

Table 1 Molecular weights and molecular weight distributions of the diblock copolymers PEG-*b*-PA444 and PEG-*b*-PMAazo444

	M_n /Da (NMR)	Hydrophilic/hydrophobic weight ratio (NMR)	DP_n (NMR)	M_n /Da (SEC)	M_w/M_n (SEC)
PEG- <i>b</i> -PA444	6700	30/70	45 (PEG), 7 (PA444)	6800	1.09
PEG- <i>b</i> -PMAazo444	9200	22/78	45 (PEG), 12 (PMAazo444)	8300	1.09

macroinitiators[‡] were then used to polymerize the liquid crystalline monomer A444 and MAazo444 by ATRP.[†]

The molecular weights and molecular weight distributions of the diblock copolymers were first measured by size exclusion chromatography (SEC)[§] calibrated with polystyrene standards (see Table 1). The SEC experiments give an indication of the polydispersity index (M_w/M_n) of the block copolymers with a reasonable approximation.⁸ Nevertheless, the values of M_n measured by SEC can not be used to characterize the molecular weights of the block copolymers because of the very different chemical structures of the block copolymers compared to that of the PS standard. Therefore, the molecular weights of the diblock copolymers were also analysed by NMR.[¶] The ratio between the integration of the aromatic signals ($\delta = 6.90$ – 8.06) in the LC hydrophobic block and the integration of the signal of the terminal methyl ($\delta = 3.38$) in the PEG block was used to calculate the molecular weights of the PA444 and PMAazo444 blocks (see Table 1). From these molecular weights, the hydrophilic/hydrophobic weight ratios of the diblock copolymers (PEG/PA444 = 30/70 and PEG/PMAazo444 = 22/78) were calculated. The mesomorphic properties of the diblock copolymers in bulk were studied by thermal optical polarizing microscopy and differential scanning calorimetry (DSC). PEG-*b*-PA444 showed birefringent textures upon heating ($1\text{ }^\circ\text{C min}^{-1}$) from room temperature to $59\text{ }^\circ\text{C}$ and it became isotropic after $59\text{ }^\circ\text{C}$. Upon cooling the birefringent texture reappeared at $58\text{ }^\circ\text{C}$. Similar phenomena were observed for PEG-*b*-PMAazo444: the LC–isotropic transition temperature was $65\text{ }^\circ\text{C}$ upon heating and $61\text{ }^\circ\text{C}$ upon cooling. These transition temperatures were confirmed by DSC analysis. The pure homopolymers PA444 and PMAazo444 exhibit a nematic mesophase,^{8,9} but the block copolymers formed from a nematic polymer and a flexible amorphous polymer may present self-assembled structures triggered by microsegregation such as lamellar phases.⁸ The self-assembled phases of the diblock copolymers in bulk will be studied by other techniques like X-ray diffraction and electron microscopy and presented in a subsequent paper.

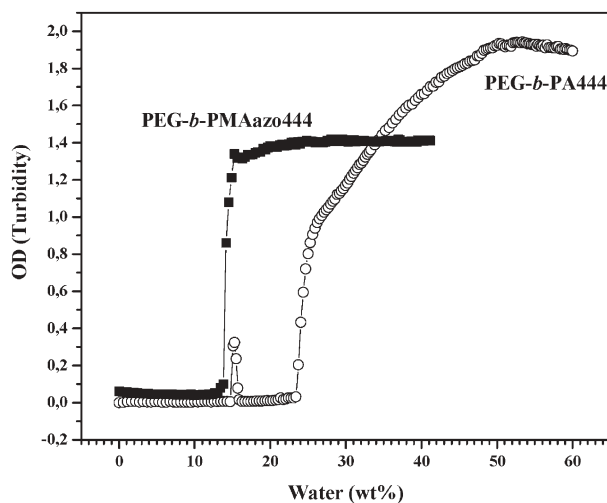
The polymer vesicle preparation and turbidity measurements were performed according to published procedures.¹⁰ The diblock copolymer was dissolved in dioxane, a common solvent for the two polymer blocks, at a concentration of 1.0 wt%. Deionized water was then added to the solution very slowly (2 – $3\text{ }\mu\text{L}$ of water per minute to 1 mL of polymer solution) with slight shaking. After every addition of water, the solution was left to equilibrate for 20 minutes. The turbidity was then measured at a wavelength of 650 nm using a quartz cell (path length 2 cm) with a Unicam UV/vis spectrophotometer. The cycle of water addition, equilibration and turbidity measurement was continued until the increase in turbidity upon water addition was very small. The solution was then dialyzed against water for 3 days to remove dioxane using a Spectra/Por regenerated cellulose membrane with a molecular

weight cut-off of 3500. This turbid polymer solution was then ready for the morphological analysis.

Fig. 1 shows the turbidity diagrams obtained for PEG-*b*-PA444 and PEG-*b*-PMAazo444. The diagrams show one jump in turbidity occurring at water content of 24% (w/w) for PEG-*b*-PA444 and of 14% (w/w) for PEG-*b*-PMAazo444. This jump corresponds to the apparition of polymer vesicles.

These polymer vesicles were observed by cryo-transmission electron microscopy after preparative vitrification of the polymer solution in liquid ethane (Fig. 2(a) and (c)). The size of observed vesicles is rather heterogeneous, with diameters ranging from 40 to 500 nm for PEG-*b*-PA444 vesicles and from 140 to 760 nm for PEG-*b*-PMAazo444 vesicles. Nevertheless, the membrane thickness is homogeneous: 10–11 nm for PEG-*b*-PA444 vesicles and 14–15 nm for PEG-*b*-PMAazo444 vesicles. Considering the molecular weight measured by NMR, the PA444 block has a degree of polymerization of 7 (monomer mass = 632 Da) and the PMAazo444 block a degree of polymerization of 12 (monomer mass = 602 Da). The mesogen length is 2.6 nm as measured by X-ray diffraction.¹¹ The LC hydrophobic block length is therefore approximately 4.4 nm for PA444 and 5.6 nm for PMAazo444, assuming that the mesogens are parallel to and distributed around the extended backbone.¹² These values are close to the half values of the membrane thickness. We conclude that the membrane has a bilayer structure as shown in the schematic representation in Fig. 2(b) and the polymer vesicles are unilamellar vesicles.

Work is in progress to obtain giant vesicles and then study their responsive properties under the action of external stimuli like temperature, light and magnetic field.

**Fig. 1** Turbidity diagrams of 1.0 wt% PEG-*b*-PA444 and of 1.0 wt% PEG-*b*-PMAazo444 in dioxane upon addition of water.

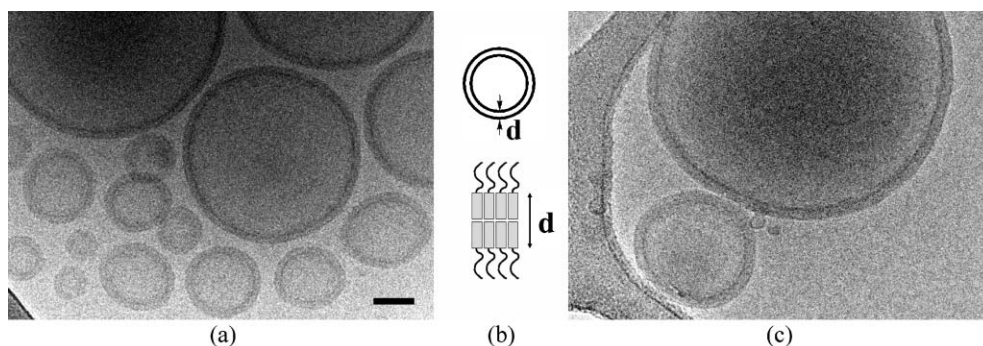


Fig. 2 Cryo-electron micrographs of vesicles formed in water by PEG-*b*-PA444 (a) and by PEG-*b*-PMAazo444 (c). The scale bar at lower right of (a) is 50 nm and the scale is the same for (c). The mean lamellar thickness is 10–11 nm for PEG-*b*-PA444 and 14–15 nm for PEG-*b*-PMAazo444. (b) is the schematic representation of diblock copolymers with bilayer structure in the membrane (the rectangles represent the LC blocks).

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Notes and references

‡ Macroinitiator MPEG2000-Br (R = H) ^1H NMR (300 MHz, CDCl_3): δ 4.38 (q, $J = 9$ Hz, 1H, CH_3CHBr), 4.30 (t, $J = 3$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{OCO}$), 3.51–3.87 (m, $n\text{H}$, OCH_2CH_2), 3.36 (s, 3H, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}$), 1.81 (d, $J = 6$ Hz, 3H, BrCHCH_3).

§ For SEC, we used Waters Styragel HR5E columns and a Waters 410 differential refractometer with THF as eluent at a flow rate of 1.0 mL min^{-1} at 40°C . SEC chromatograms are shown in the ESI.†

¶ PEG-*b*-PA444 ^1H NMR (300 MHz, CDCl_3): δ 6.90–8.06 (m, 11×7 H arom.), 3.81–4.07 (m, $\text{C}_6\text{H}_3\text{COOCH}_2$ and $\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.54–3.64 (m, $-(\text{OCH}_2\text{CH}_2)_n-$), 3.38 (s, 3 H, $\text{CH}_3-(\text{OCH}_2\text{CH}_2)_n-$), 0.95–2.17 (m, OCOCHCH_3 and other H aliph.); PEG-*b*-PMAazo444 ^1H NMR (300 MHz, CDCl_3): δ 6.82–8.04 (m, 11×12 H arom.), 3.88 (broad, COOCH_2 and $\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.51–3.66 (broad, $-(\text{OCH}_2\text{CH}_2)_n-$), 3.38 (s, 3 H, $\text{CH}_3-(\text{OCH}_2\text{CH}_2)_n-$), 0.86–1.71 (m, $\text{OCOC}(\text{CH}_3)_2$ and other H aliph.). ^1H NMR spectra are given in the ESI.

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