



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

Publication details, including instructions for authors and subscription information:

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Version of record first published: 24 Sep 2006

To cite this article: Gen-Ichi Konishi & Yoshiki Chujo (2000): Preparation of Polymer Complexes by Coordination of 2,2'-Bipyridyl-Modified Organic Polymer with Ruthenium Ion, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 342:1, 87-90

To link to this article: <http://dx.doi.org/10.1080/10587250008038249>

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Preparation of Polymer Complexes by Coordination of 2,2'-Bipyridyl-Modified Organic Polymer with Ruthenium Ion

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Novel metal-containing hydrogels or metal-centered star shaped polymers were prepared by coordination of 2,2'-bipyridyl-modified organic polymers with ruthenium ion. The resulting polymer complexes are a new class of organic-inorganic polymer hybrids.

Keywords: ruthenium; 2,2'-bipyridyl; hydrogel; star-shaped polymer; self-assembly; MLCT absorption; organic-inorganic polymer hybrid

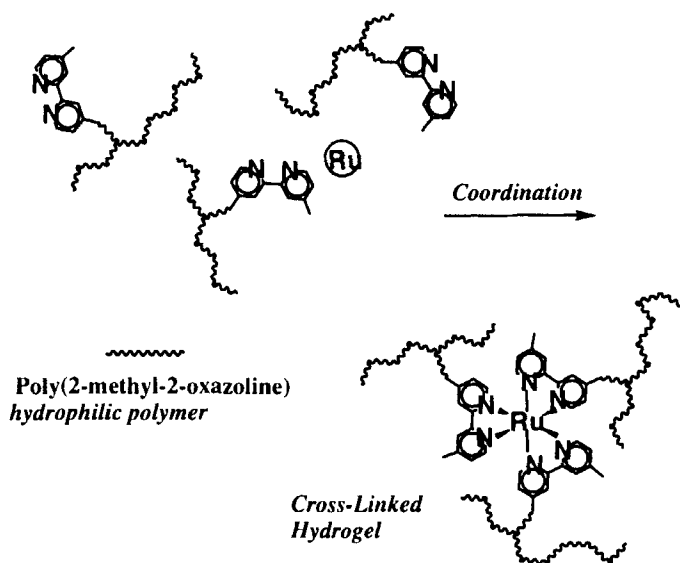
Polymer complexes having transition metal complexes in the main chain or in the side chain have been extensively investigated from synthetic viewpoints [1-3]. In particular, the construction of polymer structure *via* coordination between transition metal ions and ligands should be a simple and fruitful synthetic method. The polymer complexes can also be expected to show characteristic properties derived from transition metal complex.

Synthesis and properties of low molecular weight ruthenium complexes have been extensively investigated in recent decades [4].

Ru(II)-polypyridine complexes are known to be highly stable against heating, acid, base, and ligand exchange reactions. These complexes also show a strong metal-to-ligand charge transfer (MLCT) absorption around UV/Vis region and have considerable potentials such as photocatalyst, solar energy transformation, and luminescent materials. The construction of polymer complex using metal complexation between ruthenium and polypyridyl ligand is interested in both synthetic and application viewpoints.

In this paper, the preparation of metal-containing hydrogels or metal-centered star-shaped polymers by means of coordination of 2,2'-bipyridyl-modified organic polymers with ruthenium ion is described.

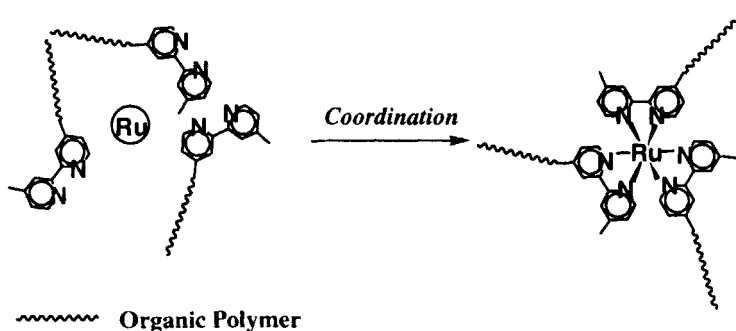
We have previously reported the formation of cross-linked hydrogel by coordination of poly(2-methyl-2-oxazoline) [hydrophilic polymer] having 2,2'-bipyridyl ligands in the side chain with ruthenium ion [5]. (**Scheme 1**) The key step of gelation is a formation of "inert



Scheme 1

metal center” of Ru(II)-2,2'-bipyridyl complex. Other transition metal ions such as nickel, cobalt and iron enable to give the cross-linked hydrogels by using this type of 2,2'-bipyridyl-modified polymer [5, 6]. This strategy is not only a brief synthetic method for hydrogel but also combination of a hydrogel with the property of transition metal complexes.

We also reported the synthesis of Ru(II)-centered star-shaped polymers by coordination of 2,2'-bipyridyl-terminated organic polymers with ruthenium ion [7, 8]. (**Scheme 2**) Several commodity polymers such as poly(ethylene glycol), poly(propylene glycol), polystyrene and poly(2-methyl-2-oxazoline) are available for the preparation of this type of star-shaped polymers. The coordination between 2,2'-bipyridyl-terminated organic polymers and ruthenium ion efficiently proceeded and then the desirable star-shaped polymers were obtained in high yields. These polymers showed strong MLCT absorptions in a UV/Vis region ($\lambda_{\text{max}} = \text{ca. } 460 \text{ nm}$). The solubility and processability of these star-shaped polymers were found to be similar to those of the corresponding polymer arms. As an extension of this chemistry, we also reported the preparation of the chromium(III)- β -diketone complex-centered star-shaped polymer by coordination of β -diketone-terminated poly(oxyethylene) with chromium ion [9].



Scheme 2

These types of polymer complexes might be one of the homogeneous organic-inorganic polymer hybrids on molecular level and have considerable potentials such as electronic, magnetic, and photochemical materials, polymer blends and precursors for organic-inorganic composite materials. They are also expected to reveal a novel function distinguished from the starting materials.

In general, the metal-containing polymers were prepared by coordination of "polymer ligand" with "ruthenium ion." It should be noted that "metal complexation" is a strong tool for self-assembly of a polymer ligand as well as low molecular weight ligands. Self-assembly of functionalized organic polymers induced by metal complexation is a fruitful methodology for the preparation of a new class of polymer structures or metal containing materials.

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