



# Metallo-supramolecular complexes mediated thermoplastic elastomeric block copolymer



Haixia Li, Wei Wei, Huiming Xiong\*

Department of Polymer Science, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

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## ABSTRACT

Orthogonal multi-phase strategy has been applied to generate a novel type of thermoplastic elastomeric block copolymer which was obtained *via* anionic polymerization. Functional terpyridine groups which can potentially form metallo-supramolecular complexes with a variety of metal ions has been introduced to the polystyrene-*b*-polyisoprene (PS-PI) living chain ends through the termination reaction in an optimized condition. Iron(II), cobalt(II) and zinc(II) metal ions have been used to form metal-ligand complexes with the terpyridine end groups, which can phase separate from the polymer matrix to form hybrid clusters. The formation of metallo-supramolecular hybrid clusters have dramatic effects on the micro-phase separated structures of the PS-PI diblock copolymer, which have been characterized by transmission electron microscopy, small-angle X-ray scattering and atomic force microscopy. This type of hybrid material containing hard PS nanophase and metal-ligand clusters exhibit distinct mechanic properties such as increased modulus, higher yield strength and improved toughness, which is further discussed in light of nature of the metal-ligand bonds and the liability of the clusters. The utilization of metallo-supramolecular complex and its high tunability is potential to fabricate new types of supramolecular nanocomposite materials.

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## 1. Introduction

Supramolecular chemistry has advanced into a variety of fields over the last decades [1]. Supramolecular interactions typically encompass non-covalent bonds such as hydrogen-bonding, electrostatic interaction and metal-ligand complexation. The integration of supramolecular chemistry with polymeric materials can potentially enhance their performances in terms of reversibility, functionality and processability [2–20]. In principle, these features are also highly desirable in thermoplastic elastomers which require a good processability at elevated temperature like plastics, yet keep elastomeric at ambient temperature [21]. Therefore, this joint can significantly broaden the scope and applicability of thermoplastic elastomeric materials [5,6].

Polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) triblock copolymer is a well-known thermoplastic elastomeric block copolymer, which was commercialized decades ago [21]. In this ABA type triblock copolymer system, phase separated polystyrene (PS) “hard”

domains are bridged by “soft” rubbery polyisoprene (PI) chains at room temperature. The chain ends of the PI blocks are pinned in the “hard” domains, while the maximization of the connected chain configuration entropy leads to the elasticity. The “hard” PS domains prevent macroscopic deformation of the network, whereas they soften once the temperature above their glass transition temperature ( $T_g \sim 100$  °C). In this work, we aim to design and introduce a variety of metal-ligand complexes into styrenic block copolymers to generate metallo-supramolecular thermoplastic elastomers in the spirit of orthogonal multi-phase strategy [22,23]. Particularly, the metal-ligand motifs based on terpyridine (Tpy) metal complex chemistry are introduced into a PS-PI diblock copolymer through end-functionalization of PI chains in anionic polymerization process. This functionalized diblock copolymer composed of multiple phases represents a novel type of thermoplastic elastomers with distinct mechanic properties.

The reason to choose Tpy metal complex chemistry in this work is two-fold. Firstly, Tpy can easily form complexes with a wide range of metal ions of vastly different binding constants and readily construct versatile, stable and inert, yet reversible supramolecular architectures [24–26]. Therefore, the mechanic properties of the resulted material can be systematically tuned and the

\* Corresponding author. Tel.: +86 21 34202544.

E-mail addresses: [hmxiong@sjtu.edu.cn](mailto:hmxiong@sjtu.edu.cn), [hmxiong@yahoo.com](mailto:hmxiong@yahoo.com) (H. Xiong).

functionalities such as photophysical or electrochemical applications can be potentially achieved [27–30]. Secondly, the utilization of metal–ligand binding as the driving force of the self-assembly offers a facile route to generate organic/inorganic hybrid materials. The hybrid complexes have a high potential to phase separate from the surrounding matrix. As known, mechanic properties can be enhanced by phase separation induced by crystallization and stacking of associating motifs [31–34]. For example, cylindrical metal–ligand rich domains were observed in the polymer bound with metal–ligand complexes, which improved the modulus, stability and strength of the polymer [34]. In our design, an orthogonal combination of two types of phase-separated microstructures is anticipated: one originates from the intrinsic incompatibility between the glassy PS domains and soft PI matrix; another is ascribed to polar moieties of Tpy complexes, which tend to form clusters or aggregates immersed in the PI soft domain. These metallo-supramolecular complexes could thus act as extra physical cross-links, imparting the material elastomeric behavior through the connectivity of the network. Furthermore, the polar ionic clusters could function as effective nano-fillers and reinforce the material similar to that of nanocomposites with enhanced properties. For instance, ten-time increase of polymer modulus in comparison to the prediction of rubber elasticity theory was found in the metallo-supramolecular network [33]. However, the research on the tunable mechanical properties of metallo-supramolecular polymers is still limited. How the nature of the metal–ligand bond, and the effects of phase separated structures on multiple length scales influence the ultimate mechanic properties of this type of materials deserve further investigation.

Herein, we report the synthesis and preparation of a series of end-functionalized metallo-supramolecular diblock copolymer (PS-PI) coordinated with three different metal ions, Fe(II), Co(II) and Zn(II), which have descending binding strength with Tpy [25,35,36]. The integrity of this material is revealed to be directly related to the nature of the supramolecular interaction and the lability of the metal–ligand hybrid clusters. The influences of metal–ligand binding strength and formation of clusters on their mechanic properties are investigated. The presence of two types of “hard” domains imparts this type of materials distinct mechanic properties in terms of modulus, tensile strength and toughness.

## 2. Experimental

### 2.1. Materials

Calcium hydride (Sigma–Aldrich, 95%), dibutylmagnesium (1.0 M in heptane, Sigma–Aldrich), sec-butyllithium (1.3 M in heptane, Energy Chemical), 4'-chloro-2, 2':6',2''-terpyridine (Sigma–Aldrich, 99%), Iron (II) chloride tetrahydrate (Aladdin Reagents Ltd, 99.95%), Cobalt (II) acetate tetrahydrate (Alfa Aesar, 98%), Zinc chloride (J&K Scientific Ltd, 98%) and ammonium hexafluorophosphate (J&K Chemical, 99.4%) were used as received. Styrene (J&K Chemical Ltd.) was dried over calcium hydride powder for 24 h, and further purified by distillation under reduced pressure into another flask that contained dibutylmagnesium (1.0 M in heptane, Sigma–Aldrich) and stirred for 1 h at room temperature. Isoprene (Tokyo Chemical Industry) was dried by calcium hydride. Further purification was carried out by distilling the monomers under reduced pressure into another flask that contained dibutylmagnesium and stirred for 1 h at room temperature. Afterwards, the isoprene was distilled into a flask contained n-butyllithium and stirred for 30 min at 0 °C and ready for immediate use. Cyclohexane (J&K Chemical Ltd., 99%) was stirred with concentrated sulfuric acid for three days. The acid was then removed and neutralized with saturated sodium bicarbonate solution, followed by washing with

deionized water for several times. Anhydrous magnesium sulfate powder was added to remove the residual water. The resulted solution was filtered, then stirred over sodium overnight and subjected to several freeze-thawed cycles before use. Toluene was stirred with sodium over 24 h, then distilled into a high-vacuum flask, and thawed three times. All other solvents were purified by distillation.

### 2.2. Synthesis of Tpy end-functionalized PS-PI block copolymer (SI-Tpy)

Anionic polymerization was carried out in cyclohexane at room temperature. A high-vacuum reactor flask was placed on the high vacuum line and flame dried three times. 80  $\mu$ L sec-butyllithium (1.3 M in hexane) was added in the flask, followed by the addition of 0.75 mL (6.5 mmol) pre-purified styrene monomer. 200 mL cyclohexane was distilled into the flask on the vacuum line. The color soon became deep yellow as forming poly(styryl)lithium anions. After the completion of the polymerization of PS (~12 h), 6 mL (60 mmol) isoprene was introduced into the reactor flask, resulting in the deep pale yellow solution. The reaction was kept for additional 60 h at 40 °C to complete the second-stage polymerization. 42 mg 4'-chloro-2, 2':6',2''-terpyridine (156 mmol in toluene) was then added into the reactor, resulting in a deep blue color. The reactor flask was then kept at 8 °C overnight. Finally, methanol was distilled into the reactor to terminate the reaction. The blue color of the mixture immediately vanished. The polymers were purified by precipitation into methanol three times, and dried in high vacuum for further use.

### 2.3. Preparation of metallo-supramolecular block copolymers

The complexes of SI-Tpy with iron (II), zinc (II) and cobalt (II) ions were obtained by adding stoichiometric amount of FeCl<sub>2</sub>·4H<sub>2</sub>O, ZnCl<sub>2</sub> and Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O in methanol to the SI-Tpy chloroform solution in a molar ratio of 1:2 (metal ion:Tpy). Preparation of iron(II) complexed polymer (SI-Fe) is taken as an example. Stock solution of FeCl<sub>2</sub>·4H<sub>2</sub>O (111.5 mg, 0.56 mmol) in 10 mL methanol solution was freshly prepared first. 17.42  $\mu$ L FeCl<sub>2</sub> solution (0.001 mmol) was then added into 30 mL SI-Tpy chloroform (100.2 mg, 0.002 mmol) solution. The color of the solution became purple promptly. The solution was stirred for 6 h at room temperature and isolated by precipitation into methanol after counter-ion exchange by ammonium hexafluorophosphate. The dissolution and precipitation were repeated for three times. The obtained sample was dried in high vacuum. Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and ZnCl<sub>2</sub> were used as reactants for preparation of SI-Co, SI-Zn in a similar procedure. The orange and pale yellow colors were observed in these two systems, respectively. The film specimens for structural measurements and mechanical experiments were obtained by casting their toluene solution on Teflon drying pan in a covered glass vessel and evaporated slowly for 24 h. The films were further annealed at 80 °C in high vacuum for 3 h.

### 2.4. Characterization methods

Gel permeation chromatography (GPC) with a multi-angle laser light scattering detector (Wyatt Dawn EOS) plus a differential refractometer detector (Waters Model 2414) has been used to determine the molecular weights of the polymers and their polydispersities. Polymer samples for the GPC analysis were dissolved in tetrahydrofuran (THF) at an appropriate concentration (~1.0 mg/mL). The flow rate of the mobile phase was 1 mL/min. The NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz <sup>1</sup>H NMR) spectrometer with chemical shifts reported in ppm relative

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