Electronic Supplementary Material (ESI) for RSC Advances

# Cation-Sensitive Compartmentalization in Metallacarborane Containing Polymer Nanoparticles

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# CryoTEM micrographs of star-like copolymers

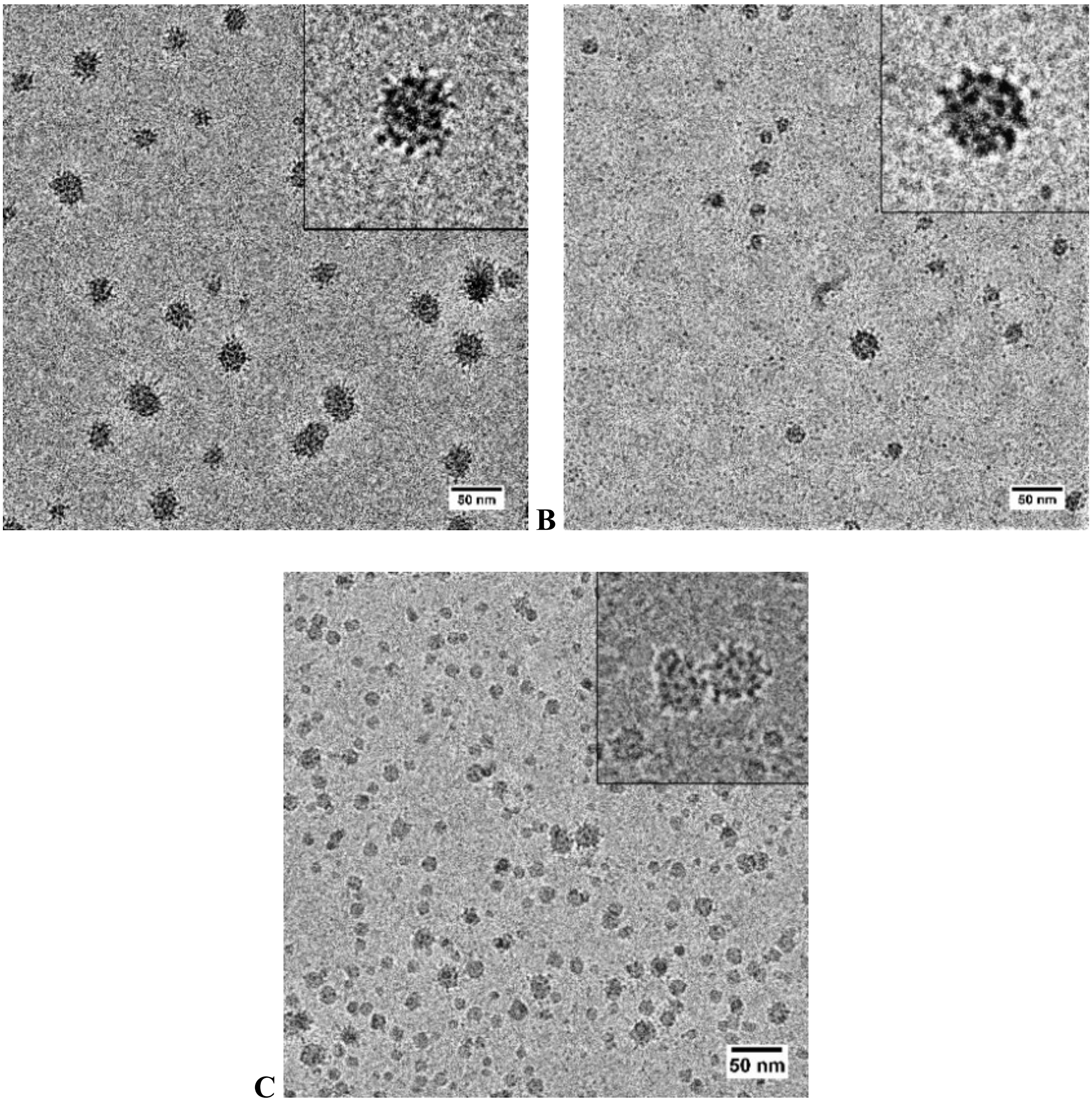
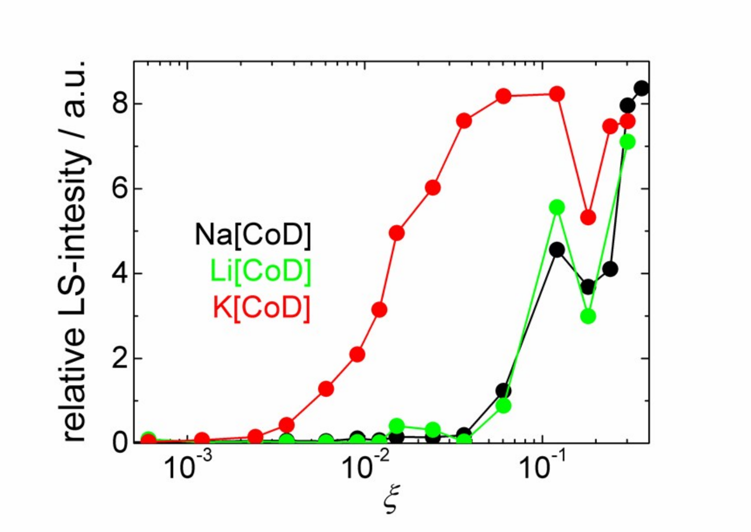
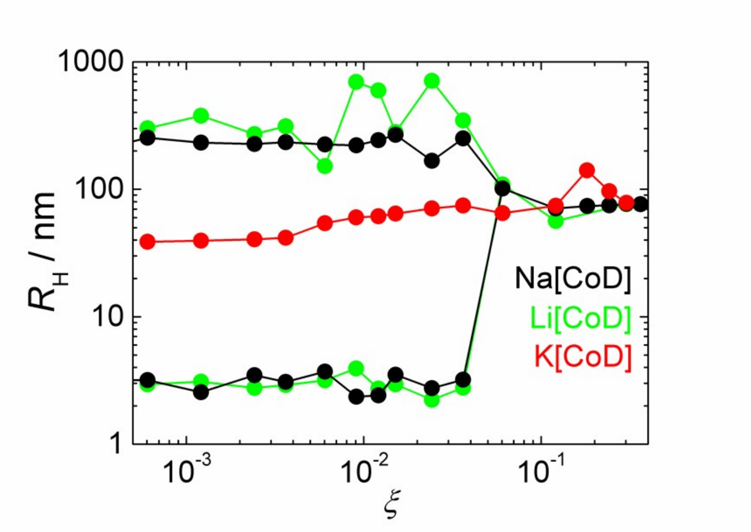



**Figure S1**. CryoTEM micrographs of (**A**) $[PEO\text{-}POX]_4$/Na[CoD] in 0.154 M NaCl, (**B**) $[PEO\text{-}POX]_4$/Li[CoD] in 0.154 M LiCl, and (**C**) $[PEO\text{-}POX]_4$/K[CoD] in 0.154 M KCl (polymer concentration 10 g/L).

# Light scattering and SANS analysis




**A**




**B**

**Figure S2** (**A**) Light scattering intensity and (**B**) hydrodynamic radius after addition of M[CoD] (c = 0.019 M) in 0.154 M MCl to PEO-POX (2g/L) in 0.154 M MCl solution, where M is Na (black), Li (blue), and K (red).

In Figure S2, there is a comparison of the relative LS-intensity and hydrodynamic radius, $R_H$, for Li- and K-systems with previously studied Na-one as functions of $\xi$, which is defined as [CoD]-to-number of polymer segments ratio. In all three cases, the formation of compact hybrid nanoparticle is accompanied by a substantial increase of LS-intensity. However, the nanoparticles in the K-medium appeared in earlier stages of titration than for the Na- and Li-systems. The $R_H$ *vs.* $\xi$ dependence (Figure S2B) in the K-medium has a different shape but the same mean size after saturation as compared to the Li- and Na-systems. Two modes in the unstable region merge into one close to the saturation point in the Na-medium and stable compact nanoparticles form as a result. Thus, LS-study indicates that counterions play a role in the process of nanoparticle formation. In this case, the presence of $K^+$ accelerates a formation of the compact nanoparticles.

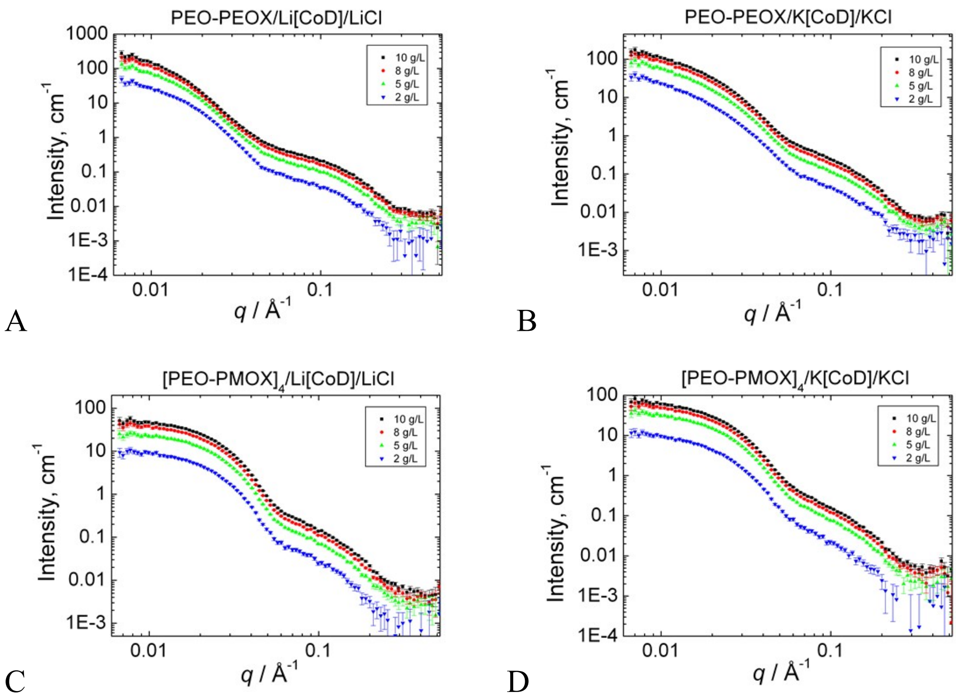



**Figure S3** SANS curves of (**A**) PEO-POX/Li[CoD] in 0.154 M LiCl, (**B**) PEO-POX/K[CoD] in 0.154 M KCl, (**C**) $[PEO\text{-}POX]_4$/Li[CoD] in 0.154 M LiCl, and (**D**) $[PEO\text{-}POX]_4$/K[CoD] in 0.154 M KCl. Polymer concentration was 10 g/L.

**Table S1** Results of SANS fitting of curves in Figure S3 extrapolated to zero angle, where $R_{g,1}$ and $R_{g,2}$ are radii of gyration of particle 1 and 2 in the "two particle" model; and $R_{sph}$ is radius of sphere, $R_c$ and $l_c$ are radius and length of cylinder in the "spheres and cylinders" model.

| **Sample** | **Fitting Model** | | | | |
|---|---|---|---|---|---|
| | **2 Particles** | | **Spheres with attached Cylinders** | | |
| | $R_{g,1}$ / nm | $R_{g,2}$ / nm | $R_{sph}$ / nm | $l_c$ / nm | $R_c$ / nm |
| PEO-POX/Li[CoD] | 14.86 | 2.80 | - | - | - |
| PEO-POX/K[CoD] | 14.26 | 1.59 | - | - | - |
| $[PEO\text{-}POX]_4$/Li[CoD] | - | - | 7.49 | 2.60 | 1.47 |
| $[PEO\text{-}POX]_4$/K[CoD] | - | - | 5.14 | 2.23 | 1.47 |

The SANS curves for the Li- and K-systems are shown in Figure S3 and the results of the fitting procedure in Table S1. A presence of two types of particles is clearly evident, where the large ones correspond to compact particles, and the small ones can be assigned to a mixture of compartments, M[CoD] micelles and small pre-aggregates. An absence of correlation peaks in SANS curves for nanoparticles with otherwise distinct compartmentalization indicates a low level of ordering of the compartments within the nanoparticles.

# Nanoparticles with the mix of cations

We also studied different combinations of counterions of PEO-POX/M[CoD] in MCl (M = Na, K or Li). The same amounts of Na[CoD] as in the standard experiments were added to 10 g/L polymer solutions in 0.154 M LiCl or KCl. Analytical concentration of $Na^+$ was thus 2.45 mM and 7.35 mM (respectively for increasing $\xi$). A comparison of the fraction of frozen polymer segments from NMR experiments for the Li-systems with added Na[CoD] or Li[CoD], and for the K-systems with added Na[CoD] or K[CoD], together with cryoTEM micrographs are shown in Figure S3:

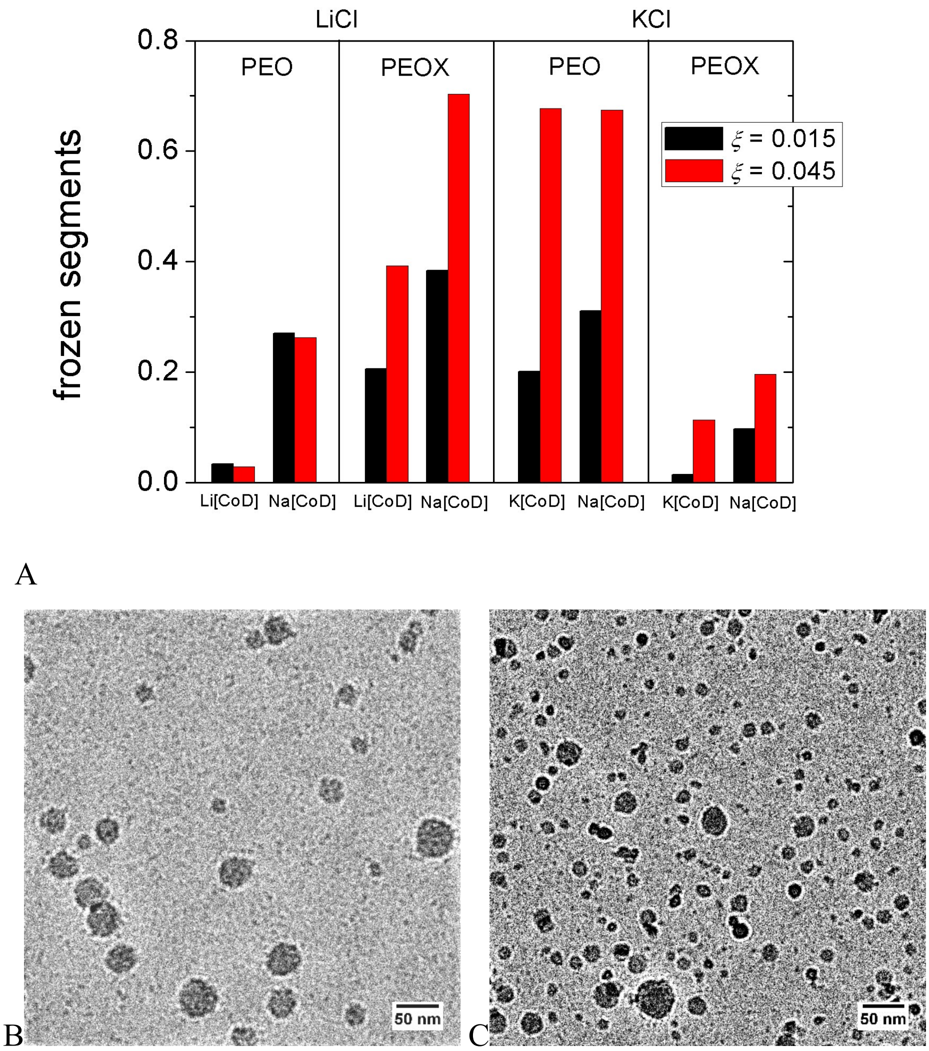



**Figure S4** (**A**) The fraction of frozen PEO-POX polymeric segments in 0.154 M LiCl and KCl differing in amount of M[CoD] (M = Na, K, or Li) as indicated with the graph calculated from a decrease of corresponding $^1$H NMR signals related to pure PEO-POX and *t*-butanol (internal standard). Cryo-TEM micrographs of (**B**) PEO-POX/Na[CoD] in 0.154 M LiCl, and (**C**) PEO-POX/Na[CoD] in 0.154 M KCl.

In Figure S4B,C cryoTEM micrographs of PEO-POX/Na[CoD] in 0.154 M LiCl and PEO-POX/Na[CoD] in 0.154 M KCl are shown, respectively. Both large and small particles are slightly larger than in solution with only one type of cation, compartments in lithium salt are less visible and even disappeared in KCl. Average diameter of small particles and compartments of Na[CoD] in LiCl was 6 nm (while for Li[CoD] in LiCl it is only 3.8 nm) and size of small particles of Na[CoD] in KCl was 7.8 nm (while for K[CoD] in KCl it is 4.9 nm).

# Titration of KCl, NaCl and LiCl to PEO-POX/Li[CoD] in LiCl nanoparticles

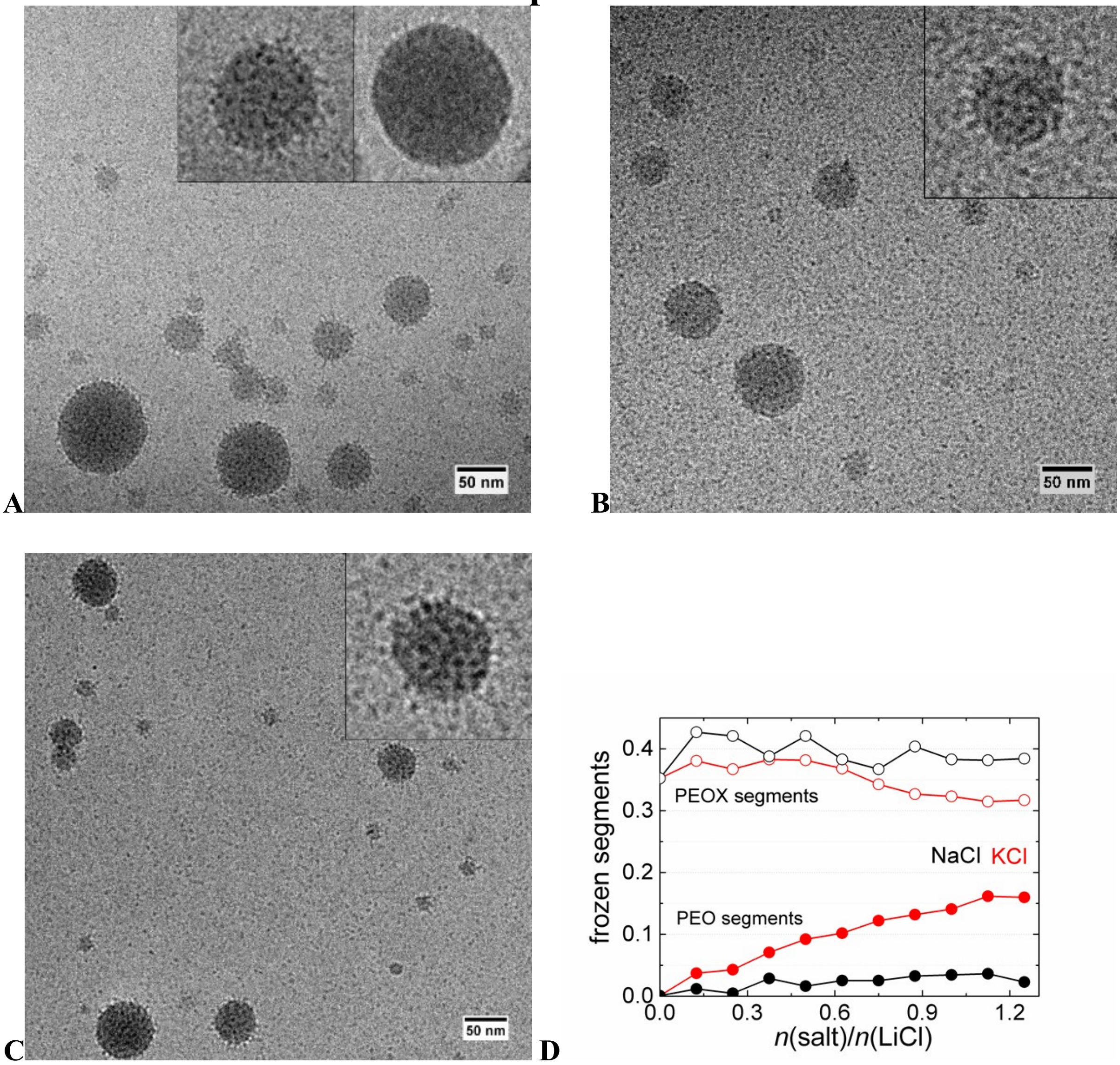



**Figure S5**. CryoTEM micrographs of PEO-POX/Li[CoD] in 0.154 M LiCl after titration with 0.154 M (**A**) NaCl; (**B**) LiCl and (**C**) KCl. (**D**) Fraction of frozen polymeric segments in PEO-POX/Li[CoD] in 0.154 M LiCl ($\xi = 0.045$) during the titration by 0.154 M NaCl (black curves) and 0.154 M KCl (red curves), calculated from a decrease of corresponding $^1$H NMR signals related to pure PEO-POX and *t*-butanol (internal standard).

The samples from the ITC experiment were analyzed also by means of cryoTEM (see Figure S5A-C). The nanoparticles after the "K to Li" process are compartmentalized in a similar way as original nanoparticles in Li-medium, and it is quite difficult to distinguish any differences. However, in the sample after the "Na to Li" addition, a fraction of nanoparticles without compartments was observed. They are very similar to those of PEO-POX/Na[CoD] in NaCl and they coexist with the multicompartmentalized ones. In order to understand what processes take place during the titration, $^1$H NMR technique was employed. We choose PEO-

POX/Li[CoD] in LiCl with lower value of $\xi$ (0.045) to better detect changes in $^{1}$H NMR spectra. The changes in fractions of frozen segments during the “Na(K) to Li” additions are shown in Figure S5D. We can see that “K to Li” leads to the situation similar to that in pure K-medium. Ratio of frozen PEO segments is increasing (up to 16 %) in opposite to POX, which has slightly decreasing tendency (from 35 to 31 %). This is in agreement with our assumption that potassium supports interaction with PEO and suppresses interaction with POX. In the case of “Na to Li”, the changes are however almost insignificant.