

Synthesis and characterization of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex and its polymerization via ATRP method

E.K.Pefkianakis¹, N.P.Tzanetos¹, T.Fillipopoulos², P.Fallaras² and J.K.Kallitsis¹

1. Department of Chemistry, University of Patras, 26500, Patras, Greece

2. NCSR Demokritos, Inst Chem Phys, Athens 15310, Greece

The recent research in polymeric materials bearing metal complexes, has arise scientific interest, while at the same time has create a novel extensive field of macromolecular chemistry. The combination of inorganic metal groups with macromolecules has lead to supramolecular structures with interesting physical and chemical properties. Thus the main objective is to create materials that combine the desired properties that arise from both the polymers and the inorganic metal groups.

Due to the strong affinity of the chemical bond that exists between the ions of the transition metals and 2,2'-bipyridyl (bpy) or 2,2':6',2''-terpyridine units (tpy), the later have been used as moieties capable for introduction of metals into polymers^{1,2}. Among the various transition metal ions, such as the ions of Ru, Os, Co, Zn, Cu, Fe the Ru(II) ion is the most promising for use in the area of polymer complexes, since it allows the direct synthesis of both symmetric or non-symmetric systems^{2,3}. The produced inorganic-organic hybrid systems are nowadays very tempting and promising, since they are able to combine both the properties of the metals (oxidoreductive, optoelectronic, catalytic) and those of the polymers (process ability, mechanical stability, and formation of thin films). Control over molecular architecture is one of the most important goal in this field of polymer science, since this determines to a great extend the properties of the final supramolecular material. Moreover this control of the supramolecular polymers gives birth to "intelligent" materials through molecular recognition of the supramolecular units.

In recent literature the use of such polymeric materials in optoelectronics is extensively reported i.e. Light Emitting Diodes (LEDs) or Photovoltaic Cells (PC) and Lasers. In an attempt to replace traditional inorganic systems the (2, 2'-bipyridyl)Ru(II) complex seems to be the most promising^{1,3,4}.

Most emphasis is given to the introduction of bipyridyl complexes into a polymeric backbone, making it possible to synthesize polymer structures with well defined architecture, since the bpy group has been used as a ligand for a large variety of ions of the transition metals¹.

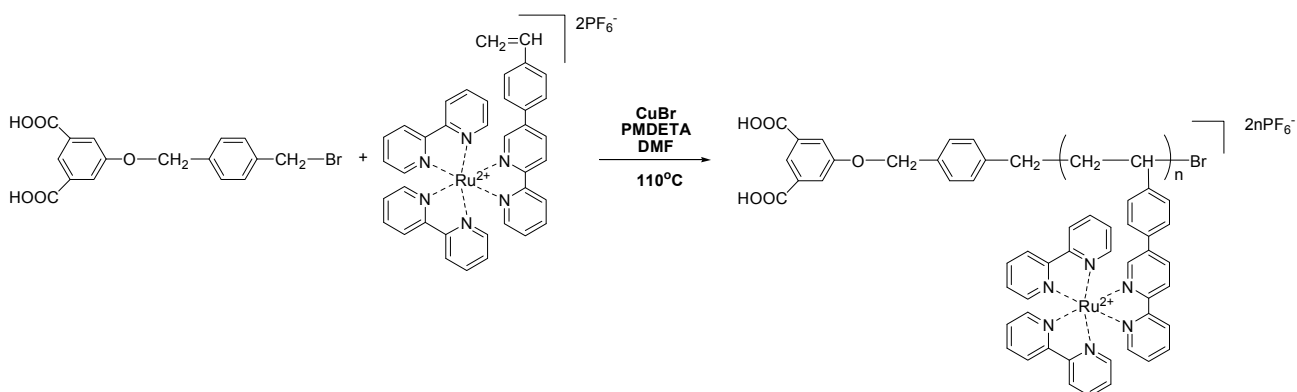


Fig. 1: Example of ATRP polymerization with functional initiator

In this work we present the synthesis of a new vinylic monomer of 2, 2'-bipyridyl, starting from 2-bromopyridine and converting it to a stanyl pyridine unit, which then reacts with 2,5-dibromopyridine trough a Stille coupling. Then via a Suzuki coupling

with styryl-boronic acid we result in the desired vinyl monomer. This in sequence is transformed to a $(2, 2'-bipyridyl)_3Ru(II)^{2+}$ complex by reacting with $Ru(bpy)_2Cl_2$. Polymerization of this monomer using ATRP conditions, combined with functional initiators has lead to the synthesis of such homopolymers, making it possible for use in applications such as Hybrid Photovoltaic Cells (PC) and Polymeric Light Emitting Diodes (PLEDs) . The resulting polymer structure is confirmed via NMR. The optical properties of these new polymers are studied using UV-Vis and Photoluminescence.

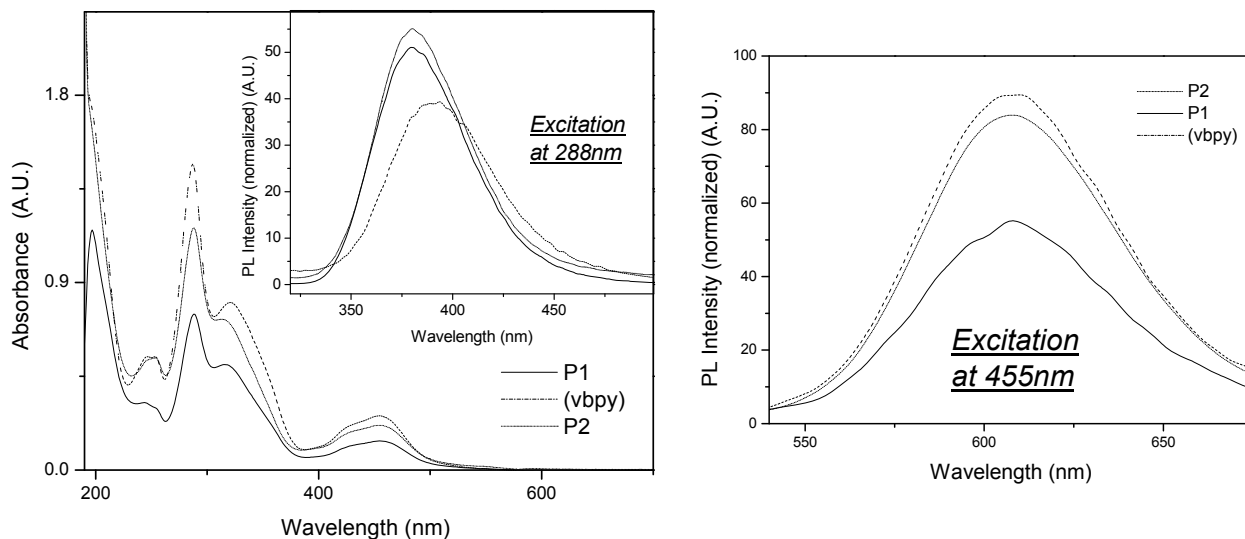


Fig. 2: UV-Vis and PL spectra of monomer and polymers P1, P2

Homopolymer P1, which is bearing a functional initiator with two carboxylic groups, was able to be attached onto TiO_2 and tested in a single photovoltaic cell. Photovoltaic performance exhibit a short circuit photocurrent density of $J_{sc} = 39 \mu A/cm^2$, open circuit potential $V_{oc} = 350$ mV, fill factor $ff = 0.39$ and a power conversion $\eta = 0.005\%$.

Aknowledgement:

Financial support for this project from the Greek Ministry of Development under the research grant PENED 03ED118 "Organic Solar Cells" is gratefully acknowledged. This research project (PENED) is co-financed by E.U.-European Social Fund (75%) and the Greek Ministry of Development-GSRT (25%)

References:

1. Schubert U.S., Eschbaumer C., *Angw. Chem. Int. Ed.* **2002**, *41*, 2892
2. Fraser C.L., Smith A.P., *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 4704
3. a)Chen, B.; Sleiman, H. F. *Macromolecules* **2004**, *37*, 5866 b)Serin, J.; Schultze, X.; Adronov, A.; Fréchet, J. M. J. *Macromolecules* **2002**, *35*, 5396

Synthesis and Characterization of a vinylic $[\text{Ru}(\text{bpy})_3]^{2+}$ monomer and its Polymerization via ATRP Method

E.K. Pefkianakis¹, N.P. Tzanetos¹, A. Philipopoulos², P. Falaras² and J.K. Kallitsis¹

1. Department of Chemistry, University of Patras, 26500, Patras, Greece

2. NCSR Demokritos, Inst Chem Phys, Athens 15310, Greece

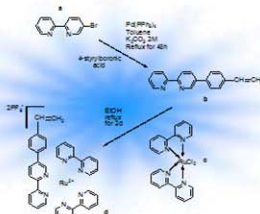
Introduction

The recent research in polymeric materials bearing metal complexes, has arise scientific interest, while at the same time has create a novel extensive field of macromolecular chemistry. The combination of inorganic metal groups with macromolecules has lead to supramolecular structures with interesting physical and chemical properties. Thus the main objective is to create materials that combine the desired properties that arise from both the polymers and the inorganic metal groups.

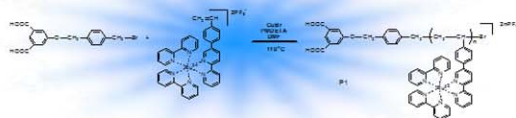
Due to the strong affinity of the chemical bond that exists between the ions of the transition metals and 2,2'-bipyridyl (bpy) or 2,2',6',2''-terpyridine units (tpy), the later have been used as moieties capable for introduction of metals into polymers^{1,2}. Among the various transition metal ions, the Ru(II) ion is the most promising for use in the area of polymer complexes, since it allows the direct synthesis of both symmetric or non-symmetric systems^{2,3}. In recent literature the use of such polymeric materials in optoelectronics is extensively reported in Light Emitting Diodes (LEDs) or Photovoltaic Cells (PV) and Lasers. In an attempt to replace traditional inorganic systems the tris-bipyridyl-Ru(II) complex seems to be the most promising^{1,3-6}. Working in the direction of PV, a novel vinylic monomer of $(\text{bpy})_3\text{Ru(II)}$ was synthesized and polymerized using ATRP conditions. A dicarboxy functionalized initiator has been used and the synthesized functional homopolymer has the proper characteristics for its application in hybrid solar cells. Both the monomer and homopolymer synthesized, were characterized by ¹H-NMR, UV-Vis, PL and viscosity measurement. Moreover the polymer was tested for its PC performance in a single photovoltaic cell.

Synthesis

Suzuki coupling of 5-bromo-2, 2'-bipyridine (a) with 4-styryl boronic acid in the presence of Pd(PPh₃)₄ as catalyst, produces 5-(p-vinylphenyl)-2,2'-bipyridyl (vbpy)(b). Dichloride (2,2'-bipyridine)-Ruthenium(II) ($(\text{Ru}(\text{bpy})_2\text{Cl}_2)$ (c) was synthesized by reacting 2,2'-bipyridine with (Ru(II)Cl_2) in DMF. $[\text{Ru}(\text{bpy})_2(\text{vbpy})](\text{PF}_6)_2$ (d) was produced by complexation of b and c in EtOH at 80°C (Scheme 1). Polymerization of monomer d using ATRP conditions with CuBr as catalyst, PMDETA as base and a functional initiator in DMF at 110°C, produced the first homopolymer of $(\text{bpy})_3\text{Ru(II)}$ complex (Scheme 2).



Scheme 1: Chemical structure and synthesis of the vinyl monomer $[(\text{vbpy})(\text{bpy})_2]\text{Ru}$ (d)



Scheme 2: Atom Transfer Radical Polymerization of monomer d with a functional initiator

Acknowledgement

Financial support for this project from the Greek Ministry of Development under the research grant PENED 03ED118 "Organic Solar Cells" is gratefully acknowledged.

References

- Schubert U.S., Eschbauer C., *Angew. Chem. Int. Ed.* **2002**, *41*, 2892
- Fraser C.L., Smith A.P., *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 4704
- a) Chen, B.; Sleiman, H. F., *Macromolecules* **2004**, *37*, 5865 b) Serin, J.; Adronov, A.; Fréchet, J. M. J., *Macromolecules* **2002**, *35*, 5396
- Jones, W. E., Jr.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J., *J. Am. Chem. Soc.* **1993**, *115*, 7363
- Andreopoulos A.K., Kallitsis J.K., *Eur. J. Org. Chem.* **2005**, 2005 4448
- Tzanetos N.P., Kallitsis J.K., *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 1049

Characterization

The vinylic monomer $[\text{Ru}(\text{bpy})_2(\text{vbpy})](\text{PF}_6)_2$ d and the homopolymer P1 were characterized by ¹H-NMR spectroscopy (Figure 1). The ¹H-NMR spectra proves the successful synthesis of d, as well as P1, since the olefinic peaks at 5.33, 5.94 and 6.75 of the monomer are not present at the polymers' ¹H-NMR graph. Viscosity measurements were performed for P1, and d in DMF at 30°C (Figure 2), showing the viscosity behavior of P1 and d; an increase in the reduced viscosity is evident as the concentration decreases. Such behavior can be explained in terms of the polyelectrolyte nature of the polymer, due to the presence of the Ru(II) and the PF₆⁻ counter ions. Moreover this novel vinylic monomer and homopolymer are studied with respect to their optical properties using UV-Vis and Photoluminescence (Figure 3,4). Finally P1 was applied in a single photovoltaic cell and tested for its performance (Table 1).

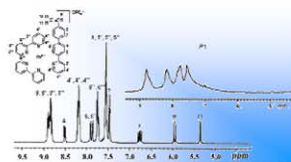


Figure 1: ¹H-NMR of monomer d and polymer P1 in DMSO-*d*₆

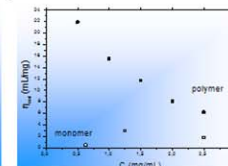


Figure 2: Viscosity measurements of polymer P1 and monomer d

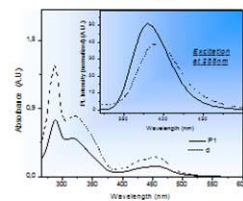


Figure 3: UV-Vis spectra of monomer d and polymer P1. The inset shows the PL spectra after excitation at 288nm

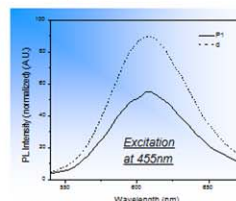


Figure 4: PL spectra of d and P1 after excitation at the absorption maxima of the metal complex (454nm).

J_{sc} ($\mu\text{A}/\text{cm}^2$)	V_{oc} (mV)	ff	n (%)
39	350	0.39	0.005

Table 1: Photovoltaic performance of solid state DSSCs using P1 as a polymeric dye and a PEO/TiO₂/I₃⁻ composite polymer redox electrolyte.

Conclusions

- Successful synthesis of a novel vinylic-Ru-(bpy)₃ monomer and the first reported homopolymer via the ATRP method for such complexes, using a functional initiator. ¹H-NMR spectra and viscosity measurement proves the desired structures.
- Characterization of the monomer and polymers' optical properties via UV-Vis and PL.
- The PL spectra of P1 after excitation at 545nm, shows emission at 607nm, which is in the red region of the visible spectra.
- Tested in a single photovoltaic cell for its performance, P1 exhibits a short circuit photocurrent density of $J_{sc} = 39 \mu\text{A}/\text{cm}^2$, open circuit potential $V_{oc} = 350 \text{ mV}$, fill factor $ff = 0.39$ and a power conversion $n = 0.005\%$.

Development of new Polymers and Composite Materials for Organic Photovoltaics and Dye Sensitized Cells

E.K. Pefkianakis, A.A. Stefopoulos, A.K. Andreopoulou, C.L. Chochos, N.P. Tzanetos, S.P. Economopoulos, V.G. Gregoriou, J.K. Kallitsis

**Department of Chemistry, University of Patras, Patras 26500, Greece*

**Foundation for Research and Technology Hellas, Institute of Chemical Engineering and High Temperature Processes (FORTH-ICEHT)*

The technology of renewable energies, aims in the long run, to efficiently contribute to the solution of the energy problem both economically and environmentally friendly. In respect to the materials science, the interest for the development of energy related materials, is of great interest and one of the main achievements focused into Organic Solar Cells. These are categorized to Cells of Organic Molecules, Polymeric/Plastic Cells (OPVs) and Dye Sensitized Cells (DSSCs). Our group is mainly focused in the development of the two latter systems, the Plastic and the Dye Sensitized Solar Cells.

In the field of OPVs, our group is focused on producing polymers that shall act as p-n type heterojunctions over a conductive polymeric substrate, and semi-conductive polymers that will function as hole or electron acceptors/transporters respectively.

For the electron donor/acceptor or even transporter segments, derivatives of oxadiazole, carbazole, quinoline, fluorene and thiophene monomers are utilized. These moieties are producing specific polymeric “architectures” and they are extensively characterized in respect to their molecular characteristics and optoelectronic properties. Such polymers/copolymers and block copolymers, are produced through controlled radical polymerization techniques like Atom Transfer Radical Polymerization and Heck coupling polymerization.

Our main objective in DSSCs is to replace the commonly used dyes (complexes of transition metal ions with organic molecules) with polymeric dyes, thus utilizing the advantages of the polymers’ character in a sensitized Solar Cell. Such polymers produced, consist of polymeric complexes of the Ruthenium (II) ion, with tridentate or bidentate ligands like 2,2':6',2''-terpyridine and 2,2'-bipyridine respectively.

Recently our laboratory has been involved in the rapidly evolving technology of Carbon Nanotubes (CNTs) modification. In this direction polymer modifications of Single Wall Carbon Nanotubes was attempted, in order to develop new composite materials that combine the electron donor or acceptor properties of the polymers with those of the CNTs. The final product is characterized with the conventional methods used for CNTs, as well as for their optoelectronic properties.

Aknowledgement:

Financial support for this project from the Greek Ministry of Development under the research grant PENED 03ED118 “Organic Solar Cells” is gratefully acknowledged. This research project (PENED) is co-financed by E.U.-European Social Fund (75%) and the Greek Ministry of Development-GSRT (25%)

Development of new Polymers and Composite Materials for Organic Photovoltaics & Dye Sensitized Solar Cells

E.K. Peftianakis, A.A. Stefanopoulos, A.K. Andreopoulou, C.L. Chochos, V.G. Gregoriou and J.K. Kallitsis

Department of Chemistry, University of Patras, 26500, Patras, Greece & Foundation for Research and Technology-Hellas, Institute of Chemical Engineering and High-Temperature Processes (FOKTH-ICEHT), Patras 26500, Greece

In the emerging area of Solar Cells, our group has mainly focused on the development of novel polymer materials for flexible and dye sensitized solar cells. In the field of Photoconductive, we have so far developed new polymers with electron acceptor properties, which have been combined with polymer donors, leading to bulk heterojunction architectures. In the section photoconductor or donor (acceptor) segments, the features of conductive, electron accepting, flexible and photoreversible nature have been studied. The combinations of these modified polymer "building blocks" with complete separation and well selectively characterized in respect to their molecular characteristics and applications in specific. Both heteropolymers and random or block copolymers were prepared through radical polymerization techniques (e.g. both Transfer Radical Polymerization) and cross-linking polymerizations.

Our main objective in Dye Sensitized Cells, has been the replacement of commonly used dyes (complexes of transition metal ions with small organic molecules), with polymers dyes, exploiting the advantages of polymers in Dye Sensitized Cells. Thus, an emphasis is given to synthesizing a variety of highly tunable, soluble metal-free complexes of the ruthenium (II) ion, with moderate to extensive ligands like π -conjugated or π -conjugative copolymers, bearing carboxylate (or other) ligands involved in the rapidly existing technology of Surface Plasmon Resonance (SPR). In this direction polymer modification of large well defined nanoparticles, via sequentially attempted, is used to develop new composite materials that combine the photo-conductive or acceptor properties of the covalently attached polymers with those of the dyes. The final products were fully characterized with all the conventional methods employed for dyes, as well as for their application properties.

OPVs

Polymers, Copolymers and Blends of Donor-Acceptor Architecture

Electron Donor - Acceptor Polymer Blends

Material parameters of the polymer blends (measured at room temperature):

Blend	Open Circuit Voltage (V)	FF (%)	Power Conversion Efficiency (%)
P1/P2	0.60	0.55	0.20

Material parameters of the polymer blends (measured at room temperature):

Blend	Open Circuit Voltage (V)	FF (%)	Power Conversion Efficiency (%)
P3/P4	0.60	0.55	0.20

Material parameters of the polymer blends (measured at room temperature):

Blend	Open Circuit Voltage (V)	FF (%)	Power Conversion Efficiency (%)
P5/P6	0.60	0.55	0.20

Material parameters of the polymer blends (measured at room temperature):

Blend	Open Circuit Voltage (V)	FF (%)	Power Conversion Efficiency (%)
P7/P8	0.60	0.55	0.20

DSSCs

Material parameters of the polymer blends (measured at room temperature):

Blend	Open Circuit Voltage (V)	FF (%)	Power Conversion Efficiency (%)
P9/P10	0.60	0.55	0.20

CNTs

Material parameters of the polymer blends (measured at room temperature):

Blend	Open Circuit Voltage (V)	FF (%)	Power Conversion Efficiency (%)
P11/P12	0.60	0.55	0.20

Acknowledgements

- Grant of the NSRF (Ministry of Science, Tech. & Innov.)
- Prof. G. Patrinoiu, Corneil University, USA
- Dr. P. Arora, IIT Kanpur, India

This work was partially supported from:

- Greek Ministry of Development under the research grants:
 - ΠΕΠ2 (ΕΥΡΩΠΕΪΚΟ ΓΕΝΙΚΟ ΚΑΤΑΣΤΡΟΦΟΛΟΓΟ) (2007-2009) and
 - ΠΕΡΑ (11) "Development of Flexible Photovoltaics (2007-2009)
- Institute Technologies Inc. of Lowell, MA, USA

References

1. Peftianakis, E.K., Stefanopoulos, A.A., Andreopoulou, A.K., Chochos, C.L., Gregoriou, V.G., Kallitsis, J.K. *Journal of Applied Polymer Science* 2007, 10, 3121

2. Peftianakis, E.K., Stefanopoulos, A.A., Andreopoulou, A.K., Chochos, C.L., Gregoriou, V.G., Kallitsis, J.K. *Journal of Applied Polymer Science* 2007, 111, 1872

3. Peftianakis, E.K., Stefanopoulos, A.A., Andreopoulou, A.K., Chochos, C.L., Gregoriou, V.G., Kallitsis, J.K. *Journal of Applied Polymer Science* 2008, 10, 1880

4. Peftianakis, E.K., Stefanopoulos, A.A., Andreopoulou, A.K., Chochos, C.L., Gregoriou, V.G., Kallitsis, J.K. *Journal of Applied Polymer Science* 2008, 10, 1880

5. Peftianakis, E.K., Stefanopoulos, A.A., Andreopoulou, A.K., Chochos, C.L., Gregoriou, V.G., Kallitsis, J.K. *Journal of Applied Polymer Science* 2007, 10, 1880

6. Peftianakis, E.K., Stefanopoulos, A.A., Andreopoulou, A.K., Chochos, C.L., Gregoriou, V.G., Kallitsis, J.K. *Journal of Applied Polymer Science* 2007, 10, 1880