Supporting information:

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

Pengfei Zhang$^{1,2,3}$, Marc Behl$^{1,3}$, Xingzhou Peng$^{1,2,3}$, Maria Balk$^{1}$ and Andreas Lendlein$^{1,2,3}$*

$^{1}$Institute of Biomaterial Science, Helmholtz-Zentrum Geesthacht, Kantstr. 55, 14513, Teltow, Germany

$^{2}$Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany

$^{3}$Tianjin University – Helmholtz-Zentrum Geesthacht Joint Laboratory for Biomaterials and Regenerative Medicine, Weijin Road 92, 300072 Tianjin (China) and Kantstr. 55, 14513 Teltow, Germany

*Corresponding author: E-Mail: andreas.lendlein@hzg.de

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† Deceased
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I. Experimental

No unexpected risks or significant hazards are known by the authors. The authors refer to the Material Safety Data Sheets and the technical description of the instruments for safe handling of chemicals and devices used in this reported work.

Materials

\( n \)-Butyl acrylate (\( n \)-BA) (purity \( \geq 99.5\% \)), chloro(1,5-cyclooctadiene)rhodium(I) dimer \([\text{RhCl(COD)}]_2\) (purity \( \geq 98\% \)), 4-(diphenylphosphino)styrene (DPPST) (purity 97%), polypropylene glycol dimethacrylate (PPGDMA), acetone-\( d^6 \) (purity \( \geq 99.9\% \) atom D), chloroform (\( \text{CHCl}_3 \)) (purity \( \geq 99.9\% \)), triphenylphospine (\( \text{Ph}_3\text{P} \)) (purity \( \geq 99\% \)), diphenyl(2, 4, 6-trimethylbenzoyl)-phosphine oxide (purity \( \geq 97\% \)) and chlorodiphenylphosphine (purity \( \geq 99\% \)) (all Sigma-Aldrich, Steinheim, Germany) were used without further purification. 2,2’-Azobis(2-methylpropionitrile) (AIBN) (purity \( \geq 98\% \)) (Fluka, Steinheim, Germany) was recrystallized from ethanol before use.

Characterization

\(^1\)H-NMR spectra were recorded at room temperature with a 500 MHz Avance spectrometer (Bruker GmbH, Karlsruhe, Germany) using acetone-\( d^6 \) as solvent. The spectra were referenced to the small amounts of the protonated species (\( \delta = 2.00 \) ppm) acting as internal standard.
The gel content \( (G) \) was determined gravimetrically according to equation (1), in which \( m_d \) is the mass of extracted sample and \( m_{iso} \) is the mass of unextracted sample. \( \text{CHCl}_3 \) was used as solvent for extraction.

\[
G = \frac{m_d}{m_{iso}} \times 100\% \quad (1)
\]

Degree of swelling \( (Q) \) was calculated according to equation (2), in which \( m_d \) is the mass of the dry sample, \( m_{sw} \) is the mass of sample swollen in \( \text{CHCl}_3 \), \( \rho_1 \) is the specific density of the \( \text{CHCl}_3 \), and \( \rho_2 \) is the specific density of the dry sample.

\[
Q = 1 + \rho_2 \times \left( \frac{m_{sw}}{m_d \times \rho_1} - \frac{1}{\rho_1} \right) \quad (2)
\]

\(^{31}\text{P}-\text{NMR}\) spectra were recorded with a Bruker 400 spectrometer (Bruker GmbH, Rheinstetten, Germany) using aceton-\( \text{d}^6 \) as solvent at 25 °C. \( \text{UV-VIS} \) absorption spectra were recorded with a Cary 100 spectrophotometer (Agilent, Darmstadt, Germany). Samples were placed in a quartz cuvette and scanned in the range of 300-800 nm at ambient temperature. Rheological investigations were performed on a Haake Rheowin Mars II (Thermo Scientific, Karlsruhe, Germany) with parallel plates (Platte PP20 Ti) of 2 cm diameter in chloroform at 25 °C. The amplitude sweep was firstly carried out to determine the linear viscoelasticity region. Afterwards all frequency sweep measurements were performed over a frequency range of 1 to 10 Hz at a constant shear strain \( (\gamma) \) of 0.001. At this strain, it can be ensured that all samples were in the linear viscoelastic region according to the amplitude sweep. Scanning Electron Microscopy (SEM) was conducted using a Quanta 250 FEG (FEI Deutschland GmbH, Dreieich, Germany) at an acceleration voltage of 6 kV in high vacuum and a BSE-detector. Samples were sputtered with
SEM images of the films were sputtered with carbon as conductive coating layer (~ 10 nm). The elemental composition of the samples was studied by energy dispersive X-ray (EDX) spectrometry detector (Octane Elect Plus, Ametek, Wiesbaden), coupled to the SEM instrument with a linescan of 320 dots (distance ~ 0.7 µm) along the crosssection of the sample and was analyzed with Genesis Software.

**Synthesis of poly[(n-BA)-co-DPPST-co-PPGDMA] network (PN-(x))**

A mixture of n-BA, DPPST, PPGDMA, and AIBN was injected between two glass plates separated by a 0.5 mm Teflon™ spacer (feed of monomers were listed in Table S1), and afterwards polymerized at 70 °C for 8 h. The obtained poly[(n-BA)-co-DPPST-co-PPGDMA] network (PN-(x)) was extracted with CHCl₃ for 12 h and dried under vacuum at ambient temperature for 48 h until constant weight was achieved. The composition of the PN-(x) was determined by $^1$H-NMR, according to the integrals of the signals at $\delta = 3.70$-$4.10$ ppm (-O-CH$_2$- protons from n-BA) and the signals at $\delta = 6.90$-$7.65$ ppm (benzene rings from DPPST).

**Table S1. Monomer feed for synthesis of PN-(x).**

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>PN-(5)</td>
<td>0.95</td>
<td>0.05</td>
<td>0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>PN-(10)</td>
<td>0.90</td>
<td>0.10</td>
<td>0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>PN-(14)</td>
<td>0.86</td>
<td>0.14</td>
<td>0.001</td>
<td>0.005</td>
</tr>
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</table>
Synthesis of covalently crosslinked rhodium-phosphine coordination polymer network (RhPN-(x))

The swollen PN-(x) sample was immersed into 20 mL [RhCl(COD)]$_2$/chloroform solution at ambient temperature for 12 h, from which a dark yellow colored RhPN-(x) was obtained. The required amount of [RhCl(COD)]$_2$ to complex PN-(x) was calculated according to equation (3). $M_{\text{Rh}}$ is the molecular weight of [RhCl(COD)]$_2$, $M_{\text{BA}}$ is the molecular weight of $n$-BA, $M_{\text{DPPST}}$ is the molecular weight of DPPST, and $M_{\text{PPGDMA}}$ is the molecular weight of PPGDMA. $C_{\text{DPPST}}$ is the molar concentration of DPPST in PN-(x) (in mol%), $C_{\text{BA}}$ is the molar concentration of $n$-BA in PN-(x) (in mol%), $C_{\text{PPGDMA}}$ is the molar concentration of PPGDMA in PN-(x) (constant 0.1 mol%), and $m_d$ is the mass of the dry PN-(x) sample (in g), the parameter $8$ results from the metal-to-phosphorous stoichiometry (1:4) and the molecular structure of [RhCl(COD)]$_2$.

$$m_{\text{Rh}} = \frac{M_{\text{Rh}} \times C_{\text{DPPST}} \times m_d}{8 \times (C_{\text{DPPST}} \times M_{\text{DPPST}} + C_{\text{BA}} \times M_{\text{BA}} + C_{\text{PPGDMA}} \times M_{\text{PPGDMA}})} \quad (3)$$

Chemo-responsive experiment of RhPN-(x)

RhPN-(x) samples were immersed into the Ph$_3$P/CHCl$_3$ solutions (Ph$_3$P concentration: 0.1 mol·L$^{-1}$ or 0.01 mol·L$^{-1}$) at ambient temperature for 12 h, from which the Ph$_3$P treated RhPN-(x) (Ph$_3$P-RhPN-(x)) were obtained.

Selectivity experiments with metal salts based on iridium and platinum

The swollen PN-(x) sample was folded to an angle of 0° under application of an external force. Afterwards, the deformed PN-(x) strip was immersed into 20 mL of a metal salt solution
([IrCl(COD)]_2/chloroform or [PtCl_2(COD)]/chloroform solution, utilized amount of metal salt was calculated in accordance to equation 3) at ambient temperature for 12 h while application of external force was maintained. When the external force was removed, IrPN-(x) or PtPN-(x) was obtained. In the shape-transformation experiment, the sample in its programmed shape was immersed into Ph_3P/CHCl_3 solution for 12 h. The directed movement of the material was documented via photographical pictures.

**Selectivity experiments with phenyl phosphine components**

The swollen RhPN-(x) samples in their programmed state (folding of the material to an angle of 0° and fixation by means of [RhCl(COD)]_2 addition) were immersed into a phenyl phosphine/CHCl_3 solution for 12 h (as phenyl phosphine component diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide or chlorodiphenylphosphine in a concentration of 0.1 mol·L^{-1} was used).

**Cyclic bending tests to quantify the repeatability of chemo-responsiveness**

Cyclic bending tests were performed on the series of RhPN-(x) polymer networks according to the procedure described for the quantification of the shape-transformation. Here, after addition of the Ph_3P/CHCl_3 solution (recovery process), the resulting polymer network was reprogrammed by refolding to an angle of 0° under application of an external force, was fixed with the [RhCl(COD)]_2/chloroform solution, and the shape shift was again obtained after addition of the Ph_3P/CHCl_3 solution.
UV-VIS calibration curve of Rh-Ph₃P complex in Ph₃P/CHCl₃ solution for calculation of Rh ion release

The immersion of the RhPN-(x) into the Ph₃P/CHCl₃ solution caused the release of Rh ion from the RhPN-(x) into the Ph₃P/CHCl₃ solution by Rh-Ph₃P complexes. Therefore, to quantify the rhodium ion release, the UV-VIS calibration curve of Rh-Ph₃P complex in Ph₃P/CHCl₃ solution (Ph₃P concentration: 0.1 mol·L⁻¹ or 0.01 mol·L⁻¹) was created. Here, the preparation of UV-VIS calibration curve of Rh-Ph₃P complexes in 0.1 mol·L⁻¹ Ph₃P/CHCl₃ solution is described as an example: a series of 0.1 mol·L⁻¹ Ph₃P/CHCl₃ solutions containing various concentrations of Rh-Ph₃P complex (Rh concentration: 0, 5.0×10⁻⁵, 1.0×10⁻⁴, 1.5×10⁻⁴, and 2.0×10⁻⁴ mol·L⁻¹) was prepared by mixing 5.0 mL Ph₃P/CHCl₃ solution (0.2 mol·L⁻¹) and 5.0 mL [RhCl(COD)]₂/CHCl₃ solutions containing different [RhCl(COD)]₂ concentrations (0, 0.025, 0.05, 0.075, and 0.1 μg·mL⁻¹, respectively). The mixed solutions were shaken for 40 min to ensure the complete coordination of the rhodium ions with Ph₃P and afterwards the UV-VIS spectra of the solutions were recorded. Finally, the calibration curve was determined from the molar concentration of rhodium ion (C) and its corresponding UV-VIS absorbance at 370 nm (Abs). The UV-VIS calibration curve of Rh-Ph₃P complexes in 0.01 mol·L⁻¹ Ph₃P/CHCl₃ solution was prepared by the same method. As shown in Figure S9, the calibration curve of Rh-Ph₃P complexes in 0.1 mol·L⁻¹ Ph₃P solution is: \( \text{Abs} = 4010 \cdot C + 0.0108 \) \( (R^2 = 0.9996) \) and in 0.01 mol·L⁻¹ Ph₃P solution is: \( \text{Abs} = 3401 \cdot C + 0.0071 \) \( (R^2 = 0.9994) \).
Calculation of the rhodium ion release

The UV-VIS absorbance at 370 nm (Abs) of Ph₃P/CHCl₃ solution after immersion of RhPN-(x) was monitored by UV-VIS spectra. The amount of Rh-Ph₃P complexes in Ph₃P/CHCl₃ solution after immersion of RhPN-(x) was determined by the Abs of UV-VIS spectra according to the calibration curve. The rhodium ion release from RhPN-(x) to Ph₃P/CHCl₃ solution can be calculated according to equation (4). C is the concentration of Rh-Ph₃P complexes in Ph₃P/CHCl₃ solution, calculated from the calibration curve. Vₚ is the volume of Ph₃P/CHCl₃ solution. n_Rh ion is the amount of substance of rhodium ions in RhPN-(x), and can be calculated from equation (5).

\[
\text{Rhodium ion release} = \frac{C \times V_s}{n_{Rh \text{ ion}}} \times 100\% \quad (4)
\]

\[
n_{Rh \text{ ion}} = \frac{2 \times m_{Rh}}{M_{Rh}} \quad (5)
\]

The \(m_{Rh}\) and \(M_{Rh}\) are obtained from equation (3), parameter 2 results from the molecular structure of [RhCl(COD)]₂.

Bending test to quantify the programmed shape-transformation of RhPN-(x)

A straight strip (angle 180°) of the swollen PN-(x) was folded to an angle 0° under application of an external force. Afterwards, the deformed PN-(x) strip was placed in [RhCl(COD)]₂/CHCl₃ solution (the amount of [RhCl(COD)]₂ was calculated according to equation 3) at ambient temperature for 12 h while application of external force was maintained. Finally, the external force was removed and the angle after programming (\(\theta_{prog}\)) of the strip was determined. In the shape-transformation experiment, the sample in its programmed shape was immersed into
Ph₃P/CHCl₃ solution for 12 h, from which the angle after shape-transformation (θ_{tran}) was recorded.

**General description of errors analysis**

Data were reported as mean value ± standard deviation. The standard deviation was obtained by repeating each test three times.
II. Composition and gel content of PN-(x)

Figure S1. $^1$H-NMR spectra of PN-(5) in acetone-d$_6$.

![NMR spectrum]

Table S2. Monomer composition and gel content (G) of PN-(x).

<table>
<thead>
<tr>
<th>Sample-ID</th>
<th>$C_{\text{DPPST}}$</th>
<th>G $^b)$</th>
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</thead>
<tbody>
<tr>
<td>PN-(5)</td>
<td>4.3 ± 0.1</td>
<td>92 ± 2</td>
</tr>
<tr>
<td>PN-(10)</td>
<td>9.4 ± 0.1</td>
<td>89 ± 2</td>
</tr>
<tr>
<td>PN-(14)</td>
<td>13.5 ± 0.1</td>
<td>94 ± 1</td>
</tr>
</tbody>
</table>

$^a)$ $C_{\text{DPPST}}$ is the molar concentration of DPPST in PN-(x), which was calculated from the ratio between the integrals of -O-CH$_2$- protons at δ = 3.70-4.10 ppm and those of benzene rings at δ = 6.90-7.65 ppm in $^1$HNMR spectra. The determined $C_{\text{DPPST}}$ were in good agreement with the molar concentration of the monomer feeds. $^b)$ The G values of PN-(x) were determined by equation (1).

III. Formation of Rh-PCB in RhPN-(x)
Figure S2. $^{31}$P-NMR spectra of PN-(5) (black solid line) and RhPN-(5) (red solid line) in acetone-d$_6$.

Figure S3. Electron microscope analysis showing elemental distribution. White line: scan line, red: carbon, green: oxygen, magenta: phosphorous, dark green: chloride, cyan: rhodium a) PN-(5) before complexation. 250x enlargement, b) Rh-PN-(5) after complexation. 500x enlargement, c) enlargement of elemental distribution of b) for phosphorous and rhodium.
Figure S4. Degree of swelling of PN-(x) (black square) and RhPN-(x) (red circle) in CHCl₃.

Figure S5. Frequency-dependent storage moduli ($G'$) of the PN-(x) and RhPN-(x) in CHCl₃. Hollow square: PN-(5); solid square: RhPN-(5); hollow circle: PN-(10); solid circle: RhPN-(10); hollow up triangle: PN-(14); solid up triangle: RhPN-(14).
## Table S2. Netpoint density before and after complexation

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Netpoint density [mol·cm(^{-3})](^a))</th>
<th>Sample ID</th>
<th>Uptake of Rh-salt from solution [%]</th>
<th>Uptake of Rh-salt from solution [mol Rh·g(^{-1})]</th>
<th>Netpoint density [mol·cm(^{-3})](^a))</th>
<th>Increase of netpoint density caused by Rh complexation [mol·cm(^{-3})](^b))</th>
<th>Netpoint density caused by Rh complexation, dry state [mol·g(^{-1})](^c))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN(5)</td>
<td>1.87 ± 0.11 · 10(^{-6}) Rh-PN(5)</td>
<td>74.6 ± 2.3</td>
<td>6.81 ± 0.21 · 10(^{-5})</td>
<td>3.13 ± 0.13 · 10(^{-6})</td>
<td>1.26 ± 0.12 · 10(^{-6})</td>
<td>2.49 ± 0.23 · 10(^{-5})</td>
<td></td>
</tr>
<tr>
<td>PN(10)</td>
<td>1.98 ± 0.10 · 10(^{-6}) Rh-PN(10)</td>
<td>79.3 ± 2.7</td>
<td>1.36 ± 0.05 · 10(^{-4})</td>
<td>4.55 ± 0.16 · 10(^{-6})</td>
<td>2.57 ± 0.13 · 10(^{-6})</td>
<td>4.25 ± 0.27 · 10(^{-5})</td>
<td></td>
</tr>
<tr>
<td>PN(14)</td>
<td>1.92 ± 0.08 · 10(^{-6}) Rh-PN(14)</td>
<td>89.5 ± 1.9</td>
<td>2.07 ± 0.04 · 10(^{-4})</td>
<td>6.23 ± 0.18 · 10(^{-6})</td>
<td>4.31 ± 0.13 · 10(^{-6})</td>
<td>6.28 ± 0.22 · 10(^{-5})</td>
<td></td>
</tr>
</tbody>
</table>

\(^a)\) Determined by vc = G/R x T; samples swollen to equilibrium in chloroform
\(^b)\) Difference between netpoint density of PN(x) and RhPN(x), samples swollen to equilibrium in chloroform
\(^c)\) calculated by means of netpoint density caused by Rh in the swollen state and swelling / shrinkage behavior in chloroform

## Table S3. Ratio of complexation

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Mol P / g polymer network [mol·g(^{-1})](^a))</th>
<th>Mol Rh / g polymer network [mol·g(^{-1})](^b))</th>
<th>P : Rh ratio(^b))</th>
<th>Mol Rh / g polymer network [mol·g(^{-1})](^c))</th>
<th>P : Rh ratio(^c))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-PN(5)</td>
<td>3.6568·10(^{-4})</td>
<td>6.8·10(^{-5})</td>
<td>5.4</td>
<td>2.49·10(^{-5})</td>
<td>3.7</td>
</tr>
<tr>
<td>Rh-PN(10)</td>
<td>6.9077·10(^{-4})</td>
<td>13.6·10(^{-5})</td>
<td>5.1</td>
<td>4.25·10(^{-5})</td>
<td>4.1</td>
</tr>
<tr>
<td>Rh-PN(14)</td>
<td>9.4765·10(^{-4})</td>
<td>20.7·10(^{-5})</td>
<td>4.6</td>
<td>6.28·10(^{-5})</td>
<td>3.8</td>
</tr>
</tbody>
</table>

\(^a)\) determined by NMR
\(^b)\) determined by back weighting the rhodium salt solution after complexation
\(^c)\) determined from back weighting and rheology
IV. Chemo-responsivity of RhPN-(x)

Figure S6. Photographs of Ph$_3$P/CHCl$_3$ solution and CHCl$_3$ before (left) and after (right) the RhPN-(14) sample was immersed at room temperature into the Ph$_3$P/CHCl$_3$ solution and CHCl$_3$ for 8 hours.

Platinum complex: $\theta_{\text{prog}} = 72^\circ$ $\theta_{\text{trans}} = 178^\circ$
Iridium complex: $\theta_{\text{prog}} = 103^\circ$ $\theta_{\text{trans}} = 143^\circ$

Figure S7. Bending test to demonstrate the generality of the chemoresponsive MPN. Programmed shape-transformation of bar-shaped samples from PtPN-(10) and IrPN-(10) treated with Ph$_3$P.
Figure S8. Bending test to demonstrate the selectivity of the chemoresponsive system.

Programmed shape-transformation of bar-shaped samples from RhPN-(10) treated with solutions with concentrations of a) diphenyl(2, 4, 6-trimethylbenzoyl)phosphine oxide and b) chlorodiphenylphosphine.

\[ \text{Ph}_3 \text{BzPO}: \text{diphenyl(2, 4, 6-trimethylbenzoyl)phosphine oxide; } c = 0.1 \text{ mol L}^{-1} \]
\[ \text{Ph}_2 \text{PCl}: \text{chlorodiphenylphosphine; } c = 0.1 \text{ mol L}^{-1} \]
Figure S9. Bending test to explore the minimum concentration to induce shape recovery of bar-shaped samples from RhPN-(10). A noticeable recovery occurs up to concentrations of PPh3 of up to 0.0025 mol·L⁻¹/CHCl₃.

Figure S10. Degree of swelling of Ph₃P-RhPN-(x) in Ph₃P/CHCl₃ solutions as a function of immersion time period. Black hexagon: in 0.1 mol·L⁻¹ Ph₃P/CHCl₃ solution, red pentagon: in 0.01 mol·L⁻¹ Ph₃P/CHCl₃ solution. a) Ph₃P-RhPN-(10). b) Ph₃P-RhPN-(5).
Figure S11. Frequency-dependent storage moduli of Ph₃P-RhPN-(x) samples after immersion at room temperature in 0.1 mol∙L⁻¹ Ph₃P/CHCl₃ solution after different 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. a) Ph₃P-RhPN-(10). b) Ph₃P-RhPN-(5).

Figure S12. UV-VIS spectra of Ph₃P/CHCl₃ solution after immersion of RhPN-(14) at room temperature. Black solid line: $t = 0$ h; red solid line: $t = 0.5$ h; green solid line: $t = 1$ h; blue solid line: $t = 2$ h; cyan solid line: $t = 3$ h; magenta solid line: $t = 4$ h; purple solid line: $t = 6$ h; olive solid line: $t = 8$ h; orange solid line: $t = 12$ h. a) 0.1 mol∙L⁻¹ Ph₃P/CHCl₃ solution. b) 0.01 mol∙L⁻¹ Ph₃P/CHCl₃ solution.
Figure S13. a) UV-VIS calibration curve of Rh-Ph₃P complex in 0.01 mol·L⁻¹ Ph₃P/CHCl₃ solution. b) UV-VIS calibration curve of Rh-Ph₃P complex in 0.1 mol·L⁻¹ Ph₃P/CHCl₃ solution.