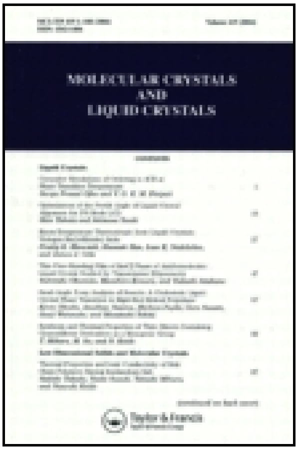

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Synthesis and Characterization of New π-Conjugated Polymer Complexes with Transition Metal Fragments

Hiroki Fukumoto [a] , Naoki Hayashida [a] , Tsukasa Maruyama [a] & Takakazu Yamamoto [a]

[a] Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

To cite this article: Hiroki Fukumoto, Naoki Hayashida, Tsukasa Maruyama & Takakazu Yamamoto (2000): Synthesis and Characterization of New π-Conjugated Polymer Complexes with Transition Metal Fragments, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 342:1, 237-240

To link to this article: http://dx.doi.org/10.1080/10587250008038271

Mol. Cryst. Liq. Cryst., 2000, Vol. 342, pp. 237-240
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Printed in Malaysia

Synthesis and Characterization of New π-Conjugated Polymer Complexes with Transition Metal Fragments

HIROKI FUKUMOTO, NAOKI HAYASHIDA,
TSUKASA MARUYAMA and TAKAKAZU YAMAMOTO

*Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226–8503, Japan*

Poly(2,2'-bipyridine-5,5'-diyl) (PBpy) (**1**) and a polymer of 2,2'-bipyrimidine (PBpym) (**2**) afford polymer complexes (**3**) and (**4**) coordinated with $[Ru(bpy)_2]^{2+}$ fragments, respectively. The UV-vis spectrum of (**4**) in conc. H_2SO_4 is considerably different from **2** in conc. H_2SO_4. The poly(6,6-dimethylbipyridine-5,5'-diyl) (P6MeBpy) (**5**) reacts with a ruthenium complex, $[RuClCp^*]_4$, (Cp^* = pentamethylcyclopentadienyl) to give a new ruthenium complex (**6**).

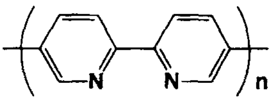
Keywords: π-conjugated polymer; π-conjugated polymer complex; ruthenium complex; poly(2,2'-bipyridine-5,5'-diyl); poly(2,2'-bipyrimidine-5,5'-diyl)

INTRODUCTION

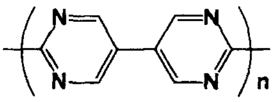
Synthesis and properties of π-conjugated heteroaromatic polymers such as polythiophene and polypyridine have rapidly progressed due to their high potential in material science. In these polymers, nitrogen and sulfur have the capability of forming various transition metal complexes, which gives new types of polymer complexes based on pπ-dπ interaction of transition metal fragments with the π-conjugated polymer.[1] In order to investigate basic function of the π-conjugated polymer ligand to form metal complexes, we have prepared polymers of 2,2'-bipyridine (bpy) and 2,2'-bipyrimidine (bpym).[1-3] Herein we report synthesis of ruthenium complexes of the polymeric π-conjugated ligands and properties of the ruthenium complexes.

RESULTS and DISCUSSION

PBby (**1**) and PBpym (**2**) prepared by dehalogenatation polycondensation [1-3] were used in this study.

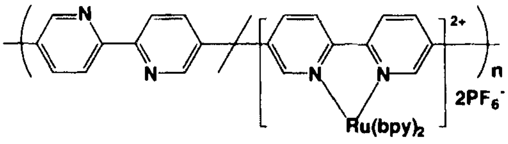


PBpy (1)

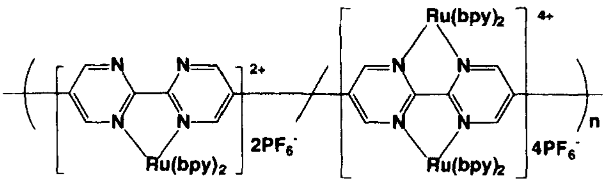


PBpym (2)

As reported previously,[2] polymers **1** and **2** form Ru complex in reactions with [$RuCl_2(bpy)_2$] in aqueous solutions. UV–vis spectroscopic study on the complexes in conc. H_2SO_4 have been investigated.



Ru–PBpy complex (3)



Ru–PBpym complex (4)

Figure 1 exhibits UV–vis spectra of PBpym (**2**) and the Ru–PBpym complex (**4**) in conc. H_2SO_4. The lower energy π-π* absorption band along the main chain (345 nm) is not observed in the UV–vis spectrum of the Ru–PBpym complex, presumably due to the breaking of the π-conjugation system of the polymer by coordination of an excess amount of $Ru(bpy)_2$ to the polymer which causes twisting out of the main chain.[2a] However, on leaving of **4** in conc. H_2SO_4, the intensity of the peaks at 275 and 345 nm increased. These data suggest that partial liberation of the $[Ru(bpy)_2]^{2+}$ units from the PBpym in conc. H_2SO_4 leads to reconstruction of the main chain π-conjugation system of PBpym. In contrast to **4**, there is no change of UV–vis spectrum of Ru–PBpy complex **3** and $[Ru(bpy)_3]$ $[PF_6]$ in conc. H_2SO_4, indicating these complexes are more stable than the Ru–PBpym complex **4**.

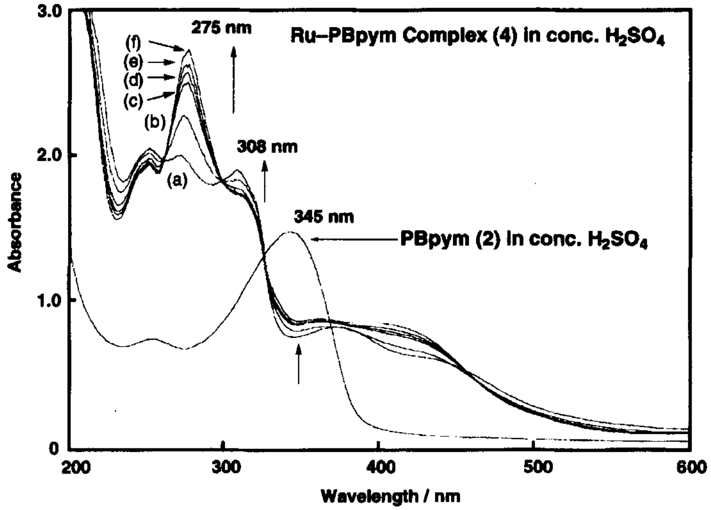
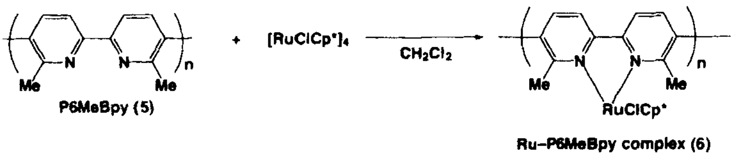


FIGURE 1 Change in UV–vis spectrum of **4** after dissolution in conc. H_2SO_4: (a) 0 h, (b) 2 h, (c) 4 h, (d) 6 h, (e) 8 h, and (f) 16 h.

On the other hand, an alkyl derivative of PBpy, poly(6,6-dimethyl-bipyridine-5,5'-diyl) (P6MeBpy)[3], react with a ruthenium complex[4, 5], $[RuClCp^*]_4$, (Cp^* = pentamethylcyclopentadienyl) to form a new complex. When $[RuClCp^*]_4$ was added to a suspension of P6MeBpy in CH_2Cl_2 at room temperature, the complex forming reaction proceeded instantly with a color change from off-white to deep red. The resulting solution gave the polymer complex **6** with the coordinated RuClCp* fragments, as a deep red solid in a moderate yield. Elemental analysis of **6** indicated that most of dimethyl-2,2'-bipyridine unit of P6MeBpy participated in complex formation with [RuClCp*].



The UV-vis spectrum of **6** exhibited a π-π* transition bands of the main chain of P6MeBpy at 334 nm in $CHCl_3$, shifted to 17 nm longer wavelength from that of polymer **5** at 317 nm in $CHCl_3$. Complex **6** showed an absorption peak at 537 nm assigned to a MLCT band.

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