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Asymmetric A-B-A' Metallo-Supramolecular Triblock Copolymer Linked by Ni^{2+} Bis-terpyridine Complexes at One Junction

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Metallo-supramolecular triblock copolymer polystyrene-*b*-polyisoprene-[Ni^{2+}]-polystyrene (SI-[Ni^{2+}]-S') has been efficiently prepared in a one-pot, two-step procedure, where the blocks are held by bis-terpyridine complexes at the junction of SI-S'. This specific metallo-supramolecular chemistry is demonstrated to be a robust approach to potentially broaden the diversity of block copolymers. The location of the metal-ligand complexes has a profound influence on the phase separation of the triblock copolymer in the bulk, which results in a distinctive phase segregation among the end blocks and leads to an unexpected asymmetry of the triblock copolymer. The metal-ligand complexes are found to preferentially locate on the adjacent spherical domain and form a core-shell structure. The resulting multiphase material exhibits distinct elastomeric properties with significant toughness and creep recovery behavior. This type of triblock copolymer is anticipated to be a novel class of hybrid thermo-plastic elastomeric materials with wide tunability and functionality.

1. INTRODUCTION

Supramolecular polymers are fascinating materials that may be designed using principles of both polymer science and supramolecular chemistry.[1-5] In contrast to its covalent analogues, it is held by non-covalent interaction including van der Waals forces,[6] hydrogen bonding,[7-13] metal-ligand coordination[14-25] and host-guest interaction,[26-31] which are inherently stimuli-responsive to circumstance due to their reversible nature. Once the external stimuli removed, the supramolecular bonds can reform and the materials regain their original properties. This has been considered as a new avenue to create functional materials, for example, thermo-plastic elastomers[32-34] and self-healing materials.[33-40] In particular, metal-ligand coordination has been extensively studied, not only because its strength can be tuned in a broad range with choice of various metal ions, ligands and counter-ions, but also metal-ligand complexes themselves can be functional as well, for example, endowed with optoelectronic,[19,36] magnetic,[24] and catalytic[19] properties. Among them, tridentate pyridine-based ligands such as terpyridine (Tpy) and its derivatives have been the focus of increasing interest.[18-20,23,36,38] For instance, sophisticated architectures can be designed and generated through quantitative self-assembly and chemistry of various metallo-Tpy compelexes.[20] Metallo-supramolecular polymers based on an optically active Tpy derivative have shown to be mendable through exposure to light.[36] The light-heat conversion was demonstrated to be quick and efficient in defect healing.

When Tpy motifs are incorporated into polymeric materials or serve as building entities of metallo-supramolecular polymers, the polar moieties of the metal-ligand complexes tend to form clusters and phase separate from the surroundings.[36,41-46] De-mixing between the metal-ligand complexes and the soft rubbery polymers can lead to the formation of an ordered, phase separated structure, which yields a thermo-plastic elastomer with a high modulus.[36] Cylindrical metal-ligand rich domains have been observed in polymers attached with pendent metal-ligand complexes when mixed with unbound metal-ligand complexes, where the π-π interaction and Coulombic forces each plays a role in holding the bound and unbound complexes together.[45] This design has led to an enhanced modulus. In our previous work,[46] Tpy ligand had been attached to the end of polyisoprene block in polystyrene-*b*-polyisoprene (SI) diblock copolymer. Introduction of various metal ions resulted in SI-[M]-IS type block copolymers, where the metal-ligand complexes were found to form isolated clusters dispersed in the PI matrix with a low glass transition temperature, together with glassy PS spheres at room temperature. These clusters are also stress bearing points or the “hard” phase responsible to the elastomeric properties. Inevitably, their integrity in terms of metal-ligand bond and phase separated structure impacts the mechanic properties of the metallo-supramolecular polymers.

Of particular interest is the ability to adjust the packing and distribution of the metal-ligand complexes, and thus to efficiently control and tune the elastic response and energy dissipation of metallo-supramolecular materials. The relationship between the self-assembled structures and mechanical properties deserves further studies. In the present contribution, we design a new type of metallo-supramolecular triblock copolymer, SI-[M]-S', with metal-ligand complex directly linked to the glassy polystyrene (S') block. In contrast to SI-[M]-IS, the metal-ligand complexes in SI-[M]-S' are

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Electronic Supplementary Information (ESI) available: [Details of characterizations by using MALDI-TOF, GPC, UV-vis titration and AFM are described]. See DOI: 10.1039/x0xx00000x expected to locate intimately to the S' "hard" spheres. We explore how the spatial arrangement of metal-ligand complexes affects the self-assembly behavior and the hierarchical structure of this multiphase supramolecular triblock copolymer in the bulk. Especially, this type of block copolymer is a novel modification of commercialized thermo-plastic elastomer SIS, where the phase separated PS "hard" domains are bridged by "soft" rubbery PI chains that contribute to the elasticity of the material through configurational entropy.[47] With the introduction of dynamic metal-ligand bonds along with the sufficient chain mobility of PI, hard supramolecular self-healing materials may become feasible in this multiphase design.[34,39] This structural design is anticipated to open an avenue to potentially construct a new library of hybrid thermo-plastic block copolymers with diverse functionalities imparted by metal-ligand motifs.

2. EXPERIMENTAL SECTION

2.1 Materials

Dibutylmagnesium (Sigma-Aldrich, 1.0 M in heptane), calcium hydride (Taitan chemical, 95%), sec-butyllithium (Energy Chemical, 1.3 M in heptane), nickel chloride hexahydrate (Aladdin Reagents Ltd, 98%), ammonium hexafluorophosphate (J&K Chemical Ltd, 99.4%) were used as received. Isoprene (Tokyo Chemical Industry) was dried over calcium hydride for 24 h and distilled into a flask containing dibutylmagnesium, and stirred for 1 h at room temperature. It was then distilled into another flask containing *n*-butyllithium and stirred for 30 min at 0 °C, and ready for immediate use. Styrene (J&K Chemical Ltd) was dried over calcium hydride for 24 h, and further purified by distilling under reduced pressure into another flask containing dibutylmagnesium and stirred for 1 h at room temperature, then ready for immediate use. Cyclohexane (J&K Chemical Ltd., 99%) was stirred with concentrated sulfuric acid for three days. It was then washed with saturated sodium bicarbonate solution and deionized water for several times. Anhydrous magnesium sulfate powder was added to remove the residual water. The filtered solution was stirred over sodium overnight and subjected to several freeze-thawed cycles before use. 4'-chloro-2, 2':6', 2"-terpyridine was recrystallized with methanol for three times, and dried in vacuum before use. 1,1-diphenylethylene (Sigma-Aldrich, 99%) was stirred over calcium hydride, then distilled into a flask containing *n*-butyllithium and stirred for 1 h for immediate use. All solvents were purified by distillation.

2.2 Synthesis of Tpy end-functionalized PS (S'-Tpy) and PS-b-PI block copolymer (SI-Tpy)

Synthesis of Tpy end-functionalized PS was performed as following: 210 μL *sec*-butyllithium (1.3 M in hexane) was added into a reactor flask, followed by distillation of 2 mL styrene monomer and 200 mL cyclohexane into the reactor on the vacuum line. The color of the solution then turned into deep yellow. After 12 h, pre-purified 1,1-diphenylethylene in 1.5 molar excess to *sec*-butyllithium was introduced into the reactor. The color of the solution immediately changed into red, indicating the formation of 1,1-diphenylethenyllithium. 92.5 mg Tpy in toluene was then added into the reactor, the color of the mixture immediately became deep blue. Finally, the reaction was terminated by methanol. The polymer was purified by precipitation into methanol three times, and dried in high vacuum. The synthesis of SI-Tpy follows the same procedure as previously reported,[46] except the higher molecular weight of PI block was designed.

2.3 Preparation of metallo-supramolecular block copolymers SI-[Ni^{2+}]-S'

S'-Tpy and $NiCl_2$ $6H_2O$ were dissolved in dimethylformamide (DMF). Equal molar amounts of DMF solutions of S'-Tpy and $NiCl_2$ $6H_2O$ were mixed and stirred for one minute, then an equal molar amount of SI-Tpy chloroform solution was immediately added. The mixture was stirred for 12 h at room temperature. 10-fold excess of NH_4PF_6 was added and stirred for 1 h to exchange counter-ions. The final product was purified by precipitation into dioxane/methanol mixture (10:1 in volume) for three times, and dried in vacuum for further use. The bulk samples were generally prepared by slow evaporation of their toluene solutions, followed by annealing at 80 °C in high vacuum for 3 h.

2.4 Characterization

The ^1H NMR spectra were recorded on a Varian MERCURY plus-400 spectrometer (400 MHz, ^1H NMR; 100 MHz, ^{13}C NMR). UV-vis spectra were collected on a Perkin-Elmer 950. Gel permeation chromatography (GPC) measurement was performed with a multi-angle laser light scattering detector (Wyatt Dawn EOS) plus a differential refractometer detector (Waters Model 2414). Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 mL/min. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) was conducted on a Shimadzu AXIMA Performance MALDI-TOF/TOFMS in a linear mode. Dithranol was served as the matrix, and silver trifluoroacetate was the cationization salt. Transmission electron microscopy (TEM) experiments were carried out on a JEOL 1200 with an accelerating voltage of 120 kV. A Leica UC6 ultramicrotome was used to microtome the sample at -120 °C in a liquid nitrogen atmosphere. The slice of the sample around 50 nm in thickness was picked up onto a 400-mesh lacey carbon grid. It was further stained in the vapour of OsO_4 aqueous solution for 1 h. Atomic force microscopy (AFM) measurement was conducted on a DI instrument in the tapping mode. The sample was prepared by casting its toluene solution in a concentration of 1 mg/mL on a silicon wafer, followed by slow evaporation and then annealing in vacuum at 80 °C for 3h. Small-Angle X-ray Scattering (SAXS) experiments were carried out on the synchrotron X-ray beam line, BL16B1, in Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of the X-ray beam is 1.239 Å. The scattering vector q ($q = 4\pi\sin\theta/\lambda$, where λ is the X-ray wavelength and 2θ is the scattering angle.) is calibrated using silver behenate. A MarCCD was used. Tensile measurements were performed on a Zwick Z010 Universal Tensile Tester. The sample bar was 20 mm in length, 4 mm in width, and its thickness was in the range of 0.2 ~ 0.5 mm. The gauge length of each specimen was 5 mm. The crosshead speed was kept at 5 mm/min. The measurements of each sample were repeated at least three times. Creep recovery experiments were performed on NETZSCH TMA 402F1 at room temperature. The film was elongated at various stresses for 60 min, the stress was then released and the film recovered for another 60 min. After that, the film kept relaxed in an argon atmosphere for 60 h at room temperature, the creep recovery measurement was repeated at a stress of 0.1 N for comparison.

3. RESULTS AND DISCUSSION

Herein, we present a heteroleptic metallo-supramolecular triblock copolymer SI-[Ni^{2+}]-S', which is designed through complexation of Tpy end-functionalized polystyrene (S'-Tpy) with Ni^{2+} precursors and polystyrene-*b*-polyisoprene diblock copolymer (SI-Tpy) by a one-pot,

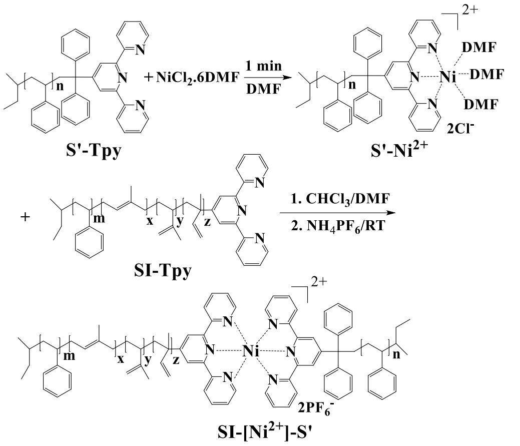

Figure 1. Synthetic route of metallo-supramolecular triblock copolymer SI-[Ni^{2+}]-S'.

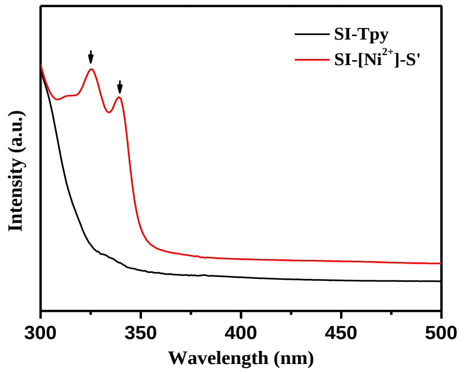

Figure 2. UV-vis spectra of SI-Tpy and SI-[Ni^{2+}]-S' solution in chloroform

two-step procedure.[48] This approach takes advantage of characteristic kinetic stabilities of Ni^{2+}-Tpy mono-complexes and bis-complexes to control the synthesis of heteroleptic Ni^{2+} bis-Tpy complexes, which was first demonstrated by Mugemana and coworkers in 2010.[49] In their work, amphiphilic PS-[Ni^{2+}]-PEO diblock copolymers has been generated and the micellization behavior was studied in selective solvent. In our synthetic route, Ni^{2+} mono-complex was first generated through the coordination of Ni^{2+} metal ions in DMF with S'-Tpy, subsequent introduction of SI-Tpy resulting in the heteroleptic bis-complexes, as shown in Fig. 1.

The end-functionalization of PS-*b*-PI block copolymer with Tpy (SI-Tpy) can be achieved through an efficient termination step during anionic polymerization process.[46] The detailed synthesis process is similar to the previous report[46] and its characterizations are described in the Supporting Information. In order to synthesize S'-Tpy, 1,1-diphenylethylene (DPE) was introduced just before the termination step.[50] The activity of poly(styryl)lithium can thus be reduced due to the steric hindrance of DPE.[51] Potential coupling reaction has been successfully avoided, as elucidated by MALDI-TOF and GPC measurements in the Supporting Information [Fig. S1, S2]. The GPC traces clearly show that SI-Tpy and S'-Tpy are highly monodisperse polymers. The molecular weight of S'-Tpy is 14 kg/mol, which is consistent with the MALDI-TOF result [Fig. S1]. The molecular weights of SI-Tpy and S'-Tpy were further determined by UV-vis titration experiments as described in the Supporting Information (Fig. S3 and S4). The molecular weights of PS and PI blocks in SI-Tpy were determined to be 9.4 kg/mol and 105.2 kg/mol, respectively.

Ni^{2+} ions was then introduced to prepare the heteroleptic SI-[Ni^{2+}]-S'. Ni^{2+} dichloride was first dissolved in DMF to form a precursor.[52] Equal mole of S'-Tpy was then added and the reaction was conducted for a limited period of time, typically on the order of minute, to yield mono-complex. SI-Tpy was subsequently introduced and reacted overnight to form the heteroleptic SI-[Ni^{2+}]-S' bis-complex. Finally, the chlorine counter-ions were exchanged with hexafluorophosphate. In order to remove any possible unreacted S'-Tpy mono-complexes and/or its homoleptic complexes, dioxane/methanol mixed solvent (10/1 in volume) was used to precipitate the sample three times. Dioxane is a good solvent for PS and a theta solvent for PI. This mixed solvent can efficiently precipitate SI-[Ni^{2+}]-S'. Meanwhile, it can dissolve S'-Tpy mono-complexes, its homoleptic complexes and a trace amount of SI-Tpy. The UV-vis spectrum of the purified sample is shown in Fig. 2. There clearly appear two new bands at 325 nm and 339 nm in comparison to SI-Tpy, which belong to ligand-centered band and metal-to-ligand-transfer band of the complexes, respectively. The GPC profile in Fig. S4 also shows that the evolution volume of the complexed sample shifts towards a lower value compared to SI-Tpy, suggesting a higher molecular weight than that of SI-Tpy. No sign of S' homopolymer can be detected. The broadness of the profile should be caused by the metal-ligand complexes in the metallo-supramolecular polymers during the elution.

In order to further confirm the complexation reaction and the chemical composition of SI-[Ni]-S', ^{1}H NMR characterization of SI-[Ni^{2+}]-S', SI-Tpy and S'-Tpy have been compared in Fig. 3. For SI-Tpy and S'-Tpy, the resonances of the Tpy end group can be identified in the chemical shift regime of 7.8-9.0 ppm. Upon the occurrence of complexation, those characteristic resonances belonging to Tpy totally disappeared due to the paramagnetic effect of Ni^{2+} bis-Tpy complexes, suggesting the complete complexation reaction during the preparation process. Moreover, it is found that the mass fraction of PS block in SI-[Ni^{2+}]-S' is ~ 20%, in contrast with that of PS block in SI-Tpy which is ~ 8.2%. This discrepancy is attributed to the formation of the heteroleptic SI-[Ni^{2+}]-S' with S'-Tpy introduced. The value is consistent with the stoichiometry of SI-[Ni^{2+}]-S' with theoretical mass fraction of PS ~ 19%, which is a direct evidence of the success in producing SI-[Ni^{2+}]-S'. This specific metallo-supramolecular chemistry is proved to be a robust approach to generate heteroleptic copolymers.

It is worth noting the mechanism of the selective formation of the heteroleptic Ni^{2+} bis-Tpy complexes, which has been investigated

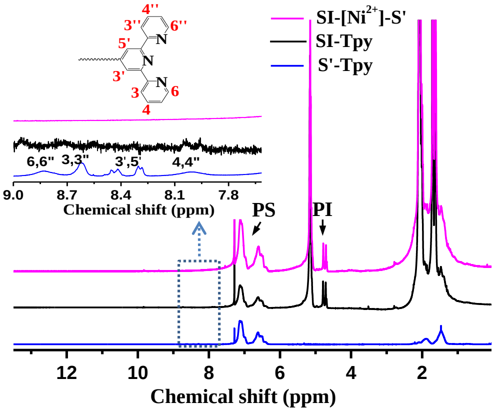

Figure 3. ^{1}H NMR of S'-Tpy, SI-Tpy and SI-[Ni^{2+}]-S' in $CDCl_3$. Inset is the chemical shift regime related to Tpy groups.

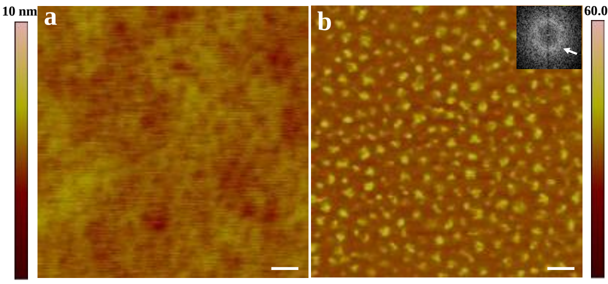

Figure 4. AFM height image (a) and phase image (b) of SI-[Ni^{2+}]-S'. The scale bar represents 100 nm. Inset in (b) is the Fast-Fourier-Transformation of the phase image.

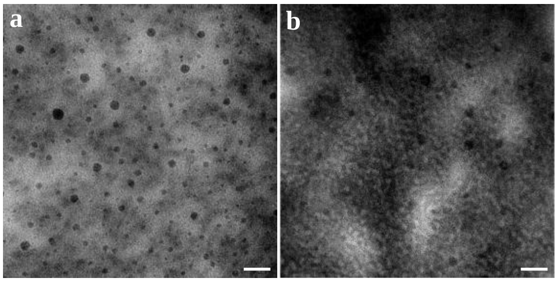

Figure 5. TEM images of SI-[Ni^{2+}]-S' without staining (a) and after staining (b). The scale bar represents 100 nm.

previously.[53] It is crucial to first yield the mono-complex between equal mole of Ni^{2+} ion and S'-Tpy. The kinetic aspect has to be taken into account as well as the thermodynamic stability of the mono- and bis- Ni^{2+}-Tpy complexes, whose association constants (K) are lgK$_1$ ~10.7 and lgK$_2$ ~ 11.1,[54] respectively. The thermodynamic stability of the mono-complex is only slightly lower than that of the bis-complexes in contrast to the most other transition metal ions.[23] The unique inertness of the Ni^{2+}-Tpy mono-complex has been ascribed to its high stability against disproportionation and at least none-enhancement in forming bis-complexes.[55,56] Particularly, the selection of DMF as the solvent can also tentatively enhance the kinetic stability of the mono-complex.[52,54] Under the kinetic control of introducing the second uncomplexed Tpy species into the system, stable heteroleptic bis-complexes can be generated with a rather large stability constant. Our work directly proves this selectivity, with a small modification using chloroform solution of SI-Tpy in the second step. This strategy has been also utilized to fabricate functional nanoporous thin films.[57]

The polar metal-ligand complexes have a strong tendency to phase segregate from the nonpolar surroundings. Therefore, clustering of the metal-ligand complexes and phase separation among different blocks could synergistically take place in the bulk. The self-assembled structure of SI-[Ni^{2+}]-S' is first investigated by using AFM in tapping mode. In contrast to the height image (Fig. 4a) where no distinct feature is observed, the phase image of SI-[Ni^{2+}]-S' in Fig. 4b clearly shows isolated dots homogenously distributed in the matrix. No such a high contrast can be observed for SI-Tpy as demonstrated in Fig. S5. This enhanced contrast in SI-[Ni^{2+}]-S' suggests a higher modulus difference between the dots and the PI matrix, which must originate from the decoration of metal-ligand clusters on the surface of the PS spheres. This has been further confirmed by TEM experiments as illustrated below. This phenomenon is nonetheless understandable since the metal-ligand complexes are directly linked to the PS blocks. Upon the occurrence of phase separation between the PS blocks and PI block, the polar metal-ligand complexes have no way but to locate on the surface of PS domain. This leads to the enhanced hardness of PS spheres due to the hybrid nature of metal-ligand clusters on one hand; on the other hand, it makes the dots appear more irregular as observed in the phase image. The irregularity of the shape can be ascribed to the clustering of the metal-ligand complexes. It also increases the size of the dots to 20-35 nm, which is larger than the expected value of PS domain (~ 12 nm in a diameter).[58] The core-shell like structure as well as the convolution effect from the AFM tip can result in this broadening.

It is also interesting to find that the average center-to-center distance among the dots is surprisingly much larger (almost double) than the typical distance between PS spheres in SI diblock,[46] as also shown in Fig. S5 and the X-ray scattering characterization elucidated below. The fast Fourier-Transformation of the phase image shown in the inset of Fig. 4b gives the most probable distance ~ 60 nm. This observation suggests that the metal-ligand complexes coated PS spheres are not nearest neighbours directly bridged by PI chains, other PS domains must exist in between despite that they could not be distinctly resolved by AFM due to their lower modulus contrast as already demonstrated before. This strongly suggests that the metal-ligand complexes should preferentially locate on the S' domain where they are directly linked and there exists a phase segregation between the PS end blocks due to the presence of metal-ligand bond in one junction. In conventional covalent block copolymer SIS where PS blocks form typical phase separated spherical structures, PI chains of the middle block can either form bridges between different PS spheres, or loops where PS end blocks are located in the same PS sphere.[47] In SI-[Ni^{2+}]-S', although both the end blocks are PS with similar molecular weights, the polar metal-ligand complexes in the SI-S' junction are found to make these two blocks different and dramatically affect its self-assembly behavior.

The morphological structure of SI-[Ni^{2+}]-S' is further characterized by TEM experiments, where the microtoned thin slice (~ 50 nm in thickness) of the sample was used. As shown in TEM micrograph without staining in Fig. 5a, dark dots are found to uniformly distribute throughout the whole sample. They should be S' domains, which contrast originates from the Ni^{2+}-Tpy complexes on their surface. The distance among the dark dots is in the range of 50-90 nm, consistent with AFM image. It is noteworthy that two types of PS domains in this triblock copolymer are anticipated. One is S domain, another is S' domain coated with Ni^{2+}-Tpy complexes. In order to reveal the existence of S domains, staining of the sample by OsO_4 was conducted, where the PI matrix was preferentially stained. As shown in Fig. 5b, light dots can be clearly identified. The contrast between the dark dots and the matrix originally observed without staining could be lost or obscured in this staining process. Nevertheless, in some area the dark dots initially present before staining are still visible, suggesting the presence of two types of PS spheres. This experiment provides another support on the asymmetric phase separation and the resulting structures in SI-[Ni^{2+}]-S'.

SAXS experiments were conducted to investigate the structural change of the block copolymers when complexation occurs. As shown in Fig. 6, SI-Tpy shows a scattering peak at the position of q = 0.18 nm^{-1}, indicating the length of ~ 35 nm ($d = 2\pi/q$). This value represents the most probable center-to-center distance among the PS spheres, which segregate from the PI matrix in absence of long range order. In contrast, the scattering peak of SI-[Ni^{2+}]-S' shifts to a higher q value of ~ 0.19 nm^{-1}, suggesting a shorter distance. This is reasonable since A-B-A triblock copolymers are known to exhibit similar phase separated structures and dimensions to those of A-B/2 homologous diblock copolymers.[59-61] Therefore, a shorter average distance among the PS spheres is anticipated for SI-[Ni^{2+}]-S' in comparison to SI-Tpy, in which the PI block has the same chain length. For SI-[M]-IS dimer

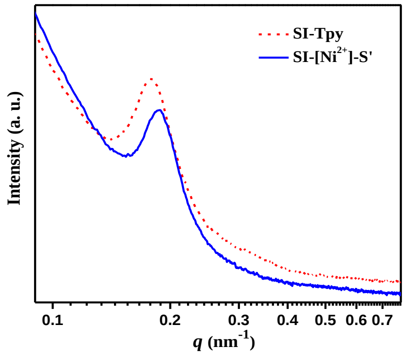

Figure 6. 1D SAXS profiles of SI-Tpy and SI-[Ni^{2+}]-S'.

system in our previous work,[46] the introduction of metal ion leads to an increase of average distance among PS spheres compared with that of SI diblock copolymer instead, where the incorporation of extra metal-ligand coordination bonds and change of conformations of the PI chains could be mostly responsible. No diffraction from the metal-ligand clusters has been observed in the wide-angle X-ray diffraction measurements. The discrepancy of the center-to-center distance of PS domains obtained from SAXS with that of Ni^{2+}-Tpy complexes coated PS domains obtained from AFM originates from the asymmetric self-assembly of SI-[Ni^{2+}]-S' and distinctive phase separation of the end blocks.

Studies on metallo-supramolecular copolymers have revealed strong influences of metal–ligand complexes on their self-assembly behaviors. For example, the presence of the metal-ligand complexes at the junction can impact the ordering process of the diblock copolymer thin film and the orientation of the cylinders with respect to the substrate.[62] The terpyridine-ruthenium complexes at the junction of amphiphilic diblock copolymers have been shown to result in an unusual scaling law of the core size of the micelle with the degree of polymerization of the blocks in the core.[63] It was also found that the insertion of point-like but strongly interacting "blocks" such as zwitterion groups,[64] or metal-ligand bonds[65,66] at the junction of diblock copolymer can enhance the immiscibility of the blocks having a finite incompatibility originally. This observation is also in line with the theoretical work on how the size, location and interactions of block B of an ABC triblock copolymer affect the miscibility of the outer blocks A and C.[67] It was suggested that the metal-ligand complex could be thought of as a "third minority block" due to the difference in polarity between the metal-ligand complexes and the other blocks, which triggers the microphase separation. Metal-ligand complexes do affect the self-assembly of the adjacent blocks. In SI-[Ni^{2+}]-S', the poor miscibility of terpyridine-metal complexes with their non-polar surroundings and their intrinsic tendency toward aggregation driven by secondary interactions may make them prone to form separated domains together with the adjacent block S'. The enthalpy gain may overwhelm the penalty of the mixing entropy between S' and S blocks. Certainly, the interplay among various competing parameters will determine the final morphology of the metallo-supramolecular copolymer, which deserves further theoretical work. The system studied here represents an exquisite example of generation of asymmetry in the phase separation of this A-B-A' type triblock copolymer in the bulk.

The formation of metal-ligand bonds in SI-[Ni^{2+}]-S' gives rise to bridge conformations of PI chains. Accordingly, elastomeric behavior is expected. The pictures in Fig. 7a demonstrate its good elasticity and ability to return to the original state after release of the applied stress. This cycle is repeatable. The analogous SI-Tpy diblock copolymer also exhibiting a spherical nanostructure is virtually not an elastomer. Failure in SI-[Ni^{2+}]-S' occurs at a significantly large strain, ~ 7 mm/mm, as shown in Fig. 7a. In symmetrical triblock copolymer that is often used as thermo-plastic elastomer, the middle block could take either a bridge and loop conformation. The bridge/loop ratio can significantly influence its mechanical properties, in which the loops make a negligible contribution.[47] In this asymmetric triblock copolymer SI-[Ni^{2+}]-S', loop fraction should be effectively reduced, which can potentially enhance the elastic properties of this material. Design of A-B-A' type block copolymer should be favorable considering the mechanism of elasticity.

It is encouraged to make a comparison between SI-[Ni^{2+}]-S' and the commercial product SIS (Dexco Vector 4111D) with very similar composition and molecular weight,[68] which block molecular masses (kg/mol) PS/SI/PS are 11.5/105/11.5. Overall, the stress-strain curve follows the general shape of this classic thermo-plastic elastomer SIS. The strain at break of SI-[Ni^{2+}]-S' can reach the similar amplitude as SIS elastomer, while the tensile strength is comparably lower than its covalent analogues. We notice that the SIS film has been annealed at 120 ℃ for 10 days to promote long range order and equilibrium microstructure,[68] while SI-[Ni^{2+}]-S' has been annealed at 80 ºC for 3 hours. In our experiment, we found that increase of annealing time to 8 hours or annealing at 100 ℃ for 3 hours didn't make any change of the SAXS profile. Nevertheless, the dynamic, non-covalent nature of the metal-ligand coordination bond should play a role. The elastomeric properties were further characterized by creep-recovery experiments (Fig. 7b). At room temperature, a stress of 0.03 N applied to the sample for 60 min, resulting in a strain of ~ 13.7%, which increased at a rate of 1.2% per hour. After the applied stress released, the sample can recover its original dimension with a negligible residual strain. Increase of the applied stress to 0.10 N resulted in a strain of 68.5%, which increased at a rate of 15.5% per hour. Release

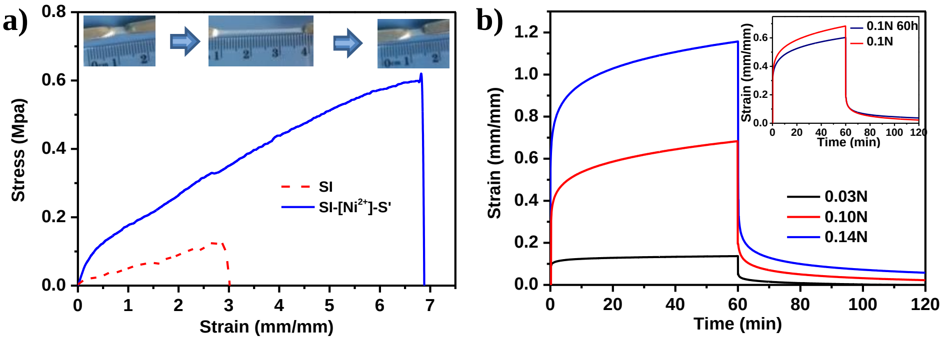

Figure 7. Stress-strain curves of SI-Tpy and SI-[Ni^{2+}]-S' at the strain rate of 5 mm/min (a). Creep-recovery behavior of SI-[Ni^{2+}]-S' at various stresses (b); inset is the comparison of the measurements at the stress of 0.1N before and after relaxation for 60h.

of the stress left a residual strain of ~ 2.5%. Applying a higher stress of 0.14 N under the same condition resulted in a strain of ~ 115.6% with an increased rate of 17.4% per hour. Removing the stress resulted in a residual strain of 6.1%. After that, the sample was set free of stress for 60 h, the creep-recovery measurement at a stress of 0.1 N was then performed again. Comparison of the creep-recovery curves in the inset of Fig. 7b shows that the film after the long time relaxation reached a smaller strain than that of the unrelaxed film, indicating a potential self-healing capability to restore the original properties. The time-dependent experiments suggest that this metallo-supramolecular triblock copolymer can indeed form a relatively stable network and sustain a load. In principle, the reversibility of metal-ligand bond can intrinsically affect the dynamic behavior of the system on multiple time scales. From another point of view, this dynamic character can be utilized in different aspects. For example, the flexibility of the PI chains linked to the metal-ligand bonds can facilitate the formation of the complexes, which can self-heal over time whenever the metal-ligand bonds are broken, where a balance between mechanical properties and dynamic self-healing might be found.

4. CONCLUSION

In conclusion, we have successfully generated the heteroleptic metallo-supramolecular triblock copolymers *via* a one-pot, two-step procedure. Morphological investigations using AFM and TEM as well as structural characterization reveal an immiscibility of the end blocks of this type of triblock copolymer, which leads to an asymmetrical phase separation. Two types of phase separated spherical domains have been observed to be dispersed homogenously in the matrix, where the metal-ligand complexes preferentially locate on one type of glassy PS domain. This specific behavior has been attributed to the special design of the metallo-supramolecular triblock copolymer, where the polar metal-ligand complexes located at one junction. This construction has dramatically influenced its hierarchical self-assembly behavior and altered the microphase separation of the triblock copolymer, consequently its elastic performance. This metallo-supramolecular material shows distinct elastomeric behaviors of a large toughness and creep-recovery capability. This strategy offers a genuine way to generate hybrid thermo-plastic block copolymers which mechanic properties can be tuned and additional functionalities can be potentially imparted.

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Notes and references

‡ The authors declare no competing financial interest.

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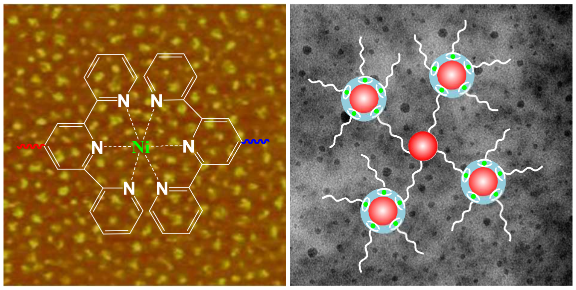

Asymmetry in SIS triblock copolymers held by a metallo-supramolecular bond at one junction comes with self-healing elastomer behavior.