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## Supporting information for:

# Effect of Core Crosslinking on the Physical Properties of Polydimethylsiloxane-based Diblock Copolymer Worms Prepared in Silicone Oil

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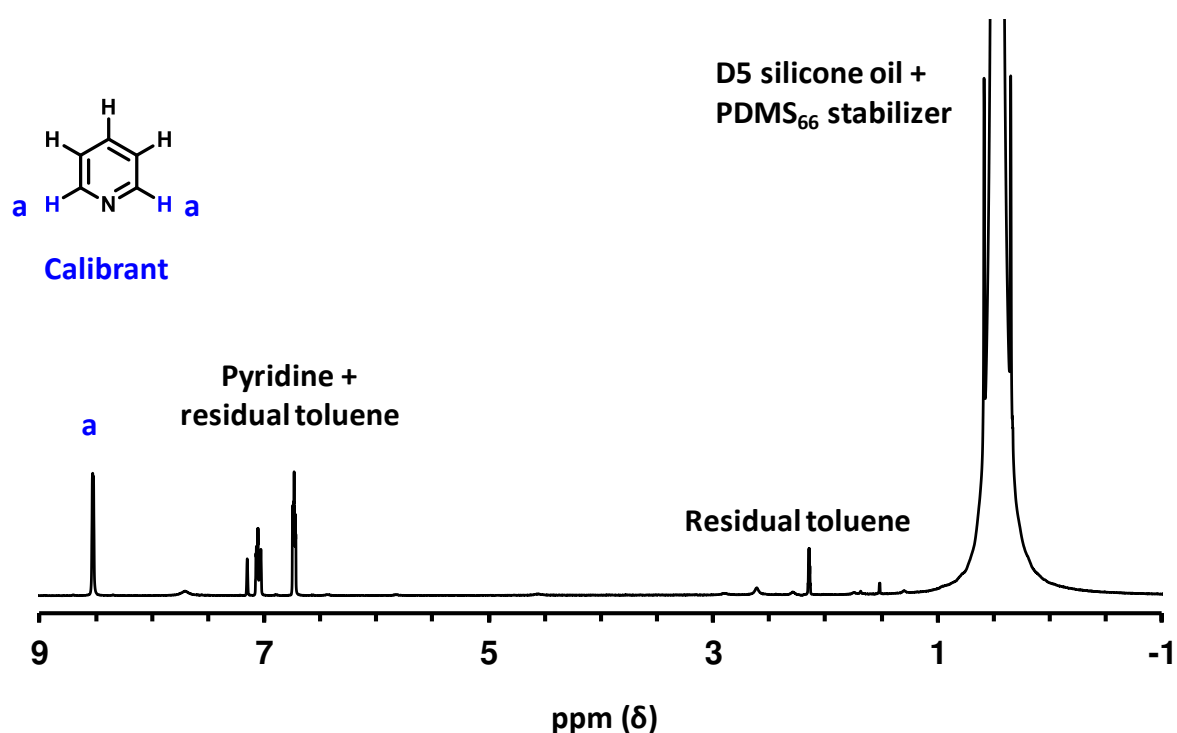
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*b.* Scott Bader Company Ltd, Wollaston, Wellingborough, Northamptonshire, NN29 7RL, UK.

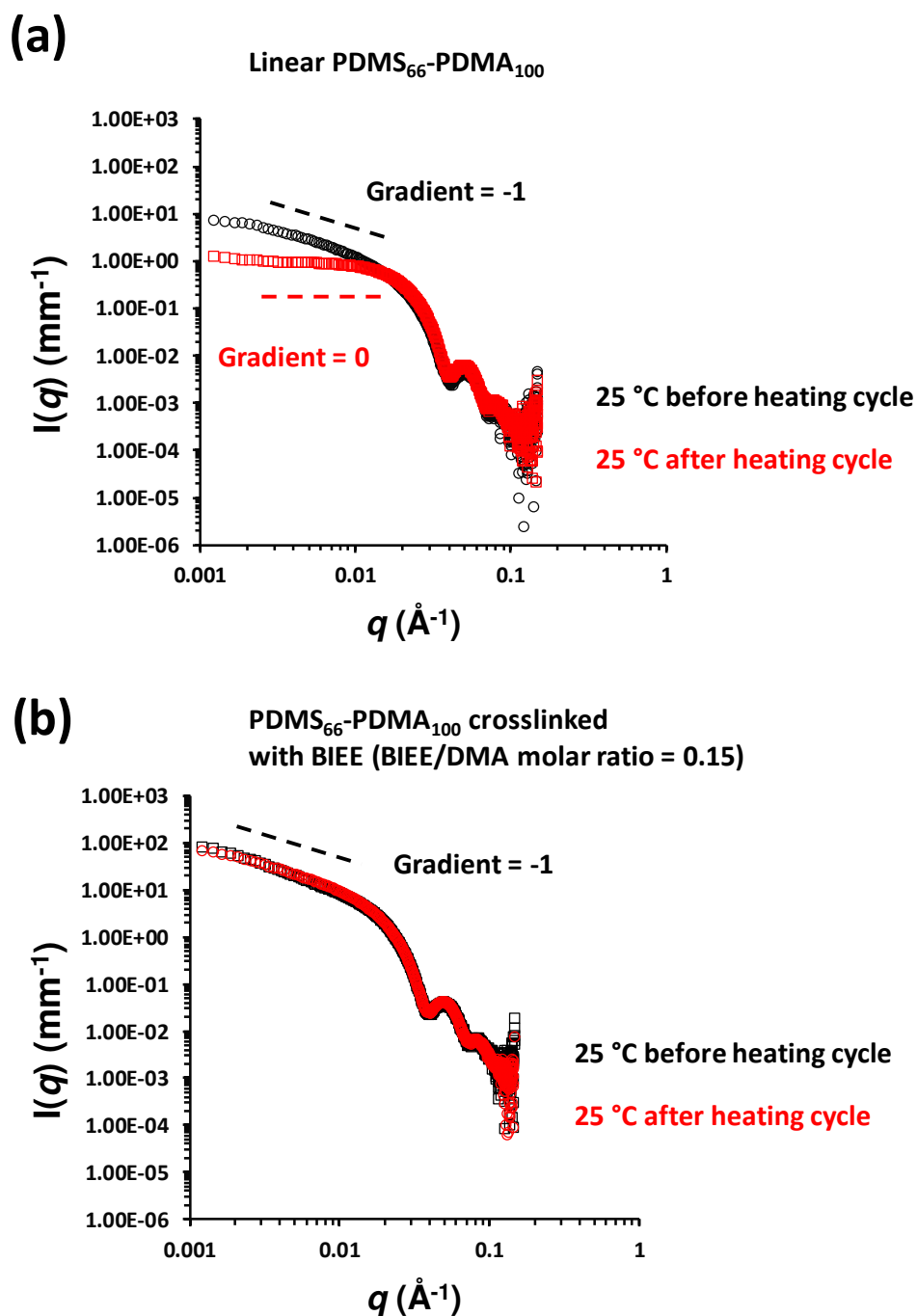
\*Authors to whom correspondence should be addressed ([s.p.arnes@sheffield.ac.uk](mailto:s.p.arnes@sheffield.ac.uk), [m.rymaruk@sheffield.ac.uk](mailto:m.rymaruk@sheffield.ac.uk)).

**Table S1.** Summary of GPC data and TEM morphology assignment for the PDMS<sub>66</sub>-PDMA<sub>105</sub> and PDMS<sub>66</sub>-PDMA<sub>190</sub> diblock copolymers examined in this study.

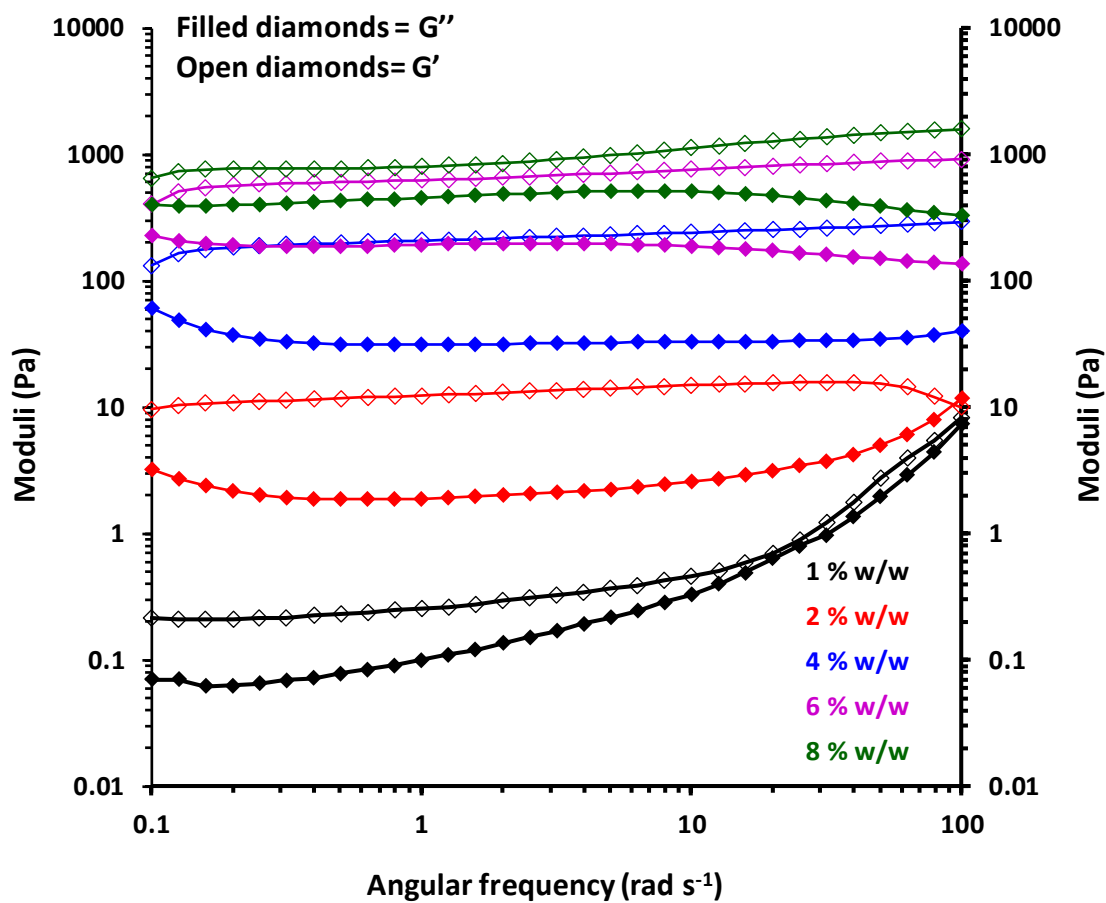
Target Block composition	DMA conversion	Actual block composition	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	TEM Morphology
PDMS <sub>66</sub> -PDMA <sub>105</sub>	95	PDMS <sub>66</sub> -PDMA <sub>100</sub>	20,900	1.21	Worms
PDMS <sub>66</sub> -PDMA <sub>190</sub>	93	PDMS <sub>66</sub> -PDMA <sub>176</sub>	35,500	1.24	Vesicles



**Figure S1.** <sup>1</sup>H NMR spectrum recorded at 20 °C (after heating to 100 °C) for a 5.0 % w/w dispersion of PDMS<sub>66</sub>-PDMA<sub>100</sub> diblock copolymer worms in D5. The NMR tube was equipped with a coaxial inner tube containing toluene-d<sub>8</sub> as a lock solvent and 0.1 M pyridine as an external standard. The lack of PDMA core-forming signals in this spectrum confirms that the increase in solvation of the core-forming PDMA block observed above 40 °C is fully reversible.

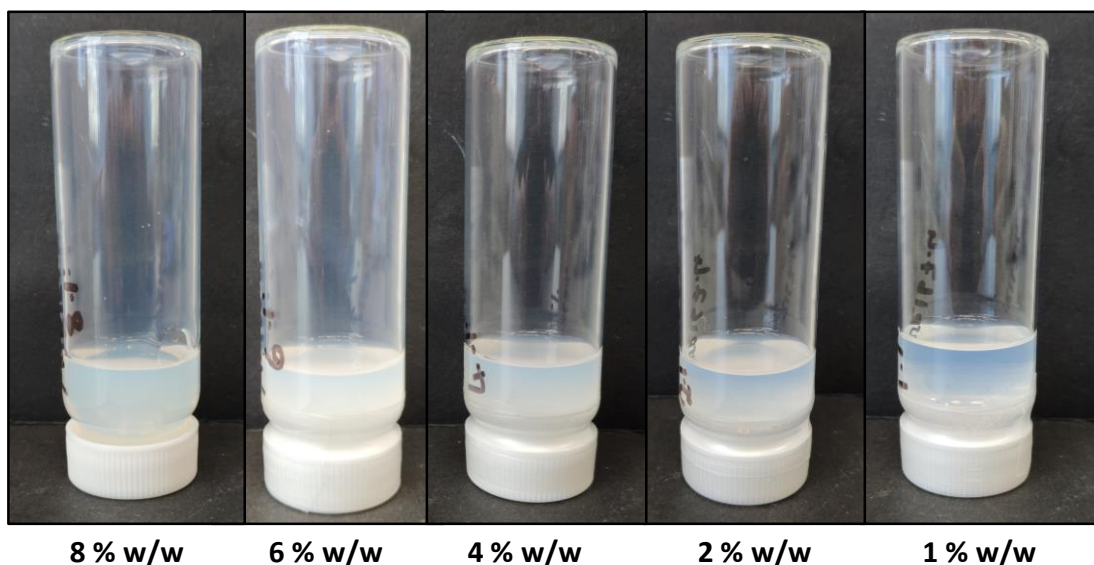


**Figure S2.** Small-angle X-ray scattering patterns recorded for: (a) a 1.0 % w/w dispersion of PDMS<sub>66</sub>-PDMA<sub>100</sub> linear worms at 25 °C, prior to heating (black open circles). The same sample was then heated to 110 °C, equilibrated for 20 min, cooled to 25 °C and equilibrated for a further 20 min before being reanalyzed (open red squares). The change in the low  $q$  gradient from approximately -1 to approximately 0 indicates a worm-to-sphere transition. Dashed lines representing gradients of -1 (black dashed line) and 0 (red dashed line) are included as a guide to the eye. (b) A 1.0 % w/w dispersion of BIEE cross-linked PDMS<sub>66</sub>-PDMA<sub>100</sub> worms (BIEE/DMA molar ratio = 0.15) at 25 °C (open black squares). The same dispersion was then heated to 110 °C, equilibrated for 20 min, cooled to 25 °C and reanalyzed (open red circles). The almost perfect overlap for these two SAXS patterns confirms that these cross-linked worms do not undergo a worm-to-sphere transition at 110 °C.

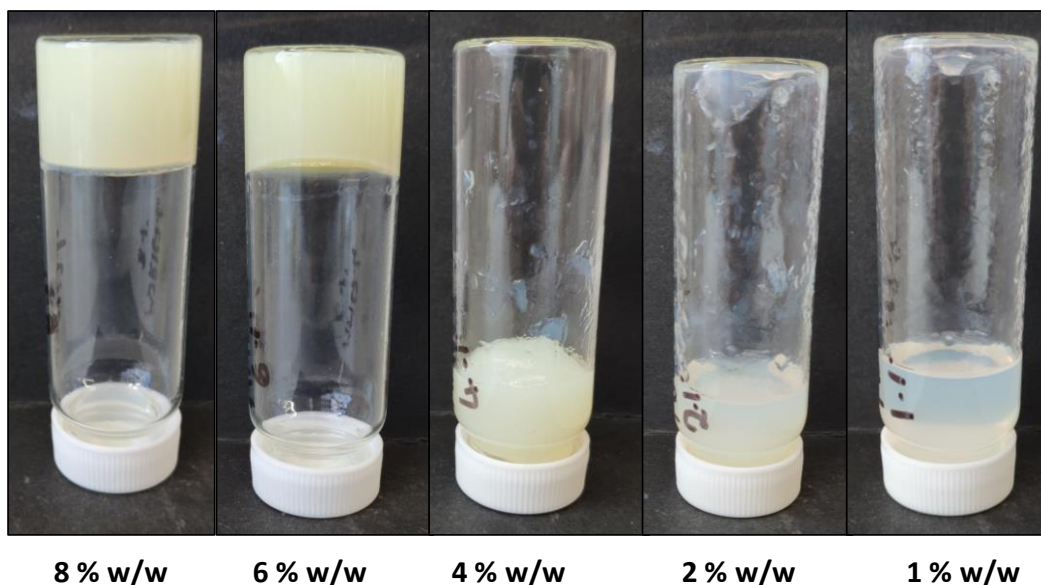


**Figure S3.** Angular frequency sweep conducted at an applied strain of 1% for a series of BIEE cross-linked PDMS<sub>66</sub>-PDMA<sub>100</sub> worm dispersions (BIEE/DMA molar ratio = 0.15) at copolymer concentrations of 1% w/w (black data), 2% w/w (red data), 4% w/w (blue data), 6% w/w (purple data) and 8% w/w (green data). In each case, open diamonds denote  $G'$  and filled diamonds denote  $G''$ .

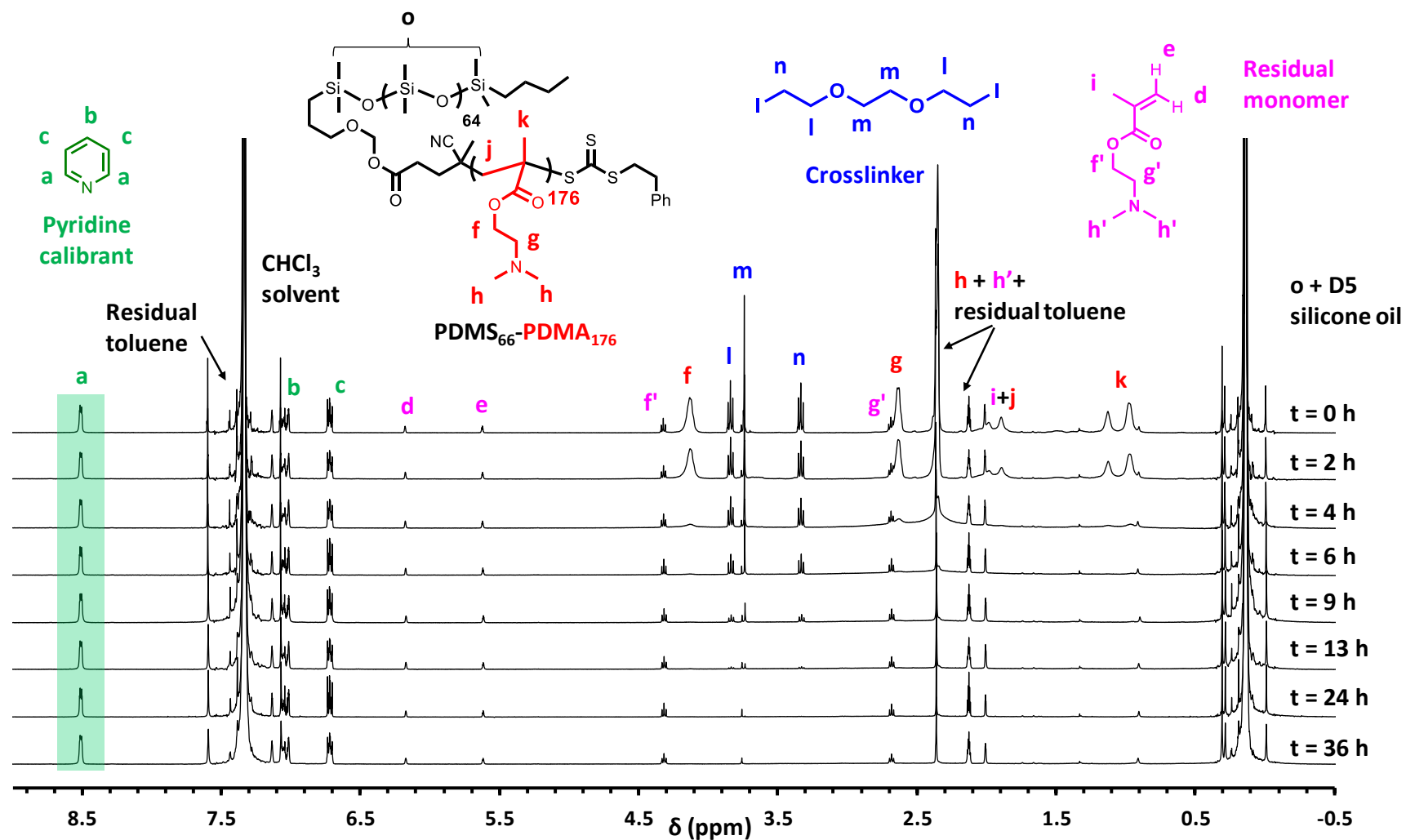
PDMS<sub>66</sub>-PDMA<sub>100</sub> diblock copolymer worms at various concentrations in D5 silicone oil



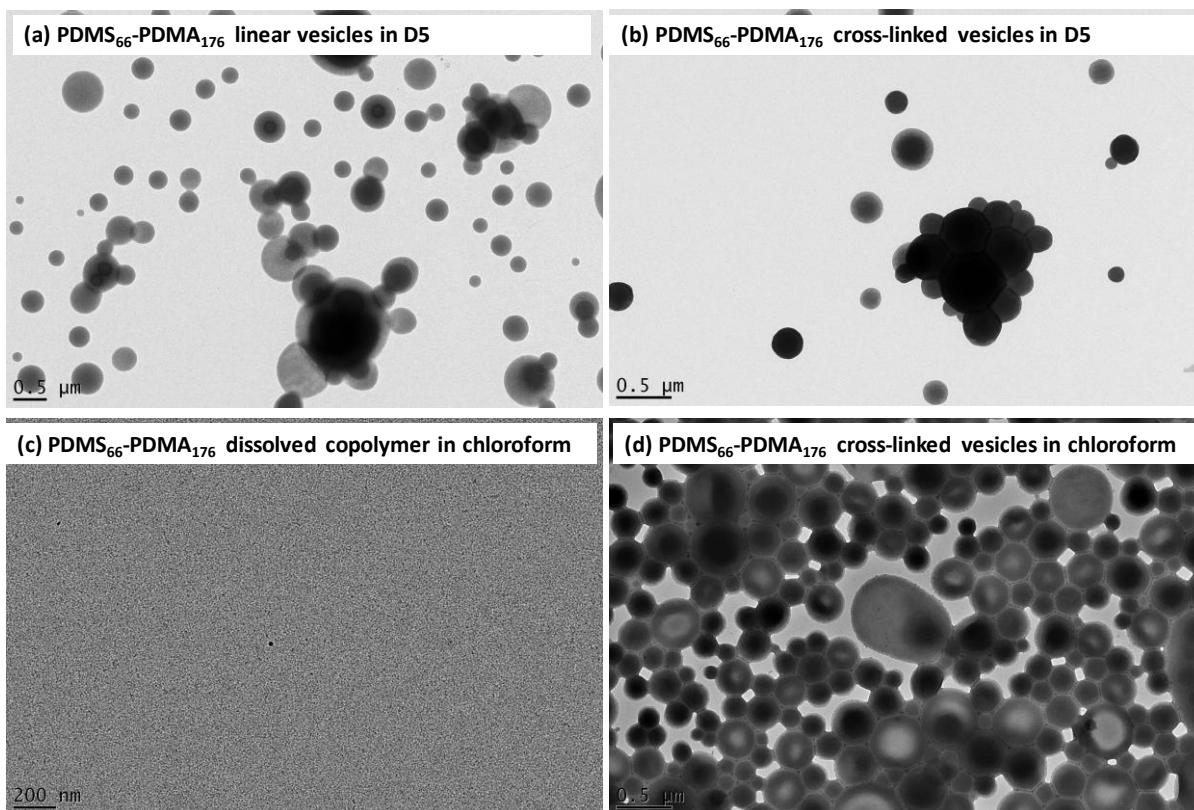
↓  
BIEE (BIEE/DMA molar ratio = 0.15)  
5 days  
20 °C



**Figure S4.** Digital photographs recorded for a series of PDMS<sub>66</sub>-PDMA<sub>100</sub> worm dispersions over a range of copolymer concentrations in D5 silicone oil. BIEE (BIEE/DMA molar ratio = 0.15) was added to each of these dispersions and quaternization was allowed to occur over 5 days at 20 °C.



**Figure S5.** Assigned  $^1\text{H}$  NMR spectra recorded during the reaction of 25% w/w PDMS<sub>66</sub>-PDMA<sub>176</sub> vesicles at in D5 silicone oil with BIEE cross-linker at 20 °C (15 mol % BIEE relative to the DMA residues). Aliquots were removed from the reaction mixture at regular intervals and diluted ten-fold in chloroform before being analyzed. Each NMR tube was equipped with a coaxial inner tube containing toluene- $d_8$  as a lock solvent and 0.1 M pyridine as an external standard. The attenuation of the oxymethylene protons assigned to the PDMA block (labeled **f**), and the protons assigned to the BIEE (**l**, **m** and **n**) were monitored relative to the pyridine external standard (labeled **a**).



**Figure S6.** TEM images recorded at a copolymer concentration of 0.25 % w/w for (a) Linear PDMS<sub>66</sub>-PDMA<sub>176</sub> vesicles in D5 silicone oil. (b) PDMS<sub>66</sub>-PDMA<sub>176</sub> vesicles cross-linked with BIEE (DMA/BIEE molar ratio = 0.15) in D5 silicone oil. (c) Linear PDMS<sub>66</sub>-PDMA<sub>176</sub> vesicles in chloroform. Chloroform is a good solvent for both the PDMS and the PDMA blocks, therefore, molecular dissolution takes place to yield diblock copolymer chains. (d) PDMS<sub>66</sub>-PDMA<sub>176</sub> vesicles cross-linked with BIEE (DMA/BIEE molar ratio = 0.15) in chloroform. The covalent stabilization afforded by the BIEE ensures the vesicles remain intact in chloroform.