

Polymer and Colloid Highlights

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Zerivalent Metallocsupramolekulare Polymere als Vorläufer für Nanokomposite

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Nanocomposites can be prepared to combine the beneficial mechanical properties of polymers with the intriguing advanced functional properties of metallic nanoparticles (NPs), and such materials have gained wide-spread interest in fields such as catalysis or soft electronics.^[1] It would be advantageous for many applications to gain control over the spatial arrangement of NPs,^[2] but this has been very difficult to achieve by *in situ* methods that afford structured nanocomposites.^[3] To address this problem, we recently reported a novel type of metallocsupramolekulare polymer (MSP) with zerovalent metal–ligand complexes and its use as a precursor for metallic nanocomposites.^[4] Many examples of MSPs with ionic complexes have been previously investigated,^[5] and zerovalent metal–ligand complexes have been integrated into polymers,^[6] but the use of the latter as precursors to nanocomposite remained unexplored.

To prepare a suitable nanocomposite precursor, we used the telechelic macromonomer (**1**) with a poly(ethylene-*co*-butylene) (PEB) core that was functionalized at the termini with diphenylacetylene ligands (Fig. 1a). The ligand-exchange reaction between the ditopic macromonomer **1** and Pt⁰(styrene)₃ then led to chain-extension under the formation of MSP **2**. The reaction was complete after addition of stoichiometric quantities of Pt⁰(styrene)₃, and our detailed investigations showed that the zerovalent metal–ligand complexes are stable under ambient conditions. However, the complexes can be dissociated upon heating or through irradiation with ultraviolet light.^[4] After dissociation of the complexes, the polymer serves as a matrix that enables the nucleation of Pt clusters and stabilized their growth into nanoparticles (Fig. 1b,c), without the formation of larger agglomerates. Moreover, we demonstrated that UV light irradiation can also trigger the NP formation, and the level of control over the incorporation of NPs was greatly improved by localized UV irradiation.^[4] The developed approach allows producing nanocomposites with Pt-NPs without auxiliary reagents or the formation of by-products. At the same time, a high level of spatial control over the nanoparticle incorporation is gained, which could be useful for the use of such materials as soft electrodes or polymer-supported catalysts. The developed approach is, hence, expected to serve as an enabling technique with potential impact in a range of different fields.

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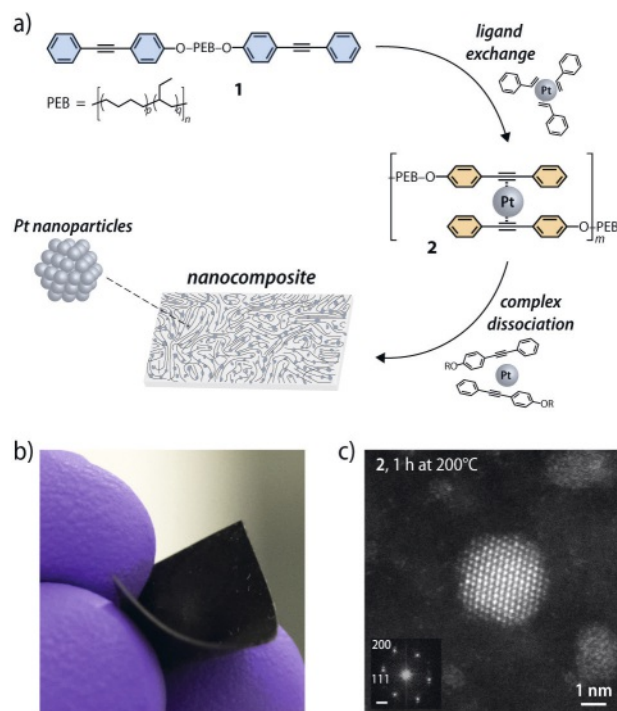


Fig. 1 a) Schematic illustration of the assembly of macromonomer **1** into the metallocsupramolekulare polymer **2** (with $p \approx 0.36$, $q \approx 0.64$, $n \approx 55$) through formation of bis(η^2 -alkyne)Pt⁰ complexes and linear chain-extension. The dissociation of **2** is triggered by heat or UV light and Pt-NPs are formed. b) Picture of a film of the nanocomposite that was prepared by heating **2** at 120 °C for 1 h. c) Scanning transmission electron microscopy image of a film of **2** after heating to 200 °C for 1 h. Fourier transform of the micrograph in the inset (scale bar = 2 nm⁻¹).

- [1] a) A. C. Balazs, T. Emrick, T. P. Russell, *Science* **2006**, *314*, 1107; b) J. Kao, K. Thorkelsson, P. Bai, B. J. Rancatore, T. Xu, *Chem. Soc. Rev.* **2013**, *42*, 2654.
- [2] a) M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, S. Minko, *Nat. Mater.* **2010**, *9*, 101; b) S. Sivaramakrishnan, P.-J. Chia, Y.-C. Yeo, L.-L. Chua, P. K. H. Ho, *Nat. Mater.* **2007**, *6*, 149; c) Y. Zhao, K. Thorkelsson, A. J. Mastroianni, T. Schilling, J. M. Luther, B. J. Rancatore, K. Matsunaga, H. Jinnai, Y. Wu, D. Poulsen, J. M. J. Fréchet, A. P. Alivisatos, T. Xu, *Nat. Mater.* **2009**, *8*, 979; d) A. K. Boal, F. Ilhan, J. E. DeRouchey, T. Thurn-Albrecht, T. P. Russell, V. M. Rotello, *Nature* **2000**, *404*, 746.
- [3] a) P. Xu, X. Han, B. Zhang, Y. Du, H.-L. Wang, *Chem. Soc. Rev.* **2014**, *43*, 1349; b) S.-W. Hsu, A. L. Rodarte, M. Som, G. Arya, A. R. Tao, *Chem. Rev.* **2018**, *118*, 3100; c) Q. Dong, Z. Meng, C.-L. Ho, H. Guo, W. Yang, I. Manners, L. Xu, W.-Y. Wong, *Chem. Soc. Rev.* **2018**, *47*, 4934.
- [4] L. M. Olachea, L. Montero de Espinosa, E. Oveisi, S. Balog, P. Sutton, S. Schrettli, C. Weder, *J. Am. Chem. Soc.* **2020**, *142*, 342.
- [5] S. W. Lee, J. R. Kumpfer, P. A. Lin, G. Li, X. P. A. Gao, S. J. Rowan, R. M. Sankaran, *Macromolecules* **2012**, *45*, 8201.
- [6] a) A. Kokil, C. Huber, W. R. Caseri, C. Weder, *Macromol. Chem. Phys.* **2003**, *204*, 40; b) M. Gianini, W. R. Caseri, U. W. Suter, *J. Phys. Chem. B* **2001**, *105*, 7399; c) K. P. Pernstich, M. Schenker, F. Weibel, A. Rossi, W. R. Caseri, *ACS Appl. Mater. Interfaces* **2010**, *2*, 639.

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