Supporting information

Block Copolymer Vesicle Permeability Measured by Osmotic Swelling and Shrinking

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\textbf{PBut-\textit{b}-PEO Characterization}

The block copolymer \textit{P}\text{But}_{46-}\textit{b}-\text{PEO}_{30} supplied by Polymer Source has been characterized by Sized Exclusion Chromatography, in THF. The molar masses are extracted from a calibration with Polystyrene Standards.

\[ M_n = 4736 \text{ g/mol}, \quad M_w = 4973 \text{ g/mol}, \quad I_p = 1.05 \]

Size exclusion Chromatogram of \textit{P}\text{But}_{46-}\textit{b}-\text{PEO}_{30} acquired in THF
The proportion of ethylene oxide and butadiene has been evaluated by $^1$H NMR, in CDCl$_3$ and is in agreement with Polymer Source data provided (40% instead of 35%). The NMR spectrum is illustrated below.

1H NMR spectrum in CDCl$_3$ of PBut$_{46}$-b-PEO$_{30}$

**DOW 5329 characterization**

The apparent Newtonian viscosity have been measured at 25°C with stress controlled rheometer MCR 301 (Anton Paar) using continuous shear rate ramp. After conversion in kinematic viscosity using the Dow density, the value obtained is in rather good agreement with value given by the manufacturer (400 centistokes instead of 360). This gives an average viscometric molar mass of 3300 g/mol instead of 3000 g/mol (manufacturer value) assuming that the viscosity scales as molar mass, which is the case for this non-entangled system.

We find a weight fraction of ethylene oxide (45%) in excellent agreement with value given by Dow corning (47%) by $^1$H NMR analysis, illustrated below.
1H NMR Spectrum in CDCl₃ obtained for Dow 5329.

The membrane thickness has been also evaluated by Cryo-TEM microscopy on extruded vesicles (polycarbonate membrane, mesh size ~100nm). Homogeneous vesicular structures are clearly observed. The envelope appears as thick homogeneous line of electron scattering matter for PDMS-g-PEO polymersomes. The characteristic thickness has been estimated to 5nm, in agreement with literature¹.

Cryo TEM Picture of PDMS-g-PEO vesicle (Dow 5329)