

Formation of polymer vesicles by simultaneous chain growth and self-assembly of amphiphilic block copolymers

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ELECTRONIC SUPPORTING INFORMATION

Materials.

4-Vinylpyridine (4VP, Aldrich, 96%) was distilled under reduced pressure before use. Acrylic acid (AA, purest grade, Arkema, stabilized with 200 ppm of hydroquinone was stored at room temperature and used without further purification). The SG1-based, oil-soluble alkoxyamine with 1-(methoxycarbonyl)eth-1-yl radical (MONAMS, 98%) and the *N-tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethylpropyl) nitroxide (SG1, 86%) were supplied by Arkema. The buffer, sodium carbonate (Na₂CO₃, Prolabo, pure) was used as received. The NaOH solution was prepared by solubilization of sodium hydroxide pellets into deionized water (41 g in 1 L). The SG1-end capped poly(acrylic acid) was synthesized according to our previous publications.^{1,2}

Emulsion Polymerization.

The macroinitiator solution was prepared by adding PAA-SG1 (1.44 g, 7.13×10^{-4} mol, 5.76 wt% based on 4VP; $M_n = 2020 \text{ g}\cdot\text{mol}^{-1}$; $M_w/M_n = 1.19$) and Na₂CO₃ (0.46 g, 3.4×10^{-3} mol) into a 1 M solution of NaOH (16.9 g), further completed with deionized water (83.1 g). 4VP was then added (25.0 g, 0.238 mol). The so-formed biphasic solution was deoxygenated for 20 min at room temperature by nitrogen bubbling under stirring and further poured into the 120 °C preheated 300 mL thermostated glass reactor (Parr/Equilabo). The internal pressure of the reactor was set to 3 bars and the mechanical stirring at 300 rpm. Time zero of the reaction was chosen when the temperature of the reaction medium reached 100 °C. Samples were periodically withdrawn for analysis and the reaction was stopped after 8 h by collecting the polymerization medium in a flask at room temperature.

Analytical Techniques.

Monomer conversion was determined by gravimetry after drying the samples first at room temperature and normal pressure overnight and then for several hours at 85 °C under vacuum. The molar mass analysis was performed by size exclusion chromatography (SEC) using DMF with added LiBr (1g L⁻¹) as an eluent at 60 °C and a flow rate of 0.8 mL min⁻¹. For this purpose, the PAA-*b*-P4VP copolymers were first methylated to give poly(methyl acrylate)-*b*-P4VP copolymers able to fully dissolve in DMF. Methylation was performed in agreement with our previously reported procedure for which THF was replaced by DMF and aqueous HCl (to turn the carboxylates into acids).^{1,2} Finally it was injected in a 100 µL loop. The steric exclusion was carried out on a pre-column PL Gel 50 x 7.5 mm and two PL Gel columns 5 µm Mixed-C 300 x 7.5 mm. The detector used was a Viscotek Dual Detector Refractometer/Viscosimeter Model 250 thermostated at 50 °C

and the data acquisition and treatment were done with the Omnisec 4.2 software. The number-average molar masses (M_n), the weight-average molar masses (M_w), and polydispersity indexes ($PDI = M_w/M_n$) were derived from the refractive index (RI) signal by a calibration curve based on polystyrene standards (from Polymer Standards Service).

The Z-average particle diameter (noted D_z) was measured by Dynamic Light Scattering (DLS) of the diluted water suspensions at an angle of 90° with a Zetasizer Nano S90 from Malvern, using a 4mW He-Ne laser at 633 nm. All calculations were performed using the Nano DTS software.

The samples were diluted in basic water prior to analysis and then deposited on a carbon-coated copper grid. Conventional transmission electron microscopy (TEM) was performed on a JEOL JEM CX II UHR microscope operating at 100 keV and equipped with a Keen View CCD camera from Soft Imaging System (Olympus) calibrated with three polystyrene particle samples (PELCO 610-SET - 91, 300, and 482 nm, Ted Pella Inc.). The acquisition was done with the iTEM software from Soft Imaging System (Olympus).

Specimens for cryo-TEM were prepared by quench-freezing thin films of suspension formed on lacey carbon films (NetMesh, Ted Pella Inc.) in liquid ethane using a Leica EMCPC cryostation. The grids were then mounted in a Gatan 626 holder cooled down with liquid nitrogen and transferred into a Philips CM200 'Cryo' microscope operating at 80 kV. The specimens were observed at low temperature (-180°C) and images were recorded on Kodak SO163 films using the Low Dose system from Philips.

Supplementary information references

- [1] C. Lefay, J. Belleney, B. Charleux, O. Guerret, S. Magnet, *Macromol. Rapid Commun.* 2004, 25, 1215–1220.
- [2] L. Couvreur, C. Lefay, J. Belleney, B. Charleux, O. Guerret, S. Magnet, *Macromolecules* 2003, 36, 8260–8267.