Electronic Supplementary Material (ESI) for Soft Matter
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SUPPORTING INFORMATIONS FOR

Hybrid polymer/lipid vesicles: fine control of the lipid and polymer distribution in the binary membrane

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DSC Experiments

A given appropriate volume of polymer/lipid solution in chloroform corresponding to a constant mass of lipid (0.5mg) was deposited in an aluminium pan, the mass of polymer being adapted to get the desired molar ratio. The solutions were evaporated under vacuum at 45°C during at least 5h and then rehydrated with an aqueous solution of sucrose at 0.1M overnight. For lipid polymer mixture with DPPC, the first 30mn of hydration were performed at 50°C *i.e.* above the main chain transition to enable the swelling of bilayers.

The thermograms were recorded after three cycles (Tmin-Tmax 5°C/min; Tmax-Tmin 5°C/min). Each experiments was done triplicate.

It has to be noted that although the average vesicle size obtained by classical film hydration (1-2 µm) is smaller than the one obtained by electroformation (10-50µm), we believe that this does not modify the lipid/polymer distribution that is mainly driven by thermodynamics. Distribution changes could eventually occur at very low size (~100nm) where the bending modulus of the membrane plays a role, although it has to be noted that in the work of Ruysschaert et al.[1] DSC analyses were performed on nanovesicles, whereas pictures of hybrid giant vesicle were also commented and no information could be collected about a possible difference of behaviours.

1. T. Ruysschaert, A. F. P. Sonnen, T. Haefele, W. Meier, M. Winterhalter and D. Fournier, *Journal of the American Chemical Society*, 2005, 127, 6242-6247.

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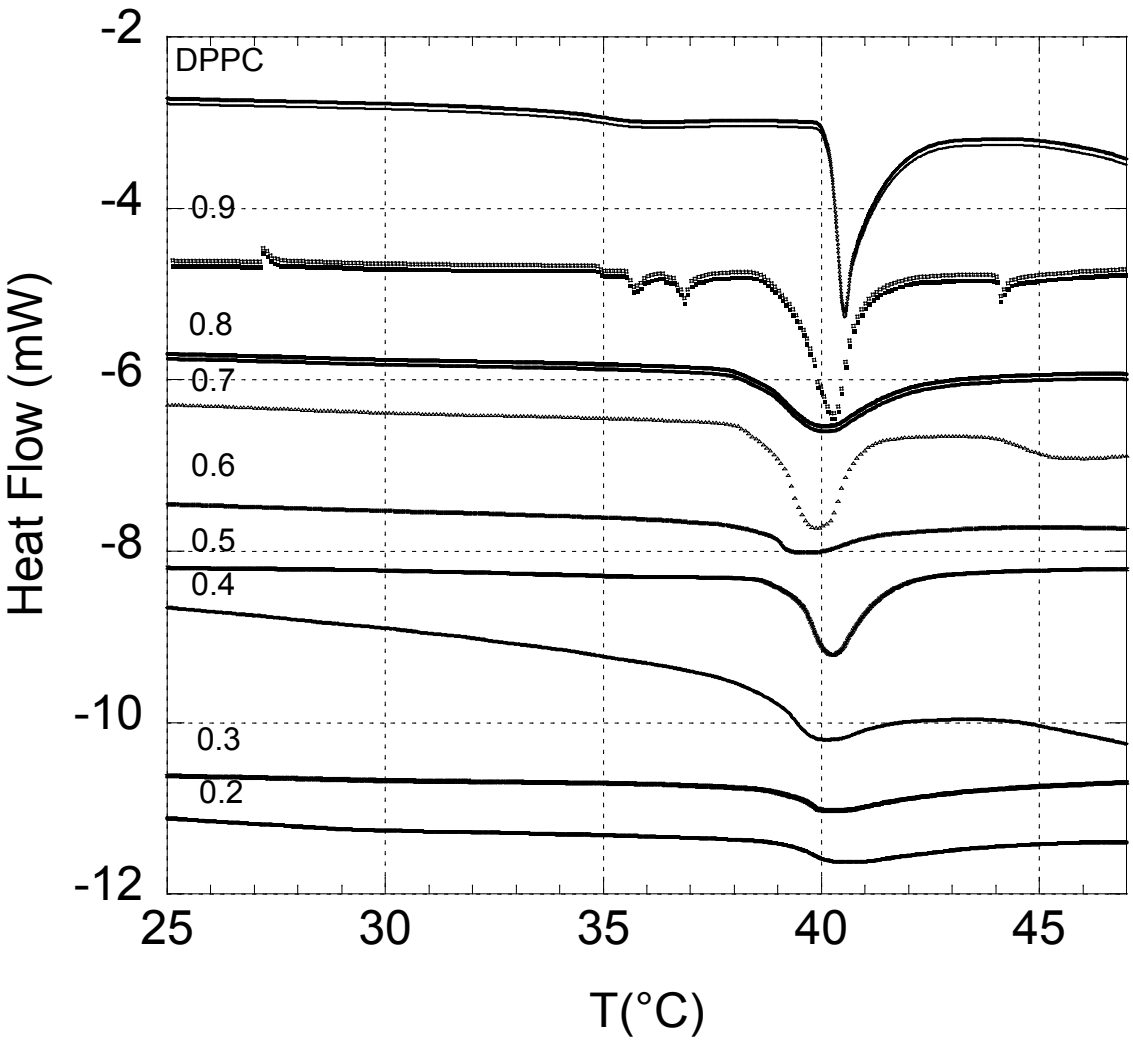

Figure S1: Thermograms obtained for vesicular suspensions of DPPC/PDMS-*g*-PEO

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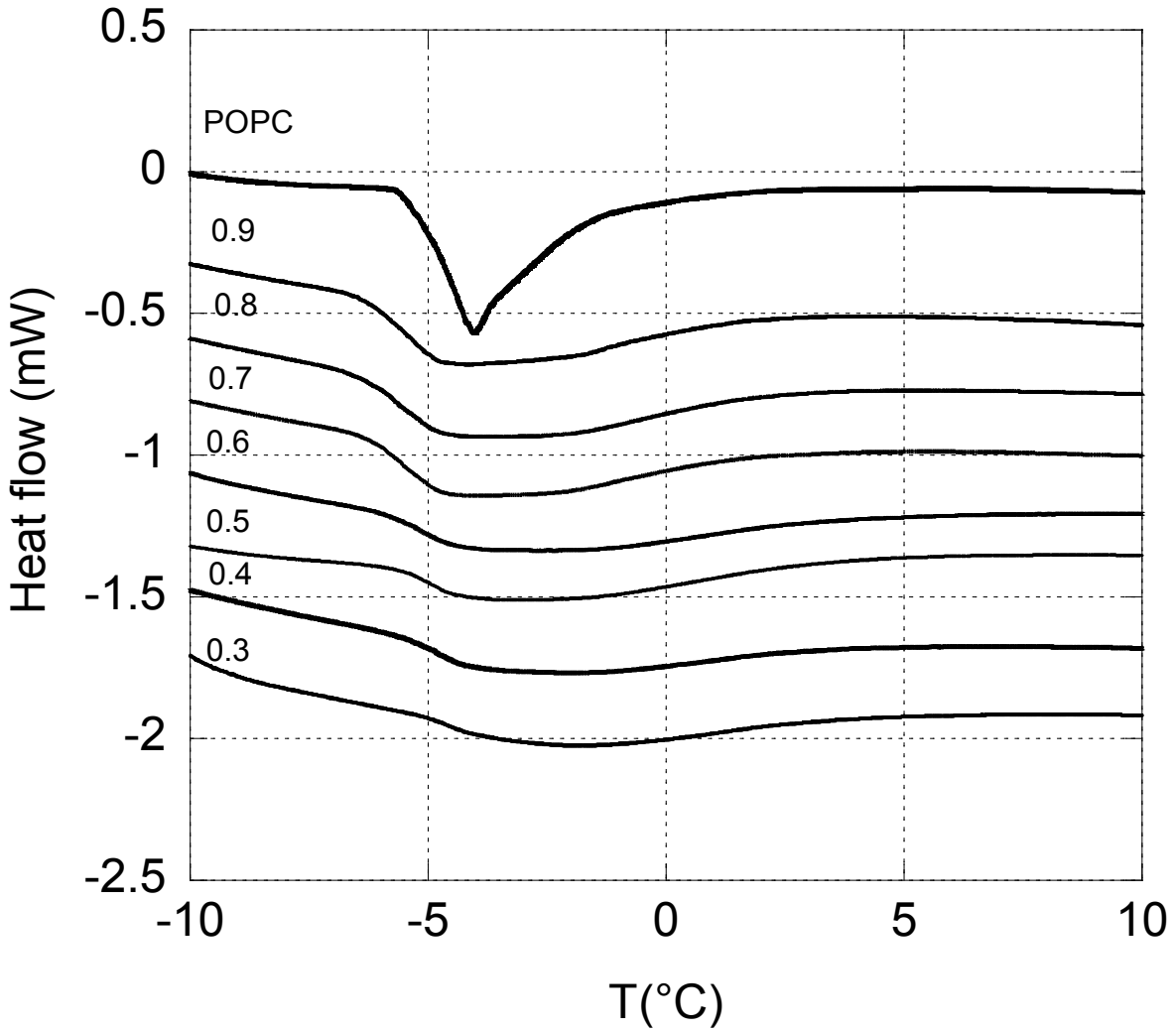

Figure S2: Thermograms obtained for vesicular suspensions of POPC/PDMS-*g*-PEO

Tagging Copolymer with Fluorescein

The PDMS-*g*-PEO in this study has been functionalized with Fluorescein using the hydroxyl end group of the PEO chains (2 hydroxyl end group in average for one PDMS-*g*-PEO copolymer chain)

The procedure was the following:

1-Mesylation of hydroxyl end group:

1g of PDMS-*g*-PEO (6.6e-4 mol of hydroxyl function) was dissolved in 20ml of dichloromethane and refrigerated at 0°C. Under magnetic stirring, 185µl (1.33e-3mol) of triethylamine (Et3N) was added at once therefore 56µl (7.3e-4mol) of mesyl chloride dissolved in 2ml of dichloromethane was added drop wise. The reaction proceeded overnight. Dichloromethane and mesylchloride in excess were removed under vacuum respectively a room temperature and at 60°C.

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2-Amination:

10ml of 28% aqueous ammonia was added directly to the flask containing PDMS-*g*-PEO mesylate. The lid was tightly closed and the reaction was vigorously stirred for 5 days at room temperature. The systems was purified by dialysis (membrane MWCO 25000Da) against MilliQ water, and dried under vacuum.

The final yield is 60% (w/w).

The amine content was checked by non aqueous titration using hydrobromic acid (1e-2M in acetic acid). The polymer was previously dissolved in a mixture of chloroform and acetic acid (50/50 vol.) and one drop of crystal violet was used as colorimetric indicator.

According to the titration, there is one amine group per PDMS-*g*-PEO copolymer chain

3-Coupling with N-hydroxysuccinimide (NHS)-Fluorescein

95mg of PDMS-*g*-PEO copolymer (3.16e-5mol of amine) was dissolved in 2ml of THF. 340µl of solution of diisopropylethylamine (DIPEA) at 12mg/ml in THF (3.16e-5mol) was added at once. 500µl of a solution of (NHS)-fluorescein at 40mg/ml in DMSO (4.22e-5mol) was added at once. The lid was tightly closed and the reaction was performed under gentle agitation during one day.

The purification was performed first by dialysis (membrane MWCO 25000Da) against basic water (pH~10) in order to facilitate the solubilisation of fluorescein in excess and therefore its removing. After 4 days, a slight yellow colour was still visible in dialysis bath. The polymer was then dried under vacuum, resuspended in basic water and purified using sephadex G25 column.

Finally the product was dried under vacuum and the final yield was evaluated at 65% (w/w).

The polymolecularity of the PDMS-*g*-PEO is not provided by the supplier (Dow corning) and its determination cannot be done by GPC using the most classical organic solvent THF. Indeed the refractive index increment of PDMS is very close to the one of THF and the resulting signal with RI detector is weak. This polymer cannot be detected with UV detector, and the molar mass is too weak to use light scattering detection.

Interestingly the resulting copolymer functionalized with fluorescein could be analysed by GPC in THF with UV detection as illustrated in the Figure S-3. The molar masses are extracted from a calibration with Polystyrene Standards

$\overline{Mn}$=3600g/mol, $\overline{Mw}$=4760 g/mol. Ip=1.32

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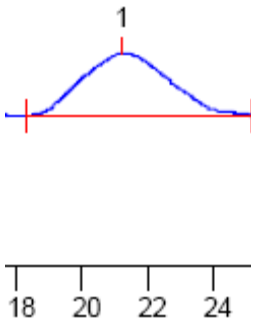
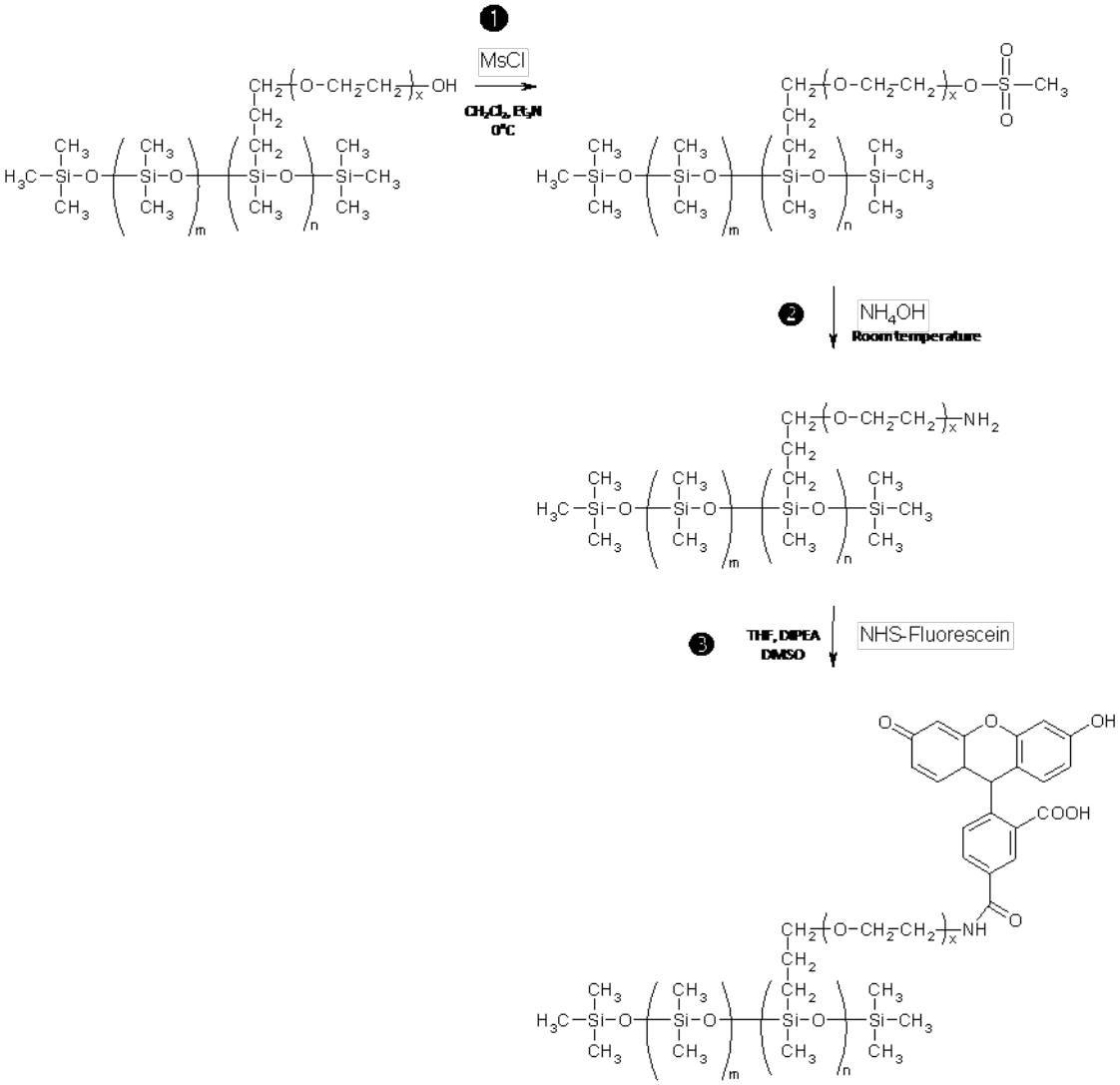


Figure S-3 Size exclusion Chromatogram PDMS-*g*-PEO-fluo acquired in THF



Scheme S-1: Reaction scheme of the tagging procedure of PDMS-*g*-PEO.

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Evidence of the presence of lipid in polymer rich phases

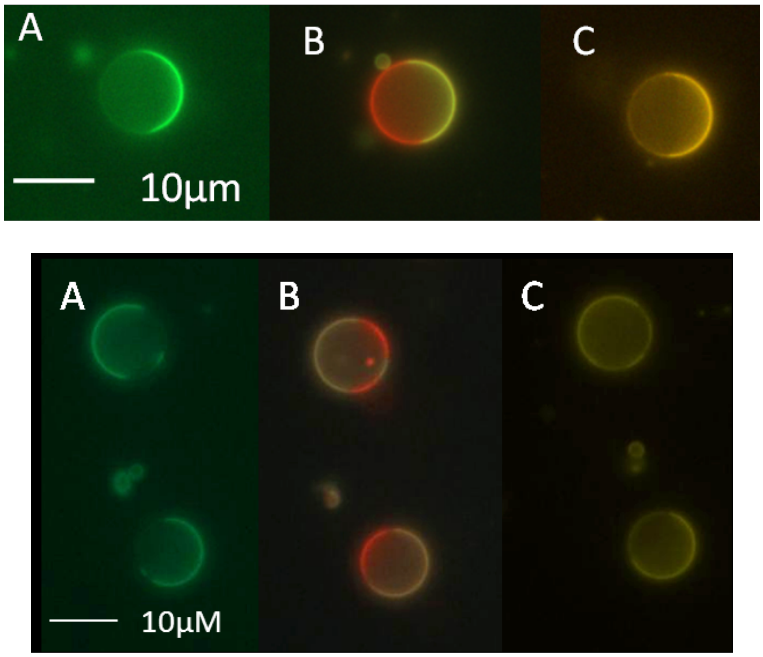

Figure S-4 Figure illustrating vesicles with heterogeneous distribution, with lipid present in the polymer-rich phase. Composition: 60 mol % DPPC/40 mol % PDMS-*g*-PEO.Filter sets: A, fluorescein; B, triple-band; C, rhodamin.

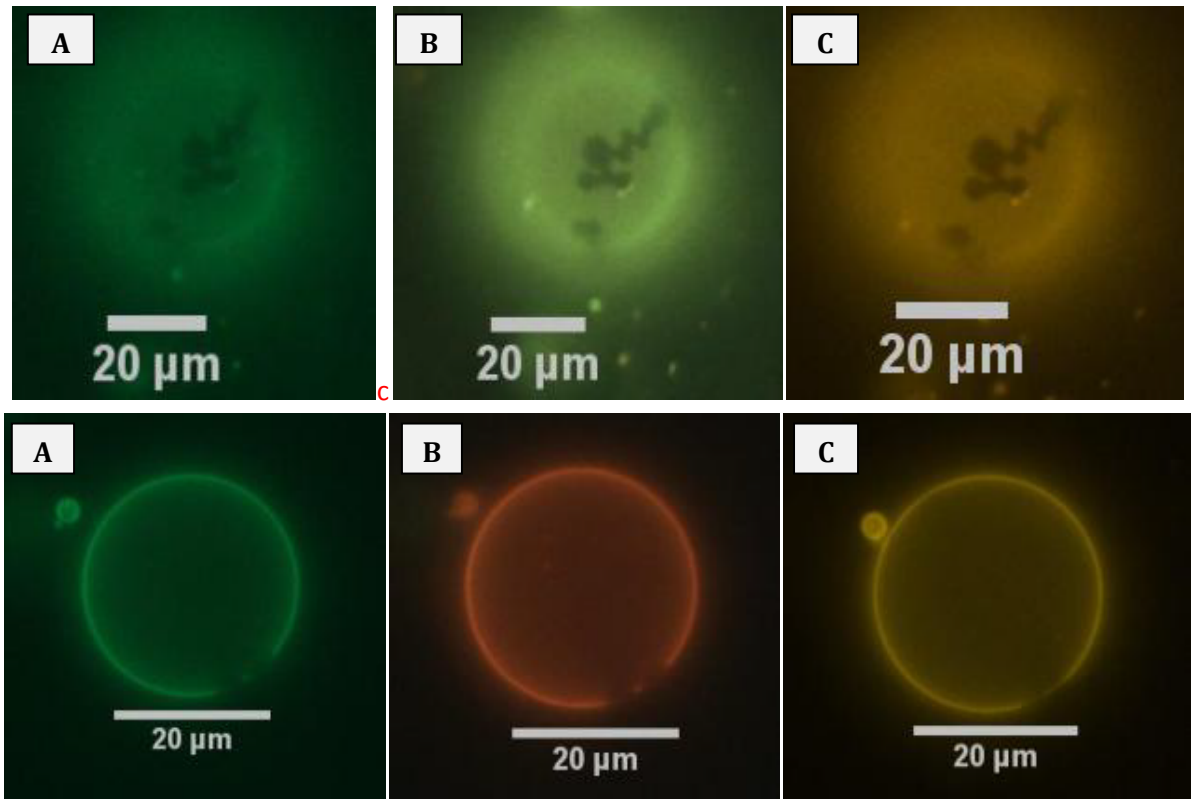

Figure S-5 Figure illustrating vesicles with heterogeneous distribution (here lipid domains in polymersome membrane), with lipid present in the polymer-rich phase. Composition: 25mol% DPPC/ 75mol% PDMS-*g*-PEO. Filter sets: A, fluorescein; B, triple-band; C, rhodamin.