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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Table S1. Summary of GPC data and TEM morphology assignment for the $PDMS_{66}$-$PDMA_{105}$ and $PDMS_{66}$-$PDMA_{190}$ diblock copolymers examined in this study.

Target Block composition	DMA conversion	Actual block composition	M_n	M_w/M_n	TEM Morphology
$PDMS_{66}$-$PDMA_{105}$	95	$PDMS_{66}$-$PDMA_{100}$	20,900	1.21	Worms
$PDMS_{66}$-$PDMA_{190}$	93	$PDMS_{66}$-$PDMA_{176}$	35,500	1.24	Vesicles

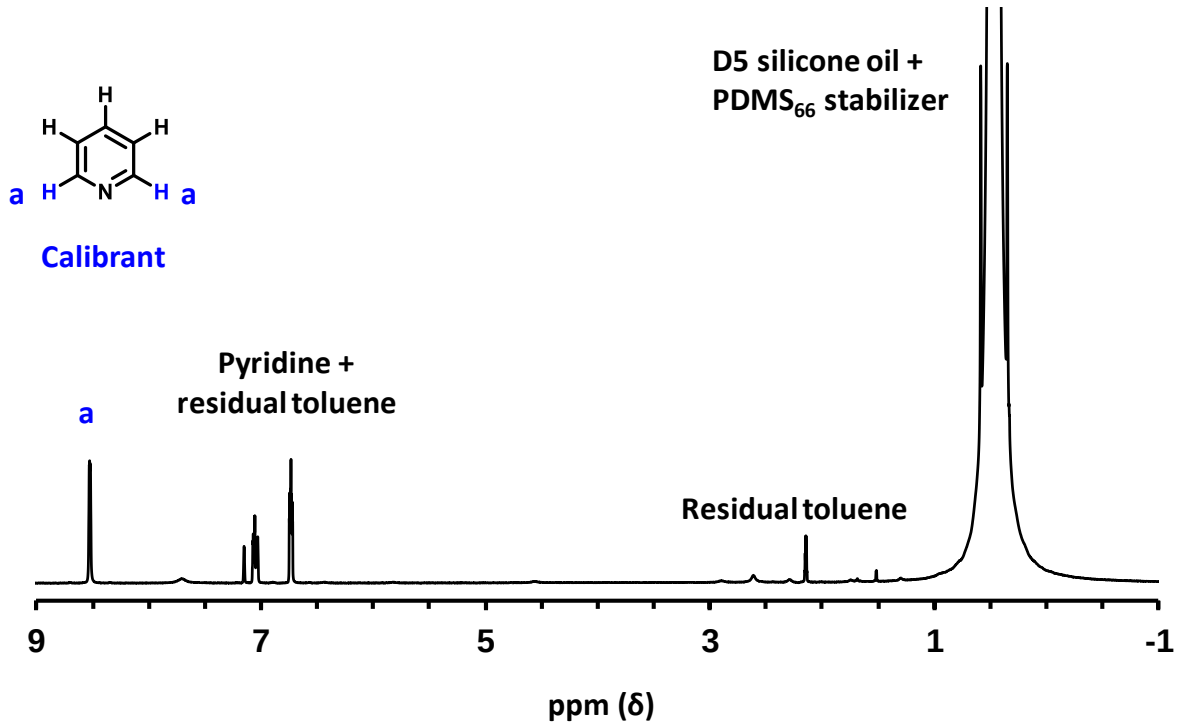

Figure S1. ^{1}H NMR spectrum recorded at 20 °C (after heating to 100 °C) for a 5.0 % w/w dispersion of $PDMS_{66}$-$PDMA_{100}$ diblock copolymer worms in D5 The NMR tube was equipped with a coaxial inner tube containing toluene-d_8 as a lock solvent and 0.1 M pyridine as an external standard. The lack 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.

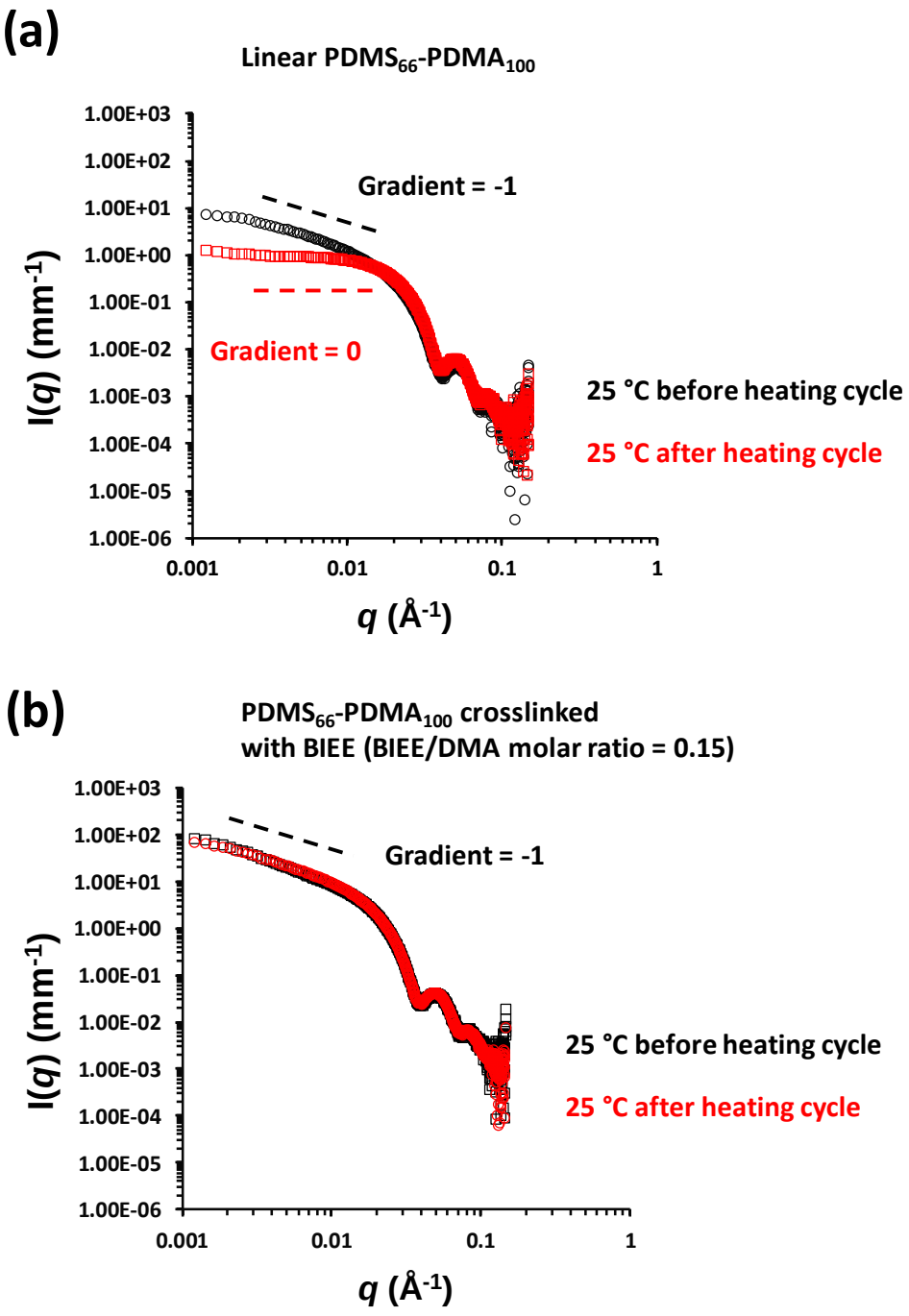

Figure S2. Small-angle X-ray scattering patterns recorded for: (a) a 1.0 % w/w dispersion of $PDMS_{66}$-$PDMA_{100}$ linear worms at 25 °C, prior to heating (black open circles). The same sample was then heated to 110 °C, equilibrated for 20 min, cooled to 25 °C and equilibrated for a further 20 min 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 $PDMS_{66}$-$PDMA_{100}$ 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.

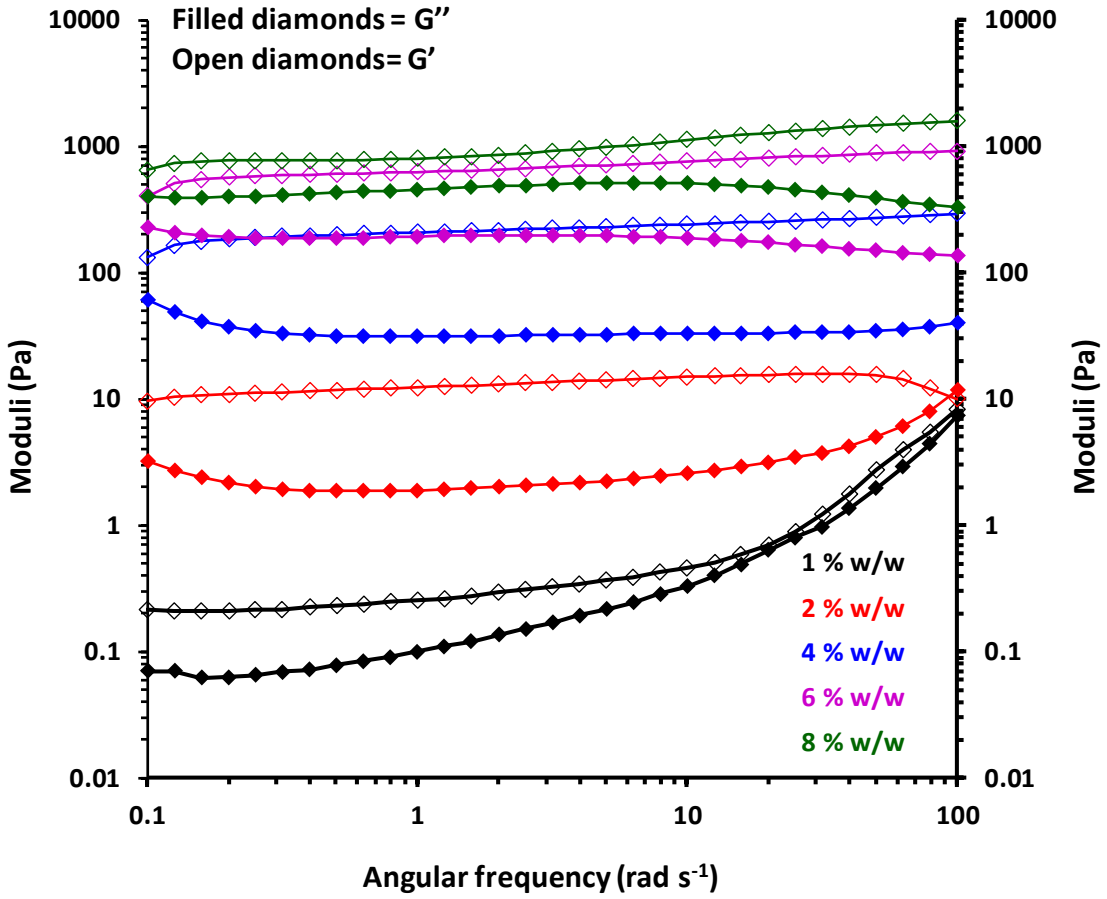

Figure S3. Angular frequency sweep conducted at an applied strain of 1% for a series of BIEE cross-linked $PDMS_{66}$-$PDMA_{100}$ worm dispersions (BIEE/DMA molar ratio = 0.15) at copolymer concentrations of 1% w/w (black data), 2% w/w (red data), 4% w/w (blue data), 6% w/w (purple data) and 8% w/w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

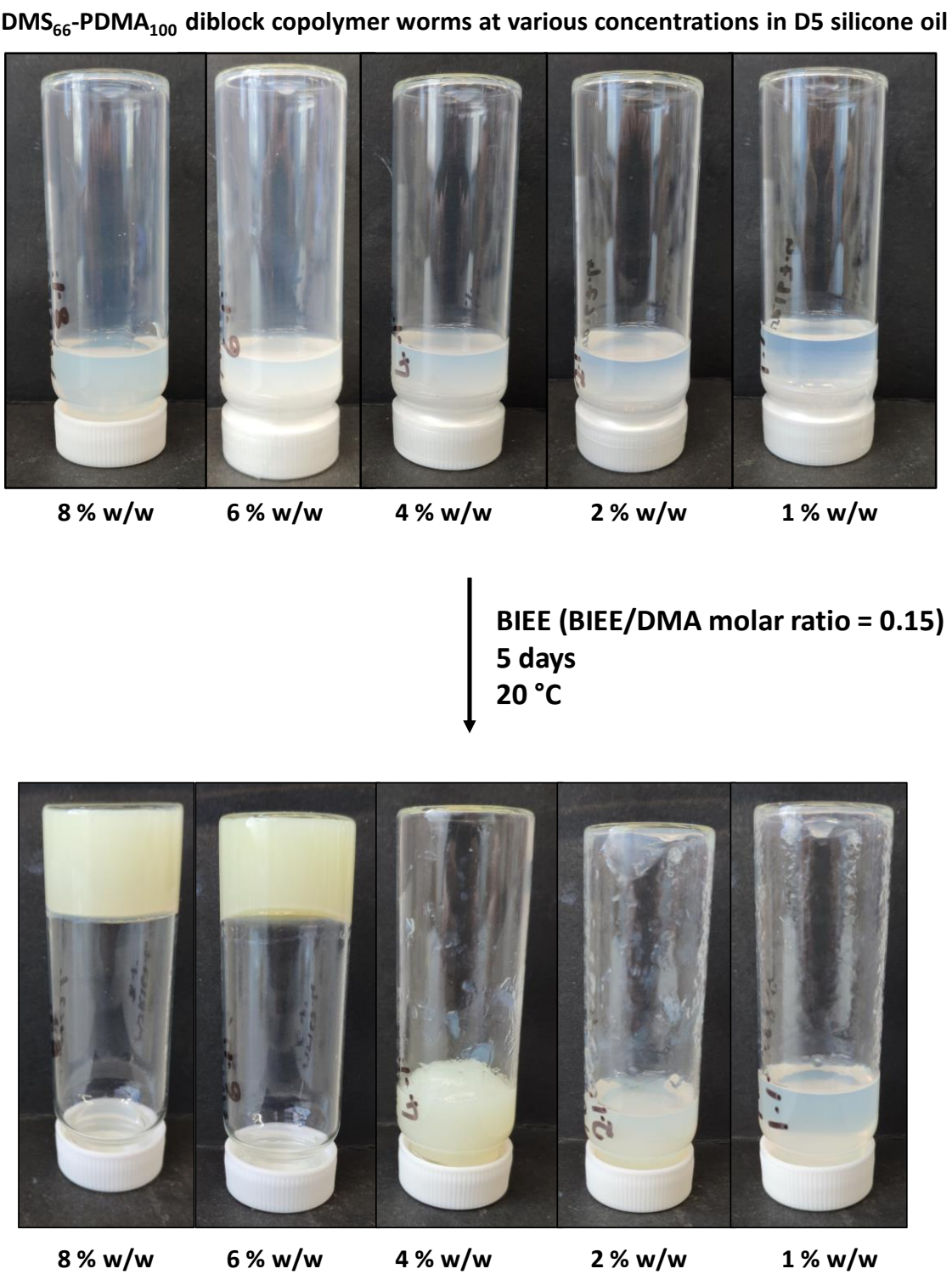

Figure S4. Digital photographs recorded for a series of $PDMS_{66}$-$PDMA_{100}$ worm dispersions over a range of copolymer concentrations in D5 silicone oil. BIEE (BIEE/DMA molar ratio = 0.15) was added to each of these dispersions and quaternization was allowed to occur over 5 days at 20 °C.

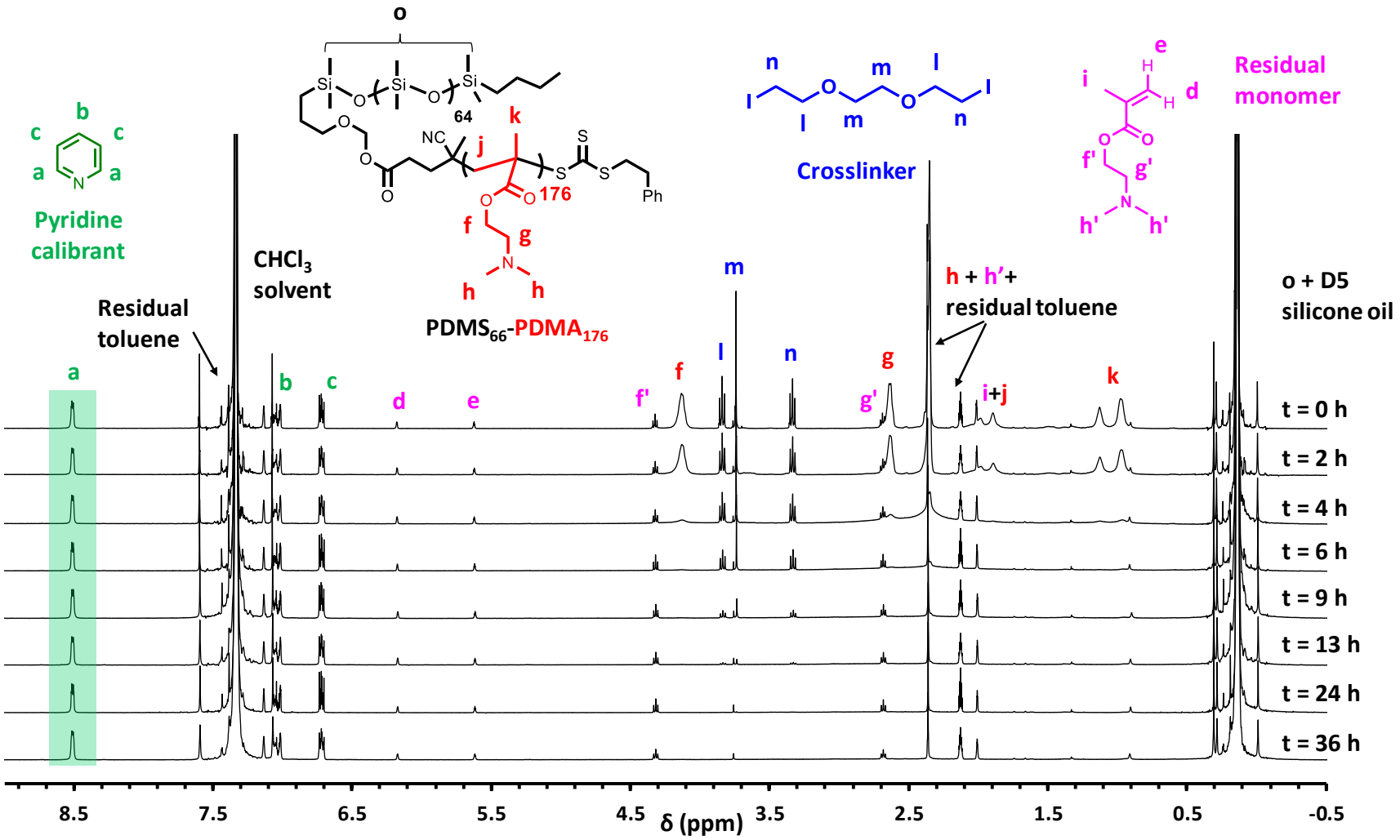

Figure S5. Assigned ^{1}H NMR spectra recorded during the reaction of 25% w/w $PDMS_{66}$-$PDMA_{176}$ vesicles at in D5 silicone oil with BIEE cross-linker at 20 °C (15 mol % BIEE relative to the DMA residues). Aliquots were removed from the reaction mixture at regular intervals and diluted ten-fold 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**).

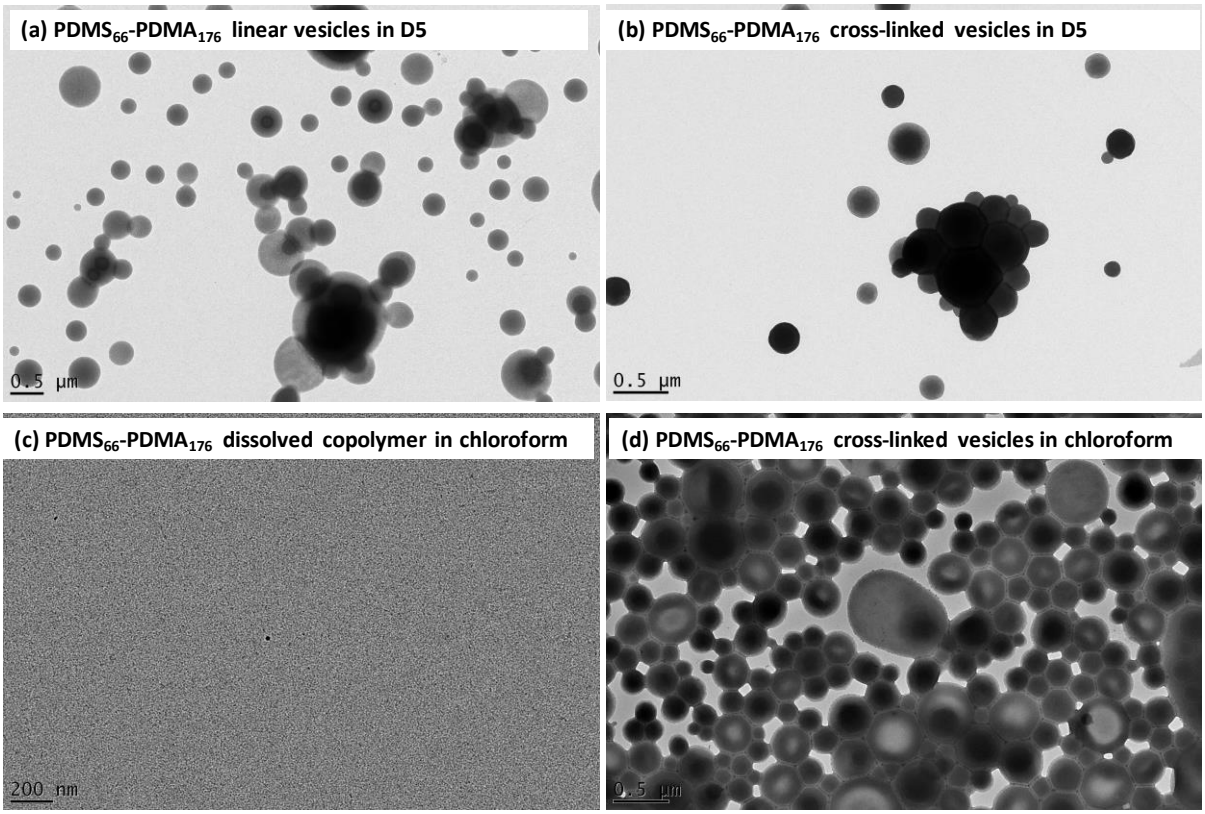

Figure S6. TEM images recorded at a copolymer concentration of 0.25 % w/w for (a) Linear $PDMS_{66}$-$PDMA_{176}$ vesicles in D5 silicone oil. (b) $PDMS_{66}$-$PDMA_{176}$ vesicles cross-linked with BIEE (DMA/BIEE molar ratio = 0.15) in D5 silicone oil. (c) Linear $PDMS_{66}$-$PDMA_{176}$ vesicles in 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) $PDMS_{66}$-$PDMA_{176}$ 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.