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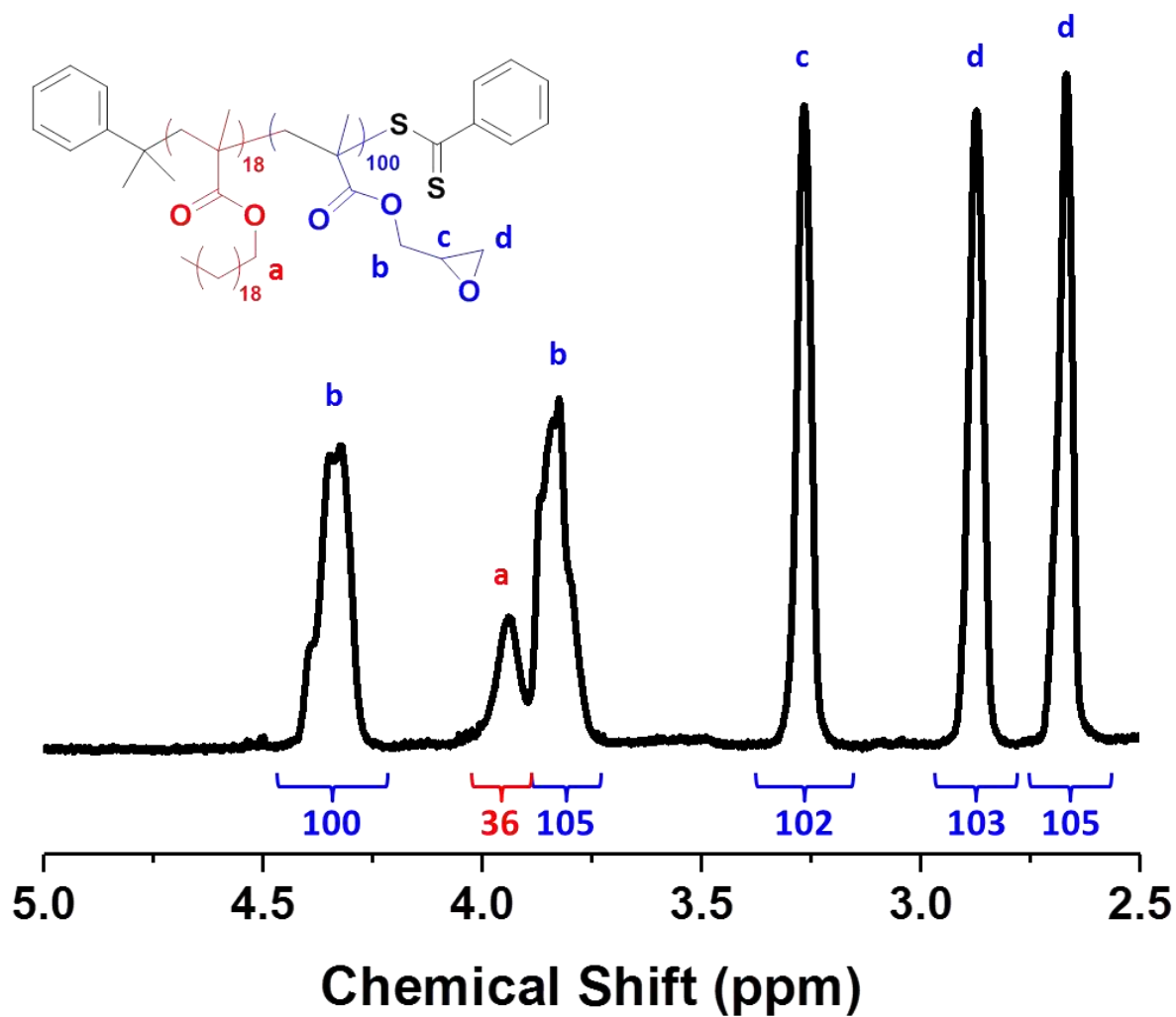
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# Supporting Information for RAFT Dispersion Polymerization of Glycidyl Methacrylate for the Synthesis of Epoxy-Functionalized Block Copolymer Nanoparticles in Mineral Oil

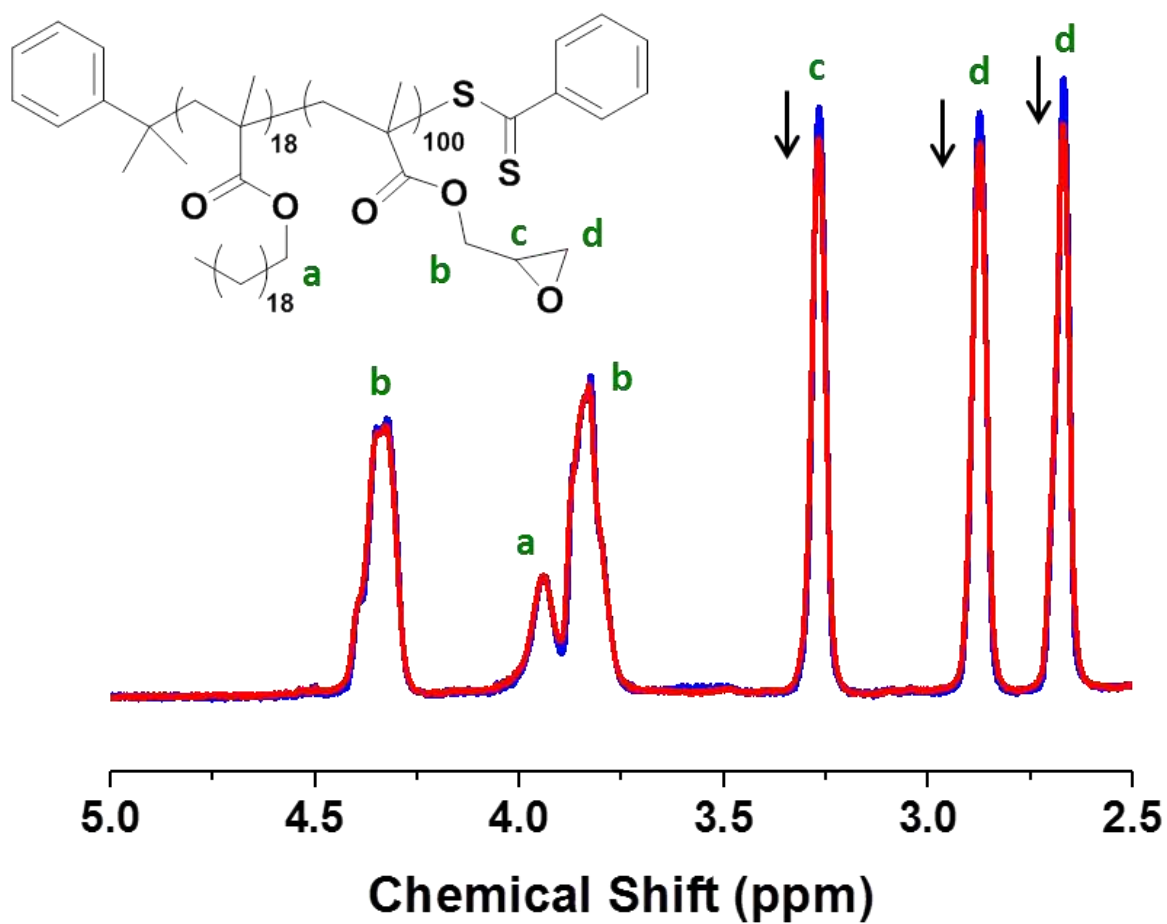
Philip J. Docherty, Matthew J. Derry\* and Steven P. Armes\*

**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.

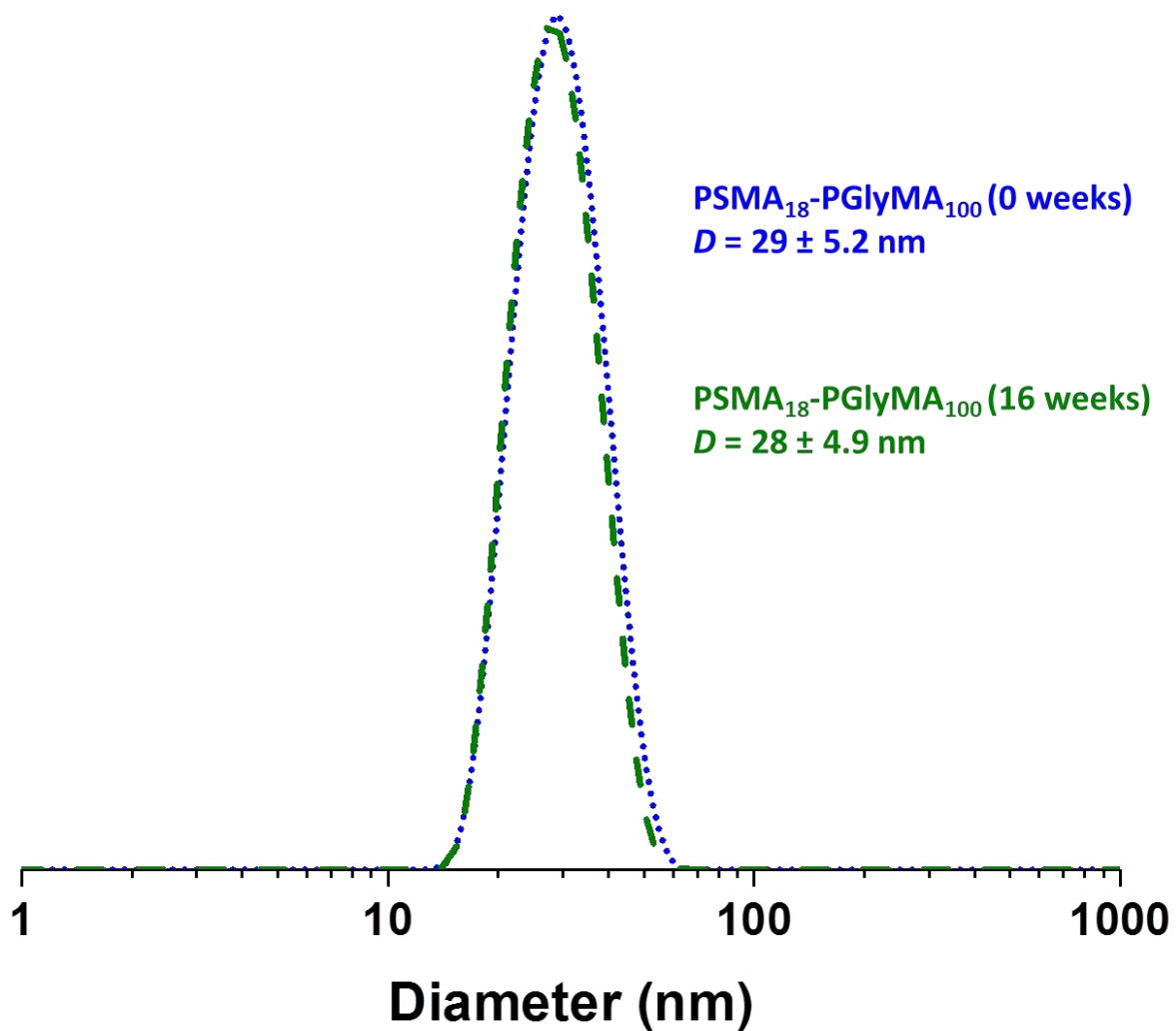
Target Composition	% GlyMA	CHCl <sub>3</sub> GPC		DLS		TEM Morphology
		M <sub>n</sub> / g mol <sup>-1</sup>	M <sub>w</sub> /M <sub>n</sub>	D / nm	PDI	
PSMA <sub>18</sub> macro-CTA	-	5,700	1.19	-	-	-
PSMA <sub>18</sub> -PGlyMA <sub>50</sub>	97	12,700	1.26	21	0.05	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>75</sub>	99	15,700	1.23	25	0.05	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>100</sub>	99	19,200	1.17	29	0.03	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>125</sub>	98	22,200	1.27	32	0.03	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>150</sub>	98	23,800	1.31	36	0.05	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>175</sub>	96	25,700	1.25	37	0.04	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>200</sub>	97	29,300	1.38	41	0.03	Spheres
PSMA <sub>18</sub> -PGlyMA <sub>300</sub>	97	40,300	1.64	51	0.03	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	0.04	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>75</sub>	95	13,600	1.17	27	0.09	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>100</sub>	96	16,100	1.19	31	0.04	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>125</sub>	94	17,400	1.18	33	0.09	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>150</sub>	94	22,100	1.22	45	0.09	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>175</sub>	97	24,400	1.33	47	0.10	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>200</sub>	98	30,700	1.24	55	0.08	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>300</sub>	98	38,900	1.38	64	0.07	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>375</sub>	96	48,300	1.31	74	0.04	Spheres
PSMA <sub>13</sub> -PGlyMA <sub>400</sub>	97	53,800	1.43	86	0.05	Spheres



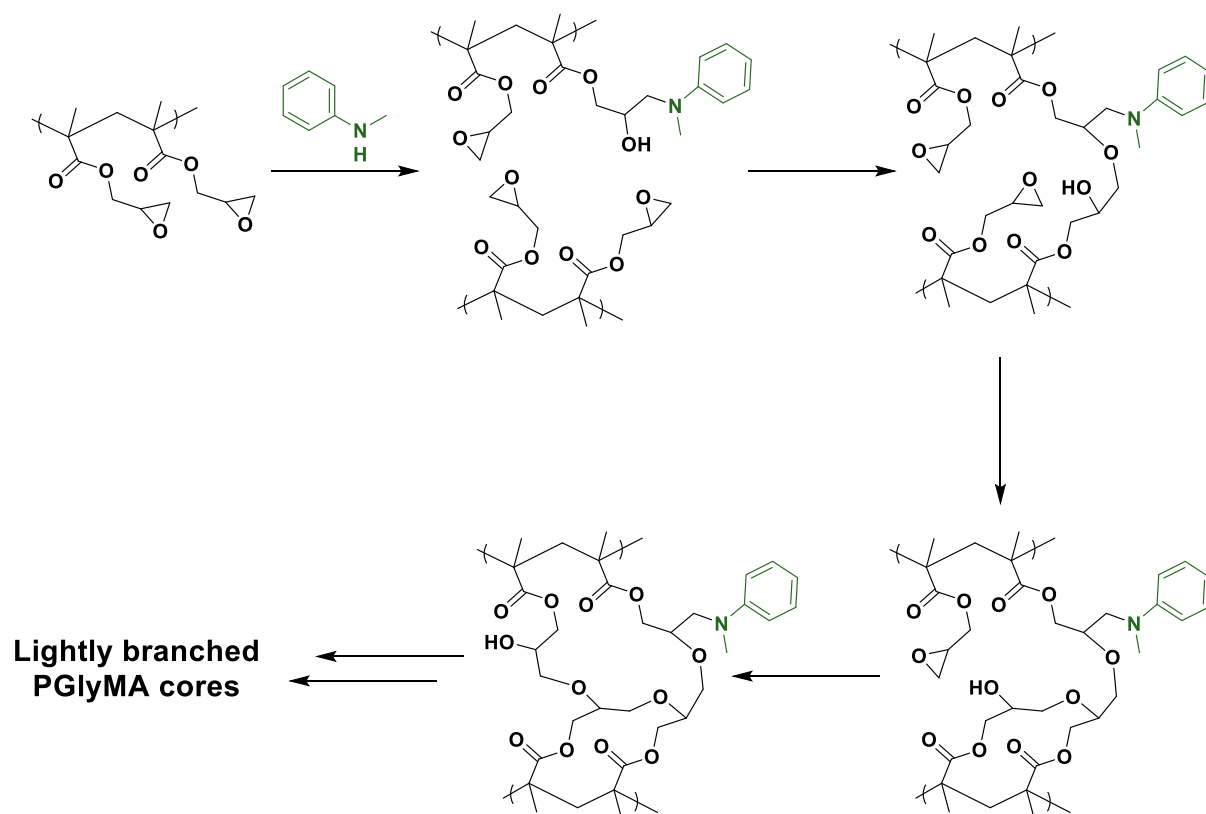
**Figure S1.** Assigned partial <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> for PSMA<sub>18</sub>-PGlyMA<sub>100</sub> directly after synthesis. Comparing the integral of the peak assigned to the PSMA oxymethylene protons at 3.9 ppm (a) with those assigned to the GlyMA residues (b, c and d) confirmed that all epoxy groups survived the RAFT dispersion polymerization in mineral oil.



**Figure S2.** 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 S3.** 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).