



Supporting Information

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# **Hierarchical Self-assembly of Complex Coacervate Core Micelles from Supramolecular Coordination Polymer and Diblock Copolymer**

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# Hierarchical Self-assembly of Complex Coacervate Core Micelles from Supramolecular Coordination Polymer and Diblock Copolymer

Yun Yan<sup>\*</sup>, Nicolaas A. M. Besseling, Arie de Keizer, Antonius T. M. Marcelis, Markus Drechsler, and Martien A. Cohen Stuart<sup>\*</sup>

## Experimental Section

### 1. Materials and methods:

#### Materials

The diblock copolymer poly(2-vinyl-N-methylpyridinium iodide)-b-poly(ethylene oxide) (PMVP<sub>41</sub>-b-PEO<sub>205</sub>) was quaternized with methyl iodide from poly(vinylpyridine)-b-poly(ethylene oxide) (Polymer Source, Mw/Mn = 1.03, Mw = 13.3 K). In a typical reaction,<sup>[S1]</sup> 1 g of diblock copolymer was dissolved in 35 ml DMF. Iodomethane (3 ml) was added, and the reaction was stirred under nitrogen for 48 h at 60 °C. Ether (110 ml) was added to precipitate the polymer (add until no more precipitation occurs). The precipitate was filtered and washed with ether (5 × 10 ml) to get a light-yellow powder. (With every washing step the polymer becomes less coloured, less sticky, and more powdery). Subsequently, the polymer was placed in a vacuum oven at 48°C to dry overnight. The degree of quaternization is higher than 90%.<sup>[S2]</sup>

The zinc(II)-1,11-bis(2,6-dicarboxypyridin-4-yloxy)-3,6,9-trioxaundecane metallo-supramolecules (Zn-L<sub>2</sub>EO<sub>4</sub> complex), is prepared according to literature.<sup>[S3]</sup> Piperazinebis(ethanesulfonic acid) (PIPES, 98%) is from Aldrich. Sodium hydroxide (NaOH) and zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) were of analytical grade. Bidistilled water was used throughout the experiments.

PMVP<sub>41</sub>-b-PEO<sub>204</sub>, L<sub>2</sub>EO<sub>4</sub>, and Zn(NO<sub>3</sub>)<sub>2</sub>, stock solutions were prepared in 20 Mm PIPES-NaOH buffer of pH 5.4 before mixing.

### **Methods:**

***Dynamic light scattering (DLS).*** Light scattering measurements were performed with an ALV light scattering-apparatus, equipped with a 400mW argon ion laser operating at a wavelength of 514.5 nm. A refractive index matching bath of filtered cis-decalin surrounded the cylindrical scattering cell, and the temperature was controlled at  $\pm 0.5$  °C using a Haake C35 thermostat. DLS measurements have been analyzed according to standard methods (method of cumulants using standard ALV software and CONTIN).

***Cryogenic transmission electronic microscope (Cryo-TEM).*** A few microliters of samples were placed on a bare copper TEM grid (Plano, 600 mesh), and the excess liquid was removed with filter paper. This sample was cryo-fixed by rapidly immersing into liquid ethane cooled to -170 to -180 °C in a cryo-box (Carl Zeiss NTS GmbH). The specimen was inserted into a cryo-transfer holder (CT3500, Gatan, Munich, Germany) and transferred to a Zeiss EM922 EFTEM (Zeiss NTS GmbH, Oberkochen, Germany). Examinations were carried out at temperatures around -180 °C. The TEM was operated at an acceleration voltage of 200 kV. Zero-loss filtered images were taken under reduced dose conditions (500-2000 e/nm<sup>2</sup>). All images were recorded digitally by a bottom-mounted CCD camera system (UltraScan 1000, Gatan) and processed with a digital imaging processing system (Digital Micrograph 3.9 for GMS 1.4, Gatan).

***Transmission electronic microscopy (TEM)*** A few microliters of diluted emulsion were placed on a fomvar coated copper TEM grid (Plano, 300 mesh), and the excess liquid was removed with filter paper. This sample was observed directly with JEOL100 (CX) operated at 80 kV.

## 2. Figures

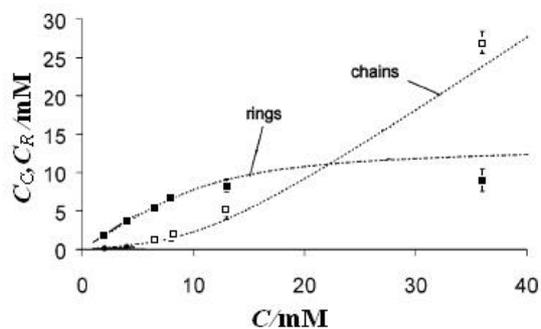


Figure S1: The concentrations of monomers in chains ( $C_C$ , ?) and rings ( $C_R$ , ! ) as a function of the monomer concentration of Zn-L<sub>2</sub>EO<sub>4</sub>(1:1ratio) at 298K, determined from the integrals of the peaks in <sup>1</sup>H NMR spectra. The curves refer to results of the theoretical model. See reference (S3) for the detailed information about this curve.

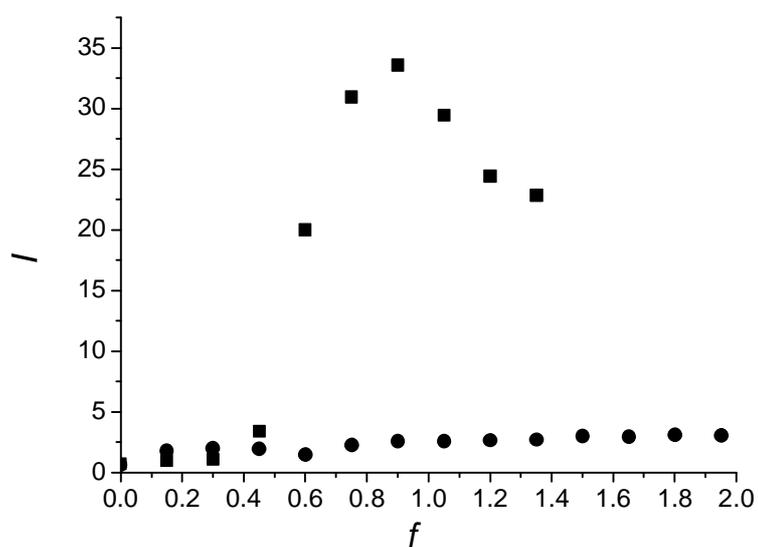


Figure S2: Variation of scattered light intensity with the mixing ratio  $f$ : Addition of Zn<sup>2+</sup> to the mixed solution of (L<sub>2</sub>EO<sub>4</sub> + PMVP<sub>41</sub>-b-PEO<sub>205</sub>) (!), where  $f = [\text{Zn}^{2+}]/[\text{L}_2\text{EO}_4]$ ; and addition of Zn-L<sub>2</sub>EO<sub>4</sub>-Zn to PMVP<sub>41</sub>-b-PEO<sub>205</sub> (?), where  $f = [\text{Zn-L}_2\text{EO}_4\text{-Zn}]/[\text{VP}^+]$ .

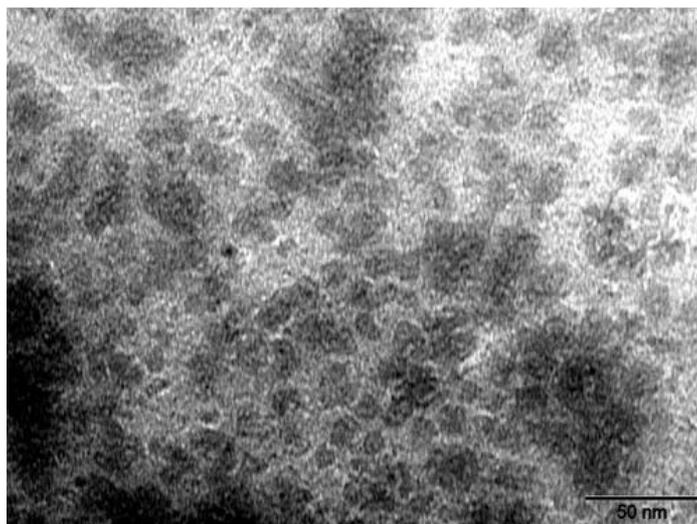


Figure S3. TEM image of Zn-L<sub>2</sub>EO<sub>4</sub>/PMVP<sub>41</sub>-b-PEO<sub>205</sub> mixed system (0.81% (wt%),  $f = 0.5$ ).

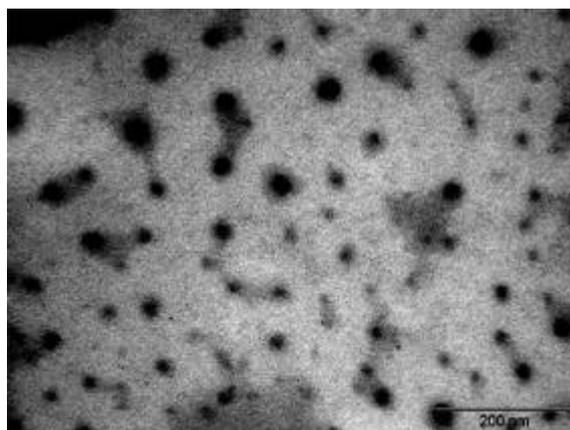


Figure S4. TEM image of Nd-L<sub>2</sub>EO<sub>4</sub>/PMVP<sub>41</sub>-b-PEO<sub>205</sub> mixed system (0.075% (wt%),  $f = 0.5$ ).

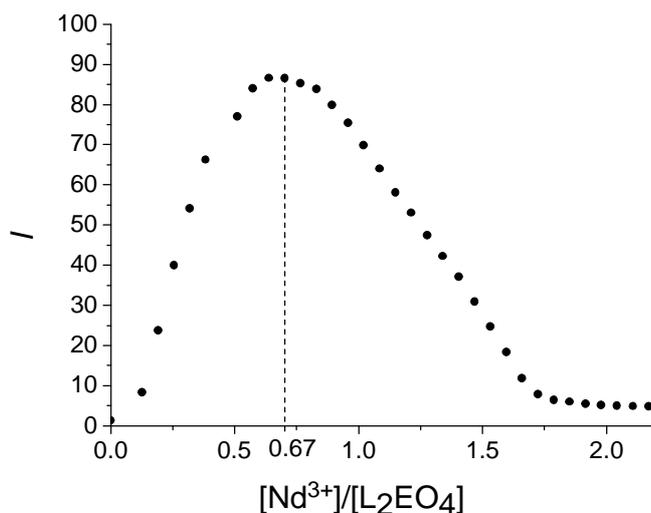


Figure S5. Variation of scattered light intensity with the molar mixing ratio of  $\text{Nd}^{3+}$  to  $\text{L}_2\text{EO}_4$  in the  $(\text{L}_2\text{EO}_4+\text{PMVP}_{41}\text{-b-PEO}_{205})$  mixed system. Due to the 9 coordination around  $\text{Nd}^{3+}$ , each coordination centre has overall three negative charges. Therefore, the maximum light intensity shows up at the molar mixing ratio of  $\text{Nd}^{3+}$  to  $\text{L}_2\text{EO}_4$  of 0.67.

## References:

- [S1]. M. Biesalski; D. Johannsmann; J. R uhe. *J. Chem. Phys.* **2004**, *120*, 8807-8814.
- [S2]. M. Biesalski and J. R uhe, *Macromolecules* **1999**, *32*, 2309-2316.
- [S3]. T. Vermonden, M. J. Van Steenberg, N. A. M. Besseling, A. T. M. Marcelis, W. E. Hennink, E. J. R. Sudh olter, M. A. Cohen Stuart *J. Am. Chem. Soc.* **2004**, *126*, 15802-15808.