

## Supporting Information

# “Self-Assembly of poly(ionic liquid)s: Polymerization, mesostructure formation and directional alignment in one step”

Jiayin Yuan,<sup>a\*</sup> Sebastian Soll,<sup>a</sup> Markus Drechsler,<sup>b</sup> Axel H. E. Müller,<sup>b</sup> and Markus Antonietti<sup>a</sup>

<sup>a</sup> Max Planck Institute of Colloids and Interfaces, Colloid Chemistry, Research Campus Golm, D-14476 Potsdam,

<sup>b</sup> Macromolecular Chemistry II, University of Bayreuth, D-95440 Bayreuth, Germany

## Experimental Part

**Materials.** 1-vinylimidazole (Aldrich 99%), 1-bromododecane (Aldrich 98%), 1-bromotetradecane (Aldrich 97%), 1-bromohexadecane (Aldrich 97%), 1-bromooctadecane (Aldrich 98%), and water-soluble nonionic azo initiator 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA86, Wake Chemicals) were used as received without further purifications. All solvents used were of analytic grade. Ionic liquid monomers (ILMs) of 3-*n*-Dodecyl-1-vinylimidazolium bromide (ILM-12), 3-*n*-tetradecyl-1-vinylimidazolium bromide (ILM-14), 3-*n*-hexydecyl-1-vinylimidazolium bromide (ILM-16) and 3-*n*-octadecyl-1-vinylimidazolium bromide (ILM-18) were prepared according to reference No. 30 (Macromolecules 2011, 44, 744-750.).

**Polymerization process.** Polymerizations were conducted in the following procedure. In a 250 ml Schlenk flask, 5 g of ionic liquid monomer, 150 mg of water-soluble initiator VA86 and 100 ml of de-ionized water were added. The mixture was completely deoxygenated by three cycles of freeze-pump-thaw procedure, and was backfilled with argon. The flask was then stirred in an oil bath thermostated at 70°C for 24 h. After cooling down to room temperature, a stable dispersion was obtained, which was further purified by serum replacement against pure water (10-fold volume). The nanoworm polymer structures (directional alignment of nanoparticles) were achieved in the same polymerization procedure, except that 10 g of ionic liquid monomer was used instead of 5g.

### Analytical instrumentation.

Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) measurements were carried out at room temperature using a Bruker DPX-400 spectrometer operating at 400.1 MHz. The solid samples were obtained by drying the nanoparticle solutions. CDCl<sub>3</sub> was used as the solvent, since it dissolved all polymers

Dynamic light scattering (DLS) was measured using an ALV-7004 multiple tau digital correlator equipped with CGS-3 compact goniometer system, 22 mW He-Ne laser (wavelength  $\lambda = 632.8$  nm) and

a pair of avalanche photodiodes operated in a pseudo-cross-correlation mode. CONTIN analyses were performed for the measured intensity correlation functions.

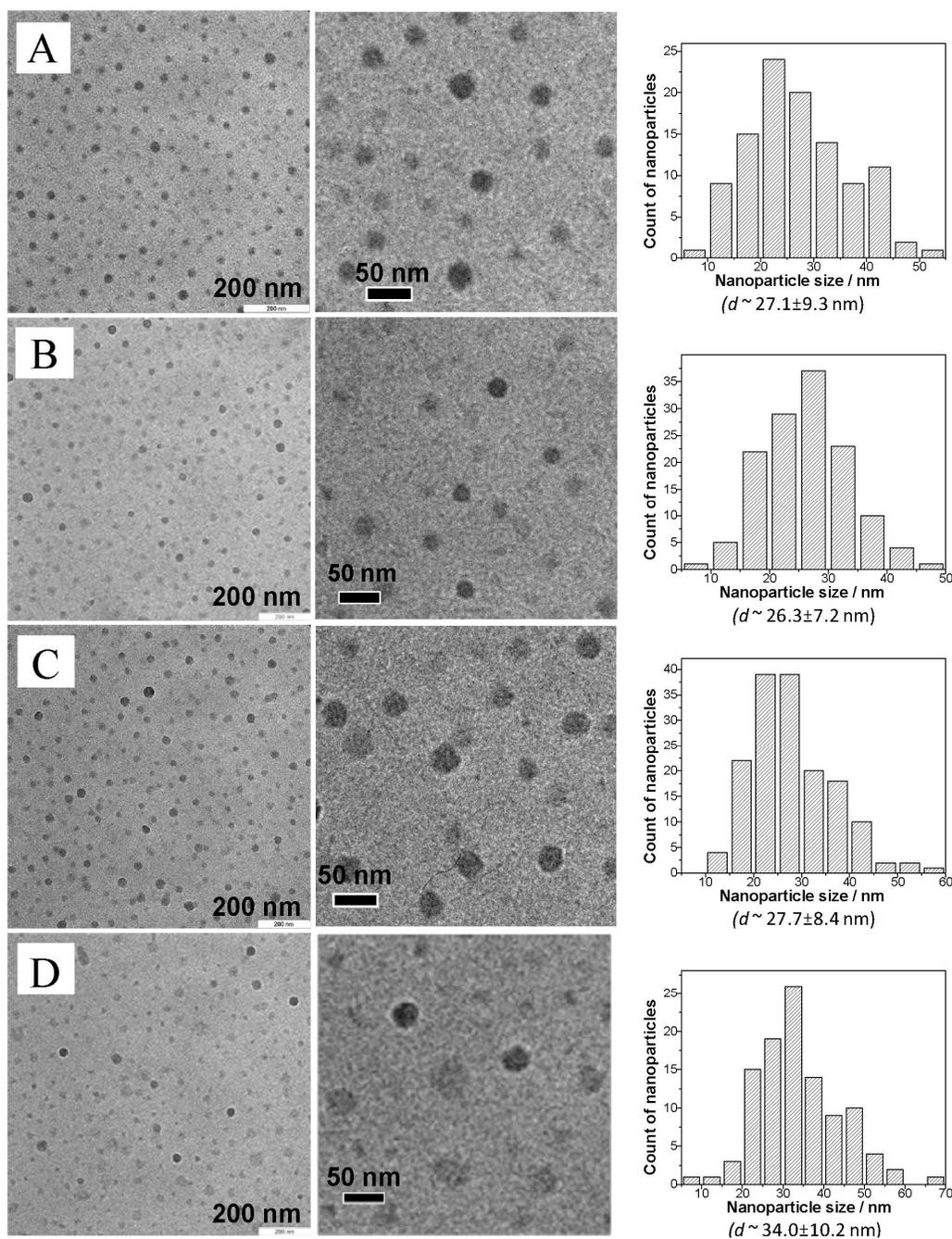
Transmission electron microscopy (TEM) was performed with a Zeiss EM 912 Omega microscope operating at 120 kV. The TEM samples were prepared by placing one drop of the diluted dispersion on a 200 mesh carbon-coated copper grid and left in air to dry.

For cryogenic transmission electron microscopy (cryo-TEM), a drop of the sample solution (c ~0.1 g/L) was placed on a lacey carbon-coated copper TEM grid (200 mesh, Science Services, München, Germany), where most of the liquid was removed with blotting paper, leaving a thin film stretched over the grid holes. The specimens were shock vitrified by rapid immersion into liquid ethane in a temperature controlled freezing unit (Zeiss Cryobox, Zeiss NTS GmbH, Oberkochen, Germany) and cooled to approximately 90 K. The temperature was monitored and kept constant in the chamber during all the preparation steps. After freezing the specimens, they were inserted into a cryo-transfer holder (CT3500, Gatan, München, Germany) and transferred to a Zeiss EM922 OMEGA EFTEM instrument. Examinations were carried out at temperatures around 90 K. The transmission electron microscope was operated at an acceleration voltage of 200 kV. Zero-loss filtered images ( $\delta E \sim 0$  eV) were taken under reduced dose conditions (100–1000 e/nm<sup>2</sup>). All images were registered digitally by a bottom mounted CCD camera system (Ultrascan 1000, Gatan), combined and processed with a digital imaging processing system (Gatan Digital Micrograph 3.9 for GMS 1.4).

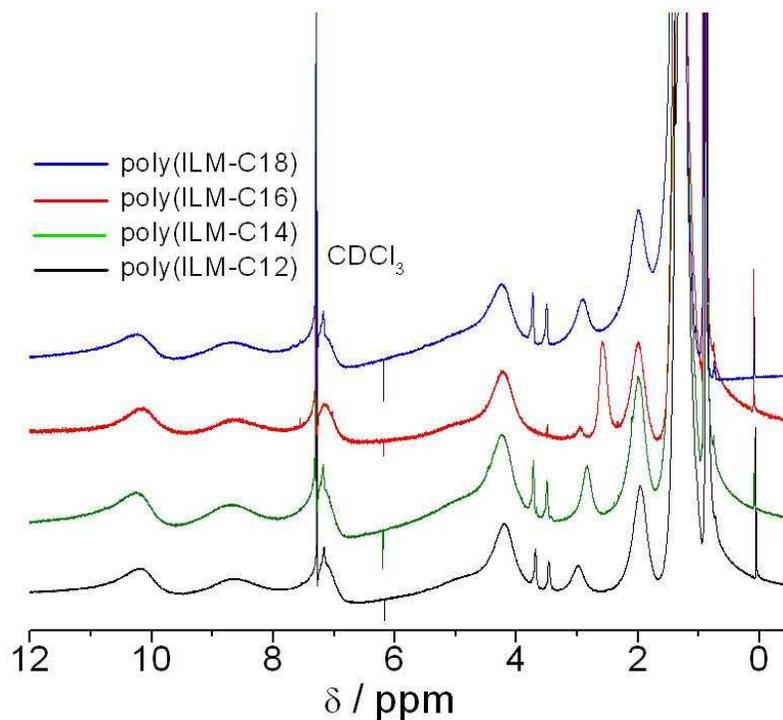
Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-1 instrument. The samples were first heated up to 150 °C, and then the samples were subjected to a cooling process from 150 to -50 °C at a cooling rate of 10 K/min. They were kept at -50 °C for 2 min. Finally, the samples were reheated to 150 °C at a heating rate of 10 K/min. The melting point of the alkyl chains in the poly(ionic liquid)s was determined by the heating curve.

SAXS experiments of the poly(ionic liquid) nanoparticle dispersion (50 g/L) in a glass capillary were performed using a NONIUS rotating anode instrument (4 kW, Cu K<sub>α</sub>) with pinhole collimation and a MARCCD detector (pixel size = 79), which was calibrated using silver behenate. The distance between the sample and detector was 33.8 cm, covering a range of the scattering vector  $q = 4\pi\lambda^{-1} \sin(\theta)$  from 0.65 to 8.9 nm<sup>-1</sup> ( $2\theta$ : scattering angle;  $\lambda = 0.154$  nm). The observed scattering patterns were corrected for empty-beam scattering. The 2D diffraction patterns were transformed into a 1D radial average of the scattering intensity using the Fit2D software.

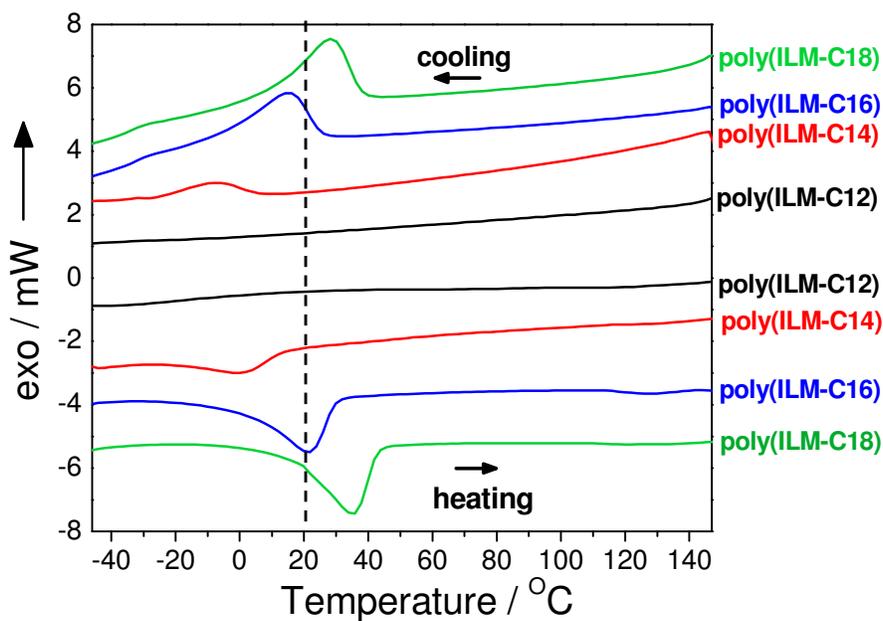
X-ray diffraction patterns were recorded on a Bruker D8 diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) and a scintillation counter.



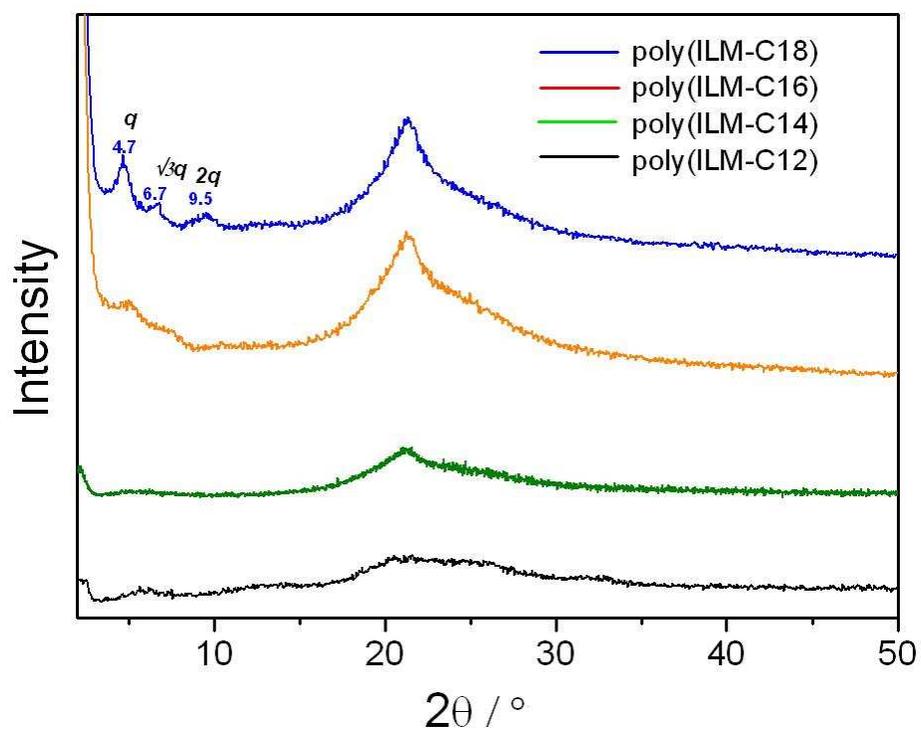
**Figure S1.** TEM images and the size distribution histograms of poly(ionic liquid) nanoparticles prepared from ILM-C12 (A), ILM-C14 (B), ILM-C16 (C), and ILM-C18 (D). The average sizes are  $27.1 \pm 9.3$ ,  $26.3 \pm 7.2$ ,  $27.7 \pm 8.4$ , and  $34.0 \pm 10.2$  nm (A→D), derived from the TEM characterization. These values are 4-7 nm smaller than that obtained from DLS measurements, due to the drying effect of the polymer nanoparticles, especially the unilamellar vesicles.



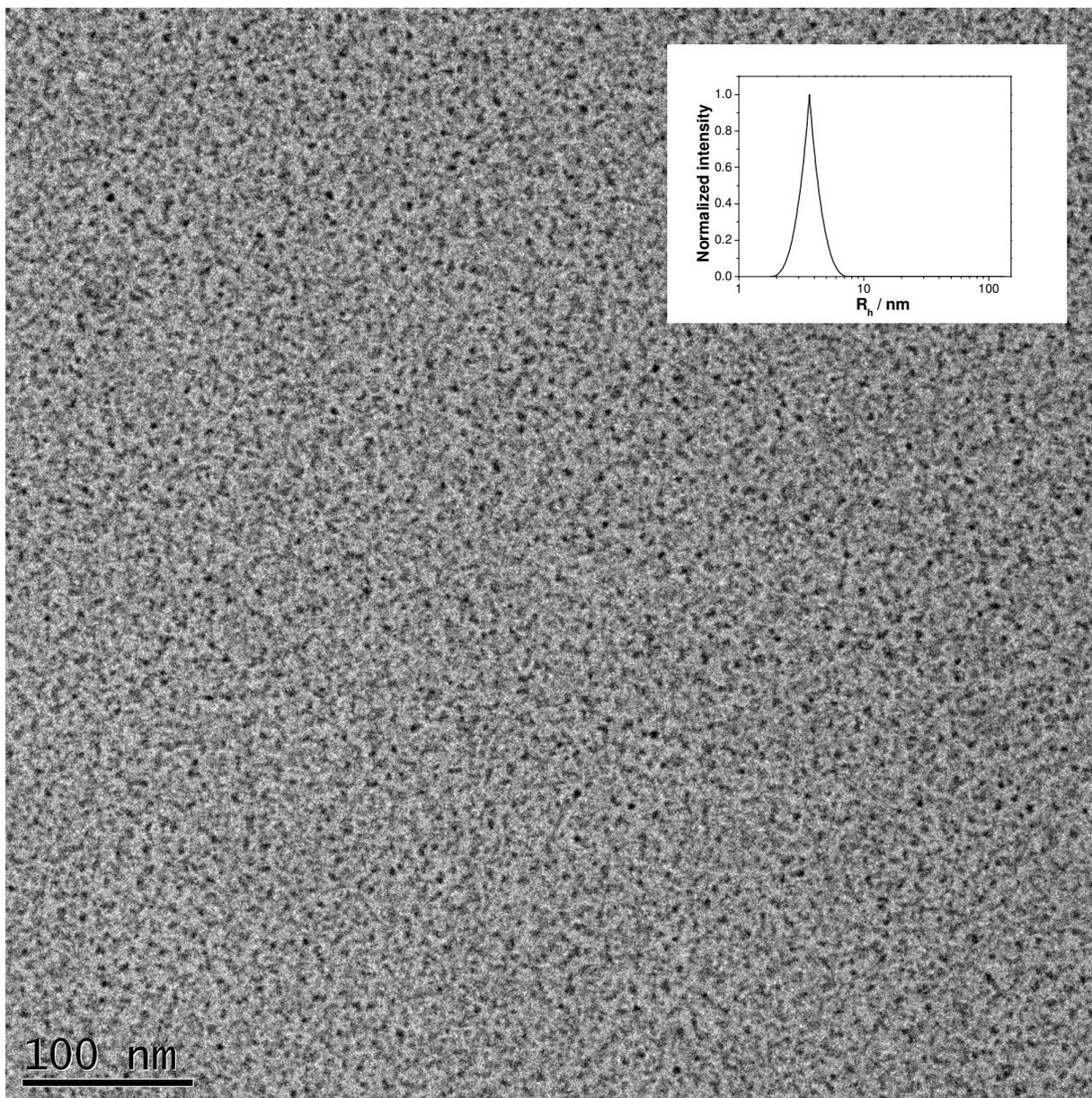
**Figure S2.**  $^1\text{H-NMR}$  spectra of the poly(ionic liquid)s in  $\text{CDCl}_3$ .



**Figure S3.** Differential scanning calorimetry curves of the solid poly(ionic liquid) polymers. (dashed line indicates the temperature at which the cryo-TEM samples were prepared). TGA characterizations showed that all poly(ionic liquid)s started to decompose at ca.  $250^\circ\text{C}$  under  $\text{N}_2$  and left a residue of  $1.0 \pm 0.5 \text{ wt}\%$  at  $1000^\circ\text{C}$ .



**Figure S4.** X-ray diffraction patterns of solid poly(ionic liquid) samples prepared by rapid freeze-drying the aqueous dispersion of poly(ILM-C12), poly(ILM-C14), poly(ILM-C16) and poly(ILM-C18),



**Figure S5.** Cryo-TEM image of aqueous solution of ILM-C14 at  $c=50$  g/L. The insert is a size distribution curve derived from dynamic light scattering measurement of the same sample. In the Cryo-TEM characterization, only micelles (dark/grey dots) were observed overall in the solution. No multilamellar or unilamellar vesicles existed. Their size was rather small, ca. 7 nm in diameter, as determined from the DLS measurements. This revealed that the multilamellar or unilamellar vesicles did not form from ionic liquid monomers before the polymerization.