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Zhang, P.; Behl, M.; Peng, X.; Balk, M.; Lendlein, A.:
Chemoresponsive Shape-Memory Effect of Rhodium–Phosphine Coordination Polymer Networks.
In: Chemistry of Materials. Vol. 31 (2019) 15, 5402 - 5407.

First published online by ACS: 26.06.2019

https://dx.doi.org/10.1021/acs.chemmater.9b00363

Chemo-responsive Shape-Memory Effect of Rhodium-phosphine Coordination Polymer Networks

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Abstract: Chemo-responsive polymers are of technological significance for smart sensors or systems capable of molecular recognition. An important key requirement for these applications is the material's structural integrity after stimulation. We explored whether covalently crosslinked metal ion-phosphine coordination polymers (MPN) can be shaped into any temporary shape and are capable to recover from this upon chemo-responsive exposure to triphenylphosphine (Ph_3P) ligands whereas the MPN provide structural integrity. Depending on the metal ion concentration used during synthesis of the MPN, the degree of swelling of the

[†] Deceased

coordination polymer networks could be adjusted. Once the MPN was immersed into Ph_3P solution, the reversible ligand-exchange reaction between the metal ions and the free Ph_3P in solution causes a decrease of the coordination crosslinks density in MPN again. The Ph_3P treated MPN was able to maintain its original shape, indicating a certain stability of shape even after stimulation. In this way, chemo-responsive control of the elastic properties (increase in volume and decrease of mechanical strength) of the MPN was demonstrated. This remarkable behavior motivated us to explore whether the MPN are capable of a chemo-responsive shape-memory effect. In initial experiments shape fixity of around 60% and shape recovery of almost 90% were achieved when the MPN was exposed to Ph_3P in case of rhodium. Potential applications for chemo-responsive shape-memory systems could be shapeable semiconductors e.g. for lighting or catalysts, which provide catalytic activity on demand.

Introduction

Stimuli-responsive polymers (SRPs) are capable to change their state in response to an external stimulus such as temperature, light, mechanical force, or chemical agents.[1-4] Various mechanisms (including phase transition, alteration in solubility, bond cleavage, formation of chemical bonds, or variation in molecular conformation) have been followed to achieve stimuli-responsibility in different types of SRPs.[1,5-9] These mechanisms can be classified by chemical or physical changes. Changes, which can be triggered by chemical agents, can enable chemo-responsiveness.[8,10] The rational design of chemo-induced chemical/physical changes in polymer systems (CRPs) is a key element to promote the development of SRPs.[2,11-14]

Metal-phosphine coordination bonds (MPCBs), as an important class of supramolecular interactions, have been widely utilized to build emission materials or semi-conductive materials because of the metal-ligand charge transfer transition.[15-17] Considering the dynamic reversibility (ligand-exchange kinetics),[18] these MPCB may also provide the opportunity to design CRPs.

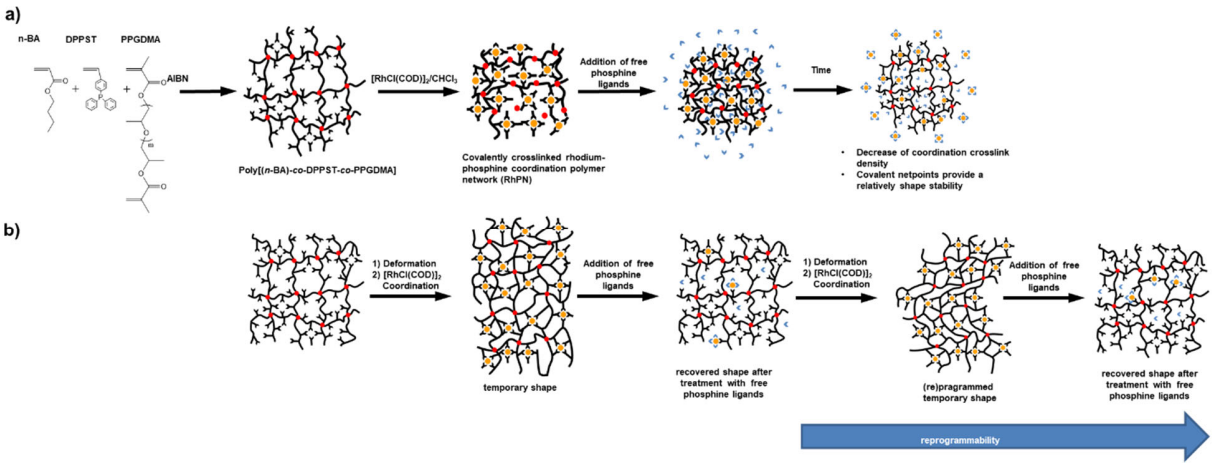
Shape-memory polymers provide the capability to be programmed into any application relevant shape from which they recover once a suitable stimulus has been applied. Heat, light, and alternating magnetic fields have been realized as stimuli. In swollen shape-memory systems, shape-memory hydrogels, sensitivity towards heat or change of pH could be implemented. E.g. a light-sensitive shape-memory effect could be realized by an elastic polymer network containing grafted cinnamylidene acetic acid moieties, which were capable to form additional covalent crosslinks once irradiated with suitable wavelengths and by doing so, are capable to fix a temporary shape. These covalent crosslinks could be cleaved again causing the elastic recovery to the original shape, when irradiated with light of other suitable wavelengths.

Inspired by the above-mentioned background, we explored, whether a polymer network containing MPCB as chemically sensitive crosslinks is capable of a chemo-responsive shape-memory effect upon treatment with phosphine ligands. We hypothesized that upon immersing the MPCB-based polymer network (MPN) into a solution of free phosphine ligands, the MPCB in the polymer network could undergo an exchange reaction, in which the metal ions are capable to coordinate with the free phosphine ligands in solution. This exchange reaction could cause a metal ion transfer/release from polymer network into the surrounding solution and hence a decrease of crosslink density in the polymer network. However, according to our hypothesis, if

the MPN would contain only MPCB as sensitive coordination crosslinks, such MPN would be completely dissolved after treatment with phosphine ligands. The loss of structural integrity would limit the applications of MPN.

We addressed the structural instability of polymer networks consisting solely of coordination crosslinks by the introduction of covalent netpoints in the MPN. A covalently crosslinked metal ion-phosphine coordination polymer network was designed (MPN, Scheme 1a), in which the metal ion-phosphine coordination bonds (M-PCB) were employed as sensitive crosslinks providing dynamic reversibility, high coordination stoichiometry, and a relative high bond energy. We hypothesized that this concept represents a general approach. Therefore rhodium, iridium, and platinum were explored as as metal ions in this material system. According to their valences, each of those metal ions can coordinate four phosphine ligands with relatively high bond energy, e.g. for Rh-PCB it is 40 kcal·mol^{-1}.[18] Poly(*n*-butylacrylate) (P*n*-BA) was selected as the main component of the polymer backbone to dilute the number of coordination sites,[19] which was copolymerized with 4-(diphenylphosphino)styrene (DPPST) and poly(propylene glycol) dimethacrylate (PPGDMA, M_n = 560 g·mol^{-1}) acting as crosslinker. We assumed that upon exposure to the free phosphine ligands, the MPN is capable of chemo-responsive change of elasticity (change of swelling behavior and modulus) as a result of the decrease of crosslink density, while at the same time the covalent netpoints of MPN maintain a certain stability of its shape (Scheme 1b). In addition to the reduction of the potential coordination sites, we speculated that the selection of P*n*-BA should enable the incorporation of another functionality in the material systems due to its high elasticity and chemical inertness. We aimed to gain a certain elastic deformability of the polymer network, which would be fixed by the additional

MCP. Based on this chemo-responsive change of elasticity we speculated that the MPN should be capable of a novel functionality, a chemo-responsive shape-memory effect, which reverses a programmed shape-deformation when exposed to free phosphine ligands. As illustrated in Scheme 1b, it was assumed that a new shape could be programmed after formation of the M-PCB based crosslinks in the deformed polymer network of this multifunctional material. Upon treatment with free phosphine ligands, the material in its programmed shape should be capable to undergo a shape-transformation because of the decrease in crosslink density. As in general the coordination sites of the polymer network should not be consumed and should be available for another coordination event, we explored whether the material could be reused for another shape-memory cycle. In this regard, we investigated the sensitivity, specificity and repeatability of this chemo-responsive shape-memory effect.



Scheme 1. a) Schematic representation of the synthesis of covalently crosslinked metal-ion—phosphine coordination polymer network (MPN) and its chemo-responsivity upon treatment with free phosphine ligands. b) Schematic illustration for programming and reprogramming as well as inducing a shape-transformation of MPN upon treatment with free phosphine ligands.

Results and Discussion

A series of poly[(*n*-BA)-*co*-DPPST-*co*-PPGDMA] networks was prepared, named as: PN-(*x*), in which *x* indicates the molar concentration of DPPST (diphenylphosphinostyrene) in the feed composition and was set to 5 mol%, 10 mol%, and 14 mol%, the PPGDMA feed was kept constant at 0.1 mol% (Table S1, S2, and Figure S1), see Experimental in Supp. Inf. for details . Afterwards, the PN-(*x*) was complexed with $[RhCl(COD)]_2$ (COD: 1,5-cyclooctadiene) in chloroform ($CHCl_3$) at a rhodium-to-phosphorous stoichiometry of 1:4, from which the targeted covalently crosslinked rhodium-phosphine coordination polymer network (named as: RhPN-(*x*)) was obtained as a dark

yellow colored swollen gel. ^{31}P-NMR spectra were recorded to confirm the formation of Rh-PCB in the RhPN-(*x*) (Figure S2, PN-(*5*) and RhPN-(*5*) were selected as representative samples). A signal at -7 ppm was observed in PN-(*5*), which can be assigned to the free DPPST ligands. In contrast, a signal at +28 ppm appeared in the ^{31}P-NMR spectra of RhPN-(*5*). This signal shift indicates the successful coordination reaction of DPPST ligands with rhodium ions. In electron microscope analysis using an EDX detector the distribution of the DPPST ligands as well as of the rhodium ions after complexation was observed. In general, the determination of the rhodium ions and of the phosphor were close to the detection limit of the detector. However, in an enlargement of the rhodium ion and phosphor distribution, the peaks indicating presence of rhodium ions and phosphor matched well, supporting complexation (Figure S3). The mechanism of complexation is also supported by an increase of netpoint density as determined by swelling experiments as well as from rheology (Table S2). In addition, the process of complexation is accompanied by a change of color from colorless to dark yellow / orange. As the gel were uniformly colored, a homogeneous distribution of the metal ion can be concluded.

By back weighing the $[RhCl(COD)]_2$ solution a P:Rh ratio between 4.6 ± 0.16 and 5.4 ± 0.23 was determined whereas in experiments using the back weighing data for the Rh content and the rheology data a P:Rh ratio between 3.7 ± 0.17 and 4.1 ± 0.29 was estimated (Table S3). Although both results fit very well with the nominal P:Rh ratio, the slightly higher value from the back weighing experiments can be explained by the fact that in this experiments the amount of rhodium that is complexed can be higher than the amount of rhodium that contributes to the crosslinks. From the rheology experiments only those units are measured, which contribute to

the crosslinking. As only two DPPST units of the polymer backbone are required to create a crosslink, this number is slightly lower than the nominal value of 4 ligands.

In the RhPN-(*x*), the Rh-PCB acted as sensitive crosslinks. The degree of swelling (*Q*) values of PN-(*x*) and RhPN-(*x*) in $CHCl_3$ were determined to confirm the change of crosslink density after rhodium coordination (Figure S4). The *Q* values of RhPN-(*x*) (ranging between 12 and 17) showed a significant decrease compared to the *Q* values of PN-(*x*) (ranging between 20 and 21), confirming an increase of crosslink density after formation of Rh-PCB. Additionally, the frequency-dependent storage moduli (*G'*) of the swollen PN-(*x*) and RhPN-(*x*) in $CHCl_3$ were examined with a rheometer to obtain a better understanding of the change of crosslink density in the polymer network (Figure S5). In the frequency range of 1-10 Hz, the *G'* values of RhPN-(*x*) exhibited a significant increase compared to those of PN-(*x*), which further verified the increase of crosslink density after coordination.

To demonstrate the chemo-responsivity of MPN-(*x*) upon treatment with free phosphine ligands, RhPN-(*x*) was immersed into $Ph_3P/CHCl_3$ solution (Ph_3P: triphenylphosphine), from which the Ph_3P treated RhPN-(*x*) (Ph_3P-RhPN-(*x*)) was obtained. After Ph_3P treatment, Ph_3P-RhPN-(*x*) displayed a shallow color as well as an increase in volume compared to RhPN-(*x*), confirming chemo-responsivity triggered by the phosphine ligands as shown for Ph_3P-RhPN-(*14*) in Figure 1a. Despite this increase in volume Ph_3P-RhPN-(*x*) was capable to maintain its original shape of a disc, which can be attributed to the existence of the covalent netpoints in RhPN-(*x*). Moreover, the $Ph_3P/CHCl_3$ solution showed a significant change of color after immersion of RhPN-(*x*) (exemplarily shown for RhPN-(*x*) in Figure S6). This result indicates that upon immersing the

RhPN-(*x*) into the Ph_3P solution, a ligand-exchange reaction of Rh-PCBs occurs and the rhodium ions in RhPN-(*x*) coordinate with the Ph_3P, causing rhodium ion release from RhPN-(*x*) into the $Ph_3P/CHCl_3$ solution and by this a decrease of coordination crosslinks density in RhPN-(*x*). Generality of the concept could be shown by chemo-responsiveness in polymer networks with PCBs based iridium or platinum, which were sensitive to PPh_3 as well (Figure S7). Cleavage of Rh-PCBs demands a free electron pair at the phosphor as demonstrated in selectivity experiments using diphenyl(2, 4, 6-trimethylbenzoyl)phosphine oxide and chlorodiphenylphosphine instead of PPh_3 (Figure S8). This chemo-responsive behavior was highly sensitive and could be observed e.g. in RhPN-(*10*) up to concentrations of PPh_3 as low as 0.0025 $mol \cdot L^{-1}$ /$CHCl_3$ (Figure S9).

The *Q* values of Ph_3P-RhPN-(*x*) in $Ph_3P/CHCl_3$ solution were monitored as a function of immersion time period to confirm the decrease of coordination crosslinks density in RhPN-(*x*) upon Ph_3P treatment. As shown in Figure 1b, the *Q* values of Ph_3P-RhPN-(*14*) displayed a rapid increase within the first 2 h after immersion and reached equilibrium after 6 h, indicating a time-dependent chemo-responsive behavior (decrease of coordination crosslinks density). At the start of the immersion, only Rh-DPPST complexes in RhPN-(*x*) and free Ph_3P ligands are present in the reaction system, from which the Rh ions in the Rh-DPPST complexes can rapidly coordinate with the free Ph_3P ligands, resulting in a fast increase of Rh-Ph_3P complex concentration. When the exchange reaction between Rh-DPPST and Rh-Ph_3P complexes reached equilibrium, the coordination crosslink density and the *Q* value of Ph_3P-RhPN-(*x*) became stable. Furthermore, the *Q* values of Ph_3P-RhPN-(*x*) immersed in solutions with varied Ph_3P concentrations were determined to explore the influence of the Ph_3P concentration on the chemo-responsivity of RhPN-(*x*) (Figure 1b). When Ph_3P-RhPN-(*14*) was immersed in Ph_3P solution with a high

concentration (0.1 mol·L^{-1}), a higher *Q* value was observed compared to Ph_3P-RhPN-(*14*) immersed in a Ph_3P solution of 0.01 mol·L^{-1}, indicating a faster coordination of Rh ions with the Ph_3P ligands in the high Ph_3P concentration solution. The same tendency of increase of *Q* values was also observed in Ph_3P-RhPN-(*10*) and Ph_3P-RhPN-(*5*) (Figure S10). Moreover, the *G'* values of the Ph_3P-RhPN-(*x*) in $Ph_3P/CHCl_3$ as function of immersion time period were also determined (Figure 1c and Figure S11). The decrease of *G*' values when the immersion period increased further demonstrated the reduction of the coordination crosslink density in Ph_3P-RhPN-(*x*) upon Ph_3P treatment.

The Ph_3P solution after immersion of RhPN-(*x*) was investigated by means of UV-VIS spectroscopy to confirm the formation of Rh-Ph_3P complexes (Figure S12). The Ph_3P solution after immersion of RhPN-(*x*) displayed a new absorbance band at 370 nm when compared to the absorbance spectrum before immersion of RhPN-(*x*). This new absorbance band can be assigned to the metal-ligand charge transfer transition of Rh-PCB and to the formation of Rh-Ph_3P complexes in Ph_3P solution. In addition, the formation of Rh-Ph_3P complexes results in the release of Rh ions from RhPN-(*x*) to the Ph_3P solution. The rhodium ion release was quantified (Figure 1d) from the value of UV-VIS absorbance of the Ph_3P solution at 370 nm (Figure S12) and the calibration curve (Figure S13). RhPN-(*14*) exhibited a rapid rhodium ion release within the first 2 h after immersion and reached equilibrium afterwards. This time-dependent tendency of rhodium ion release was in good agreement with the increase of *Q* values (Figure 1b). Moreover, it was observed that RhPN-(*14*) immersed in a 0.1 mol·L^{-1} Ph_3P solution exhibited a higher rhodium ion release compared to that immersed in a 0.01 mol·L^{-1} Ph_3P solution, further verifying that the high Ph_3P concentration is capable to accelerate the ligand exchange of Rh-PCB.

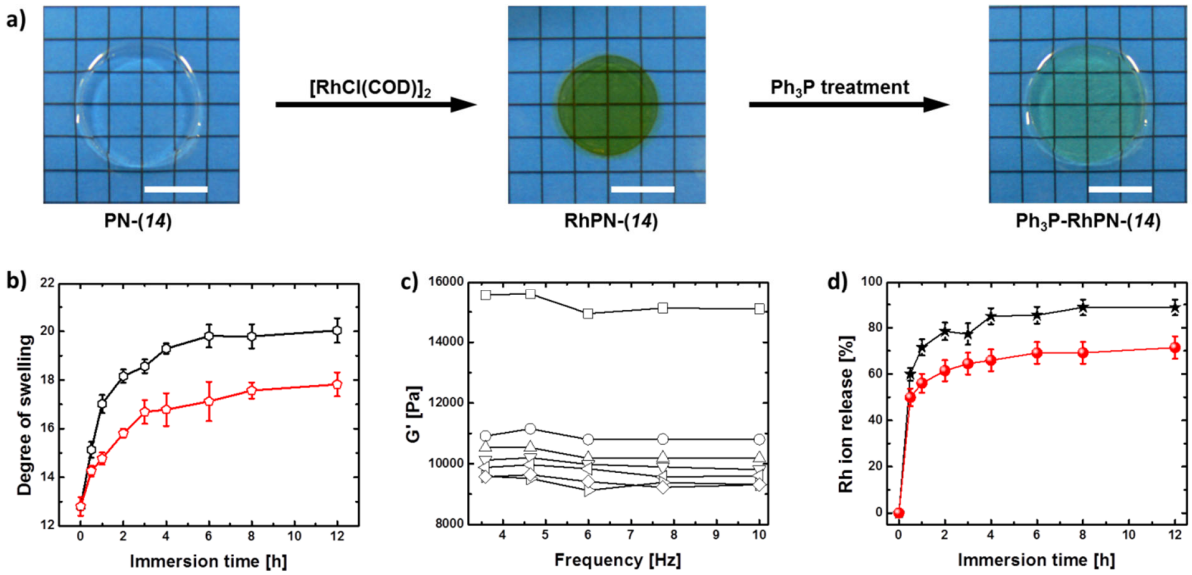


Figure 1. a) Photographs of PN-(*14*), RhPN-(*14*), and Ph_3P-RhPN-(*14*) (immersion in 0.1 mol·L^{-1} $Ph_3P/CHCl_3$ solution for 12 h). All scale bars (white solid line) are 10 mm. b) Degree of swelling of Ph_3P-RhPN-(*14*) in $Ph_3P/CHCl_3$ solutions as a function of immersion time. Black hexagon: 0.1 mol·L^{-1} $Ph_3P/CHCl_3$ solution, red pentagon: 0.01 mol·L^{-1} $Ph_3P/CHCl_3$ solution. c) Frequency-dependent storage moduli of Ph_3P-RhPN-(*14*) in 0.1 mol·L^{-1} $Ph_3P/CHCl_3$ solution at different immersion time periods (*t*). Square: *t* = 0 h; Circle: *t* = 1 h; Up triangle: *t* = 2 h; Down triangle: *t* = 4 h; Left triangle: *t* =6 h; Right triangle: *t* = 8 h; Diamond: *t* = 12 h. d) Rh ion release of Ph_3P-RhPN-(*14*) in $Ph_3P/CHCl_3$ solutions. Black star: 0.1 mol·L^{-1} $Ph_3P/CHCl_3$ solution, red sphere: 0.01 mol·L^{-1} $Ph_3P/CHCl_3$ solution.

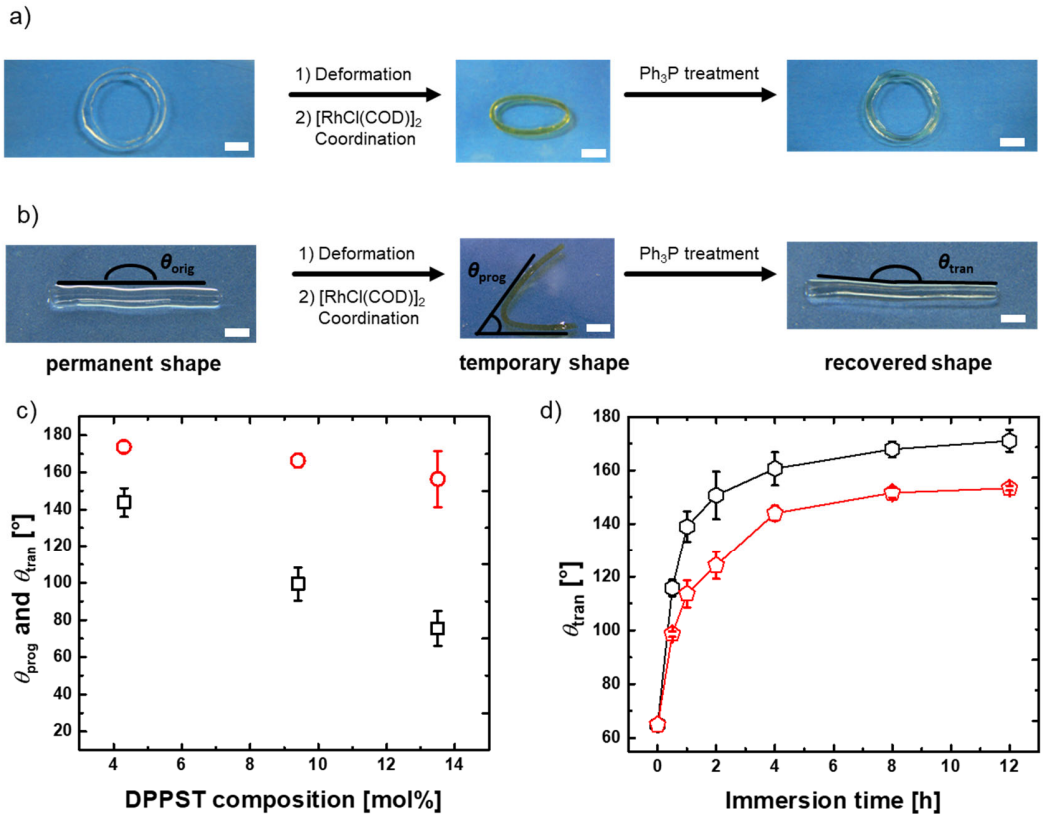


Figure 2. a) Photographs of a circular shaped sample from RhPN-(*14*) to demonstrate the programmed shape-transformation induced by Ph_3P ligands. All scale bars (white solid line) are 5 mm. b) Bending test to demonstrate the programmed shape-transformation of a bar-shaped sample from RhPN-(*14*). All scale bars (white solid line) are 5 mm. c) Angle after programming (θ_{prog}, square) and angle after shape-transformation (θ_{tran}, circle, obtained by immersing RhPN-(*x*) in its temporary shape in a 0.1 mol·L^{-1} Ph_3P solution for 12 h) of RhPN-(*5*), RhPN-(*10*), and RhPN-(*14*). d) Time-dependent θ_{tran} values of RhPN-(*14*) immersed in 0.1 mol·L^{-1} $Ph_3P/CHCl_3$ solution (hexagon) and in 0.01 mol·L^{-1} $Ph_3P/CHCl_3$ solution (pentagon).

To investigate the chemo-responsive shape-memory effect of RhPN-(*x*), we explored whether RhPN-(*x*) is capable of a programmed shape-transformation induced by the presence of Ph_3P. It was assumed that a new shape could be programmed after formation of Rh-PCBs based crosslinks in a deformed PN-(*x*), and this programmed shape is capable of a shape shift towards the original shape (before programming) upon treatment with the Ph_3P. As shown in Figure 2a and 2b, a new programmed shape was obtained after a deformed PN-(*14*) was coordinated by $[RhCl(COD)]_2$ and the programmed sample underwent the shape shift towards the original straight strip of PN-(*14*) after immersion in Ph_3P solution (0.1 $mol \cdot L^{-1}$) for 12 h, confirming the programmed shape shift of RhPN-(*x*) caused by the decrease of coordination crosslink density. A bending test was performed to quantify the efficiency of deformation fixation of RhPN-(*x*) after programming and the capability of shape-transformation of RhPN-(*x*) after Ph_3P treatment (Figure 2b). A straight strip (original angle 180°, θ_{orig}) of the PN-(*x*) was folded to an angle 0° under application of an external force. Afterwards, the deformed PN-(*x*) was placed in $[RhCl(COD)]_2/CHCl_3$ solution at ambient temperature for 12 h while the external force was still applied. Finally, the external force was removed and then the angle after programming (θ_{prog}) of the strip was determined. The sample in its programmed shape was immersed into $Ph_3P/CHCl_3$ solution for 12 h, from which the angle after shape-transformation (θ_{tran}) was recorded. The lower θ_{prog} indicates a better efficiency of deformation fixation of RhPN-(*x*) after programming, while a higher θ_{tran} suggests a better capability of shape-transformation of RhPN-(*x*) upon treatment with Ph_3P. As shown in Figure 2c, the values of θ_{prog} exhibited a significant decrease (from 143° to 65°) with the increase of molar concentration of DPPST in polymer network (from 5 mol% to 14 mol%), which can be attributed to the high molar concentration of DPPST enabling high coordination

crosslink density in RhPN-(*x*). Furthermore, all programmed samples of RhPN-(*x*) showed high θ_{tran} values (around 170°, which are almost the θ_{orig} value) after treatment with Ph_3P, indicating a good capability of Ph_3P triggered shape shift. Moreover, the influence of Ph_3P concentration on the shape shift of RhPN-(*x*) was also investigated (Figure 2d). When the RhPN-(*x*) in its programmed temporary shape was immersed in a 0.1 $mol \cdot L^{-1}$ Ph_3P solution, a higher θ_{tran} value was observed compared to the network immersed in a 0.01 $mol \cdot L^{-1}$ Ph_3P solution, which can be attributed to the fast decrease of coordination crosslink density in RhPN-(*x*) upon immersion in high Ph_3P concentration solution. The repeatability of the programming was explored by subsequent exposure to $RhCl(COD)]_2/CHCl_3$ solution for fixing a new shape and recovery by exposure to PPh_3 solution. Depending on the DPPST amount within the polymer network as well as the concentration of the PPh_3 solution, in up to 3 cycles a shape fixation and recovery could be observed (Figure 3). In future experiments it may be investigated whether the unexpected decrease in fixation and recovery is caused by a lack of coordination sites as too less $RhCl(COD)]_2$ is able to diffuse into the polymer network or a saturation of PPh_3 occurs that impedes fixation of the temporary shape.

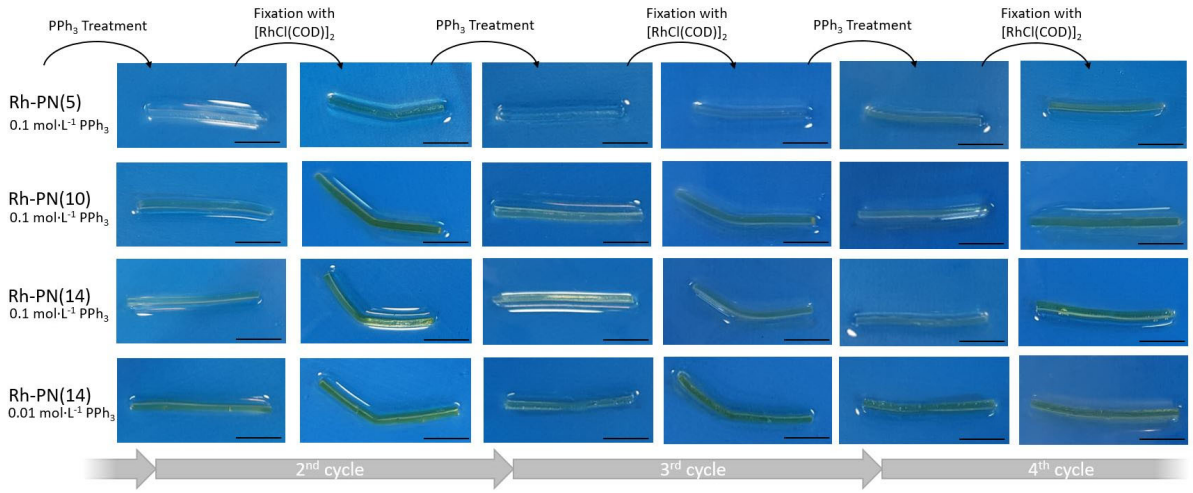


Figure 3. Bending tests to demonstrate the reprogrammability of the bar-shaped MPN, here RhPN-(*x*) with x = 5, 10, and 14, which were exposed to PPh_3 solution of 0.1 or 0.01 $mol \cdot l^{-1}$ solution. After recovery, the samples were deformed again and this new deformation was fixed again by addition $Rh[Cl(COD)]_2$. All scale bars (black solid lines) are 5 mm.

Conclusion

Covalently crosslinked metal-phosphine coordination polymers (MPN-(*x*): RhPN-(*x*), IrPN-(*x*), PtPN-(*x*)) were capable of chemo-responsive-induced shape shift and provided structural integrity upon treatment with Ph_3P. In MPN-(*x*), the M-PCBs acts as chemically sensitive crosslinks. Upon immersing the MPN-(*x*) into Ph_3P solution, the ligand-exchange of M-PCBs enables the metal ions in MPN-(*x*) to coordinate with the free Ph_3P ligands in solution, which causes the metal ion release from MPN-(*x*) into the Ph_3P solution and hence the decrease of coordination crosslinks density in MPN-(*x*). In this way, the MPN-(*x*) is capable of chemo-responsivity (increase

in volume, decrease of mechanical strength, and change of color). After Ph_3P treatment, the Ph_3P-MPN-(*x*) can maintain its original shape, indicating a certain structural integrity even after stimulation. The MPN-(*x*)s were also capable of a programmed shape shift when exposed to Ph_3P. Potential applications of RhPN-(*x*) could be intelligent switches, shape programmable semiconductors e.g. for lightning, catalyst systems able to provide catalysis on demand, or systems for Rh ion recycling (PN-(*x*) can coordinate with the Rh ions in waste solution, while the Rh ions could be released from the polymer network upon treatment with phosphine ligands).

Acknowledgements: This work has been financially supported by the Tianjin University - Helmholtz-Zentrum Geesthacht, Joint Laboratory for Biomaterials and Regenerative Medicine, which is financed by the German Federal Ministry of Education and Research (BMBF, Grant No. 0315496) and the Chinese Ministry of Science and Technology (MOST, 2008DFA51170), and the Helmholtz Association through programme-oriented funding.

Supporting Information available: Experimental part, determination of composition and gel content of PN-(x), formation of Rh-PCBs in RhPN-(x), and investigation of chemo-responsivity of RhPN-(x). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.XXXXX.

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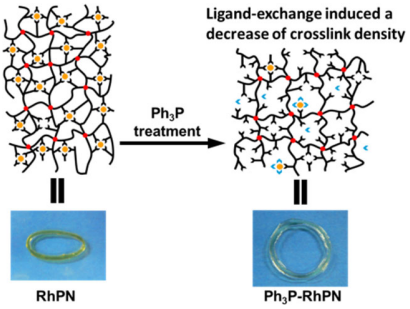
Chemo-responsive Shape-memory Effect of Rhodium-phosphine Coordination Polymer Networks

Pengfei Zhang, Marc Behl, Xingzhou Peng, Maria Balk, and Andreas Lendlein



A covalently crosslinked rhodium-phosphine coordination polymer network (RhPN) has been prepared, which is capable of chemo-responsive shape-shifts upon treatment with Ph_3P ligands.