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 $PSMA_{19}$-$PGlyMA_x$ and $PSMA_{13}$-$PGlyMA_x$ diblock copolymers prepares 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	$CHCl_3$ GPC		DLS		TEM Morphology
		M_n / g mol^{-1}	M_w/M_n	D / nm	PDI	
$PSMA_{18}$ macro-CTA	-	5,700	1.19	-	-	-
$PSMA_{18}$-$PGlyMA_{50}$	97	12,700	1.26	21	0.05	Spheres
$PSMA_{18}$-$PGlyMA_{75}$	99	15,700	1.23	25	0.05	Spheres
$PSMA_{18}$-$PGlyMA_{100}$	99	19,200	1.17	29	0.03	Spheres
$PSMA_{18}$-$PGlyMA_{125}$	98	22,200	1.27	32	0.03	Spheres
$PSMA_{18}$-$PGlyMA_{150}$	98	23,800	1.31	36	0.05	Spheres
$PSMA_{18}$-$PGlyMA_{175}$	96	25,700	1.25	37	0.04	Spheres
$PSMA_{18}$-$PGlyMA_{200}$	97	29,300	1.38	41	0.03	Spheres
$PSMA_{18}$-$PGlyMA_{300}$	97	40,300	1.64	51	0.03	Spheres
$PSMA_{13}$ macro-CTA	-	4,100	1.22	-	-	-
$PSMA_{13}$-$PGlyMA_{50}$	98	10,800	1.16	22	0.04	Spheres
$PSMA_{13}$-$PGlyMA_{75}$	95	13,600	1.17	27	0.09	Spheres
$PSMA_{13}$-$PGlyMA_{100}$	96	16,100	1.19	31	0.04	Spheres
$PSMA_{13}$-$PGlyMA_{125}$	94	17,400	1.18	33	0.09	Spheres
$PSMA_{13}$-$PGlyMA_{150}$	94	22,100	1.22	45	0.09	Spheres
$PSMA_{13}$-$PGlyMA_{175}$	97	24,400	1.33	47	0.10	Spheres
$PSMA_{13}$-$PGlyMA_{200}$	98	30,700	1.24	55	0.08	Spheres
$PSMA_{13}$-$PGlyMA_{300}$	98	38,900	1.38	64	0.07	Spheres
$PSMA_{13}$-$PGlyMA_{375}$	96	48,300	1.31	74	0.04	Spheres
$PSMA_{13}$-$PGlyMA_{400}$	97	53,800	1.43	86	0.05	Spheres

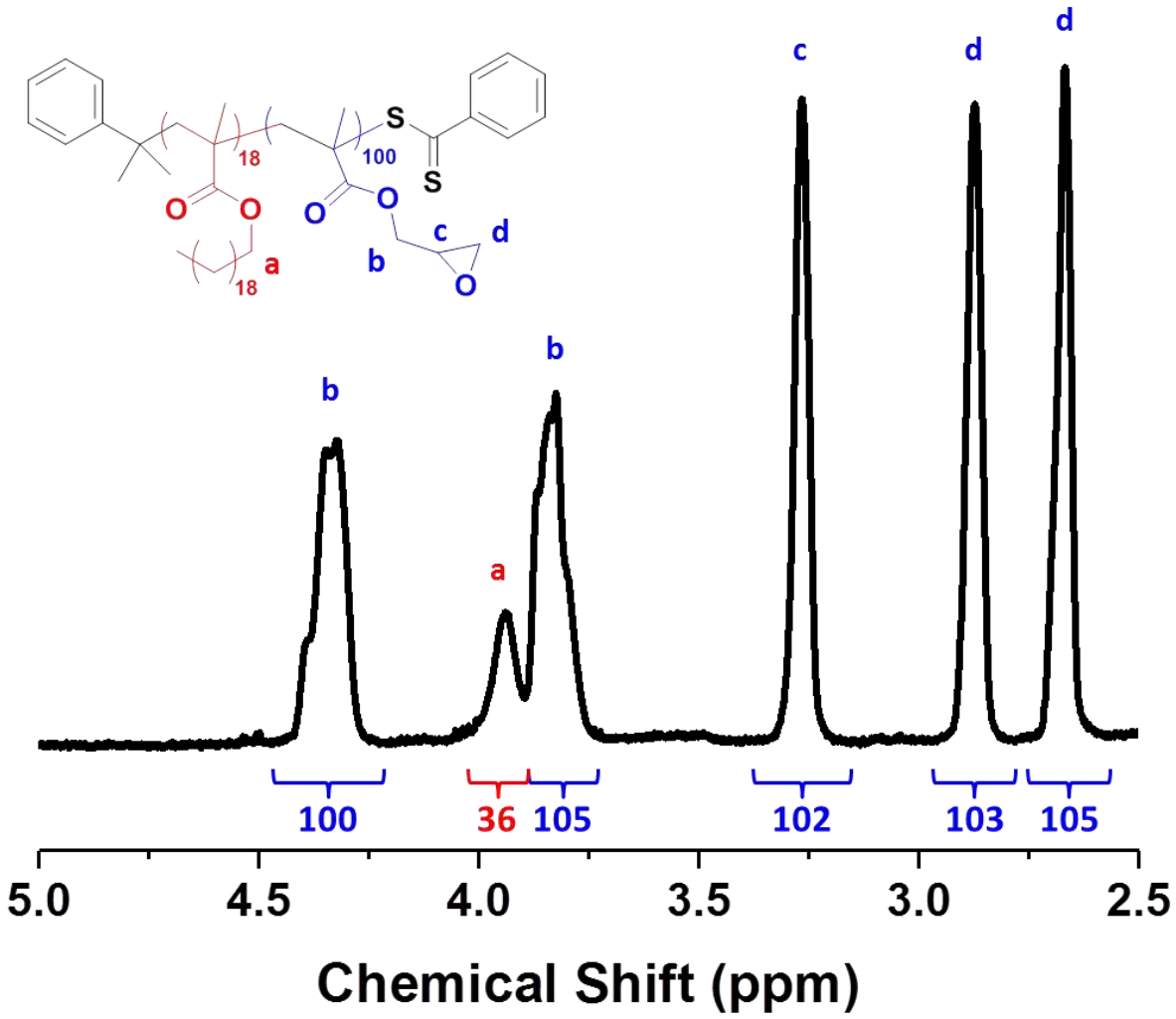


Figure S1. Assigned partial ^{1}H NMR spectrum in $CDCl_3$ for $PSMA_{18}$-$PGlyMA_{100}$ directly after synthesis. Comparing the integral of the peak assigned to the PSMA oxymethylene protons at 3.9 ppm (a) with those assigned to the GlyMA residues (b, c and d) confirmed that all epoxy groups survived the RAFT dispersion polymerization in mineral oil.

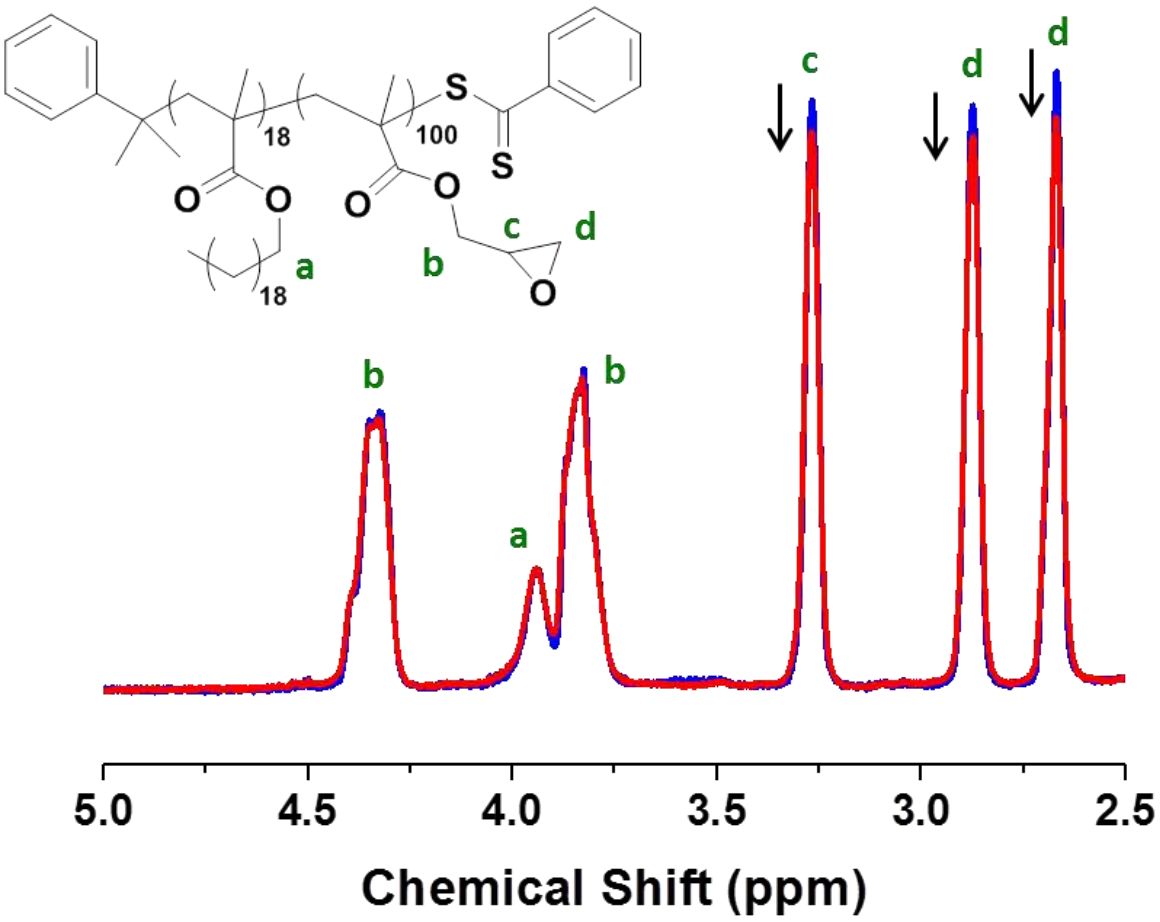


Figure S2. Assigned partial ^{1}H NMR spectrum for $PSMA_{18}$-$PGlyMA_{100}$ in $CDCl_3$ after 0 weeks (blue data) and after 16 weeks (red data). Peak integration indicated a 27% reduction of epoxide functionality after storage at 20 °C for 16 weeks.

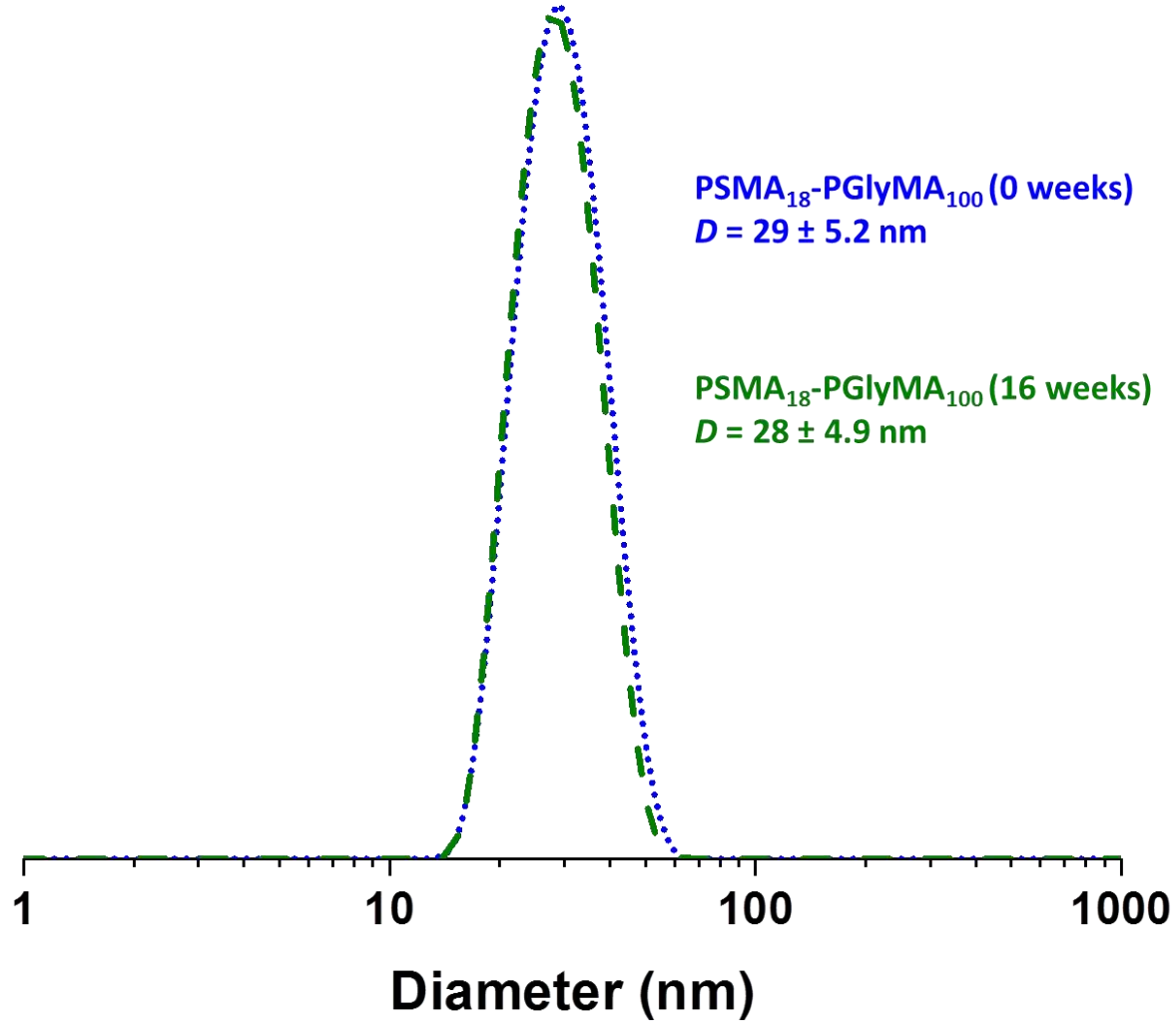
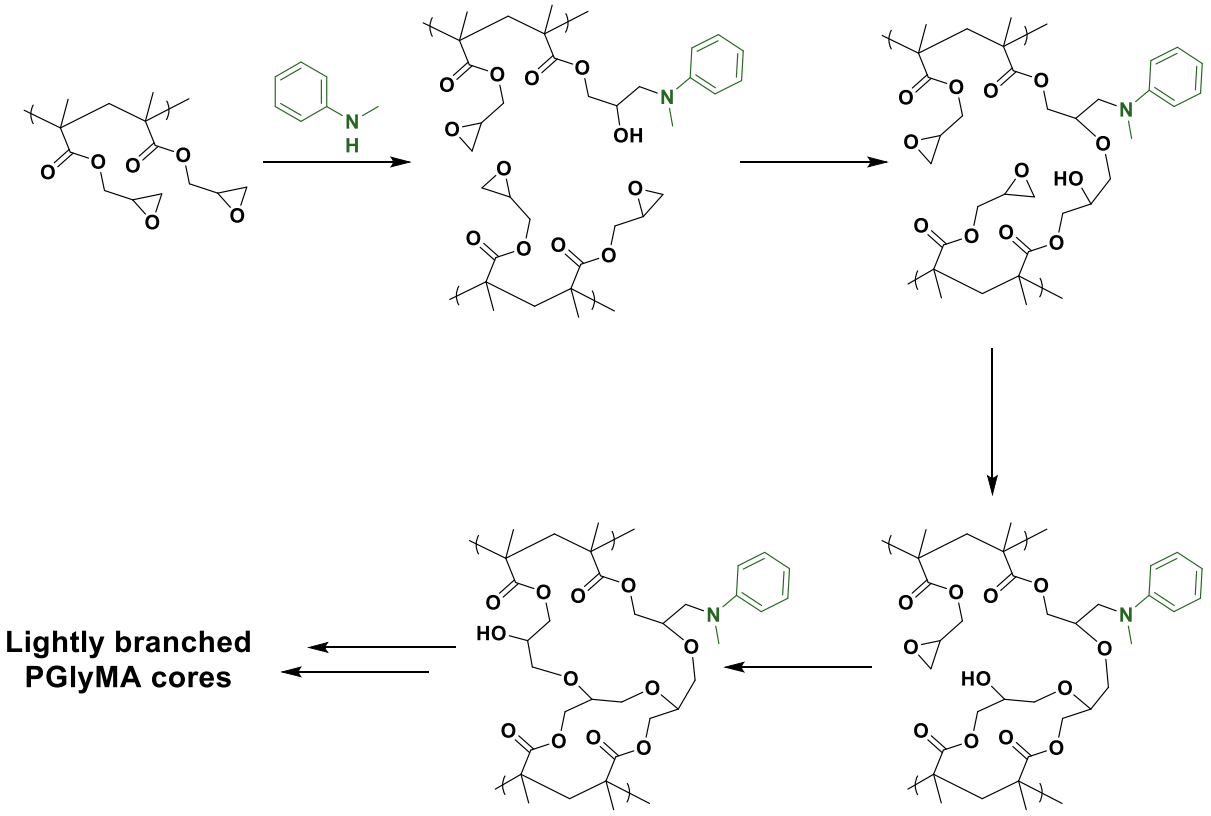


Figure S3. Intensity-average DLS particle size distributions recorded for $PSMA_{18}$-$PGlyMA_{100}$ nanoparticles immediately after synthesis (blue dotted data) and after 16 weeks (green dashed data).



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).