Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for:

Synthesis and Derivatization of Epoxy-Functional Sterically-Stabilized Diblock Copolymer Spheres in Non-Polar Media: Does the Spatial Location of the Epoxy Groups Matter?

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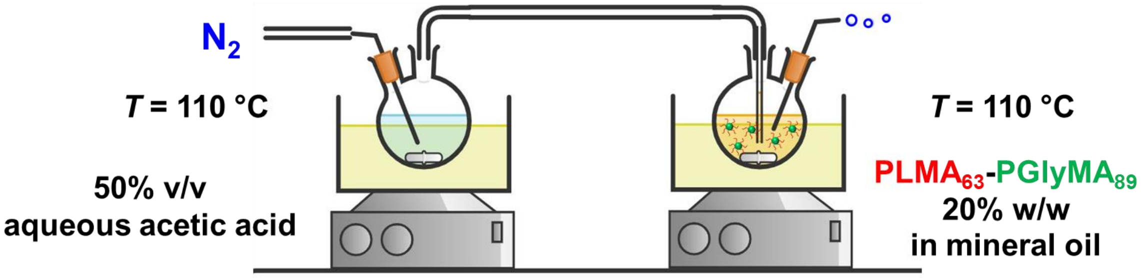


Figure S1. Experimental setup when reacting a 20% w/w dispersion of $PLMA_{63}$-$PGlyMA_{89}$ nanoparticles in mineral oil with 50% v/v aqueous acetic acid at 110 °C.

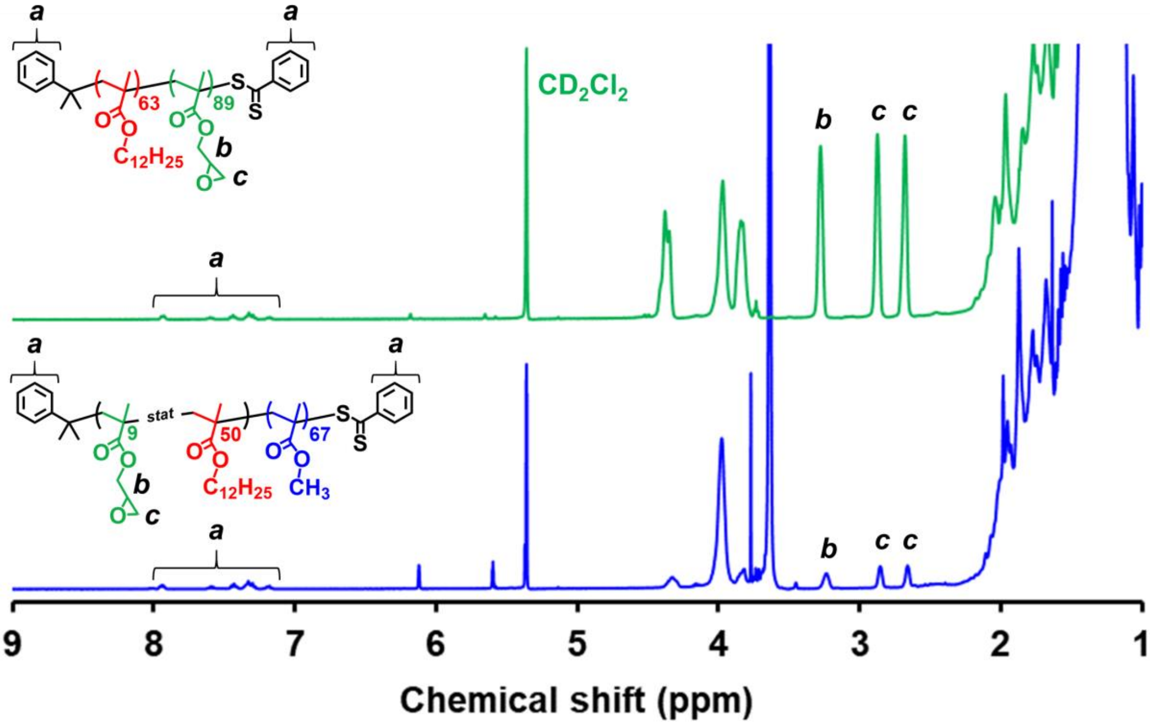


Figure S2. ^1H NMR spectra recorded in CD_2Cl_2 for the $PLMA_{63}$-$PGlyMA_{89}$ (green spectrum) and P(LMA_{50}-*stat*-$GlyMA_9$)-$PMMA_{67}$ (blue spectrum) diblock copolymers. To determine the degree of retention of the epoxy groups, the integrated aromatic proton signals *a* assigned to the copolymer end-groups at 7.10-8.00 ppm were compared to the intensity of the methine proton *b* assigned to the epoxy rings at 3.12-3.33 ppm.

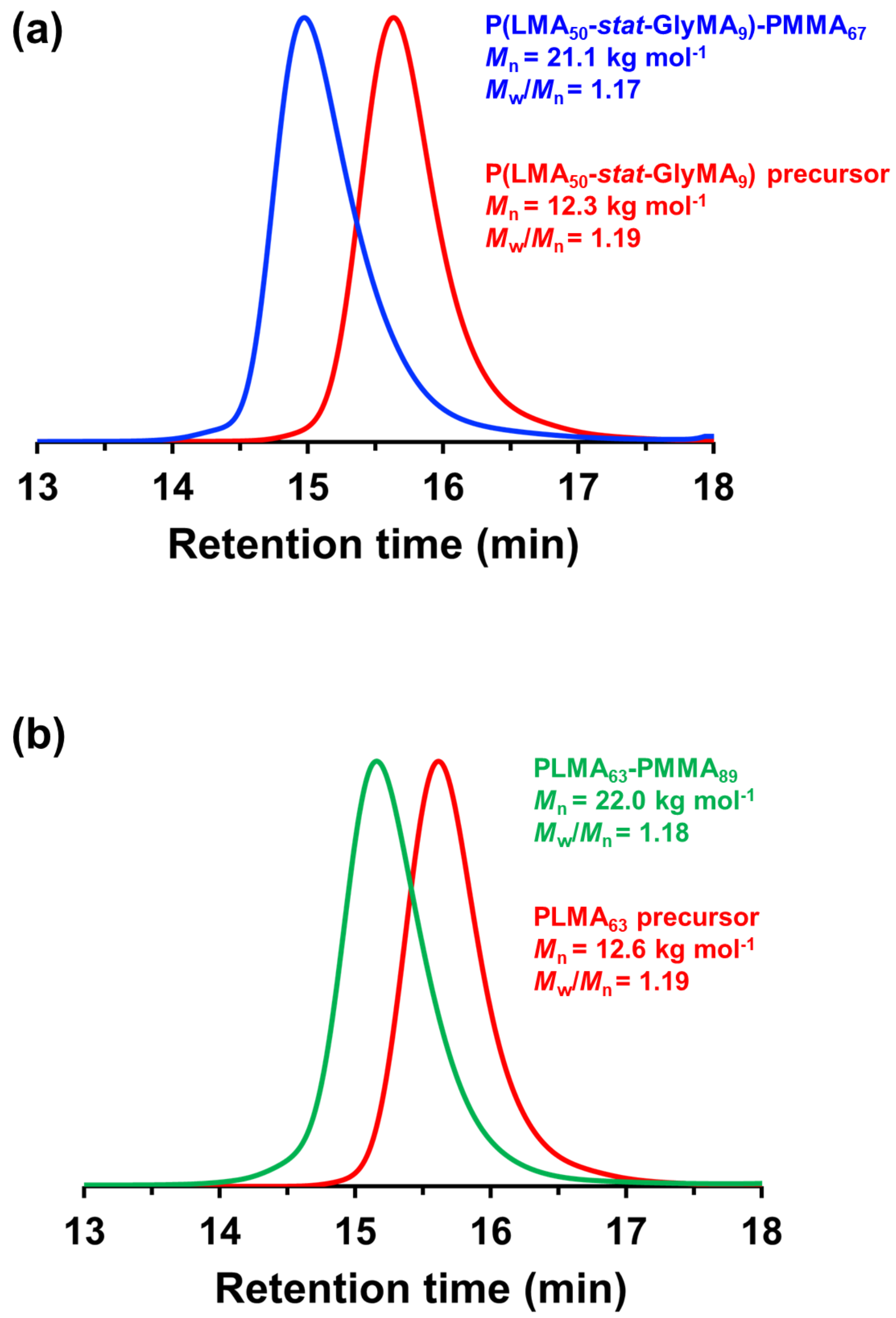


Figure S3. THF GPC curves (refractive index detector; *vs.* a series of near-monodisperse poly(methyl methacrylate) calibration standards) recorded for: **(a)** the PLMA$_{63}$ precursor and the corresponding PLMA$_{63}$-GlyMA$_{89}$ diblock copolymer; **(b)** the P(LMA$_{50}$-*stat*-GlyMA$_9$) precursor and the corresponding P(LMA$_{50}$-*stat*-GlyMA$_9$)-PMMA$_{67}$ diblock copolymer.

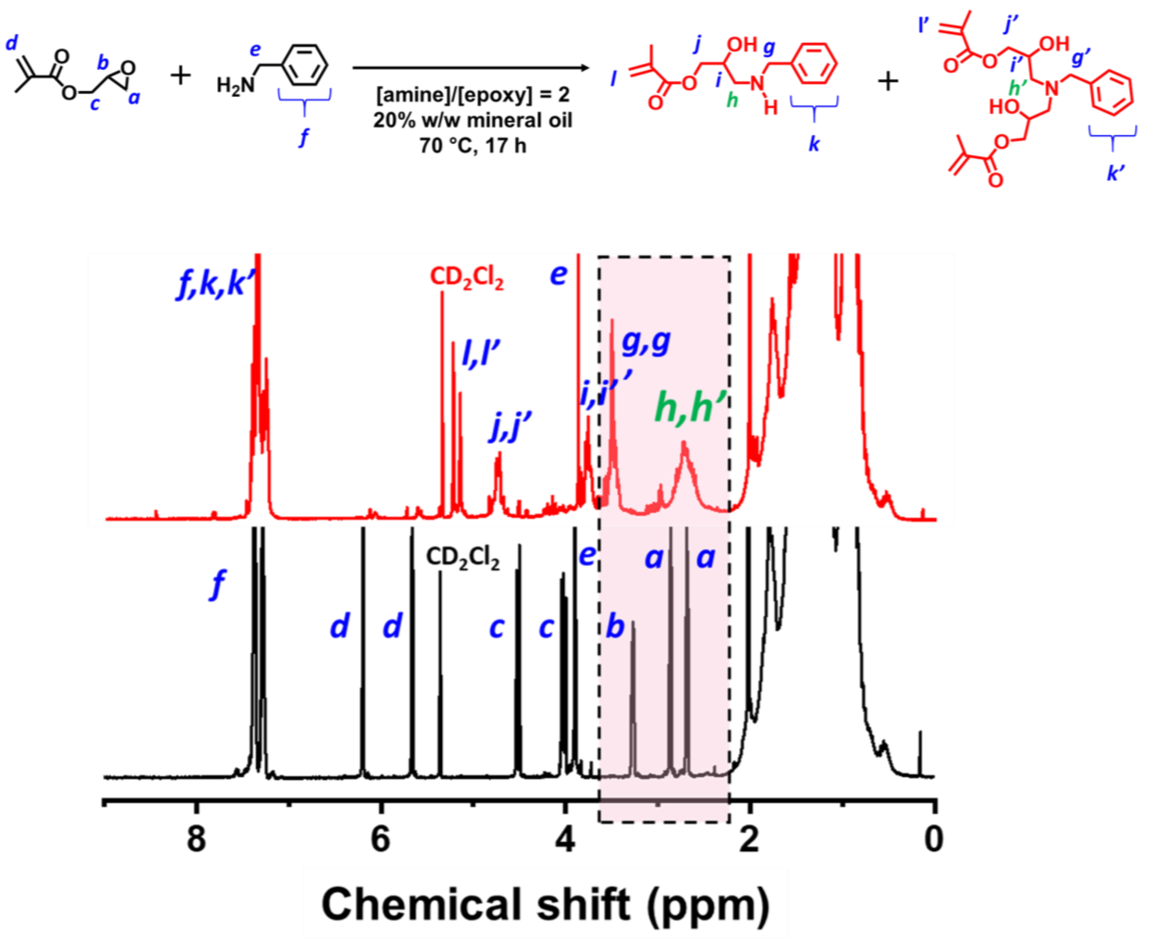


Figure S4. Assigned ^{1}H NMR spectra recorded in CD_2Cl_2 for the reaction between GlyMA and benzylamine: initial mixture (black spectrum) and after heating for 17 h at 70 °C (red spectrum). This reaction was conducted at 20% w/w solids in mineral oil using an [amine]/[epoxy] molar ratio of 2.0.

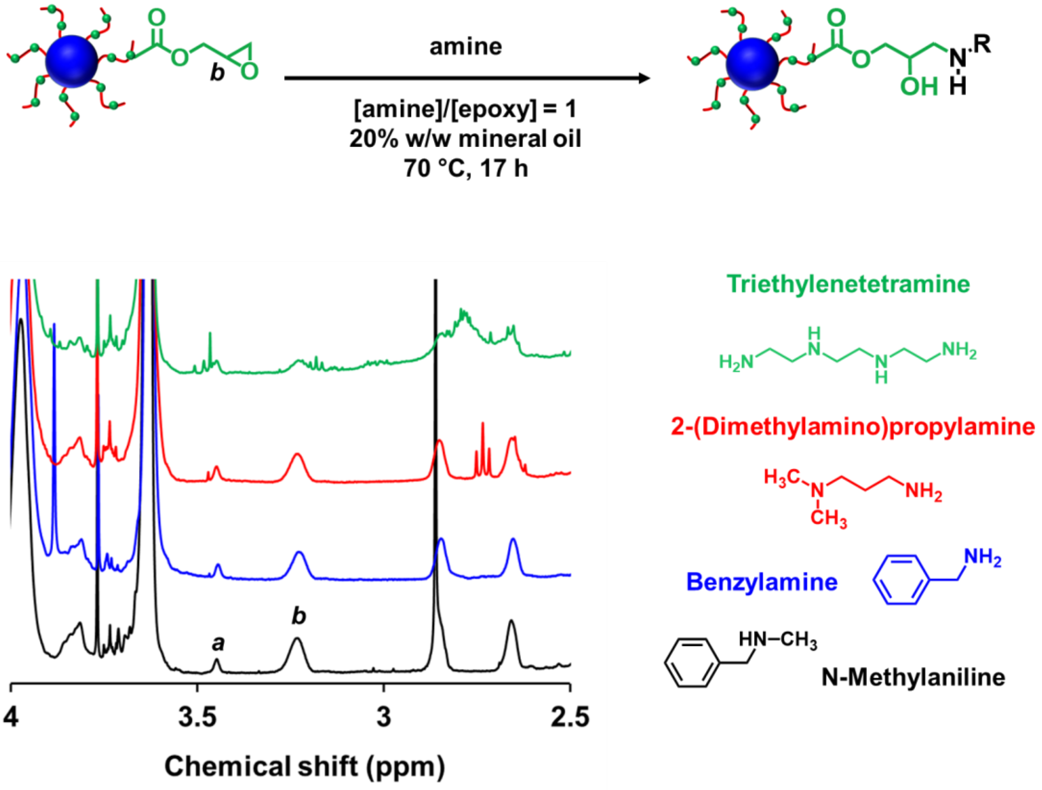


Figure S5. ^{1}H NMR spectra recorded in CD_2Cl_2 for a P(LMA$_{50}$-*stat*-GlyMA$_9$)-PMMA$_{67}$ diblock copolymer after reacting a 20% w/w dispersion of such nanoparticles in mineral oil with each of the following four amines in turn: *N*-methylaniline (black spectrum), benzylamine (blue spectrum), 2-(dimethylamino)propylamine (red spectrum) or triethylenetetramine (green spectrum). Conditions: 70 °C for 17 h, [amine]/[epoxy] molar ratio = 1.0. By comparing satellite signal *a* assigned to the PMMA backbone at 3.43-3.47 ppm to the integrated methine signal *b* of the epoxy ring at 3.12-3.30 ppm, the approximate loss of the original epoxy groups was estimated to be 12%, 16%, 23% or 68% when using *N*-methylaniline, benzylamine, 2-(dimethylamino)propylamine or triethylenetetramine, respectively.

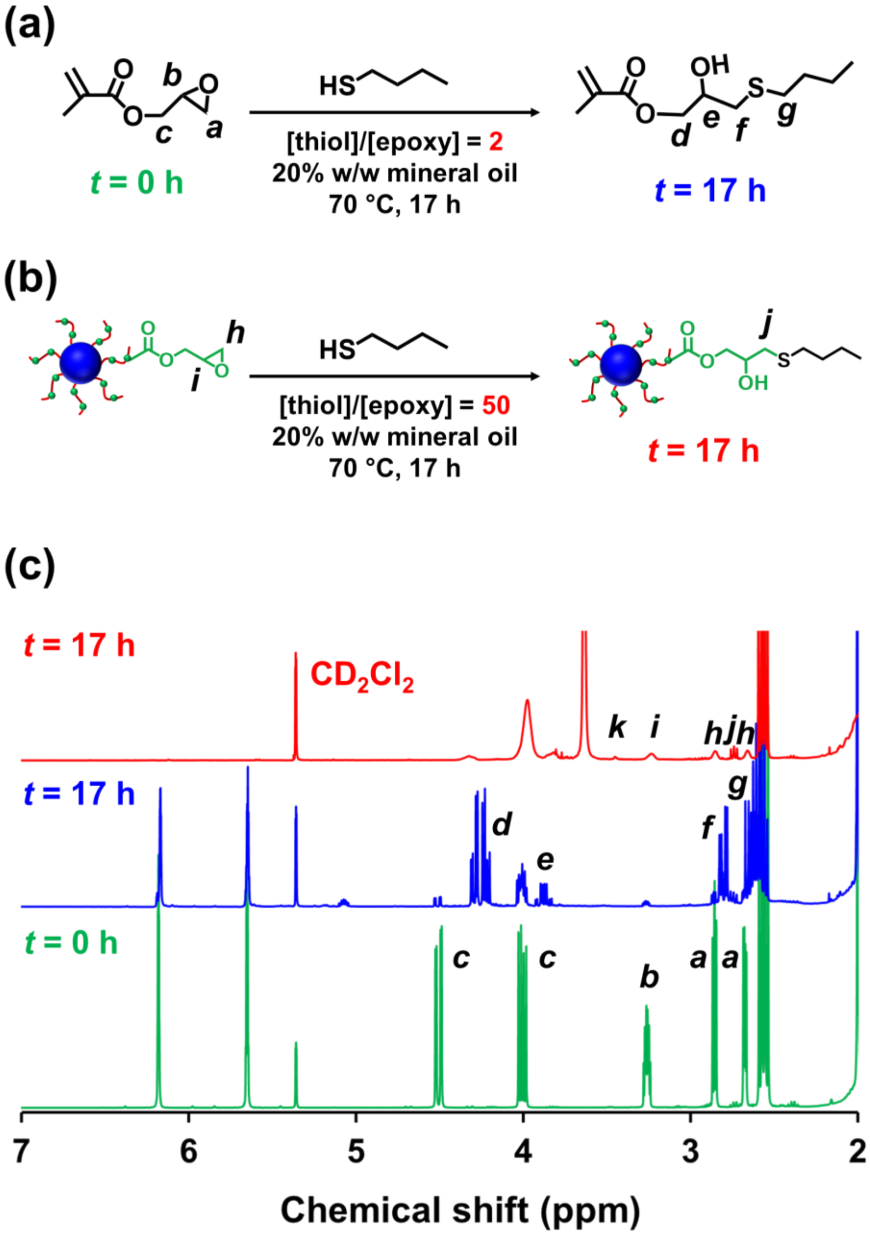


Figure S6. Schematic reaction of 1-butanethiol with **(a)** GlyMA monomer or **(b)** P(LMA$_{50}$-*stat*-GlyMA$_9$)-PMMA$_{67}$ nanoparticles. **(c)** Assigned ^{1}H NMR spectra recorded in CD$_2$Cl$_2$ for a reaction mixture containing GlyMA and 1-butanethiol at 20% w/w solids in mineral oil at 0 h (green spectrum) and after heating at 70 °C for 17 h (blue spectrum) when using an [amine]/[epoxy] molar ratio of 2.0. The red spectrum was obtained for a P(LMA$_{50}$-*stat*-GlyMA$_9$)-PMMA$_{67}$ diblock copolymer after heating the corresponding 20% w/w copolymer dispersion in mineral oil at 70 °C for 17 h using a [thiol]/[epoxy] molar ratio of 50. A % loss of epoxy groups of 13% was determined by comparing the satellite signal *k* assigned to the PMMA backbone at 3.43-3.47 ppm to the methine signal *i* corresponding to the epoxide ring at 3.12-3.30 ppm.

Figure S7. Digital photograph recorded for the original free-flowing 20% w/w dispersion of P(LMA_{50}-*stat*-$GlyMA_9$)-$PMMA_{67}$ nanoparticles (left-hand vial) and the viscous gel that is obtained after heating the same dispersion to 110 °C for 40 h (right-hand vial).

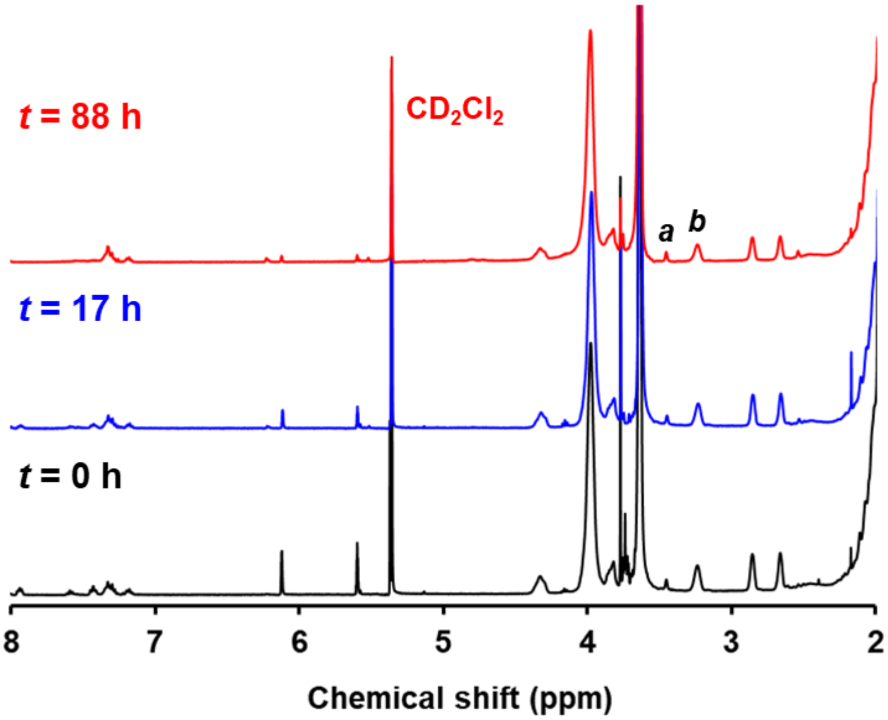


Figure S8. ^1H NMR spectra recorded in CD_2Cl_2 for the P(LMA_{50}-*stat*-$GlyMA_9$)-$PMMA_{67}$ diblock copolymer for the initial reaction mixture (black spectrum) and after heating to 110 °C for either 17 h (blue spectrum) or 88 h (red spectrum). Prior to the heating experiment, the 20% w/w copolymer dispersion was deoxygenated using a stream of N_2 gas for 30 min. A loss of epoxy groups of 21% was calculated by comparing the satellite signal *a* assigned to the PMMA backbone at 3.43-3.47 ppm to the methine signal *b* corresponding to the epoxy ring at 3.12-3.30 ppm.

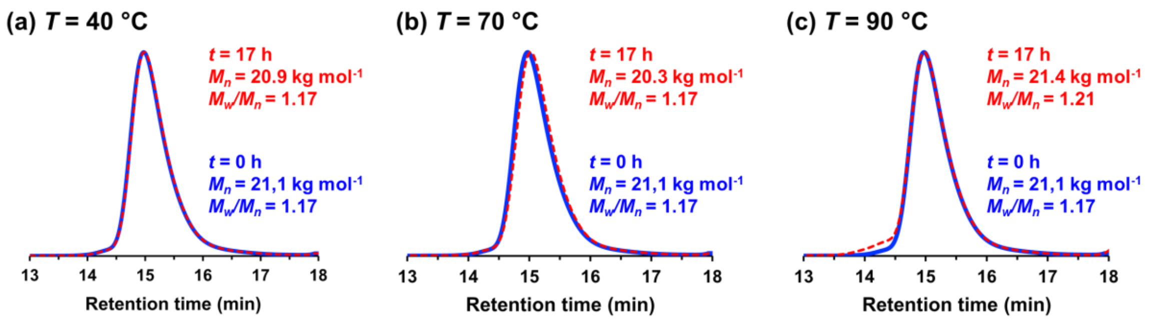


Figure S9. Comparison of the THF GPC curve recorded for the P(LMA$_{50}$-*stat*-GlyMA$_9$)-PMMA$_{67}$ diblock copolymer (prepared as a 20% w/w dispersion of nanoparticles in mineral oil at 90 °C; blue curves) with that obtained for the same copolymer (red data) after heating the 20% w/w dispersion for 17 h at **(a)** 40 °C, **(b)** 70 °C or **(c)** 90 °C, respectively.

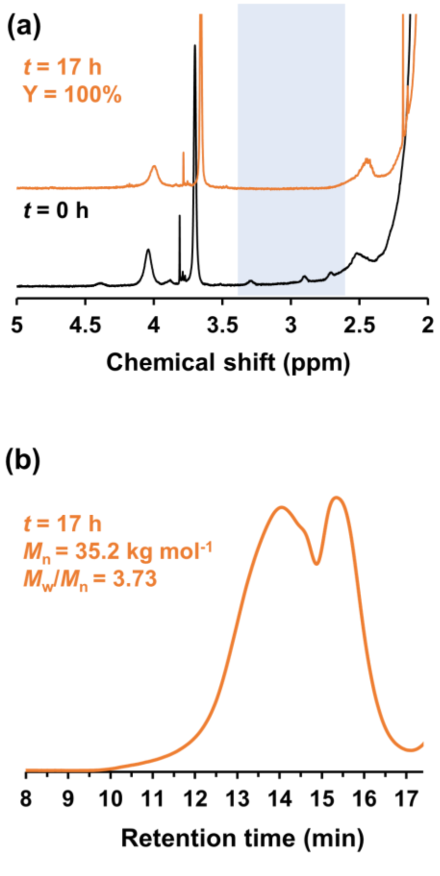


Figure S10. (a) ^{1}H NMR spectra recorded in CD_2Cl_2 for a 1.0% w/w dispersion of P(LMA$_{50}$-*stat*-GlyMA$_9$)-PMMA$_{67}$ nanoparticles initially (black spectrum) and then after heating the same dispersion to 110 °C for 17 h (orange spectrum; note the loss of epoxy signals within the shaded blue region). **(b)** THF GPC curve recorded for the diblock copolymer chains obtained after this heating protocol.

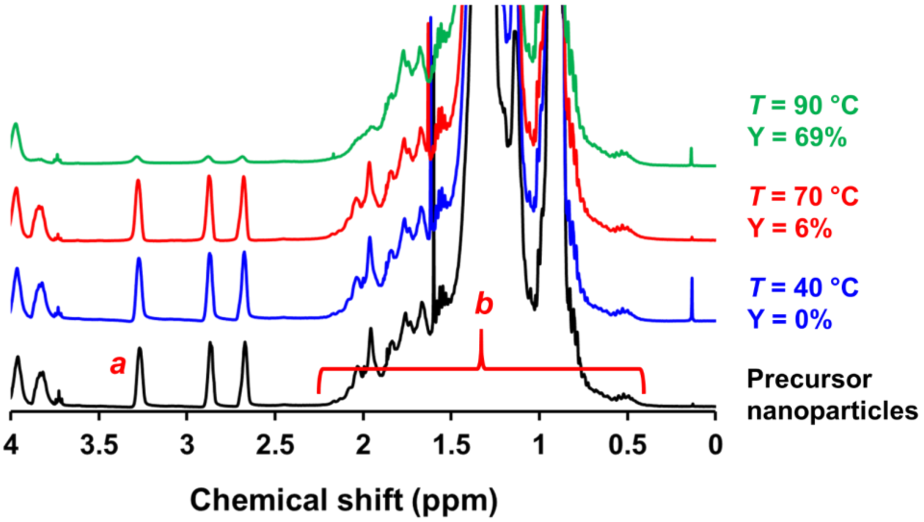


Figure S11. ^{1}H NMR spectra recorded in CD_2Cl_2 for $PLMA_{63}$-$PGlyMA_{89}$ diblock copolymer (black spectrum), the same copolymer after heating a 20% w/w copolymer dispersion in mineral oil for 17 h at 40 °C (blue spectrum), 70 °C (red spectrum) or 90 °C (green spectrum), respectively. In each case, the % loss of the original epoxy groups (Y%) was determined by comparing the aliphatic copolymer backbone at 0.30-2.30 ppm (see signal *b*) to the methine signal *a* corresponding to the epoxy ring at 3.20-3.33 ppm.

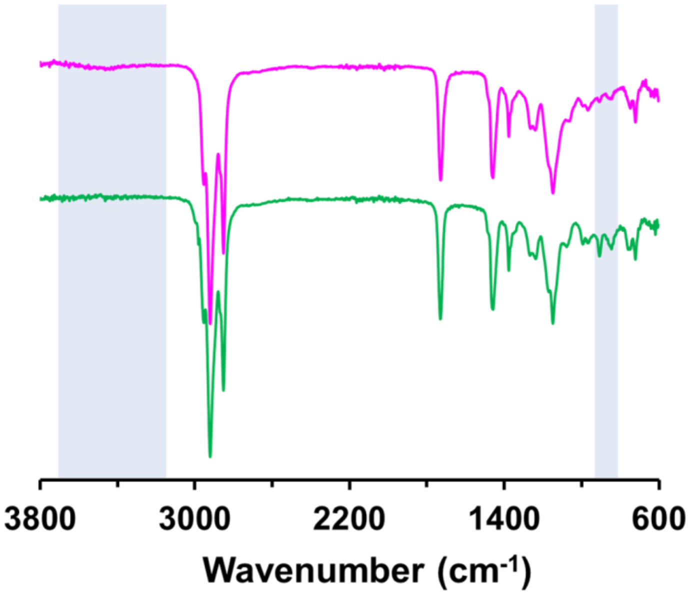
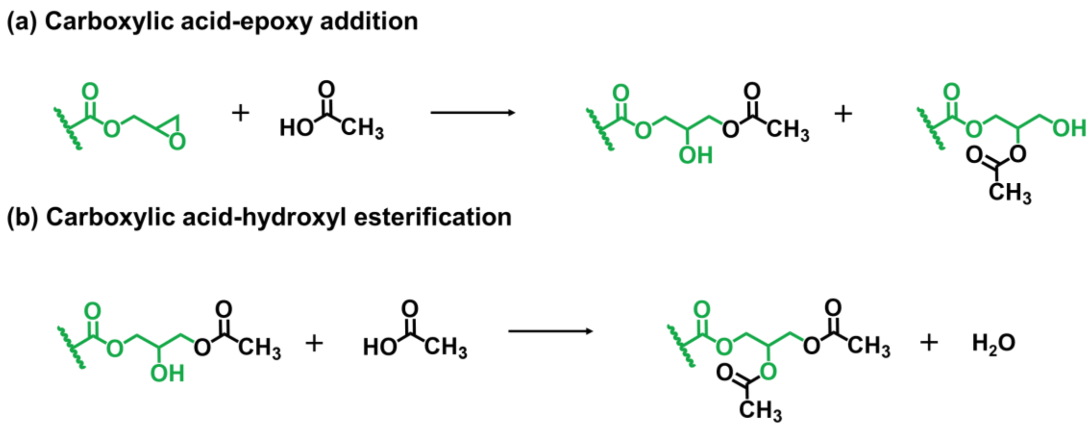


Figure S12. FT-IR spectra recorded for $PLMA_{63}$-$PGlyMA_{89}$ diblock copolymer (green spectrum) and the same copolymer (pink spectrum) after heating to 110 °C for 17 h in the presence of water.


(a) Carboxylic acid-epoxy addition

(b) Carboxylic acid-hydroxyl esterification

Scheme S1. Possible side-reactions that might occur when reacting PLMA$_{63}$-PGlyMA$_{89}$ nanoparticles with 50% v/v aqueous acetic acid: **(a)** epoxy ring-opening with acetic acid and **(b)** esterification between acetic acid and the pendent hydroxyl groups.