

Metallo-Supramolecular Cyclic Polymers

Ke Zhang,^{†,‡} Yongping Zha,[†] Bo Peng,[‡] Yongming Chen,[‡] and Gregory N. Tew^{*,†}[†]Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, United States[‡]State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

S Supporting Information

ABSTRACT: Cyclic brush polymers represent an exciting new macromolecular topology. For the first time, this new topology has been combined with metallo-supramolecular interactions to construct novel cyclic brush polymers. Here, ring-expansion metathesis polymerization was used to synthesize a universal cyclic template with a polynorbornene backbone, which was further modified with the metal-chelating synthon terpyridine. The terpyridine side chains served as the key supramolecular unit for the creation of cyclic polymer brushes and gels. This metallo-supramolecular functionality allowed direct visualization of the cyclic brush polymers by transmission electron microscopy for the first time. This demonstration should open a new area in which supramolecular interactions are used to build an array of novel cyclic brush copolymers as well as other cyclic-polymer-based architectures generating new materials.

Cyclic polymers have received a significant amount of attention recently because of the unique properties intrinsic to their endless molecular topology.¹ Cyclic polymers have markedly different characteristics than their linear counterparts, including a smaller hydrodynamic volume and radius of gyration, lower melt viscosity, higher thermostability, and increased rate of crystallization.¹ The synthetic approaches to cyclic polymers can generally be divided into two categories: ring-closure and ring-expansion methods. In the ring-closure method, cyclic polymers are prepared by applying highly efficient coupling chemistry to end-functionalized linear telechelic polymers. Progress in combining click chemistry with controlled polymerization has increased the viability of this method for synthesizing cyclic polymers with controlled molecular weight and low polydispersity, but there are still limitations. To ensure high topological purity, ring-closure reactions require dilute conditions that lead to low yields, making them impractical for many applications. In addition, it is difficult to obtain cyclic polymers with high molecular weight by this method. Alternatively, the ring-expansion method is based on the insertion of monomer units into an activated cyclic chain. Because the cyclic polymers remain intact during the whole ring-expansion process, this method can produce high-molecular-weight cyclic polymers with high purity, even from concentrated solutions or the bulk. One disadvantage is that it can be difficult to control the molecular weight and polydispersity of the resultant cyclic polymers.

The above methods have enabled the preparation of many types of cyclic polymers, such as cyclic polystyrene,^{2a} polymethacrylate,^{2b} polyacrylate,^{2c} polyacrylamide,^{2d} polyester,^{2e} polycyclooctene,^{2f} and polynorbornene.^{2g} In addition, cyclic polymers with complex architectures have been developed, including those with theta,^{3a} eight,^{3a} tadpole,^{3b} block,^{3c} and brush^{3d–f} shapes. However, as far as we know, all of the cyclic-polymer-based materials reported to date have been completely organic and formed by covalent bonds, with one exception.⁴

Supramolecular chemistry, which is based on non-covalent associations such as ionic and metal–ligand interactions as well as hydrogen bonds, provides a powerful set of tools for building complex molecules and drives the self-assembly of many natural materials. Because of the dynamic and reversible characteristics of non-covalent bonds, supramolecular materials can demonstrate “living” and “smart” behavior in response to certain external stimuli.⁵ Hybrid materials are fabricated by integrating organic and inorganic components into the same material at the molecular level. Compared with solely organic materials, the addition of inorganic components, which increases the structural complexity, has been shown to endow hybrid materials with advanced functionalities and expanded applications.⁶ Taking advantage of supramolecular interactions to expand upon the already interesting topology and properties of cyclic polymers through the incorporation of stable yet dynamic metal complexes will enable the development of a wide variety of hybrid materials with different architectures and unique properties. To date, this exciting concept has remained unexplored.

The present work sought to reveal some of the possibilities in this promising area. Ring-expansion metathesis polymerization (REMP)^{2f} and activated ester chemistry were combined to develop a unique universal cyclic polymer template bearing side groups terminated with terpyridine, a prototypical supramolecular synthon. By virtue of the metallo-supramolecular interactions between the terpyridine ligands and transition-metal ions, two novel classes of cyclic polymer/metal hybrid materials were obtained: metallo-supramolecular cyclic brush polymers and metallo-supramolecular cyclic gels.

Figure 1 summarizes the synthetic scheme used to generate these metallo-supramolecular materials. The related ¹H NMR spectra are shown in Figures S1 and S2 in the Supporting Information (SI). The synthesis of the functional norbornene-based monomer **1** is detailed in the SI, and the corresponding ¹H NMR spectrum and peak assignments are shown in Figure S3A.

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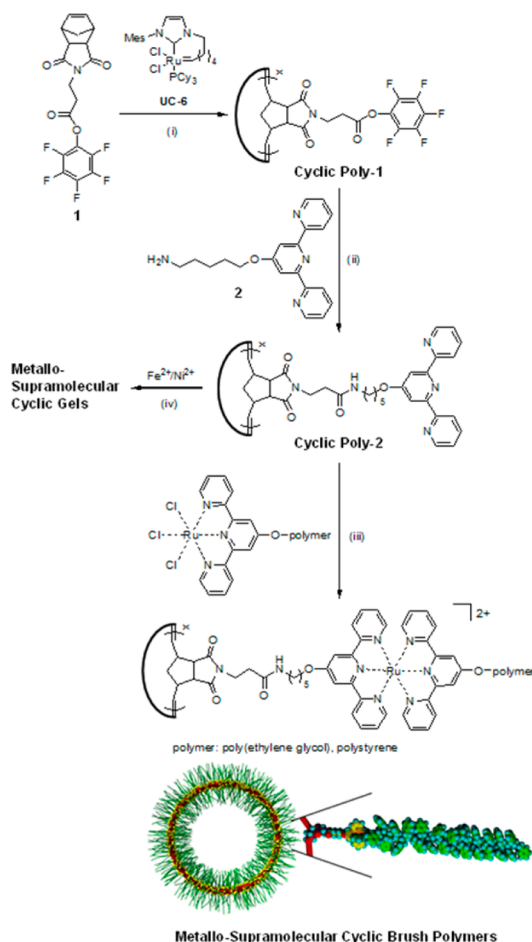


Figure 1. Synthetic scheme for the metallo-supramolecular cyclic brush polymers and cyclic gels. Conditions: (i) DMF, 55 °C, 12 h; (ii) DMF, room temperature, 24 h; (iii) *N*-ethylmorpholine, 70 °C, 12 h in 5/1 (v/v) CHCl₃/ethanol for the PEG brush polymer or 5/1 (v/v) DMF/ethanol for the PS brush polymer; (iv) DMF, room temperature, [Poly-2]₀ = 0.05 M.

With UC-6 as the catalyst,⁷ cyclic Poly-1 was obtained by REMP in 12 h at 55 °C [Figure 1(i)]. The ¹H NMR spectrum of the Poly-1 polymerization solution, without purification, (Figure S3B) showed the complete disappearance of the peak at 6.32 ppm (peak a in Figure S3A, ascribed to $-\text{CH}=\text{CH}-$ in monomer **1**) and the new broad peak at 5.40–5.90 ppm (peak a' in Figure S3B, due to $-\text{CH}=\text{CH}-$ in Poly-1) indicated that the polymerization was carried out with quantitative monomer conversion. The gel-permeation chromatography (GPC) curve of cyclic Poly-1 (black curve in Figure S4) is monomodal and corresponds to a number-average molecular weight (M_n) of 697 000 g/mol and a polydispersity index (PDI) of 1.74.

Cyclic Poly-1 was designed to have activated pentafluorophenyl ester side groups, which facilitate the incorporation of numerous functional side groups via the highly efficient nucleophilic substitution of activated esters with amines.^{3f,8} Postfunctionalization of Poly-1 with terpyridine-functionalized amine **2** yielded cyclic Poly-2 with terpyridine side groups [Figure 1(ii)]. The activated ester approach was preferred because the direct polymerization of a terpyridine-functionalized norbornene by UC-6 was inefficient. To ensure a quantitative reaction, a 3-fold excess of **2** relative to pentafluorophenyl ester side groups in Poly-1 was used. Figure 2B shows the ¹H NMR spectrum of the resultant Poly-2 and its peak assignments. In

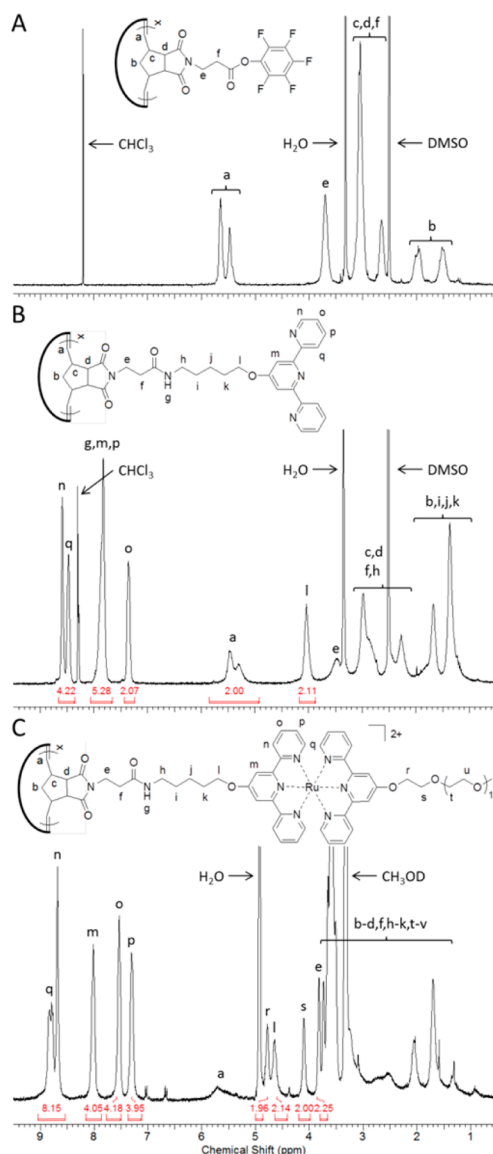


Figure 2. ¹H NMR spectra of (A) Poly-1 (in DMSO-*d*₆), (B) Poly-2 (in DMSO-*d*₆), and (C) the corresponding metallo-supramolecular cyclic brush polymers with PEG side chains (in methanol-*d*₄).

comparison to the precursor cyclic Poly-1 (Figure 2A), a series of new peaks appeared in the range of 7.20–8.80 ppm, which were ascribed to the protons of the terpyridine rings. The area ratio of 1 between peak a at 5.10–5.70 ppm ($-\text{CH}=\text{CH}-$ in the polymer backbone) and peak l at 4.05 ppm ($-\text{CH}_2\text{O}-$ in the side groups) confirmed the quantitative reaction. Characterization by FT-IR provided further evidence for the successful synthesis of cyclic Poly-2. In the FT-IR spectrum of Poly-2 (red curve in Figure S5), the peaks at 1790 cm⁻¹ (ester C=O stretching vibration) and 1522 cm⁻¹ (C=C stretching vibration of the pentafluorophenyl aromatic ring) in the spectrum of Poly-1 (black curve in Figure S5) disappeared completely, and new peaks were observed at 1656 cm⁻¹ (amide C=O stretching vibration) and at 1582 and 1562 cm⁻¹ (C=C stretching vibrations of the pyridine rings). In the GPC curve of Poly-2 (red curve in Figure S4), for which M_n = 814 000 g/mol and PDI = 1.75, the monomodal peak shape of Poly-1 (black curve in Figure S4) was preserved, and a complete peak shift to higher molecular weight was observed. As a result, postfunctionalization of cyclic

Poly-1 with **2** successfully introduced the terpyridine side groups, affording cyclic **Poly-2**.

The terpyridine ligand is well-known for its outstanding ability to chelate transition-metal ions.⁹ In addition, the resultant terpyridine–metal ion complex is a versatile supramolecular unit that can form labile or stable complexes depending on the metal ion and conditions. Thus, **Poly-2** can serve as a template from which a range of metallo-supramolecular polymeric materials with an inherent cyclic molecular topology and tunable properties can be derived. To demonstrate this concept, **Poly-2** was used as a building block to prepare metallo-supramolecular cyclic brush polymers and cyclic gels.

As the first example, the preparation of metallo-supramolecular cyclic brush polymers was systematically studied by grafting poly(ethylene glycol) (PEG) side chains onto the main chains of cyclic **Poly-2** [Figure 1(iii)]. The synthesis of the PEG–terpyridine–RuCl₃ monocomplex side chains is detailed in the SI. The metallo-supramolecular cyclic PEG brush polymers were prepared by reacting the PEG–terpyridine–Ru(III) monocomplex with the terpyridine ligands of **Poly-2** under reducing conditions (ethanol, *N*-ethylmorpholine) to produce the stable bis(terpyridine)ruthenium(II) linkages connecting the PEG side chains and the **Poly-2** main chains [Figure 1(iii)]. The resultant hybrid cyclic PEG brush polymers were purified by dialysis and characterized by UV–vis, ¹H NMR, and FT-IR spectroscopies, transmission electron microscopy (TEM), and atomic force microscopy (AFM).

The UV–vis spectrum of the hybrid cyclic PEG brush polymer (Figure 3red) shows a new characteristic metal-to-ligand charge-

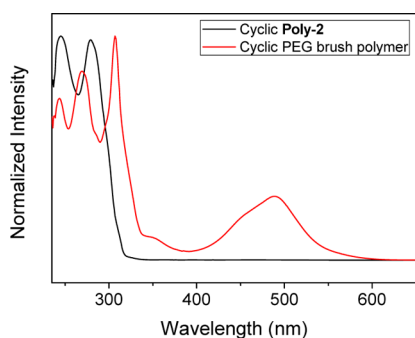


Figure 3. UV–vis spectra of (black) cyclic **Poly-2** and (red) metallo-supramolecular cyclic brush polymers with PEG side chains (in chloroform).

transfer (MLCT) band for the bis(terpyridine)ruthenium(II) complex at 490 nm that is not present for **Poly-2** (Figure 3 black). In addition, the specific π – π^* absorption bands of the free terpyridine groups in **Poly-2** at 246 and 279 nm shifted to 243, 269, and 307 nm for the bis(terpyridine) complex after grafting of the PEG side chains, as expected.¹⁰ These bands unambiguously demonstrate the successful formation of the bis(terpyridine)ruthenium(II) bridging units. In the ¹H NMR spectrum of the hybrid cyclic PEG brush polymers (Figure 2C), the value of 1 for the ratio of the peak areas from the cyclic main chains [e (NCH₂) and l (OCH₂)] to those from the PEG side chains [r (OCH₂) and s (OCH₂)] is indicative of a quantitative grafting density. FT-IR characterization (blue curve in Figure S5) provided further confirmation of the successful grafting of the PEG side chains, as the peaks at 1582 and 1562 cm^{−1} (C=C stretching vibrations of the pyridine rings in **Poly-2**) disappeared

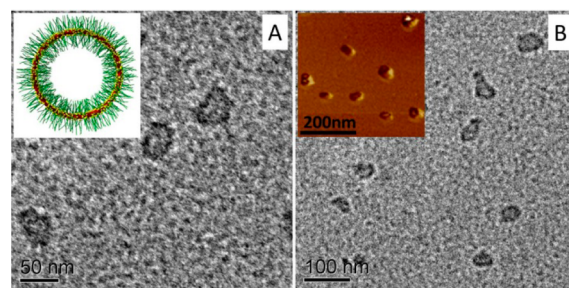


Figure 4. TEM images of the metallo-supramolecular cyclic brush polymers with PEG side chains. The inset in (A) illustrates the molecular conformation of the metallo-supramolecular cyclic brush polymers, and the inset in (B) is the corresponding AFM phase image.

completely and a new broad peak at 1110 cm^{−1} ascribed to the PEG ether bonds was observed.

The molecular conformation of the metallo-supramolecular cyclic brush polymers is illustrated in the Figure 4A inset. Because of the inherent metal-containing molecular structure, these novel supramolecular hybrid cyclic brush polymers provide an ideal model for direct imaging of single polymer chains by TEM. Figure 4 shows two representative TEM images of the hybrid cyclic PEG brush polymers, in which the cyclic molecular topology with an average diameter of ~40 nm can be seen. Although AFM has previously been used routinely by us^{3f} and others^{2g,3d} to image cyclic polymer topologies, as far as we know, this is the first time that TEM has been utilized to directly image the molecular topology of cyclic polymers. This was enabled by the unique combination of chemistries built into the molecule. The cyclic topology of these hybrid PEG brush polymers was also confirmed by AFM (Figure 4B inset and Figure S6), and the average diameter was found to be ~40 nm, consistent with the TEM analysis. This observed diameter is very close to that of cyclic organic nanostructures synthesized by REMP of a norbornene-based dendronized macromonomer.^{2g}

To demonstrate the universality of this technique for the preparation of metallo-supramolecular cyclic brush polymers, we designed and synthesized compound **4**, a model terpyridine-functionalized reversible addition–fragmentation chain-transfer polymerization (RAFT) agent that enables the incorporation of a wide range of polymer side chains (Figure S7). Subsequently, polystyrene (PS) **5** [Figures S7 (synthesis), S8 (FT-IR), S9 (GPC), and S10 (¹H NMR)] was refluxed with RuCl₃ in 3/1 (v/v) CHCl₃/methanol to form the PS–terpyridine–RuCl₃ monocomplex **6** (Figure S7). In the FT-IR spectrum of **6** (red curve in Figure S8), the characteristic peak at 1562 cm^{−1} for the C=C stretching vibration of the free pyridine rings in **5** (black curve in Figure S8) disappeared completely, indicating a high reaction conversion. The GPC curve of **6** (red curve in Figure S9) retained the monomodal peak shape of **5** (black curve in Figure S9). The *M_n* and PDI of **6** were measured to be 3200 g/mol and 1.23, respectively.

Finally, metallo-supramolecular cyclic PS brush polymers were prepared by grafting PS side chains onto the cyclic **Poly-2** main chains using **6** under reducing conditions (ethanol, *N*-ethylmorpholine) [Figure 1(iii)]. To ensure a high grafting density, **6** was used in ~3-fold excess relative to the terpyridine groups in **Poly-2**. Figure S11 shows the UV–vis spectrum of the resultant hybrid cyclic PS brush polymers (red curve). Compared with the spectrum of the cyclic **Poly-2** precursor (black curve), new bands were observed at 269, 307, and 490 nm, which are characteristic of the bis(terpyridine)ruthenium(II) linkage. In the FT-IR

spectrum of the hybrid cyclic PS brush polymers (red curve in Figure S12), the peaks at 1582 and 1562 cm^{-1} for Poly-2 (C=C stretching vibrations of the free pyridine rings) disappeared completely, verifying the high grafting density of PS side chains.

Since RAFT is one of the most widely used controlled-polymerization techniques for vinyl monomers, many kinds of polymer side chains with a terpyridine-functionalized end group could be prepared following the same procedure. As a result, this novel method provides an efficient and practical way to produce arrays of metallo-supramolecular cyclic brush polymers with various polymer side chains.

An increasingly popular strategy for modifying the mechanical and swelling properties of organic polymer gels is the incorporation of inorganic components.¹¹ We recently demonstrated the advantageous properties of gels based on cyclic polymers compared with those formed by cross-linking of linear polymers.¹² Taking advantage of the versatility of the metallo-supramolecular chemistry to cross-link cyclic polymer chains enables the creation of novel gels with the structural merits of both cyclic gels and organic/inorganic hybrid materials. Such gels are likely to have unique and interesting properties.

Here we report for the first time cyclic polymer/inorganic hybrid gels in which inorganic transition-metal ions serve to cross-link terpyridine-functionalized cyclic Poly-2 polymer templates. Two model transition-metal ions, Fe^{2+} and Ni^{2+} , were chosen to demonstrate this concept, and as shown in Figure 5A, free-standing metallo-supramolecular gels were obtained in

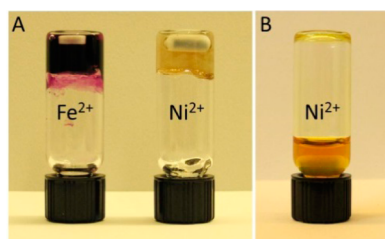


Figure 5. Pictures of (A) the metallo-supramolecular cyclic gels and (B) their stimulus response in DMF.

air at room temperature in less than 5 min using a molar ratio of 1:5 between metal ions and terpyridine groups. In addition to the “cyclic” and “hybrid” molecular structure, another appealing feature of these novel gels is the tunability of their properties under certain external stimuli, which is enabled by the characteristic reversibility of the metallo-supramolecular bonds. In one example to demonstrate this, a large excess of free 2,2';6',2''-terpyridine was added to the Ni^{2+} -cross-linked metallo-supramolecular gel, and the mixture was allowed to stand at room temperature. After ~ 20 days, the free-standing gel became fluid (Figures 5B and S13). Detailed structure–property studies of the dynamics of these novel gels are currently underway.

In conclusion, a novel cyclic polymer bearing side groups terminated with terpyridine ligands was developed by combining REMP with activated ester click chemistry. Taking advantage of the outstanding ability of terpyridine ligands to chelate transition-metal ions, this cyclic polymer served as a universal template for the preparation of various metallo-supramolecular materials with an inherent cyclic molecular architecture. Two cyclic polymer/metal hybrid materials based on this novel cyclic polymer template have been demonstrated for the first time: metallo-supramolecular cyclic brush polymers and metallo-supramolecular cyclic gels. The hybrid cyclic brush polymers

described here represent new amphiphilic architectures that are expected to have interesting assembly properties.^{3d} Exploiting metallo-supramolecular chemistry to build upon the cyclic polymer topology not only will open a new research area for cyclic polymers but is also expected to produce advanced hybrid materials with new properties.

■ ASSOCIATED CONTENT

Supporting Information

Experimental section and Figures S1–S13. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

tew@mail.pse.umass.edu

Notes

The authors declare no competing financial interest.

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