ (1111.9): C, 36.08%; H, 2.90%; N, 7.55%. Found: C, 36.00%; H, 3.22%; N, 7.67%.

MA-Derivatized Ruthenium(II) Complex (**3**)

A solution of compound **2** (200 mg, 0.18 mmol) in CH_2Cl_2 was cooled to 0 °C and then carefully treated with triethylamine (105 μL , 0.75 mmol) and methacryloyl chloride (93 μL , 1 mmol). The reaction mixture was stirred until ambient temperature was achieved. The solvent was removed under reduced pressure. The reaction mixture was extracted with a 1% (w/w) aqueous solution of NaHCO_3 (3 \times) and water (2 \times). The organic layers were then dried over Mg_2SO_4 . The solvent was removed under reduced pressure, and the crude product was redissolved in CH_2Cl_2 (5 mL) and precipitated with diethyl ether. The precipitate was stirred overnight and then filtered. To remove impurities, complex **3** was washed with a large volume of diethyl ether and additionally purified by column chromatography (acetone,

neutral aluminum oxide column, 4 cm length, 2 cm diameter). The solvent was removed under reduced pressure and the resulting dark orange-red powder was washed with *n*-hexane. The yield of **3** was 188 mg (88%).

IR (cm^{-1}): 3086, 2962, 1712 (C=O), 1619, 1604 (C=C and C=N), 1465, 1446, 1424 (CH_2 , C— CH_3 , and CH_2 —CO), 1315, 1297, 1243, 1161, 1028, 762, 731, 658. ^1H NMR (CD_3CN , δ , for assignments see refs. 23, 24): 0.92–0.94 (m, 2H, f'), 2.27–2.93 (s, 3H, a), 2.66–2.74 (m, 2H, b'), 3.17–3.27 (m, 2H, a'), 3.94–4.02 (m, 2H, c'), 5.29–5.37 (s, 1H, g'), 5.80–5.84 (s, 1H, g'), 7.07–7.00 (m, 2H, 5,5'), 7.14–7.25 (m, 4H, 5,5'-bpy), 7.30–7.35 (m, 2H, 6,6'), 7.52 (m, 4H, 6,6'-bpy), 7.84–7.90 (m, 4H, 4,4'-bpy), 8.14–8.19 (m, 2H, 3,3'), 8.26–8.29 (m, 4H, 3,3'-bpy). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , δ , for assignments see refs. 23, 24): 17.5 (Cf'), 20.3 (Ca), 28.6.2 (Cb'), 31.4 (Ca'), 63.5 (Cc'), 124.1, 124.2 (C3,3'), 125.1 (Cg'), 127.6 (C C3,3'-bpy), 128.4, 128.5 (C5,5'-bpy), 129.1 (C4,4'), 136.7 (Ce'), 150.5, 150.8 (C4,4'-bpy), 151.1, 151.6 (C5,5'), 151.6, 151.7 (C6,6'), 151.8 (C6,6'-bpy), 156.3, 156.5 (C2,2'), 157.1, 157.5 (C2,2'-bpy), 161.9 (Cd'). MALDI-TOF-MS m/z (dithranol): 945.44 ($\text{C}_{38}\text{H}_{36}\text{N}_6\text{O}_2\text{RuSbF}_6^+$). ELEM. ANAL. Calcd for $\text{C}_{38}\text{H}_{36}\text{N}_6\text{O}_2\text{RuSb}_2\text{F}_{12}$ (1179.9): C, 38.64%; H, 3.07%; N, 7.11%. Found: C, 38.94%; H, 3.07%; N, 6.60%.

General Procedure for MMA Copolymers with MA-Derivatized Ru(II) Complex (**4a–d**)

MMA and the MA derivative **3** were dissolved in 20 mL of the solvents acetonitrile for **4a** and **4b**, ethanol for **4c**, or chloroform for **4d**. The reaction mixture was heated to 60 °C, and AIBN (33 mol % for **4a**, 1 mol % for **4b–d**) in their respective solvents was added dropwise. The polymerization was continued for 48 h and quenched by precipitation into cold *n*-hexane. The crude copolymer was purified by size exclusion chromatography (CH_2Cl_2 , Bio-Beads S-X1, 50 cm length, 4 cm diameter).

Yield of **4a**: 95 mg (24% calcd in regard to MMA). IR (cm^{-1}): 2951, 1724 (C=O), 1618 (C=C and C=N), 1464, 1445 (CH_2 , C— CH_3 , and CH_2 —CO), 1242, 1148, 1050 (backbone — CH_2 —), 838, 764. ^1H NMR (CD_3CN , δ): 0.64 (br, α - CH_3 —PMMA), 0.83 (br, α - CH_3 —PMMA), 1.06 (br, α - CH_3 —PMMA), 1.65–1.80 (br, alkyl, PMMA and b'-bpy), 2.38 (br, alkyl, PMMA and a'-bpy), 2.62 (br, alkyl, PMMA and a'-bpy), 2.74 (br, alkyl, PMMA and c'-bpy), 3.42 (br, O— CH_3 —PMMA

and *c'*-bpy), 7.09–7.12 (m, 2H, 5,5'), 7.23–7.25 (m, 4H, 5,5'-bpy), 7.37–7.42 (m, 2H, 6,6'), 7.57–7.58 (m, 4H, 6,6'-bpy), 7.87–7.92 (m, 4H, 4,4'-bpy), 8.22–8.24 (m, 2H, 3,3'), 8.33–8.36 (m, 4H, 3,3'-bpy). GPC (DMF): number-average molecular weight (M_n) = 4830 g mol⁻¹, polydispersity index (PDI) = 1.09.

Yield of **4b**: 248 mg (62% calcd in regard to MMA). IR (cm⁻¹): 2995, 2951, 1724 (C=O), 1483, 1435 (CH₂, C—CH₃, and CH₃—CO), 1385 (C—CH₃ and CH₃—CO), 1270, 1239, 1190, 1050 (backbone —CH₂—), 986, 965, 841, 749. ¹H NMR (CD₃CN, δ): 0.63 (br, α-CH₃—PMMA), 0.83 (br, α-CH₃—PMMA), 1.01 (br, α-CH₃—PMMA), 1.65–1.75 (br, alkyl, PMMA), 2.43 (br, alkyl, PMMA), 2.59 (br, alkyl, PMMA), 2.71 (br, alkyl, PMMA), 3.42 (br, O—CH₃—PMMA), 7.04–7.12 (m, 2H, 5,5'), 7.18–7.29 (m, 4H, 5,5'-bpy), 7.34–7.47 (m, 2H, 6,6'), 7.50–7.66 (m, 4H, 6,6'-bpy), 7.80–7.98 (m, 4H, 4,4'-bpy), 8.16–8.26 (m, 2H, 3,3'), 8.28–8.39 (m, 4H, 3,3'-bpy). GPC (DMF): M_n = 15,540 g mol⁻¹, PDI = 1.80.

Yield of **4c**: 294 mg (74% calcd in regard to MMA). IR (cm⁻¹): 2993, 2950, 1723 (C=O), 1483, 1435 (CH₂, C—CH₃, and CH₃—CO), 1386 (C—CH₃ and CH₃—CO), 1270, 1240, 1190, 1050 (backbone —CH₂—), 986, 965, 841, 749. ¹H NMR (CD₃CN, δ): 0.64 (br, α-CH₃—PMMA), 0.83 (br, α-CH₃—PMMA), 1.01 (br, α-CH₃—PMMA), 1.65–1.80 (br, alkyl, PMMA), 2.41 (br, alkyl, PMMA), 2.60 (br, alkyl, PMMA), 2.72 (br, alkyl, PMMA), 3.42 (br, O—CH₃—PMMA), 7.07–7.12 (m, 2H, 5,5'), 7.21–7.25 (m, 4H, 5,5'-bpy), 7.41–7.42 (m, 2H, 6,6'), 7.52–7.58 (m, 4H, 6,6'-bpy), 7.81–7.92 (m, 4H, 4,4'-bpy), 8.20–8.24 (m, 2H, 3,3'), 8.31–8.36 (m, 4H, 3,3'-bpy). GPC (DMF): M_n = 21,970 g mol⁻¹, PDI = 1.98.

Yield of **4d**: 261 mg (65% calcd in regard to MMA). IR (cm⁻¹): 2994, 2951, 1724 (C=O), 1483, 1434 (CH₂, C—CH₃, and CH₃—CO), 1385 (C—CH₃ and CH₃—CO), 1270, 1239, 1190, 1050 (backbone —CH₂—), 986, 965, 841, 749. ¹H NMR (CD₃CN, δ): 0.63 (br, α-CH₃—PMMA), 0.83 (br, α-CH₃—PMMA), 1.01 (br, α-CH₃—PMMA), 1.65–1.72 (br, alkyl, PMMA), 2.38 (br, alkyl, PMMA), 2.59 (br, alkyl, PMMA), 2.70 (br, alkyl, PMMA), 3.42 (br, O—CH₃—PMMA), 7.03–7.12 (m, 2H, 5,5'), 7.21–7.25 (m, 4H, 5,5'-bpy), 7.40–7.42 (m, 2H, 6,6'), 7.57–7.58 (m, 4H, 6,6'-bpy), 7.88–7.92 (m, 4H, 4,4'-bpy), 8.22–8.24 (m, 2H, 3,3'), 8.30–8.36 (m, 4H, 3,3'-bpy). GPC (DMF): M_n = 16,770 g mol⁻¹, PDI = 1.85.

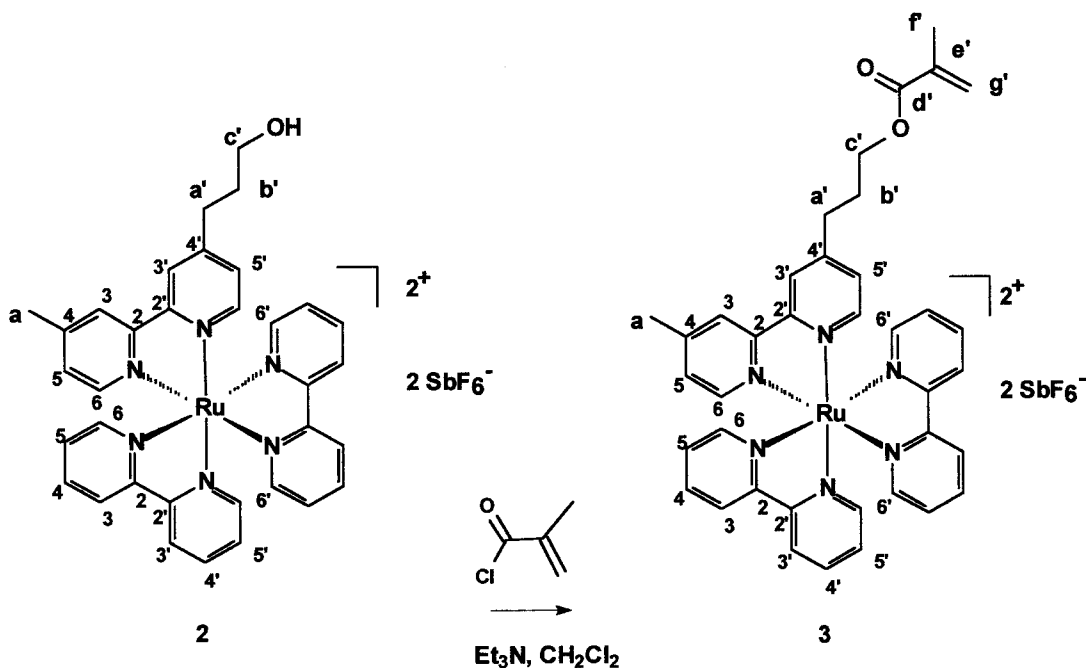
RESULTS AND DISCUSSION

New polymeric materials are currently under intense investigation for possible applications in device and display technology. In particular, organic LEDs have gained increased attention for applications as flat panel displays. Different kinds of LEDs are represented by light-emitting electrochemical cells (LECs).¹⁷ Rudmann et al. introduced a LEC simply by blending [Ru(bpy)₃]²⁺ and respective counterions with PMMA.^{8,9} One of the advantages of such systems is that they are composed of just one layer between the two electrodes. However, the blended systems suffer to some extent from reduced lifetimes because of emitter aggregation. This drawback can be overcome by copolymerization of the emitting MLCs. Therefore, we synthesized new polymerizable MLCs as shown in Schemes 1 and 2.

For the preparation of complex **2**, silver hexafluoroantimonate was added to a suspension of *cis*-(bpy)₂RuCl₂ · 2H₂O in acetone to eliminate both chlorides at ambient temperature. The silver chloride that was produced was removed by careful filtration, the modified bpy ligand **1** was added at an equivalent ratio, and the reaction mixture was subsequently refluxed in order to form complex **2** (Scheme 1). The MA-derivatized complex **3** was prepared by reacting **2** in basic conditions with methacryloyl chloride (Scheme 2). Orange crystals of complex **2** and orange-red crystals of complex **3** were obtained after precipitation in diethyl ether. Moreover, the complexes were purified by column chromatography. Both compounds were readily soluble in organic solvents of medium polarity.²³ MS, NMR, IR, and elemental analysis proved the existence and purity of **2** and **3**.

The assignments (see refs. 23, 24) of most of the proton and carbon signals in the ¹H and ¹³C{¹H} NMR spectra of **2** and **3** were achieved by using the two-dimensional (2D) techniques of correlation spectroscopy (COSY) and HMQC. The integration of the aromatic protons clearly revealed the presence of one compound **1** and two 2,2'-bpy ligands in the complex. The correlation between the aromatic protons could be recognized by a 2D COSY spectrum. The HMQC experiment allowed the assignment of the ¹³C signals with the exception of the quaternary carbon atoms. The NMR data are summarized in the Experimental section.

The UV-vis and emission spectra of complex **2** revealed the expected absorption and emission



Scheme 2. The synthesis of the methacrylate-functionalized ruthenium(II)tris-bipyridine complex **3**.

bands of $[\text{Ru}(\text{bpy})_3]^{2+}$. The absorption maximum of the metal–ligand charge-transfer (MLCT) band was found at 455 nm and the maximum of the

broad emission band was at 615 nm (Fig. 1). The bands in the IR spectra of complexes **2** and **3** are clearly shifted because of the side-chain modifica-

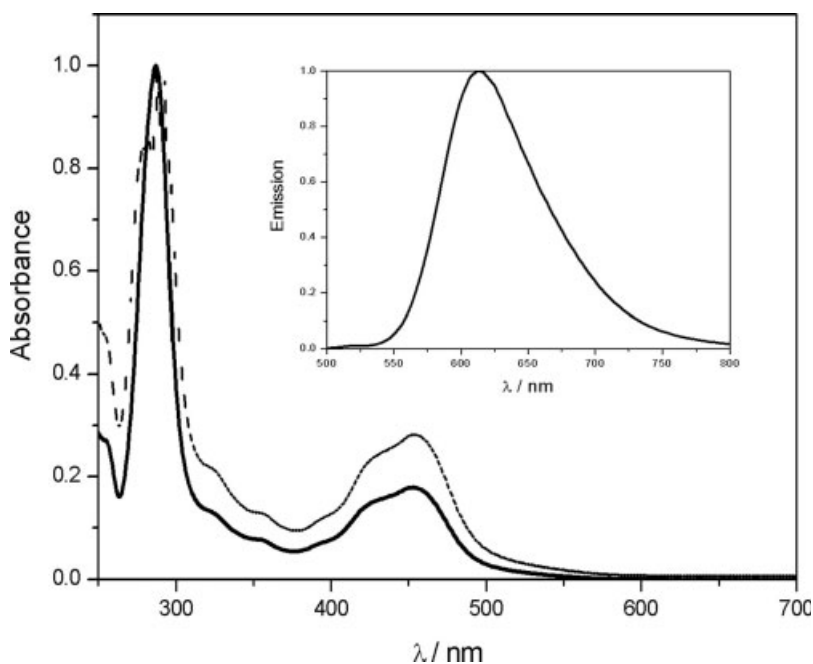


Figure 1. The selected absorption and emission properties of the prepared compounds in acetonitrile. (—) The absorption spectra representing **3** and **4b–d**. (···) The characteristic **4a** spectra. The MLCT band shows its maximum at 455 nm. (Inset) The broad and unstructured emission of **3** with a maximum at 615 nm.

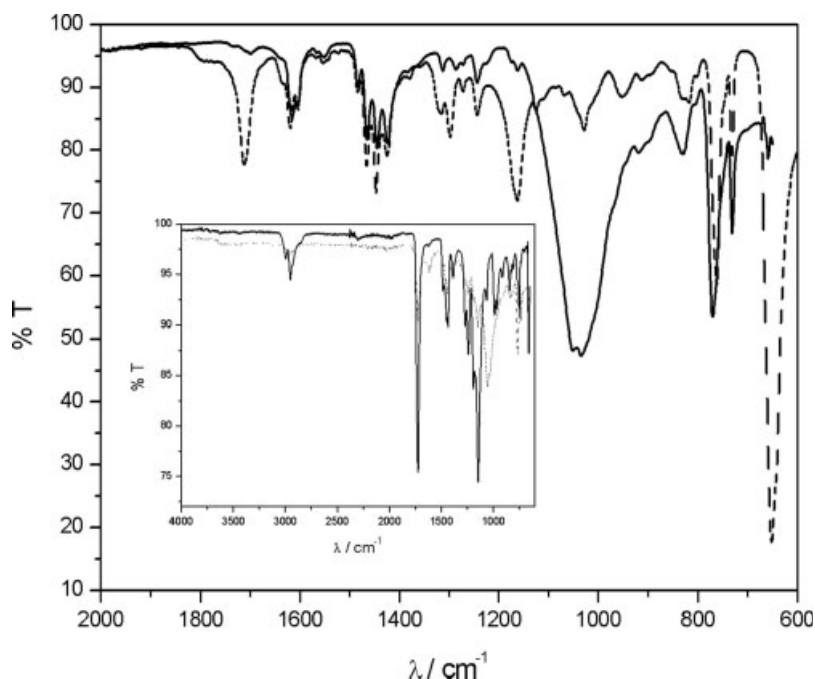


Figure 2. The IR spectra of complexes (—) **2** and (---) **3**. (Inset) The IR characteristics of (···) **4a** compared to (—) **4b-d**.

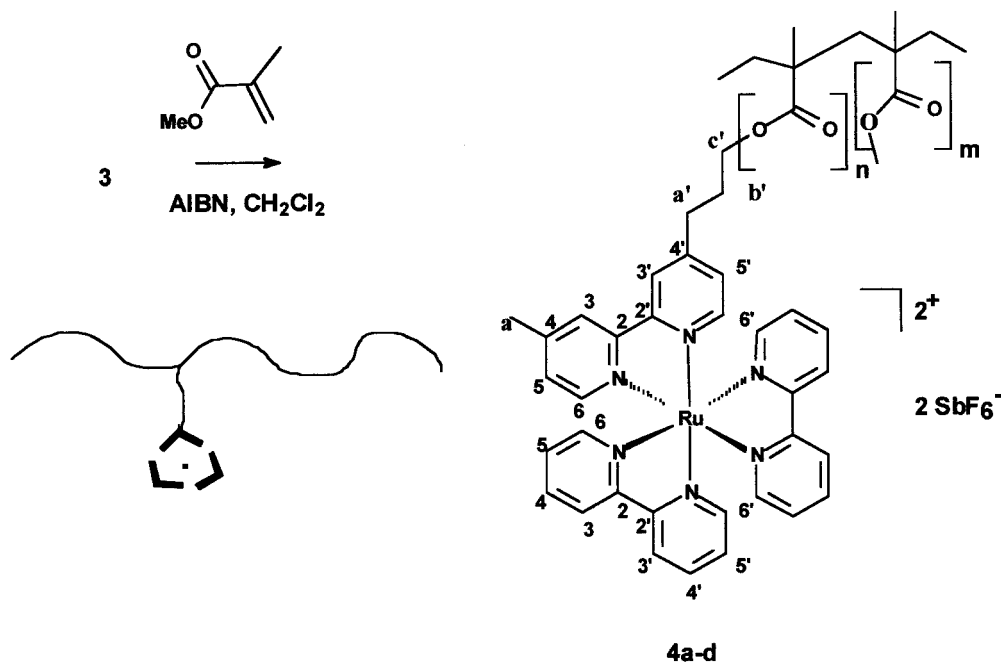
tion (Fig. 2). The new appearance of the band at 1712 cm^{-1} is significant for the C=O vibrations of the substituted bpy side chain. The primary alcohol vibration at 1033 cm^{-1} was reduced, whereas a new band at 1161 cm^{-1} appeared that could be assigned to $-\text{CH}_2-\text{O}-\text{C}=\text{O}-$ vibrations.

Free-radical polymerization with AIBN as the initiator was used for the copolymerization of **3** with MMA (Scheme 3). Except for polymer **4a** (33 mol % AIBN), all polymerizations (**4b-d**) were performed using 1 mol % AIBN as initiator. In all cases a 10^{-5} molar concentration of the MLC was utilized to ensure that concentration effects did not disturb the emission properties of the copolymerized complexes in the final materials. All orange-red copolymers revealed good processability, high solubility, and high molecular weights.

We utilized NMR, IR, and UV-vis spectroscopy and GPC to characterize the obtained copolymers. Table 1 summarizes the main features of copolymers **4a-d**. Compound **4a** synthesized in acetonitrile (33 mol % initiator) revealed all expected resonances in the ^1H NMR spectrum (Fig. 3). For this material, a Ru(II) complex content of 22% could be calculated. Moreover, we observed a 24/33/43 (*mm/mr/rr*) tacticity of $\alpha\text{-CH}_3$ protons in the PMMA backbone. GPC investigations (DMF with 10 mm NH_4PF_6) revealed a M_n of 4830 and a PDI of 1.09. The low PDI and M_n value resulted from

the fact that a large amount of initiator was utilized and that only one small fraction (the most colored band) was collected while performing preparative GPC (Bio-Beads S-X1 columns, CH_2Cl_2 eluent). Therefore, an average of one-two complexes per chain could be calculated. According to the GPC results, compound **4a** was similar to a fraction appearing in all synthesized copolymers (**4b-d**) that displayed lower molecular weights and higher MLC contents. However, with a higher amount of initiator in the case of **4a**, the yield of this second fraction was much larger than in the other cases.

Polymers **4b** (copolymerization in acetonitrile), **4c** (copolymerization in ethanol), and **4d** (copolymerization in chloroform) were synthesized utilizing 1 mol % initiator. In all cases the expected amount of MLC comonomer was inserted into the respective copolymer. Based on the ^1H NMR spectrum of compound **4b**, a Ru(II) complex content of 1.3% could be calculated, as well as a 7/31/62 (*mm/mr/rr*) tacticity of the $\alpha\text{-CH}_3$ protons of the PMMA (Fig. 3). The GPC chromatogram in Figure 4 reveals a M_n of 15,540 and a PDI of 1.80. An average value of one-two complexes per chain could be calculated. For **4c** a Ru(II) complex content of 2.2% and a tacticity of 26/27/46 (*mm/mr/rr*) was observed. The GPC results revealed a M_n of 21,970 and a PDI of 1.98 (average number of



Scheme 3. The copolymerization of complex **3** with methyl methacrylate and a schematic representation of ruthenium(II)tris-bipyridine/poly(methyl methacrylate) copolymers.

three–four complexes per chain). Finally, in the case of **4d** the obtained copolymer consisted of 2.0% Ru(II) complex **3** (tacticity = 14/29/57, M_n = 16,770, PDI = 1.85). In this case, an average of two–three complexes could be built in per chain.

Polymer **4a** displayed different behavior in the IR than compounds **4b**, **4c**, and **4d** (Fig. 2). Additional bands at 1620 cm^{-1} appeared in the first case, which were probably caused by the higher MLC content. For compounds **4b–d** the observed IR bands showed no significant change when compared to each other. The main features were intense bands of the PMMA backbone at 1724, 1434, 1190, and 1050 cm^{-1} (Fig. 2). The UV–vis data of MLCs **2** and **3** and the corresponding polymers with copolymerized MLC **3** (such as

4b–d) revealed no different UV activity compared to each other. The MLCT band remained unchanged with a maximum at 455 nm. Because of the higher content of the metal complex, copolymer **4a** showed an increased absolute MLCT band with a maximum at 455 nm. The DSC investigation revealed as the only transition a T_g of $113\text{ }^\circ\text{C}$ for **4b–d**. This T_g value is consistent with data of PMMA reported in the literature.^{4,25} Obviously, no crystalline domains of the metal complexes were formed in the amorphous matrix of **4b–d**. This result could be expected because the MLC content of the investigated materials did not exceed 2.2%.

Moreover, the obtained copolymers were investigated by utilizing GPC equipment with a mul-

Table 1. Molecular Characterization Data of Copolymers **4a–d**

Polymer No.	M_n (RI)	M_w (RI)	PDI	Yield (%)	Tacticity (mm/mr/rr)	MLC Content (%)
4a	4,830	5,280	1.09	24	24/33/43	22
4b	15,540	28,020	1.80	62	7/31/62	1.3
4c	21,970	43,510	1.98	74	26/27/46	2.2
4d	16,770	31,100	1.85	65	14/29/57	2.0

The eluent was DMF with 10 mm NH_4PF_6 .

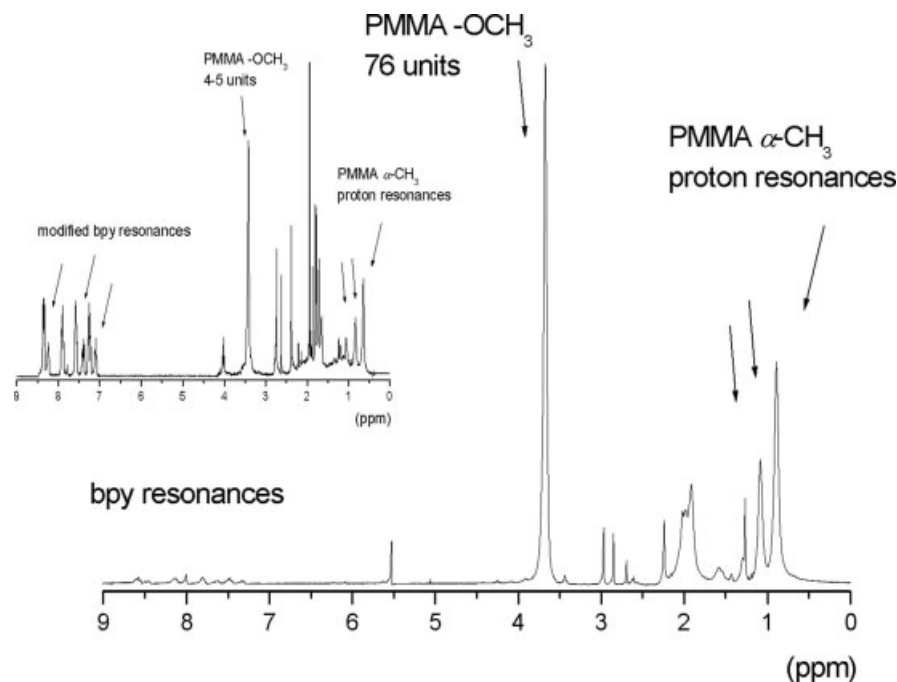


Figure 3. The ^1H NMR spectra of copolymer **4a** compared to **4b** showing the MLC contents of 22 and 1.3% (in acetonitrile).

tidiode array detector in order to proof the complete built-in (and thereof also unfragmented) complexes. Figure 5 shows the 3D plot (elution times vs wavelength of the diode array detector and UV-vis absorption intensity) of copolymer **4c**. The above described typical MLCT and $\pi-\pi^*$

transitions at 455 and 285 nm of the luminescent systems were observed, which correlate exactly with the UV-vis behavior of the precursor complex. Therefore, the existence of intact metal complexes in the copolymers can be concluded. Furthermore, the elution of the PMMA/Ru(II)tris-bpy

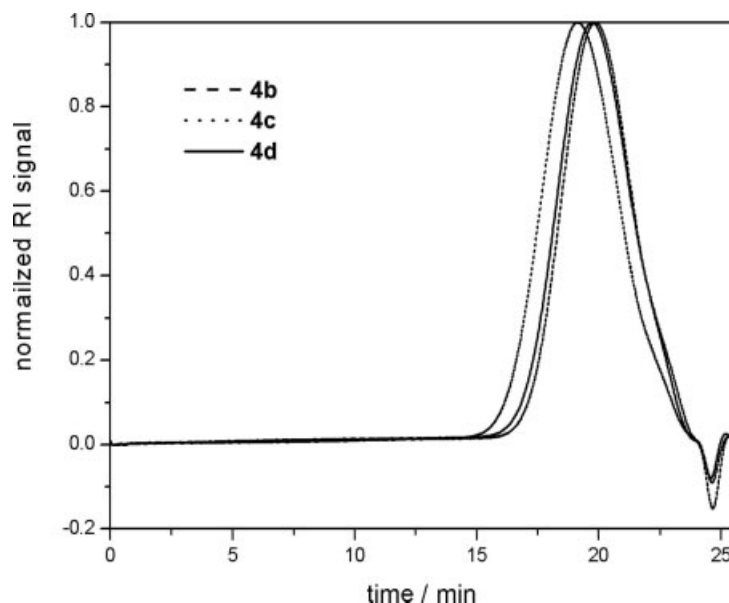


Figure 4. The GPC elution bands of **4b-d**.

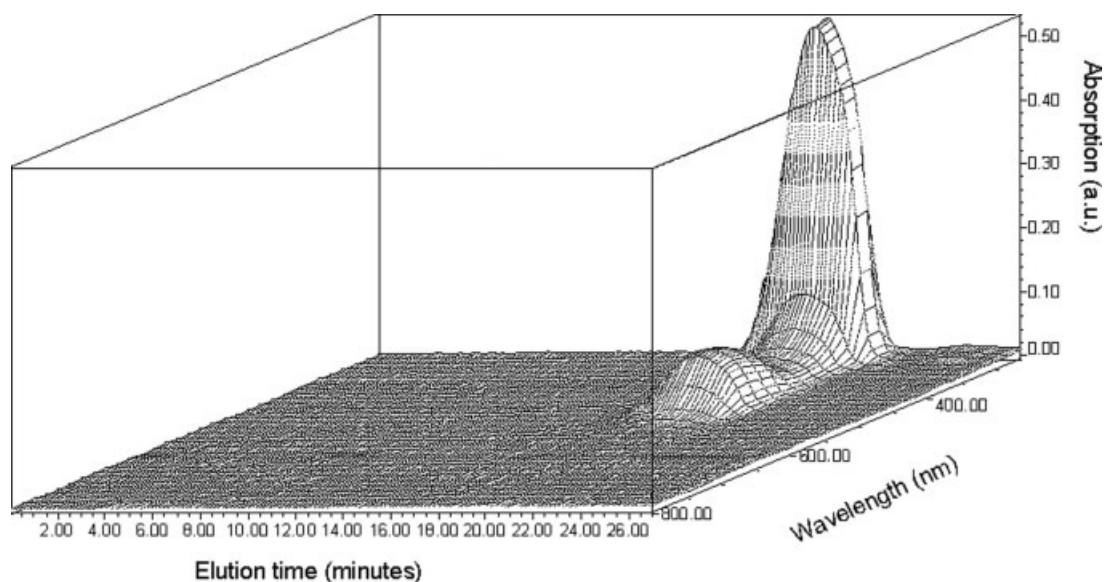


Figure 5. The GPC-coupled in-line diode array spectra of copolymer **4d**. The absorption maxima at 285 and 455 nm are clearly visible.

copolymers **4a–d** through the GPC column did not result in any fragmentation. To the best of our knowledge, this chromatogram represents the first 3D observation for copolymerized PMMA/Ru(II)tris-bpy systems.

CONCLUSION

We synthesized [4-(3-hydroxypropyl)-4'-methyl-2,2'-bpyl-bis(2,2'-bpy)Ru(II)-bis-(hexafluoroantimonate)] and its MA derivative with favorable emission properties. The substitution pattern (in the 4-position) of the modified bis(bpy)Ru(II) derivatives in combination with a flexible spacer offers the possibility to link the complex to polymers. The hydroxyl function represents an ideal moiety for subsequent reactions. This was shown by the derivatization of the hydroxyl functionality with methacryloyl chloride. Free-radical copolymerization of the new monomer opens a wide range of possibilities for the preparation of new functional materials with tunable properties. Different spectroscopic techniques and GPC were utilized in order to characterize the synthesized polymers. The $[\text{Ru}(\text{bpy}_3)]^{2+}$ containing polymers displayed favorable photochemical and photophysical characteristics of the MLCs, as well as good handling and processability because of the film forming PMMA backbone. One advantage of the new copolymers lies in the suppression of

complex aggregation as observed in blended systems. The preparation of Ru(II)PMMA devices and their detailed characterization will be part of further investigations.

The authors thank the Dutch Polymer Institute and the Fonds der Chemischen Industrie for financial support and Helene I. V. Amatdjais-Groenen (Department of Organic Chemistry, University of Nijmegen) for performing the elemental analysis measurements.

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