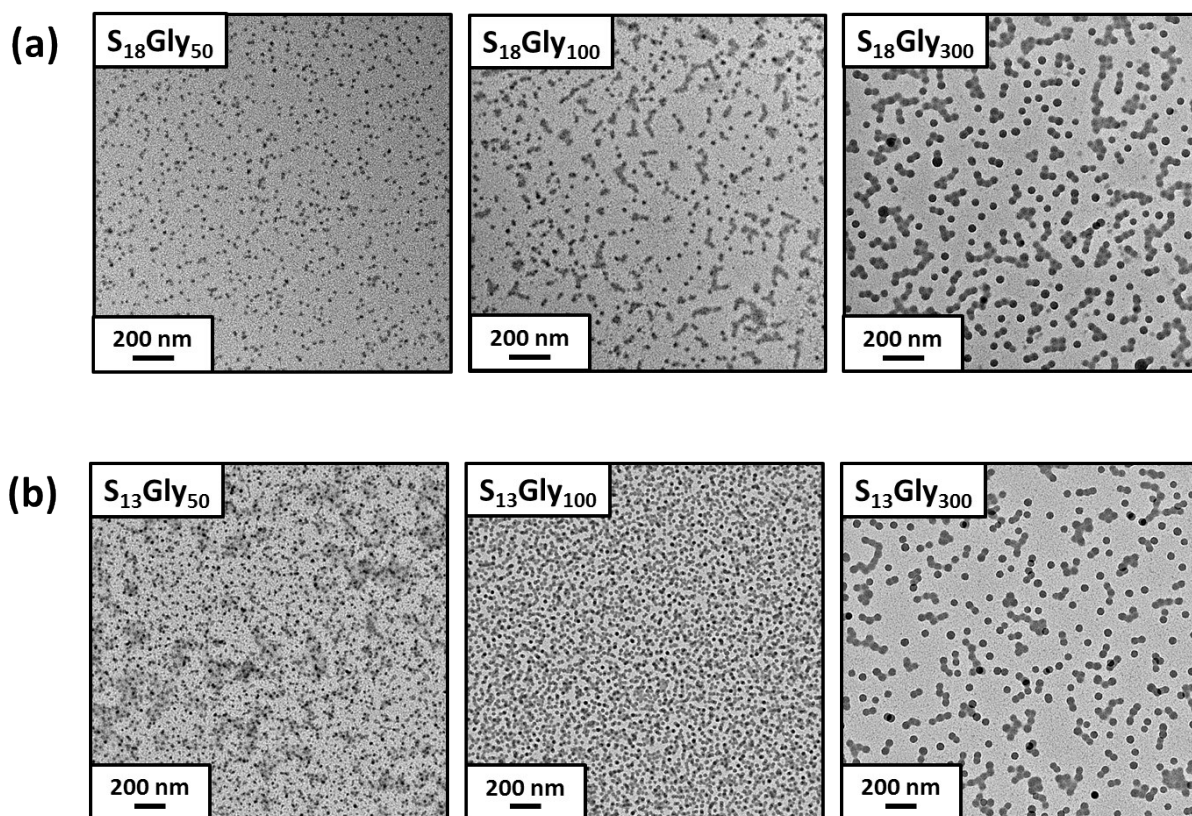


## Supporting Information for RAFT Dispersion Polymerization of Glycidyl Methacrylate for the Synthesis of Epoxy-Functionalized Block Copolymer Nanoparticles in Mineral Oil

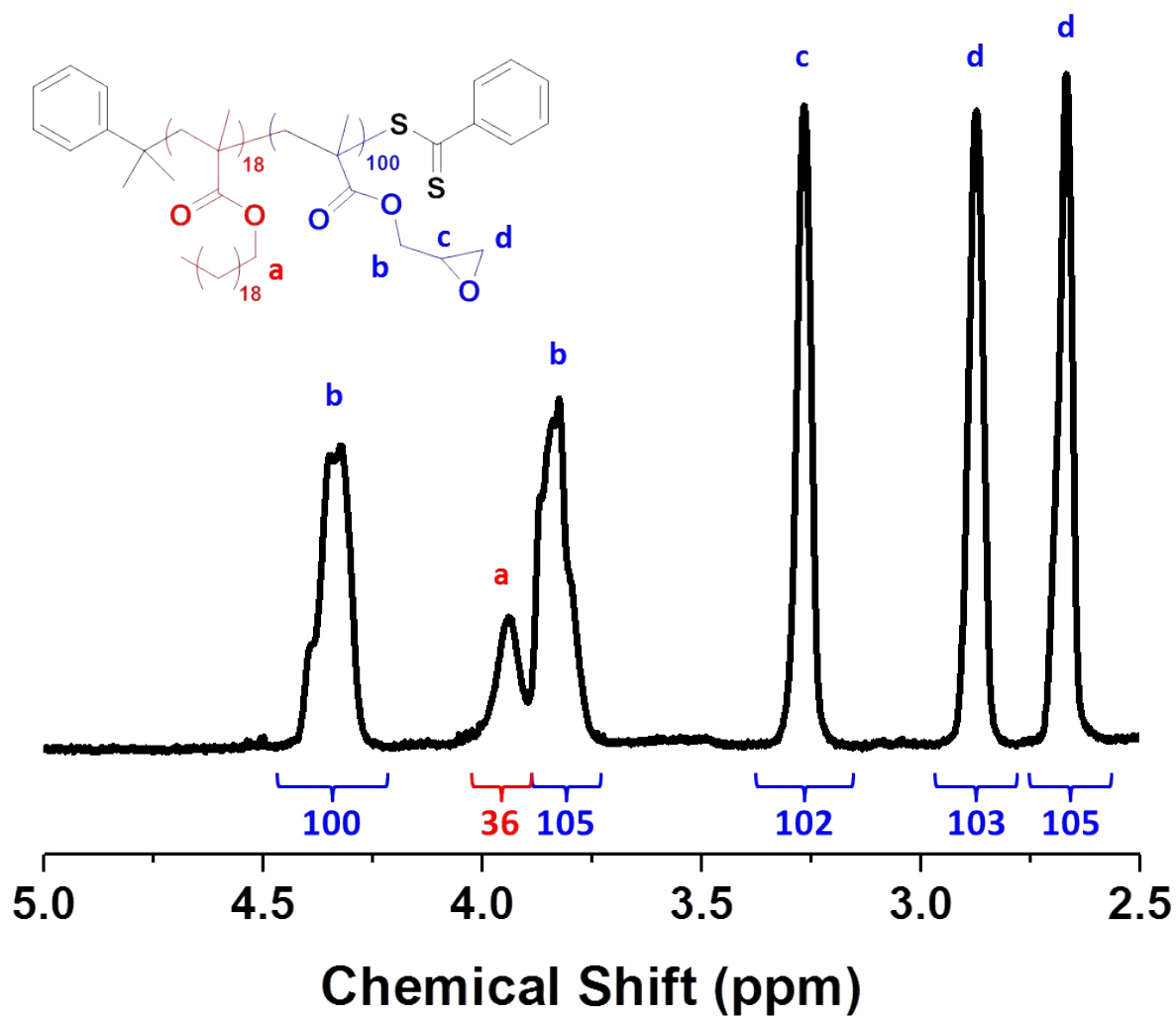
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**Table S1.** Summary of targeted (co)polymer composition, GlyMA conversions, GPC molecular weights, DLS data and observed TEM morphology for two series of PSMA<sub>19</sub>-PGlyMA<sub>x</sub> and PSMA<sub>13</sub>-PGlyMA<sub>x</sub> diblock copolymers prepared by RAFT dispersion polymerization of GlyMA in mineral oil at 70 °C using T21s initiator. Conditions: [PSMA macro-CTA]/[T21s] molar ratio = 5.0, 20% w/w total solids concentration.

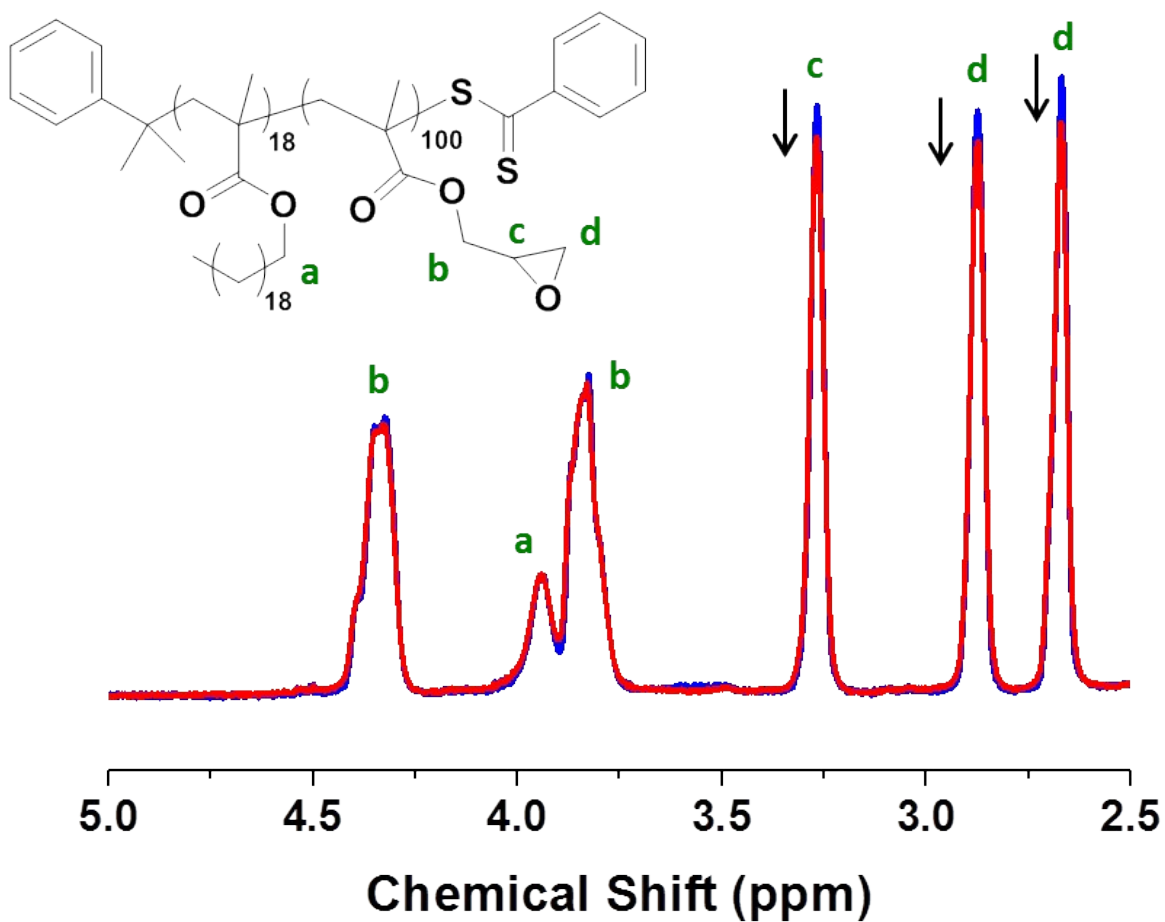
Target Composition	% GlyMA	CHCl <sub>3</sub> GPC		DLS	TEM Morphology
		$M_n / \text{g mol}^{-1}$	$M_w/M_n$	$D / \text{nm}$	
PSMA <sub>18</sub> macro-CTA	-	5,700	1.19	-	-
PSMA <sub>18</sub> -PGlyMA <sub>50</sub>	97	12,700	1.26	21 ± 4.7	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>75</sub>	99	15,700	1.23	25 ± 5.6	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>100</sub>	99	19,200	1.17	29 ± 5.0	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>125</sub>	98	22,200	1.27	32 ± 5.5	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>150</sub>	98	23,800	1.31	36 ± 8.0	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>175</sub>	96	25,700	1.25	37 ± 7.4	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>200</sub>	97	29,300	1.38	41 ± 7.1	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>300</sub>	97	40,300	1.64	51 ± 8.8	Spheres
PSMA <sub>13</sub> macro-CTA	-	4,100	1.22	-	-
PSMA <sub>13</sub> -PGlyMA <sub>50</sub>	98	10,800	1.16	22 ± 4.4	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>75</sub>	95	13,600	1.17	27 ± 8.1	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>100</sub>	96	16,100	1.19	31 ± 6.2	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>125</sub>	94	17,400	1.18	33 ± 9.9	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>150</sub>	94	22,100	1.22	45 ± 14	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>175</sub>	97	24,400	1.33	47 ± 15	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>200</sub>	98	30,700	1.24	55 ± 16	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>300</sub>	98	38,900	1.38	64 ± 17	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>375</sub>	96	48,300	1.31	74 ± 15	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>400</sub>	97	53,800	1.43	86 ± 19	Spheres



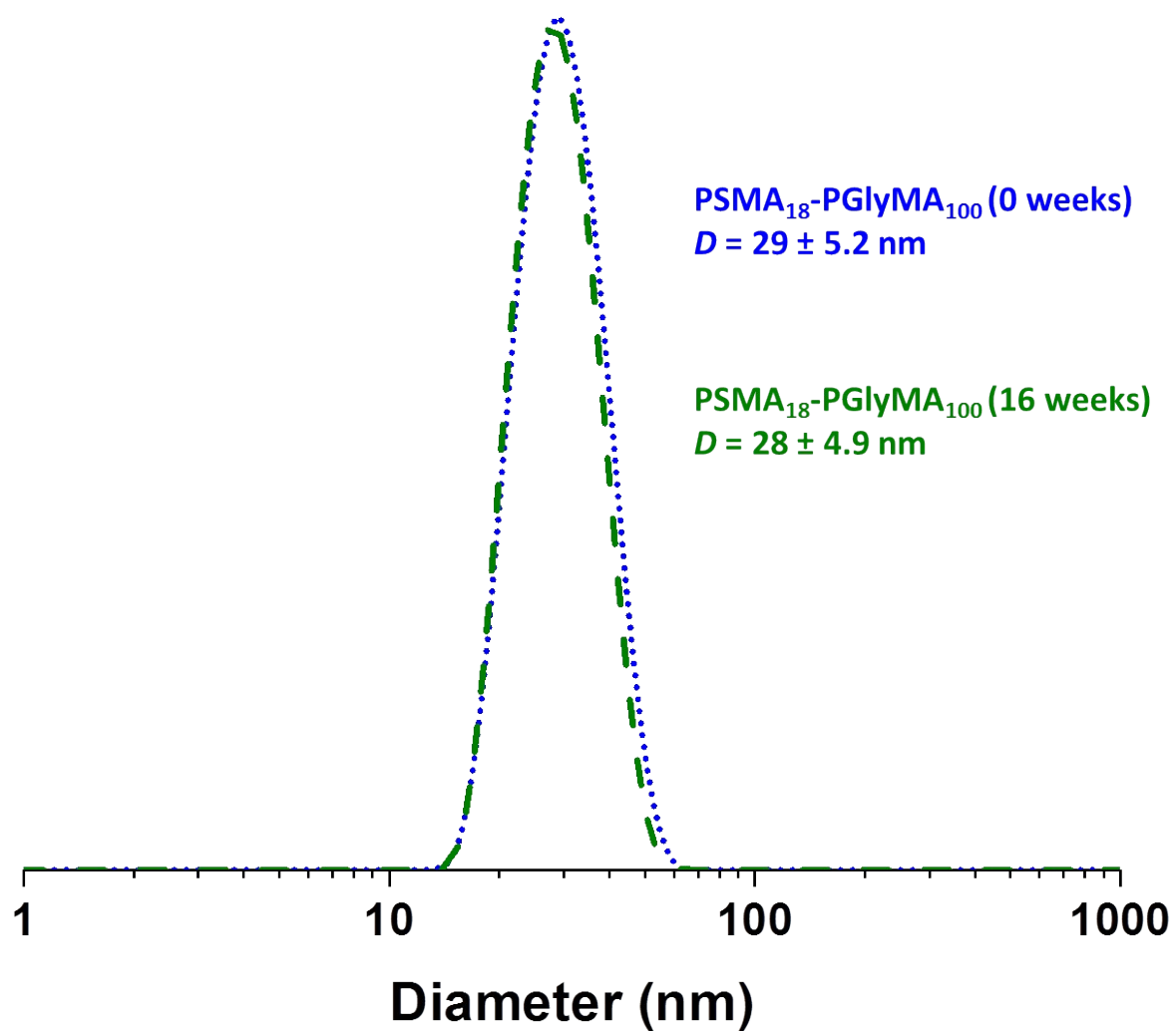
**Figure S1.** Representative transmission electron micrographs for selected (a) PSMA<sub>18</sub>-PGlyMA<sub>x</sub> and (b) PSMA<sub>13</sub>-PGlyMA<sub>x</sub> diblock copolymer spheres synthesized via RAFT dispersion polymerization in mineral oil.



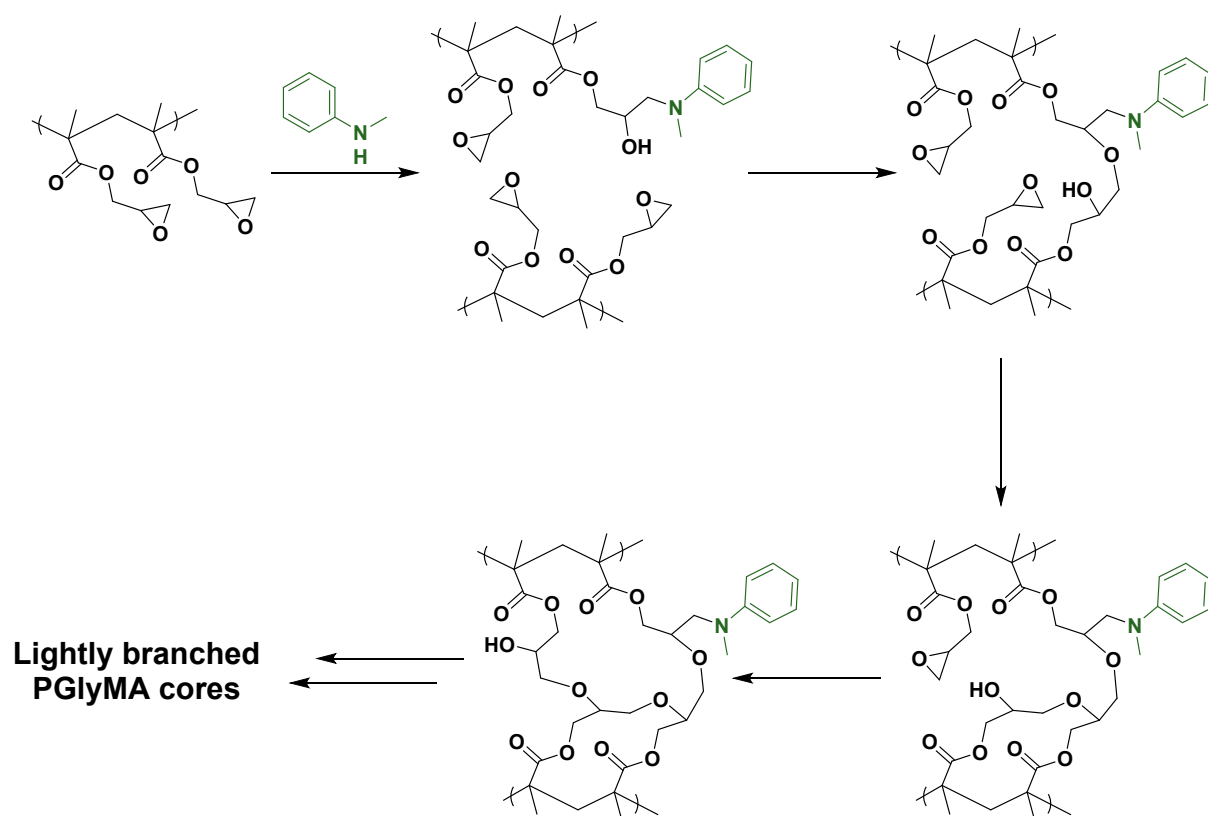
**Figure S2.** Assigned partial  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  for  $\text{PSMA}_{18}\text{-PGlyMA}_{100}$  directly after synthesis. Comparing the integral of the peak assigned to the PSMA oxymethylene protons at 3.9 ppm (a) with those assigned to the GlyMA residues (b, c and d) confirmed that all epoxy groups survived the RAFT dispersion polymerization in mineral oil.



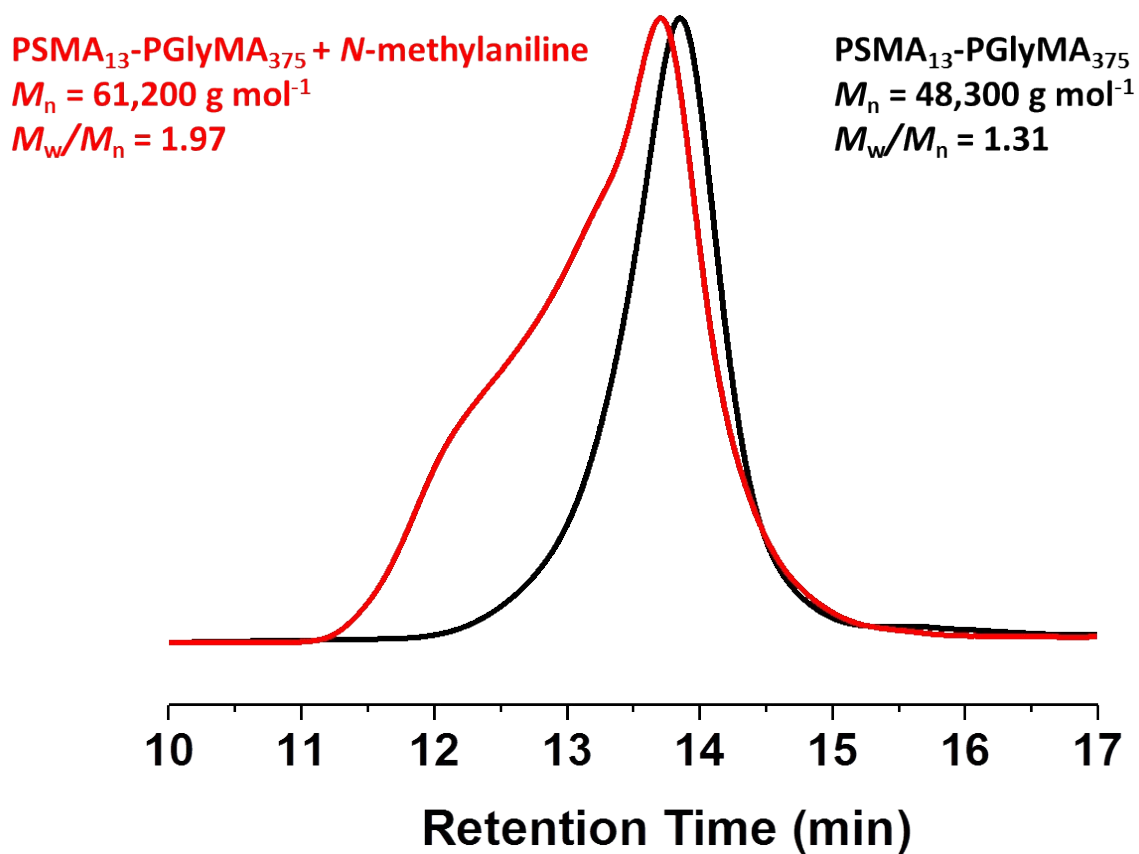
**Figure S3.** Assigned partial <sup>1</sup>H NMR spectrum for PSMA<sub>18</sub>-PGlyMA<sub>100</sub> in CDCl<sub>3</sub> after 0 weeks (blue data) and after 16 weeks (red data). Peak integration indicated a 27% reduction of epoxide functionality after storage at 20 °C for 16 weeks.



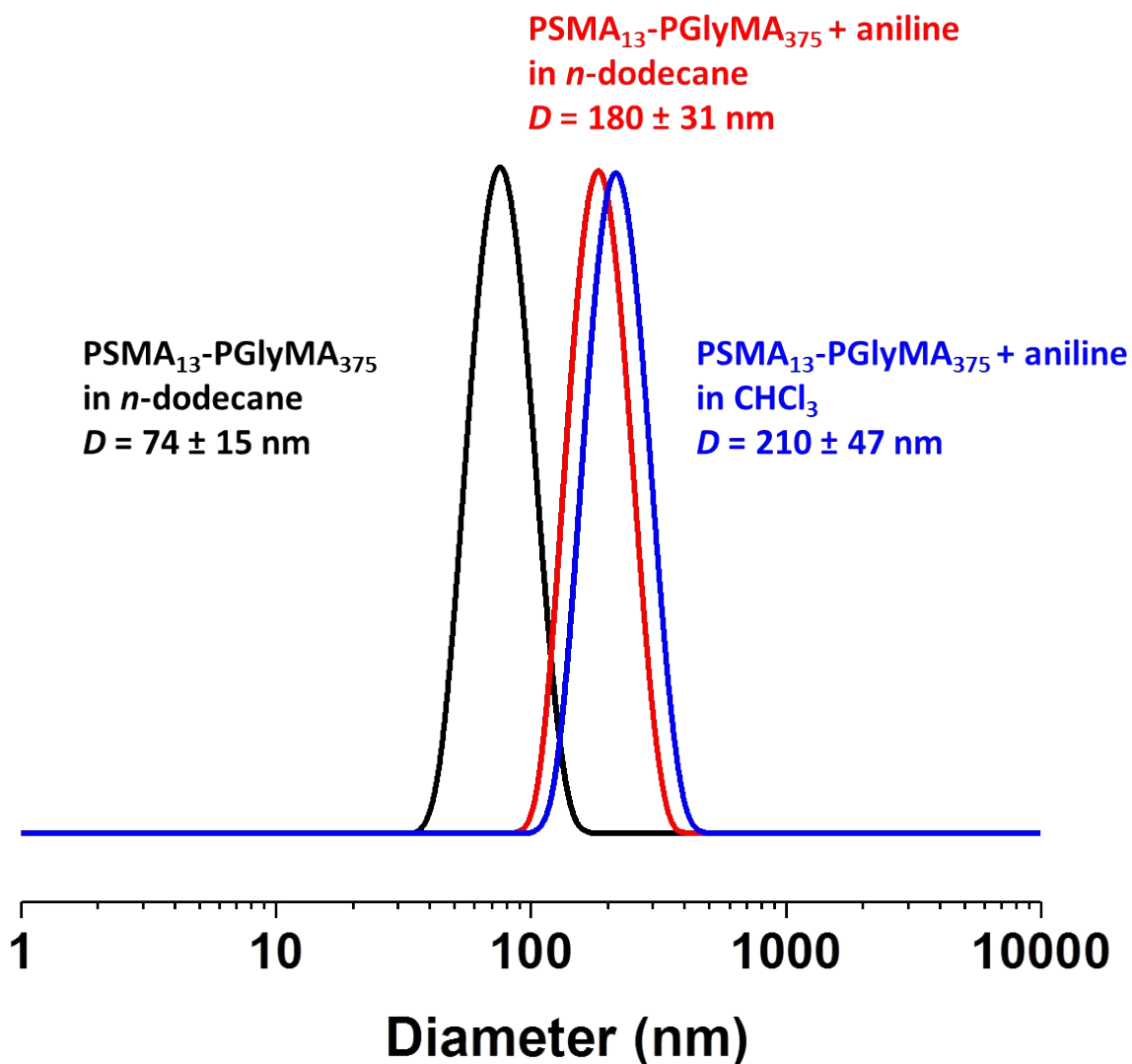
**Figure S4.** Intensity-average DLS particle size distributions recorded for PSMA<sub>18</sub>-PGlyMA<sub>100</sub> nanoparticles immediately after synthesis (blue dotted data) and after 16 weeks (green dashed data).



**Scheme S1.** Possible side-reactions involving ring-opening of epoxy groups by secondary hydroxyl groups (generated during the epoxy-amine reaction) that could lead to light chain-branching between PGlyMA chains (as suggested by GPC analysis, see Figure 4 in the main manuscript).



**Figure S5.** Gel permeation chromatograms recorded for PSMA<sub>13</sub>-PGlyMA<sub>375</sub> immediately after synthesis (black data) and after functionalization with *N*-methylaniline (red data). The shift of the main peak to higher molecular weight indicated the successful ring-opening of the GlyMA residues and thus *N*-methylaniline functionalization, whereas the significant high molecular weight shoulder confirms that numerous side reactions occurred as proposed in Scheme S1.



**Figure S6.** Intensity-average DLS particle size distributions recorded in *n*-dodecane for PSMA<sub>13</sub>-PGlyMA<sub>375</sub> nanoparticles immediately after synthesis (black data) and after functionalization with aniline (red data). In order to confirm crosslinking, DLS data were obtained on the functionalized nanoparticles in a known common solvent for both PSMA and PGlyMA blocks, CHCl<sub>3</sub> (blue data). The increase in particle size after functionalization can be attributed to the additional mass introduced to the copolymer chains, but importantly the size distribution remains narrow. On adding CHCl<sub>3</sub>, the nanoparticles swell as expected, but remain colloidally stable and thus confirms chemical crosslinking.