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Supporting Information to

Controlling the generation of bilayer and multilayer vesicles in block copolymer / epoxy blends by a slow photopolymerization process

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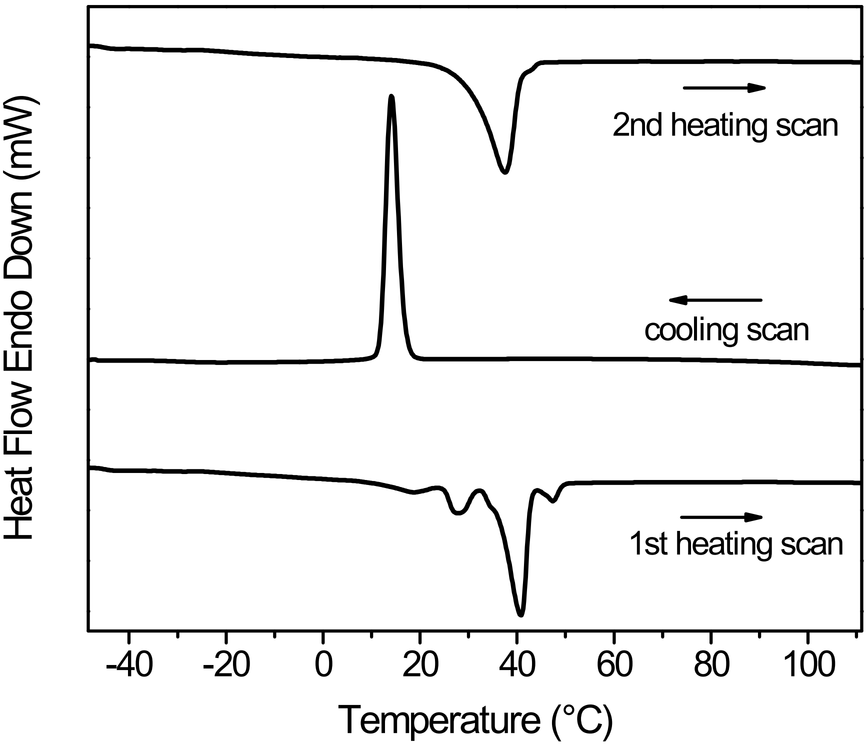


Figure S-1: DSC thermograms (at 10ºC/min) of the neat BCP.

Differential Scanning Calorimetry (DSC). The calorimetric measurement was made on a Perkin-Elmer Pyris 1 differential scanning calorimeter under a dry nitrogen atmosphere. Heating and cooling scans were made at 10ºC/min.

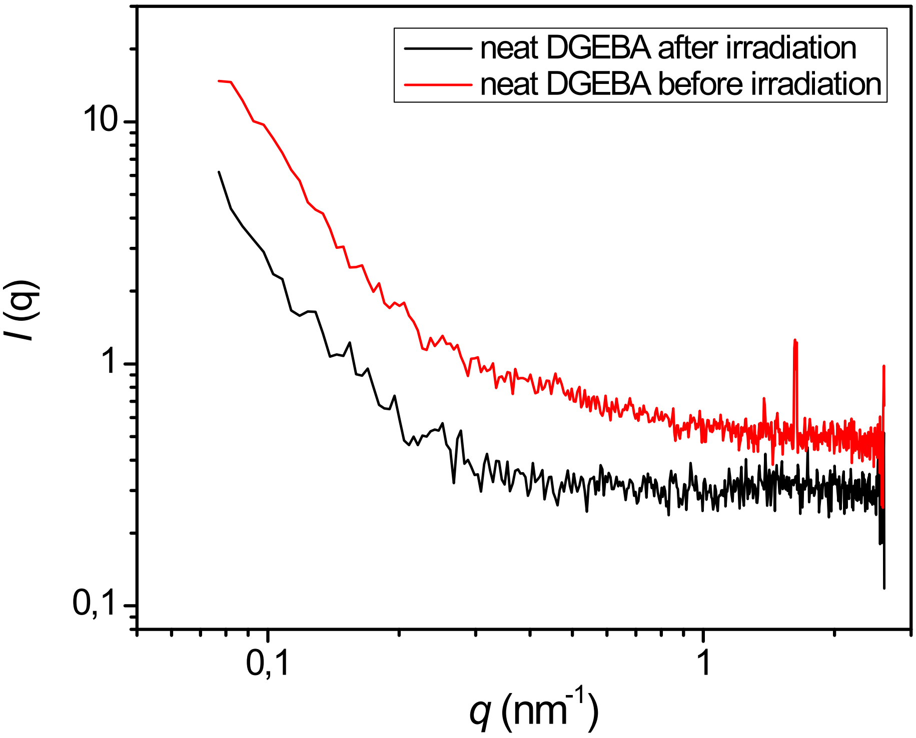


Figure S-2: SAXS measurements of the pristine epoxy resin before irradiation and after 240 min of irradiation.

Section S-3: SAXS data was fitted using the SASfit software package in the *q*-region from 0.1 to 0.7 nm^{-1}. The models used are implemented into the SASfit package and were used without modification (*Kohlbrecher, J. SASfit: A program for fitting simple sructural models to small angle scattering data. https://kur.web.psi.ch/sans1/SANSSoft/sasfit.pdf*). The models were selected taking into account the structure inferred from the Guinier analysis of the slope at the low-q region. The fitting results for the sample containing 10 wt% PEB-*b*-PEO photocured at room temperature are summarized in the following table:

Irradiation time min	**Model**	**R nm**	**R_c nm**	**L_{cyl} nm**	**t_h nm**	**t_t nm**
75	Sphere	5.6				
95	Sphere	7.2				
105	Cylinder	4.0		40.0		
135	Cylinder	4.0		44.0		
	Vesicle		9.0		4.5	3.6
145	Vesicle		12.0		5.0	3.8
195	Vesicle		12.0		5.1	4.2
235	Vesicle		12.0		4.8	4.0

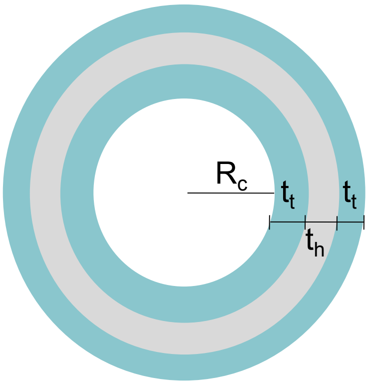
R: radius, R_c: radius vesicle core, L: length, t_h: thickness of outer part of bilayer thickness, t_t: thickness of inner part of bilayer.

For the scattering profiles obtained at 75 and 95 min a sphere model was employed. The polydispersity distribution of the radius of the spherical particles was included as a LogNormal-distribution. Also, a structure factor was needed to introduce an interparticle interaction. The fitting results obtained were the mean radius of the particle: 5.6 (standard deviation = ± 0.3 nm) and 7.2 nm (standard deviation = ± 0.7 nm) for 75 and 95 min of irradiation, respectively.

For SAXS data obtained at 105 min of irradiation, a cylinder model was used. A LogNormal radius distribution was considered. In this case, the contribution of the interparticle interaction was not required. The fitting results obtained were a mean radius of 4.0 nm (standard deviation = ± 0.4 nm) and a length of 40.0 nm.

For the scattering profile obtained at 135 min, a model using a coexistence of cylinders and bilayer vesicles was employed. For both populations, a LogNormal radius distribution was introduced. For bilayer vesicles, the introduction of a structure factor was required to taking into account the interparticle interaction. The fitting results obtained for the cylinders are a mean radius of 4.0 (standard deviation = ± 0.4 nm) nm and a length of 44.0 nm and, for the vesicles, a mean diameter of 41.0 nm ($2R_c+2t_h+4t_t$) and a bilayer thickness equal to 11.7 nm (t_h+2t_t).

The SAXs diagrams from 145 min to 235 min of irradiation were fitting using only a bilayer vesicles model. A LogNormal radius distribution and a factor structure were required to fit the data. As a result, the mean diameter ($2R_c+2t_h+4t_t$) of the overall particles could be obtained: of 49.2, 51.0 and 50.0 nm corresponding to 145, 195 and 235 min of reaction. For all these cases, the wall thickness corresponding to the bilayer membrane remained constant in approximately 13.0 nm (t_h+2t_t). The following is a representation of the vesicle with the fitting structural parameters as reference:



Section S-4: We have performed rheological measurements with the aim to estimate the conversion in the gel point for the sample modified with 10 wt % BCP. For this test, we measured the storage modulus (*G'*) and loss modulus (*G''*) for samples irradiated for different times under identical conditions to those used in the work. Measurements were performed in an Anton Paar rheometer (model Physica MCR-301) with a parallel-plate configuration (diameter D = 25 mm, gap H = 1 mm) in oscillatory mode with a 1% amplitude at a frequency of 1 Hz. The conversion vs. irradiation time data showed in Figure 2 of the manuscript were used to transform the time data of the rheology experiment into conversion data. The gel point took place at a conversion value around 30%, as determined by the crossover of G' and G''.

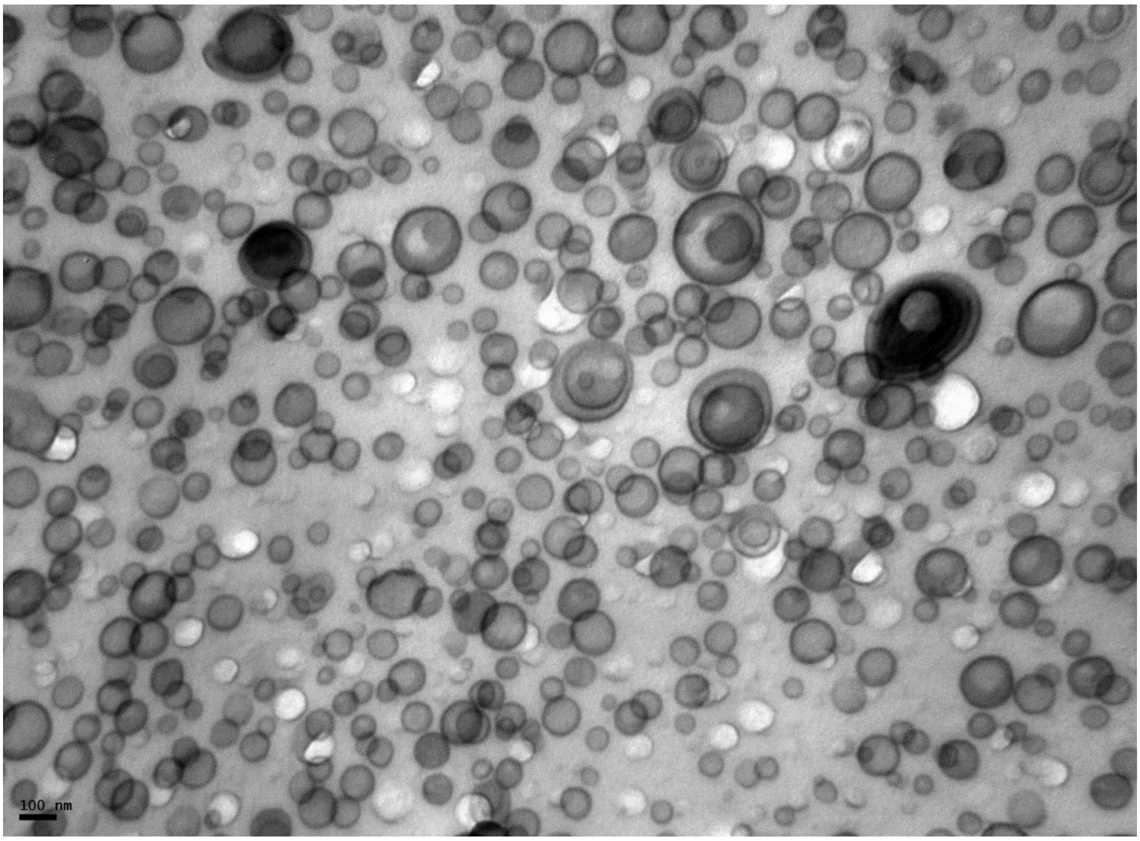


Figure S-5: TEM image of sample containing 10 wt% PEB-*b*-PEO photocured 4h at room temperature and postcured 1h at 120°C.

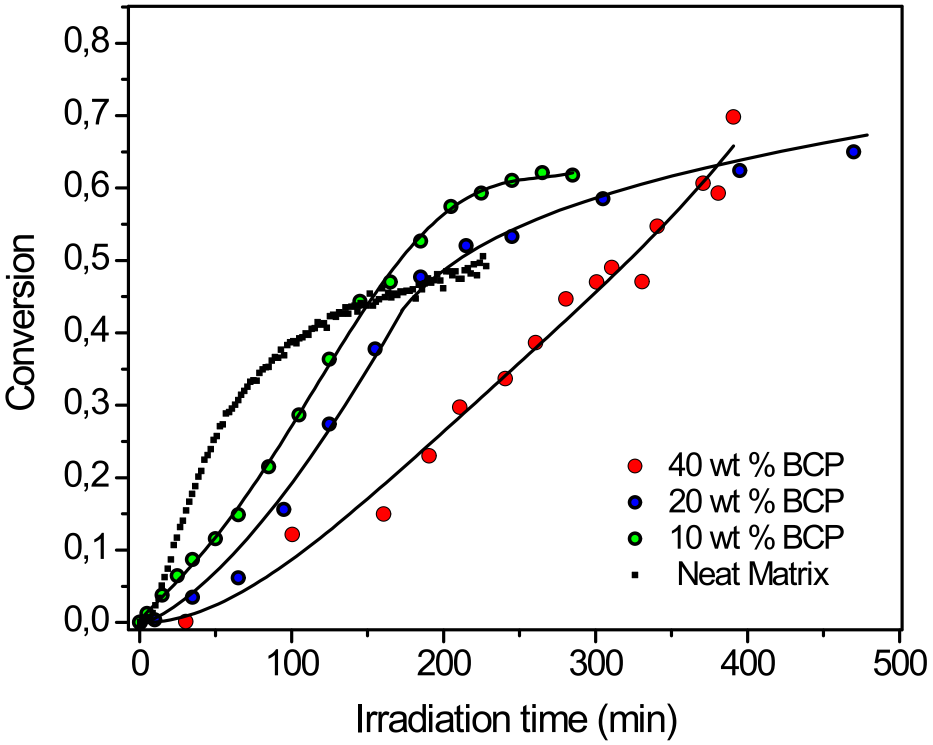


Figure S-6: Conversion of epoxy groups as a function of irradiation time for blends containing 0, 10, 20 and 40 wt % PEB-*b*-PEO photocured at room temperature. Lines are drawn to guide the eye.