Communication

Self-Healing *Metallo*-Supramolecular Amphiphilic Polymer Conetworks

Clément Mugemana,[*] *Patrick Grysan, Reiner Dieden, David Ruch, Nico Bruns and Philippe Dubois*

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Dr. C. Mugemana, P. Grysan, Dr. R. Dieden, Dr. D. Ruch
Luxembourg Institute of Science and Technology
Materials Research and Technology Department
5 rue Bommel - ZAE Robert Steichen
L-4940 Hautcharage - Luxembourg
clement.mugemana@list.lu

Prof. N. Bruns
University of Strathclyde
Department of Pure and Applied Chemistry
Thomas Graham Building
295 Cathedral Street
Glasgow - United Kingdom

Prof. P. Dubois,
Center of Innovation and Research in Materials Polymers
Laboratory of Polymeric and Composite Materials,
Université de Mons,
Place du Parc, 23B-7000 Mons – Belgium

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Introduction

One of the outstanding features of biological systems is their ability to heal damage autonomously. Inspired by this observation, the design of man-made self-healing materials has exponentially increased over the last decade.[1] Reversible interactions based on supramolecular interactions[2] have often been preferred over their covalent counterparts[3] [4] to create self-healing materials.[5] [6] Among the supramolecular interactions available, metal-ligand bonds represent an attractive motif because of the possibility to tune the interaction strength by simply choosing the appropriate metal ion and ligand. In addition to self-healing feature, the use of metal complexes enlarges the properties and functionalities of the resulting materials, including but not limited to light responsive,[7] solvatochromic,[8] conductive[9] [10] and highly stretchable polymers.[11] [12] [13] [14] Nevertheless, the current challenge in self-healing materials lies in the design of materials that combine self-healing ability and good mechanical properties.[15] [16] [17] One of the strategies that has been used to overcome this limitation is the design of phase-separated nanostructured polymers with the hard phase providing good mechanical properties while the soft one, equipped with the supramolecular bonds, endows the materials with the self-healing behavior. The use of linear block copolymers[18] or brush polymer architectures[19] [20] has led to self-healing nanostructured polymers with highly improved mechanical properties. Amphiphilic polymer conetworks (APCNs) are nanostructured materials with a unique portfolio of properties, including swellability in water and in organic solvents, robust mechanical properties, optical transparency and tunable permeability.[21] [22] [23] [24] [25] [26] Moreover, they are easy and straightforward to synthesize. The covalently interconnected [25-26] hydrophobic and hydrophilic polymer chains result in phase-separated morphologies.[27] The mechanical properties can be adjusted by tuning the polymer composition and the chemical functionality of the polymer segments.[28] APCNs have shown great potential for applications that range from contact lenses[29] to separation membranes,[30] transdermal drug delivery systems,[31] biomaterials for artificial pancreas,[32] and as support materials for catalysts.[33] [34]

Nevertheless, so far no self-healing APCNs have been reported in literature. Only self-sealing APCNs have been developed that close punctures by swelling in water.[35] However, they did not heal damage permanently. We envision that introducing reversible supramolecular interactions based on metal complexes into APCNs would lead to self-healing materials that exhibit robust mechanical properties. One of the strategy to sustain the reliability of performance is to avoid the formation of cracks arising from the formation of undetected minor damage, which would lead to complete failure of the materials. In this respect, our contribution aims at designing a *metallo*-polymer conetwork with inherent ability of healing scratch.

Results and discussion

APCNs can be prepared via the direct polymerization of hydrophilic monomers in the presence of hydrophobic macromonomer cross-linkers. However, the poor miscibility between incompatible monomers inhibits a direct polymerization. Therefore, hydrophilic monomers bearing a hydrophobic masking group have been used to prepare hydrophobic precursor conetworks.[27] [36] They are then converted into amphiphilic materials by cleavage of the masking group, leading to phase-separated nanostructured polymer networks. Recently, pentafluorophenyl acrylate (PFPA) has been reported as a suitable hydrophobically masked monomer that simultaneously is in active ester and therefore allows to prepare a wide range of functionalized poly(acrylamide)-based APCNs.[37] Thus, we used poly(pentafluorophenylacrylate)-*l*-polydimethylsiloxane (PPFPA-*l*-PDMS) precursor conetworks to prepare functionalized APCNs. It has been reported that non-chelating ligands such as imidazole [19] or histidine [38] form kinetically more labile complexes with metal ions than chelating ligands based on terpyridine[39] or bipyridine, [13] thus leading to better self-healing behavior. Therefore, pyridine and Zinc(II)-based complexes were selected as reversible bonds within the polymer conetworks with self-healing ability.
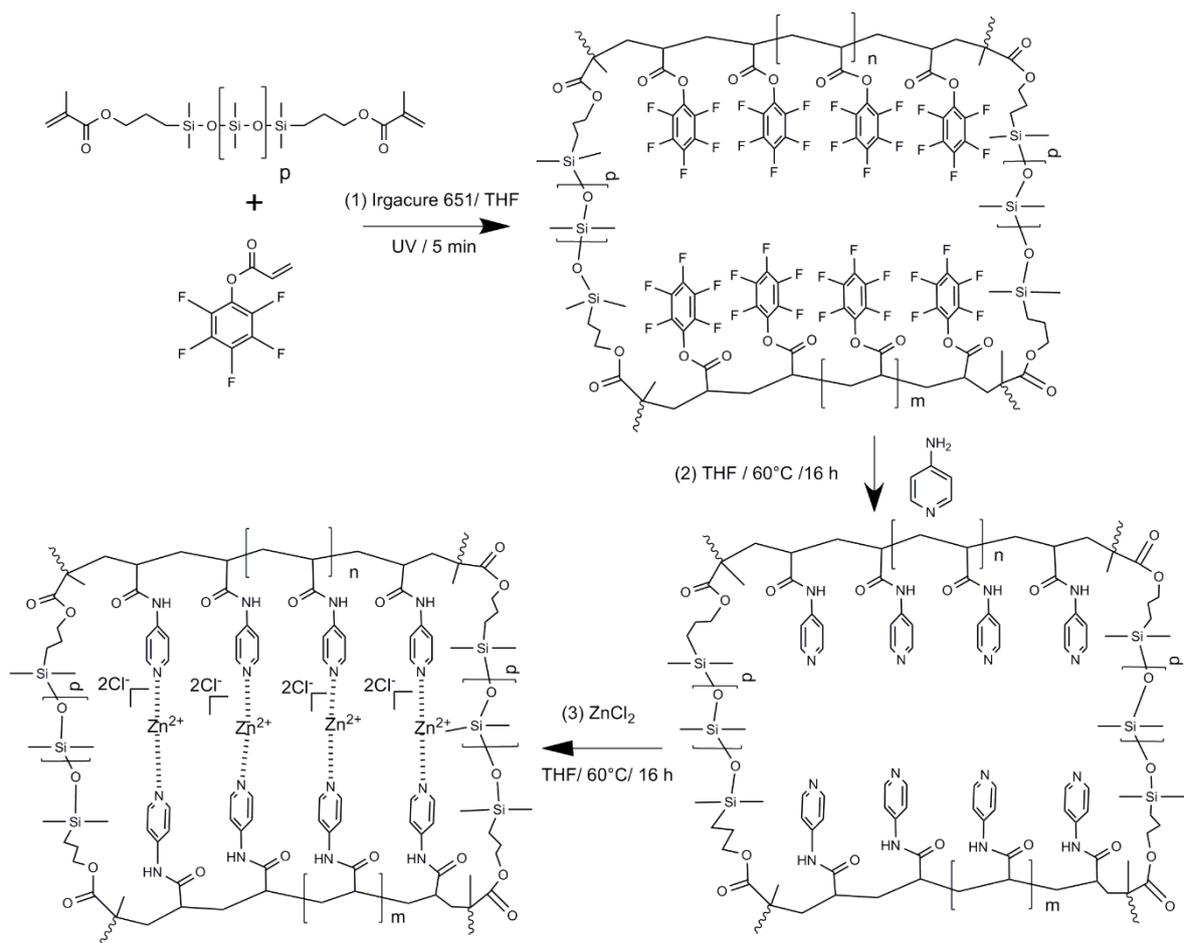
Figure 1. Three-step synthesis to prepare *metallo*-supramolecular amphiphilic polymer conetworks: simplified representations of (1) PPFPA-*l*-PDMS conetworks precursor, (2) PNP4A-*l*-PDMS polymer conetworks and (3) PNP4A-*l*-PDMS loaded with ZnCl$_2$.
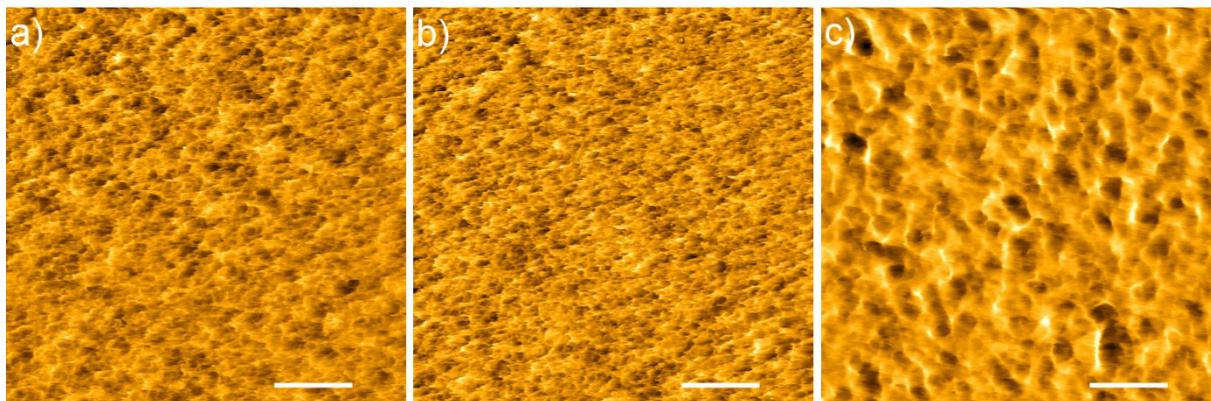
Figure 2. AFM phase mode images of the cross-section of PPFPA-*l*-PDMS (a), PNP4A-*l*-PDMS (b) and PNP4A-*l*-PDMS loaded with $ZnCl_2$ (c). (Scale bar: 100 nm)

The PPFPA-*l*-PDMS conetwork precursors were synthesized by UV-initiated polymerization in the presence of Irgacure 651 (2,2-dimethoxy-1,2-diphenylethan-1-one) according to the previously described procedure.[37] A monomer mixture containing 50 wt. % of PFPA and 50 wt. % of PDMS was prepared and further diluted with 10 wt. % of THF into which the initiator had been dissolved (Figure 1). A U-shaped 500 µm thick Teflon membrane was tighten between two glass slides covered with a brown polypropylene (PP) tape, forming a mould (Figure S2). The monomer mixture was filled into the mould and irradiated with UV light. The resulting freestanding and optically transparent film of ca. 430 µm thick was washed in THF at 60°C overnight in order to remove unreacted PFPA and PDMS cross-linker. The content of PPFPA in the polymer was 43 wt. % PPFPA as measured by elemental analysis. The FTIR spectrum of the polymer conetwork precursor revealed the characteristic absorption bands of the active ester at 1783 cm^{-1} (C=O stretch) and 1571 cm^{-1} (the fluorinated aromatic ring stretch) as shown in Figure S5. DSC analysis of the precursor conetwork revealed two distinct glass transition temperatures at ca. -120°C and 44°C. They correspond to the PDMS and active ester phases, respectively (Figure S5). This confirms the presence of phase-separated morphologies as previously reported.[27] [37] 4-Aminopyridine was reacted with the active ester-based precursor

in THF at 60°C to yield poly(*N*-(pyridin-4-yl)acrylamide)-*l*-polydimethylsiloxane (PNP4A-*l*-PDMS) APCNs. Residual content of fluorine of 2.4% was determined by elemental analysis, thus indicating the reaction completion and the extraction of pentafluorophenol residue. The same analysis allowed to estimate the content of PNP4A phase corresponding to 18.5 wt.%. According to the FTIR spectrum analysis, the peak assigned to the active ester disappeared and was replaced by the amide stretch signal at 1685 cm^{-1} and the pyridine ring vibration signal at 1592 cm^{-1} (Figure S4). DSC analysis confirmed the functionalization by revealing a new T_g at 74°C that can be assigned to the PNP4A phase (Figure S5). .The higher glass transition temperature of PNP4A arises from stronger π-π interactions inherent to *N*-heterocyclic aromatic rings.[40] It is worth noting that the T_g of the PDMS phase remained almost unchanged (ca. -118°C). The swelling ability of the polymer conetwork was tested in various organic solvents and water. One of the outstanding features of APCNs is their ability to swell both in organic solvents and in water, which can be tuned by the composition of the polymer conetwork and its chemical functionality.[21] The polymer conetwork films were immersed in THF, a good solvent of the PNP4A and PDMS phases. An average volumetric degree of swelling (S_{Vol}) of 2.14 ± 0.14 revealed a good swelling ability of the polymer conetwork in THF (Figure S7). Immersing the film in *n*-hexane, a selective solvent of PDMS, resulted in lower swelling (S_{vol} = 1.48 ± 0.10), because the PNP4A phase did not swell. A slightly lower swelling ability of S_{vol} = 1.42 ± 0.06 was determined in DMF, a selective solvent of the PNP4A phase. In contrast, when the films were immersed in water, they revealed a poor swelling ability with only a S_{vol} of 1.07 ± 0.10. Most likely, hydrophobic interactions between *N*-heterocyclic aromatic groups hindered the swelling of the polyacrylamide phase in water.

The phase morphologies of the polymer conetworks was analyzed by AFM phase mode imaging. A contrast between hard and soft phases arising from their difference in energy dissipation is expected.[27] The bulk morphology of the PPFPA-*l*-PDMS conetworks revealed phase-separated morphologies with interconnected spherical PDMS domains (ca. 10 nm in

diameter) that are homogenously dispersed in the PPFPA matrix (Figure 2 a). The PNP4A-*l*-PDMS conetworks exhibited roundish PDMS domains similar to the morphology of the active ester-based conetworks (Figure 2 b). In addition, the phase morphologies were imaged on the surface of the synthesized APCNs showing similar morphologies to bulk. (Figure S8).

The last step of *metallo*-supramolecular polymer conetworks synthesis consisted in loading metal ions into the APCNs. Zinc(II) was selected because Zn(II) complexes are inherently kinetic labile as demonstrated in previous works on *metallo*-supramolecular self-healing polymers.[7, 12, 19, 38] From a plethora of available Zinc(II) salts, $ZnCl_2$ was selected due to the high coordinating strength of chloride counter ions, in addition to the fact that they act as bridging ligand, leading to fast self-healing.[18] The reaction was performed in THF to achieve good swelling of the APCN. The polymer conetwork film (5 x 1 cm^2 and 430 μm thick) was immersed in THF (30 mL) containing 0.038 M of $ZnCl_2$, and the solution was heated to 60°C overnight. The film was then rinsed in THF, and dried overnight under vacuum. The concentration of Zn(II) in the material was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis to be 4.5 ± 0.1 wt. %. This content corresponds to a molar ratio of PNP4A to Zn(II) close to 2:1. AFM revealed spherical interconnected PDMS domains in a PNP4A-Zn(II) phase (Figure 2-c). The PDMS domains are bigger, and the hydrophilic domains appear thinner than the domains of the metal-free APCN. Thus, the incorporation of metal ions into the APCNs does not change the overall phase morphology, but increases the size of hydrophobic domains, while it decreases the size of the hydrophilic domains due to the cross-linking of the PNP4A phase.

The complexation of Zn(II) ions by poly(*N*-(pyridin-4-yl)acrylamide) ligands was confirmed by solid-state NMR analysis. As shown in Figure 3, the characteristic peaks of pyridine were shifted at 154 ppm CH(2), 148 ppm CH(4) and 128 ppm CH(3) for the PNP4A-*l*-PDMS conetwork, while for the polymer conetwork loaded with Zn(II) only two signals shifted at 152 CH (2 and 4) ppm and 130 ppm CH(3) were observed. As the pyridine carbon signals are the

most impacted by the coordination bond between the aromatic nitrogen and Zn(II), we conclude that Zn(II) ions are complexed solely by poly(*N*-(pyridin-4-yl)acrylamide) ligands.

To demonstrate the self-healing ability of the APCNs, the surface of specimen was scratched using a scalpel leading to 10 ± 3 µm scratch width and approximately 100 µm deep, representing approximately 25% of the polymer film thickness (Figure S9). Then, the sample was placed in an oven and heated to 80°C for 16 hours. Healing of the scratch was monitored by optical microscopy (Figure 4). Under these conditions, the scratch closed but did not heal completely. However, when the temperature was increased to 120°C, the healing effect improved. The entire scratch healed, even though one could still observe a scar at the scratched area.
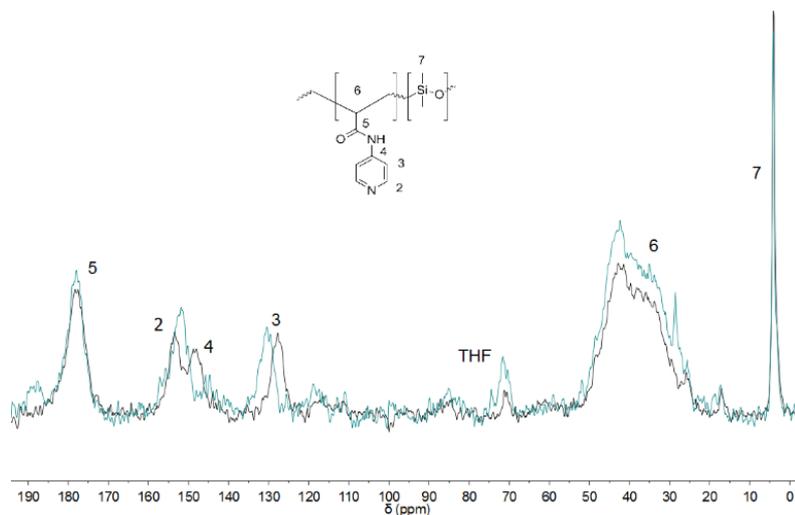

Figure 3. Solid-state ^{13}C NMR spectra of the PNP4A-*l*-PDMS (black line) and PNP4A-*l*-PDMS loaded with ZnCl$_2$ (green line).
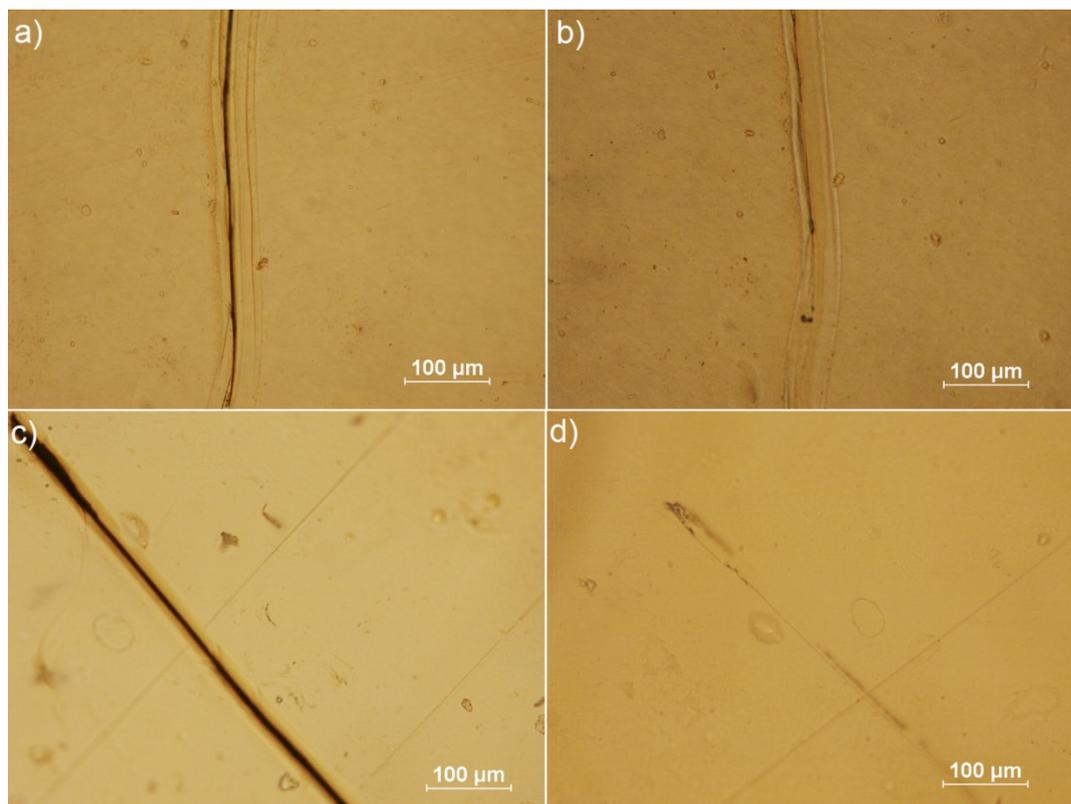
Figure 4. Self-healing of scratches in PNP4A-*l*-PDMS polymer conetworks loaded with $ZnCl_2$. Optical microscopy images of scratched free standing polymer films (a and c) and of the same specimen after 16 hours at 80°C (b) and 120°C (d).

Another possibility to assess the self-healing of materials is to measure the recovery of their mechanical properties after damage and healing. To this end, tensile tests of polymer films were carried out (Figure 5). A Young Modulus (E') of 132 ± 30 MPa with a tensile strength of 7.4 ±1.3 MPa and a strain at break of 0.31 ± 0.04 were measured at a strain rate of 10 mm min^{-1} for PNP4A-*l*-PDMS loaded with $ZnCl_2$. For comparison, the APCN without Zn(II) exhibited a lower E' of 25 ± 5 MPa and a higher strain at break of 0.5, but a lower tensile strength (4.5 ± 0.5 MPa). Thus, non-covalent cross-linking of the polymer conetwork by Zn(II) made it stiffer and strengthened it. Applying a scratch along the entire width of the strip and oriented perpendicular to the uniaxial deformation on the surface of APCN films loaded with $ZnCl_2$ reduced their mechanical properties. Polymer films broke into two parts at strain of only 0.07 ± 0.02 (Figure

5). Heating of scratched samples to 120°C for 16 hours led to a strain at break of 0.25 ± 0.03 i.e. self-heling of the scratches resulted in 80 ± 8 % recovery of strain at break. It should be noted that the polymers are covalently cross-linked in addition to the non-covalent crosslinks by the Zn(II) complexes. To demonstrate that the healing of the scratches is due to the reformation of non-covalent supra-molecular crosslinks, scratches were applied on the surface of the polymer conetwork films that do not contain Zn(II). Tensile tests analysis revealed that heating the damaged sample at 120°C for 16 hours did not improve the strain unlike the film loaded with Zn(II) as shown in Figure 5 (dotted lines).
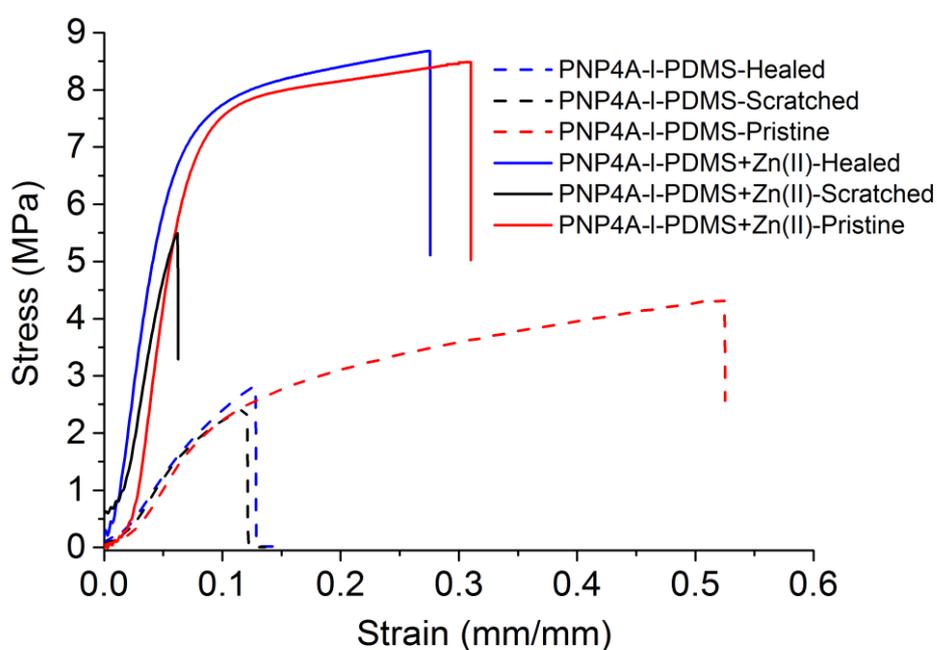

Figure 5. Uniaxial tensile tests of PNP4A-*l*-PDMS polymer conetworks loaded with ZnCl$_2$ PNP4A-Zn(II)-*l*-PDMS (solid lines) and PNP4A-*l*-PDMS polymer conetworks without Zn(II) (dashed lines) at a strain rate of 10 mm min^{-1}: Pristine samples (red), samples after scratch damage (black), and sample after healing of scratches at 120°C for 16 hours (blue).

In conclusion, *metallo*-supramolecular polymer conetworks of poly(N-(pyridin-4-yl)acrylamide)-l-polydimethylsiloxane loaded with $ZnCl_2$ were synthesized from PPFPA-l-PDMS activated ester precursor networks. Phase-separated nanostructured morphologies of interconnected PDMS domains surrounded by a continuous PNP4A phase were evidenced by AFM analysis. Loading of $ZnCl_2$ into the APCNs supramolecularly cross-linked the PNP4A phase, which improved the mechanical properties of the material. The ability of the polymer conetwork to heal scratches was demonstrated in addition to the recovery of mechanical properties. Since APCNs are optical transparent, this kind of materials could find application for self-healing coating for electronic devices and displays, in addition the loaded metal complexes would enlarge their functionality towards fouling release, antibacterial polymer films and catalytic active surfaces.

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