ELECTRONIC SUPPLEMENTARY INFORMATION

Thermo-reversible and controlled transfer of poly(oxazolines) block copolymer micelles between ionic liquids and water

Carlos Guerrero-Sanchez, Jean-François Gohy, Cecile D'Haese, Hanneke Thijs, Richard Hoogenboom and Ulrich S. Schubert

EXPERIMENTAL INFORMATION

Materials

1-Butyl-3-methylimidazolium hexafluorophospate (BMI-PF_6) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMI-CF_3SO_3) ionic liquids (ILs) were obtained from Solvent-Innovation GmbH and Merck KGaA, respectively, as kind gifts. Both ILs were synthesis grade and dried under vacuum at 40 °C at least 3 days before use. The rest of the materials were utilized as received from different suppliers.

Synthesis of block copolymer systems

The poly(2-nonyl-2-oxazoline-*block*-2-ethyl-2-oxazoline) (PNonOx-*b*-PEtOx) block copolymers were synthesized by sequential cationic ring opening polymerizations under microwave irradiation; a detailed description of this synthetic method can be found elsewhere.[i] All polymers showed narrow mono-modal molecular weight distributions as revealed by gel permeation chromatography (GPC). Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy in combination with GPC measurements were utilized for calculating the chain lengths composition of the different block copolymers.

Preparation of block copolymer nanstructures (micelles)[ii] in ILs

Self-assembled nanstructures (micelles)[ii] of the investigated block copolymers were prepared utilizing the co-solvent method as reported elsewhere.[iii] Bulk PNonOx-*b*-PEtOx block copolymers were dissolved in a thermodynamically good solvent for both blocks (acetone) at 50 °C and at a concentration of 10 wt. %. Subsequently, BMI-PF_6 or BMI-CF_3SO_3 ILs were gradually added into the polymeric solutions as selective precipitants for the block composed of PNonOx under vigorous stirring in order to reach a concentration of 0.5 wt. % of the polymeric materials. The removal of the co-solvents from the micellar dispersions was achieved by placing the vials in a vacuum oven at 40 °C for at least 24 hours.

Characterization techniques

Dynamic light scattering (DLS) measurements were performed at 25 °C at 90° on a Malvern CGS-3 apparatus equipped with a 633 nm laser. The values of refractive index for BMI-PF_6 and BMI-CF_3SO_3, used during the analysis, were 1.41 and 1.44, respectively (measured values); whereas the used values of viscosity for BMI-PF_6 and BMI-CF_3SO_3 were 352 mPa s and 115 mPa s, respectively (values obtained from the suppliers). Hydrodynamic radius and polydispersity indices of the micelles were calculated from a cumulant analysis. The distribution of the hydrodynamic radii was obtained by a deconvolution of the data with the CONTIN algorithm.

Turbidity measurements were performed in an Avantium Crystal 16 platform which is composed of 16 wells designed to hold 1.5 mL vials, each with its on-line turbidity (light transmission intensity) sensor. The wells can be magnetically stirred at a fixed speed and are grouped into four zones that can be independently heated and cooled. Block copolymer micellar systems were heated and cooled at 1 °C min^{-1} or at 5 °C min^{-1} in a temperature range from 20 °C to 95 °C (or 70 °C) using a stirring speed of 700 rpm. To verify the reproducibility of the measurements related to the thermo-reversible transfer process of the micelles between a hydrophobic IL phase (BMI-PF_6) and an aqueous phase, the heating/cooling cycle was repeated several times. The turbidity sensor of the equipment was located at the lower phase (IL phase) of the micellar systems. Additionally, the transfer of the micelles between the two mentioned phases (change in turbidity upon heating/cooling) was verified by visual inspection in a conventional oil bath setup.

Gel permeation chromatographic measurements (GPC)of the PNonOx-*b*-PEtOx block copolymers were performed on a Waters GPC system consisting of an isocratic pump, a 2414 refractive index detector, a 2996 photo diode array detector, and a Waters Stryragel HT4 column. A *N,N*–dimethylformamide solution containing 5 mM of NH_4PF_6 was used as an eluent at a flow rate of 0.5 mL min^{-1} and a column temperature of 50 °C. Molecular weights were calculated against poly(methyl methacrylate) standards.

Proton nuclear magnetic resonance spectra (^{1}H-NMR) were recorded on a Varian Gemini 400 MHz spectrometer at room temperature using deuterated chloroform ($CDCl_3$).

DYNAMIC LIGHT SCATTERING INVESTIGATIONS OF THE SELF-ASSEMBLY PROCESS OF PNonOx-*b*-PEtOx BLOCK COPOLYMER NANOSTRUCTURES (MICELLES)[ii] IN THE HYDRPHOBIC IL BMI-PF_6 AND IN THE HYDROPHILIC IL BMI-CF_3SO_3

Transmission electron microscopy[iv] or atomic force microscopy[iiia] can provide information related to the size of the cores of self-assembled block copolymer micelles, whereas dynamic light scattering (DLS) can be used to determine the hydrodynamic radius (R_h) of the micelles in solution.[iv,iv] The values of R_h obtained by DLS for the PNonOx-*b*-PEtOx block copolymers nanstructures (micelles)[ii] in the hydrophobic IL BMI-PF_6 and in the hydrophilic IL BMI-CF_3SO_3 are shown in Table A, whereas their respective scattered light intensity autocorrelation functions are displayed in Fig. A. Note that the observed diffusion timescales for the investigated systems were in the range of 0.1–1 s, which is in good agreement with other block copolymer micellar systems in ILs reported elsewhere.[iv] These large diffusion timescales are thought to be related to the relatively high viscosity of the ILs compared to usual solvents. Indeed block copolymer micelles prepared in conventional solvents typically diffuse at the millisecond timescale. [iv] According to the results of Table A, nanstructures (micelles)[ii] with relatively large R_h are observed for the investigated samples, being this effect more pronounced for the samples with a large content of PNonOx. The polydispersity index (PDI) of these systems was, in general, relatively large for all cases, in agreement with the possible formation of aggregates of micelles (nanstructures)[ii]. Nevertheless, the CONTIN analysis of these results never succeeded in resolving a population of aggregates of micelles beside the isolated nanstructures (micelles).[ii] However, CONTIN data should be considered carefully due to the fact that these results do not totally exclude the formation of such aggregates.[v] Dilutions of the initial "micellar" solutions with the respective ILs did not result in significant changes in R_h, which is in agreement with the formation of kinetically frozen nanstructures (micelles)[ii] (the results given in Table A are those obtained for the starting "micellar" solutions at a concentration of 5 g L^{-1}). Therefore, dilutions were not successful to dissociate the hypothetical aggregates (nanostructures) into isolated micelles. The observation of kinetically frozen nanstructures (micelles)[ii] in ILs is in agreement with previous results,[ivb,c] and indicates that "micellar" systems out of the thermodynamic equilibrium are obtained in ILs. This also explains why the "micellar" characteristic features are strongly dependent on the used preparation protocol as suggested elsewhere.[ivb,c]

Sample	**Block copolymer**	**Mn (kDa)**	**IL**	**Rh (nm)**	**PDI**
M1	PNonOx$_{20}$–*b*–PEtOx$_{80}$	11.9	BMI-PF$_6$	96	0.42
M2	PNonOx$_{40}$–*b*–PEtOx$_{60}$	13.8	BMI-PF$_6$	92	0.48
M3	PNonOx$_{50}$–*b*–PEtOx$_{50}$	14.8	BMI-PF$_6$	90	0.32
M4	PNonOx$_{60}$–*b*–PEtOx$_{40}$	15.8	BMI-PF$_6$	152	0.39
M5	PNonOx$_{80}$–*b*–PEtOx$_{20}$	17.8	BMI-PF$_6$	518	2.18
M6	PNonOx$_{20}$–*b*–PEtOx$_{80}$	11.9	BMI-CF$_3$SO$_3$	54	0.48
M7	PNonOx$_{40}$–*b*–PEtOx$_{60}$	13.8	BMI-CF$_3$SO$_3$	50	0.47
M8	PNonOx$_{50}$–*b*–PEtOx$_{50}$	14.8	BMI-CF$_3$SO$_3$	43	0.39
M9	PNonOx$_{60}$–*b*–PEtOx$_{40}$	15.8	BMI-CF$_3$SO$_3$	72	0.44
M10	PNonOx$_{80}$–*b*–PEtOx$_{20}$	17.8	BMI-CF$_3$SO$_3$	484	0.31

Table A. Molecular characteristics and measured properties of the investigated PNonOx-*b*-PEtOx block copolymer nanstructures (micelles)[ii] in the hydrophobic IL BMI-PF$_6$ and in the hydrophilic IL BMI-CF$_3$SO$_3$. Rh and PDI stand for the hydrodynamic radius and polydispersity indices of the systems, respectively, as measured by DLS. Sub-indices in the tags of the materials indicate the average number of monomer units incorporated into the block copolymers which were estimated by GPC measurements in combination with ^{1}H-NMR; hence the average molecular weights (Mn) and composition of the block copolymers were calculated.

According to previous reports[ivc] and to solubility tests realized on the PNonOx and PEtOx homopolymers in the investigated ILs, the investigated nanstructures (micelles)[ii] consist of a PNonOx core surrounded by a PEtOx corona. Note that the block copolymers investigated have a constant degree of polymerization (DP) and a varying monomer composition (see Table A). However, there is no clear trend of the influence of the DP of the PNonOx block (core) on the R_h of the nanstructures (micelles)[ii] in both investigated cases (nanstructures (micelles)[ii] in BMI-PF$_6$ and BMI-CF$_3$SO$_3$). In this respect, nanstructures (micelles)[ii] with an almost constant R_h value around 93 nm were observed for samples **M1**, **M2** and **M3** while the R_h increases sharply for a high PNonOx content in samples **M4** and **M5**. A similar trend could be also observed for the case where nanstructures (micelles)[ii] were prepared in the hydrophilic IL BMI-CF$_3$SO$_3$; however, in this case the R_h values of the assembled nanstructures (micelles)[ii] are smaller. An almost constant R_h value of around 49 nm was observed for samples **M6**, **M7** and **M8** while the R_h increases again sharply for a high PNonOx content in samples **M9** and **M10**. In all investigated cases the R_h values are relatively large to fit to single micelles and therefore the presence of aggregated micelles (nanostructures) could be the reason why no clear trend between the DP of the core-forming block and the R_h of the nanstructures (micelles)[ii] could be observed. The tendency for aggregation is more pronounced for samples **M5** and **M10** in agreement with the short PEtOx stabilizing coronal blocks of the corresponding nanstructures (micelles).[ii] As observed in Table A, the influence of the type of IL on the characteristic features of the nanstructures (micelles)[ii] has also been evaluated. For the investigated block copolymer nanstructures (micelles),[ii] smaller R_h values are systematically observed when the nanstructures (micelles)[ii] are prepared in the more hydrophilic IL (BMI-CF_3SO_3); compare samples **M1**-**M5** to samples **M6**-**M10** in Table A. In addition to the reported R_h, the scattered light intensity of the nanstructures (micelles)[ii] was systematically larger in BMI-PF_6 than in BMI-CF_3SO_3, supporting that smaller nanstructures (micelles)[ii] are formed in BMI-CF_3SO_3. From these experiments, it can be anticipated that the more hydrophobic IL (BMI-PF_6) has a better affinity for the PNonOx block than BMI-CF_3SO_3 (a water-soluble IL) and would therefore swell slightly more the PNonOx cores resulting in larger nanstructures (micelles).[ii] This effect has also been recently observed for similar micellar systems based on a poly(2-nonyl-2-oxazoline-*block*-2-ethyl-2-oxazoline-*block*-2-methyl-2-oxazoline) triblock copolymer.[ivc]

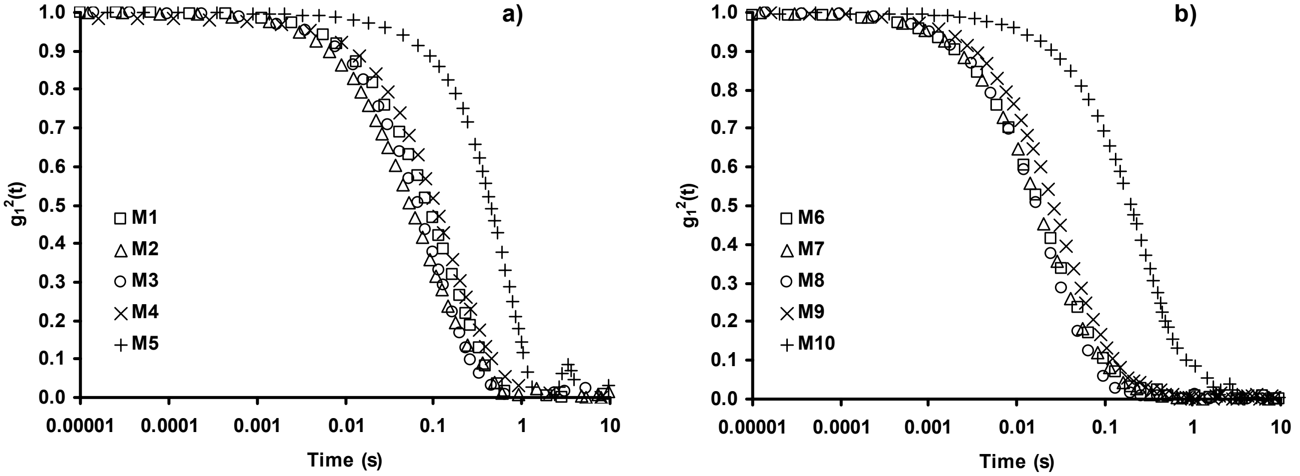

Fig. A. Normalized scattered light intensity aurocorrelation functions obtained by DLS measurements of self-assembled block copolymer nanstructures (micelles)[ii] in ILs. a) Samples **M1**-**M5** (Table A): PNonOx-*b*-PEtOx block copolymer nanstructures (micelles)[ii] in the hydrophobic IL BMI-PF_6. b) Samples **M6**-**M10** (Table A): PNonOx-*b*-PEtOx block copolymer nanstructures (micelles)[ii] in the hydrophilic IL BMI-CF_3SO_3.

REFERENCES AND NOTES

[i] a) F. Wiesbrock, R. Hoogenboom, M. Leenen, S. F. G. M. van Nispen, M. van der Loop, C. H. Abeln, A. M. J. van den Berg, U. S. Schubert, *Macromolecules*, 2005, **38**, 7957; b) R. Hoogenboom, F. Wiesbrock, H. Huang, M. A. M. Leenen, H. M. L. Thijs, S. F. G. M. van Nispen, M. van der Loop, C. A. Fustin, A. M. Jonas, J. F. Gohy, U. S. Schubert, *Macromolecules*, 2006, **39**, 4719.

[ii] The self-assembled nanostructures investigated in this work had relatively large sizes as measured by dynamic light scattering. One may estimate that the size of self-assembled core-shell micelles even with fully stretched macromolecules will not match to the sizes of the nanostructures of this study (at least not in the case of BMI-PF6; see Table A). For this reason and for scientific formality the term “nanostructures” is preferred instead of the term “micelles” throughout the discussion of the results of this contribution.

[iii] a) C. Guerrero-Sanchez, D. Wouters, C. A. Fustin, J. F. Gohy, B. G. G. Lohmeijer, U. S. Schubert, *Macromolecules*, 2005, **38**, 10185; (b) G. Riess, *Prog. Polym. Sci.*, 2003, **28**, 1107.

[iv] a) Y. He, Z. Li, P. Simone, T. P. Lodge, *J. Am. Chem. Soc.*, 2006, **128**, 2745; b) P. M. Simone, T. P. Lodge, *Macromol. Chem. Phys.,* 2007, **208**, 339; c) C. Guerrero-Sanchez, J. F. Gohy, D. Wouters, S. Hoeppener, H. Thijs, C. Ott, R. Hoogenboom, U. S. Schubert, *Polym. Mat. Sci. Eng.*, 2007, **96**, 936.

[v] O. Regev, J. F. Gohy, B. G. G. Lohmeijer, S. K. Varshney, D. H. W. Hubert, U. S. Schubert, *Colloid Polym. Sci.*, 2004, **282**, 407.