Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Oxidation-Responsive Polyether Block Copolymers Lead to Non-ionic Polymer Surfactants with Multiple Amine *N*-Oxides

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Reagents.

Solvents and reagents were generally purchased from Acros Organics, TCI, Sigma-Aldrich, or Fluka and used as received, unless otherwise stated. Deuterated solvents were received from Deutero GmbH. *N,N*-diethyl glycidyl amine was synthesized in accordance to literature.[15,18]

Instrumentation.

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker Avance III HD 300 (5 mm BBFO-Probe with *z*-Gradient and ATM). ^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance II 400 (400 MHz, 5 mm BBFO-SmartProbe with *z*-gradient and ATM, SampleXPress 60 sample changer). ^{1}H, ^{15}N HMBC spectra were recorded on a Bruker Avance III HD 400 (400 MHz, 5 mm BBFO-SmartProbe with *z*-gradient and ATM, SampleXPress 60 sample changer).

Size exclusion chromatography (SEC) was performed at 50 °C in *N,N*-dimethylformamide (containing 1 g/L lithium bromide) as an eluent on an Agilent 1100 Series equipped with Polymer Standards Service (PSS) HEMA columns with 300/100/40 Å porosity and a RI detector. Molecular weights were determined by calibration with poly(ethylene oxide) standards by PSS.

Differential scanning calorimetry (DSC) measurements were carried out under a nitrogen atmosphere, using a PerkinElmer DSC 8500 in the temperature range of -95 °C to 0 °C, with heating rates of 20 K/min for the first and 10 K/min for the second heating run. The heat flow of the second heating cycle was used for the analysis. The glass transition temperatures were determined from the inflection point of the second heating cycle.

Electrospray ionization (ESI) mass spectra were recorded on a Waters Micromass ESI QToF Ultima 3 with methanol as a solvent.

Dynamic light scattering (DLS) measurements were conducted on a Malvern Instruments Zetasizer Nano ZS with aqueous polymer solutions of 1 mg/mL at a temperature of 25 °C. The scattering at a wavelength of 633 nm was recorded at angle of 173°.

Surface tension measurements to determine the critical micelle concentration (CMC) were performed on a DTCAT 11 EC connected with TV 70 thermostat and a LDU 1/1 liquid metering pump. The surface tension was determined with RG 11 Du Noüy ring, which was annealed in a butane flame before use. The measurements were performed at a temperature at 25 °C. The CMC was determined by the intersection of two linear regressions.

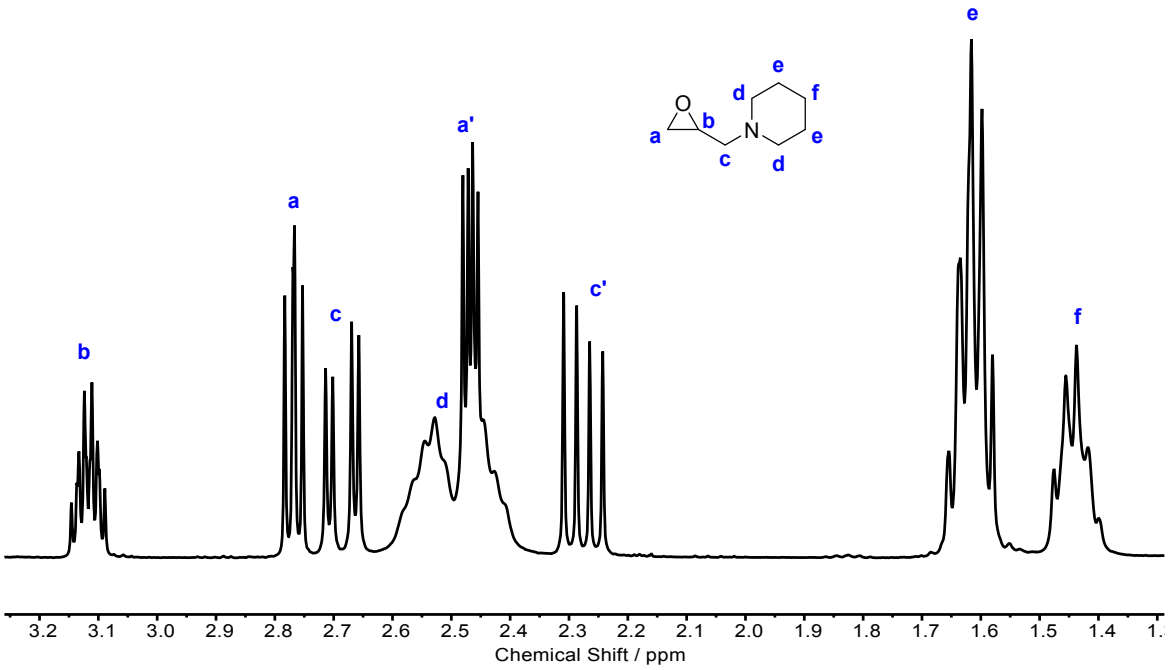

Fig. S1 ^{1}H NMR spectrum (300 MHz, C*D*Cl$_3$) of PiGA monomer.

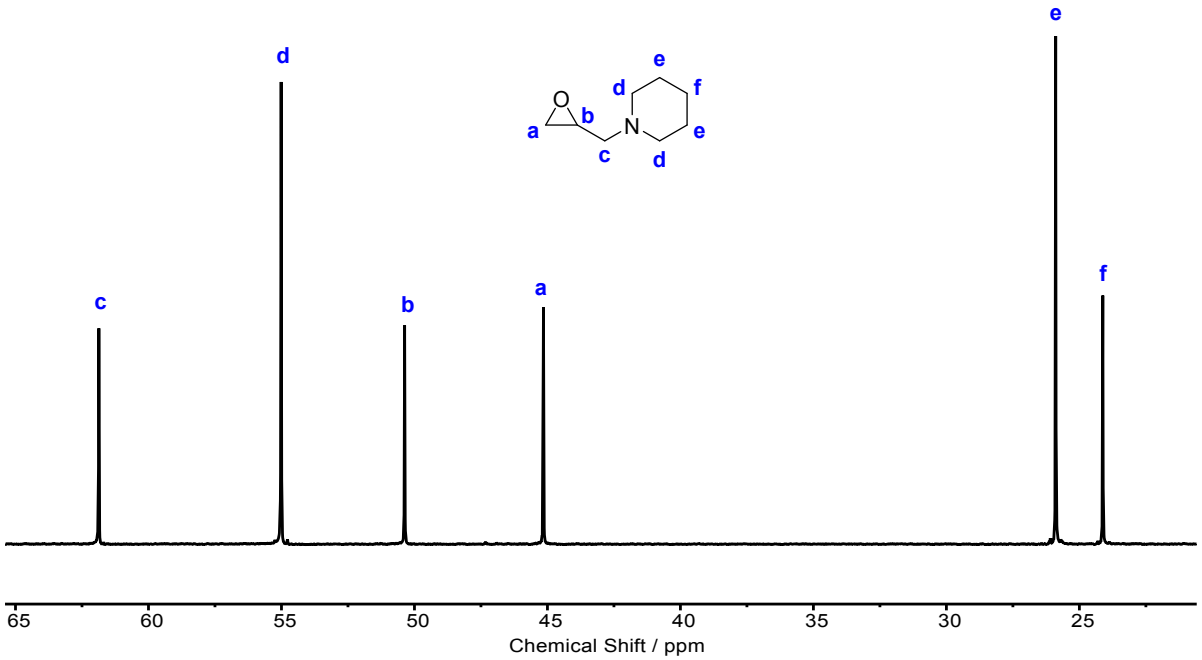

Fig. S2 ^{13}C NMR spectrum (75 MHz, C*D*Cl_3) of PiGA monomer.

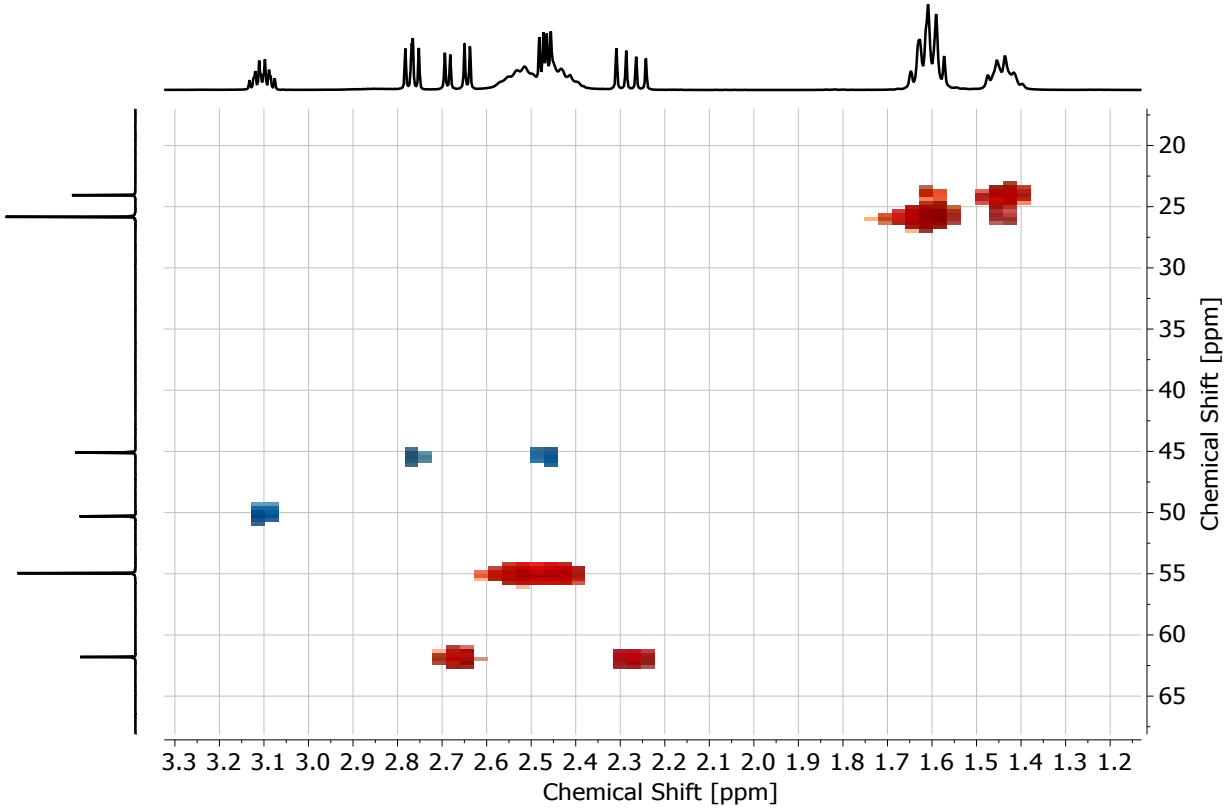

Fig. S3. ^{1}H, ^{13}C HSQC NMR spectrum (C*D*Cl_3) of PiGA monomer.

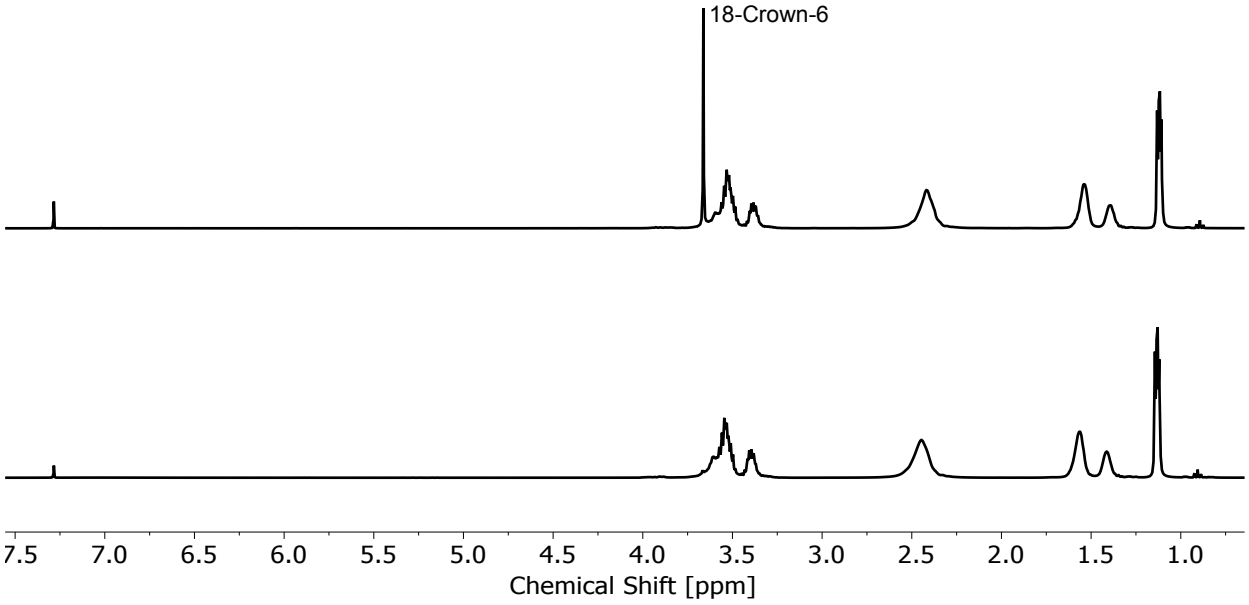

Fig. S4 ^{1}H NMR spectra (400 MHz, C*D*Cl3) of PPO_{47}-b-$PPiGA_{25}$ before (top) and after (bottom) removal of 18-crown-6 by liquid-liquid extraction.

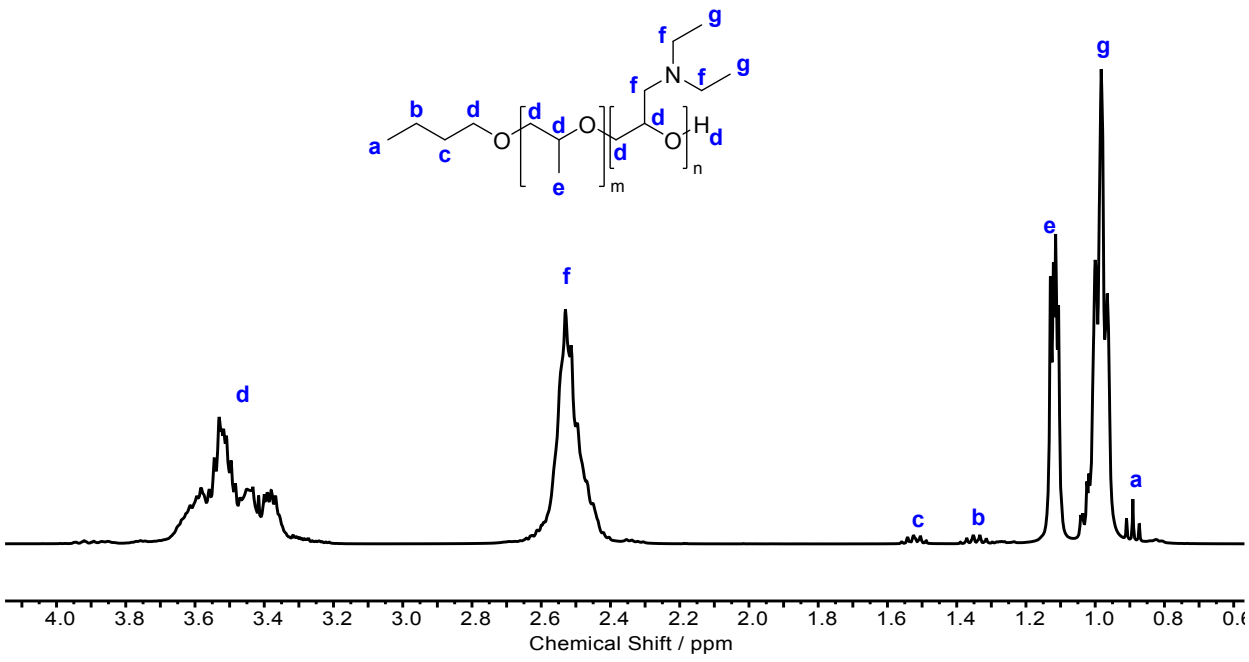

Fig. S5 ^{1}H NMR spectrum (400 MHz, C*D*Cl_3) of PPO_{21}-*b*-$PDEGA_{21}$.

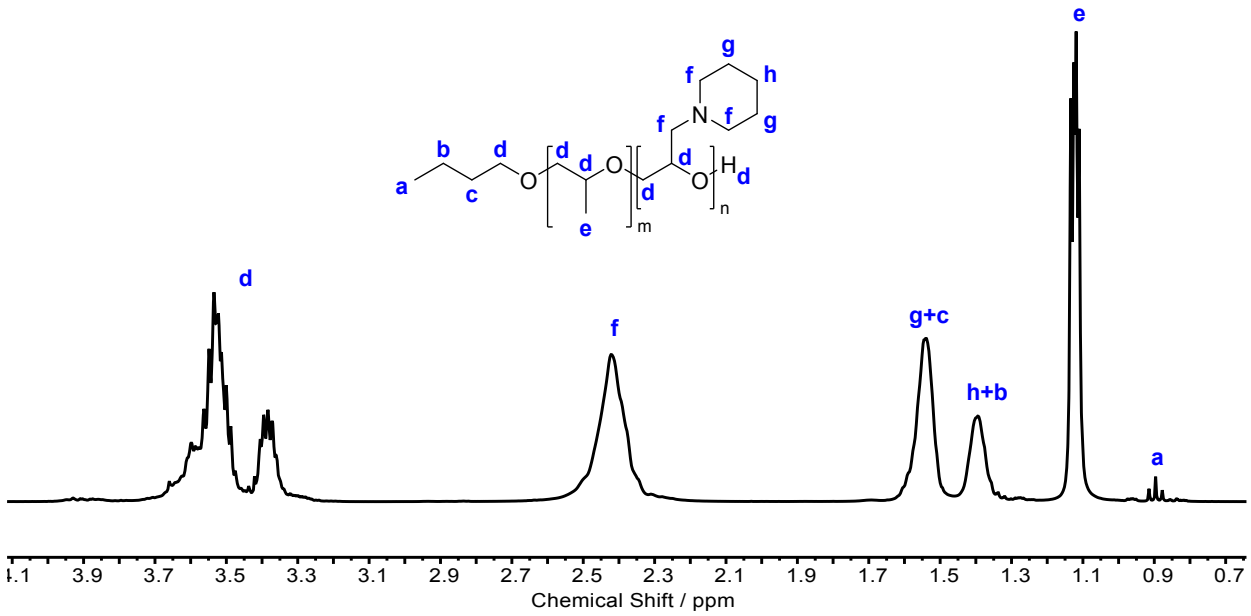

Fig. S6 ^{1}H NMR spectrum (400 MHz, C*D*Cl3) of PPO_{47}-*b*-$PPiGA_{25}$.

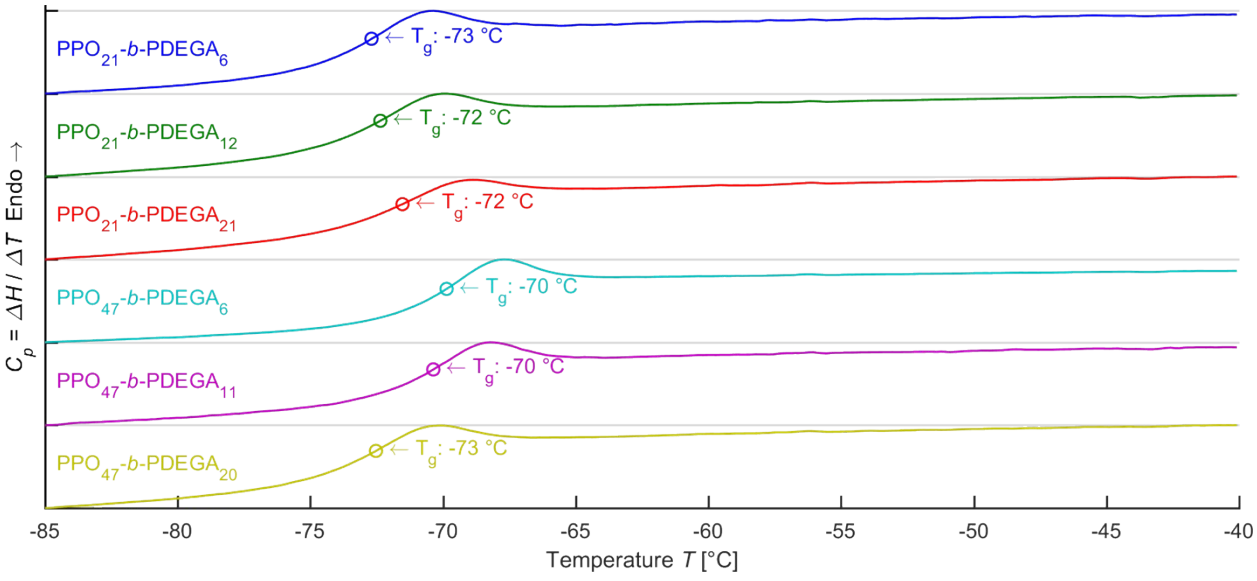

Fig. S7 DSC diagrams of PPO-*b*-PDEGA block copolymers.

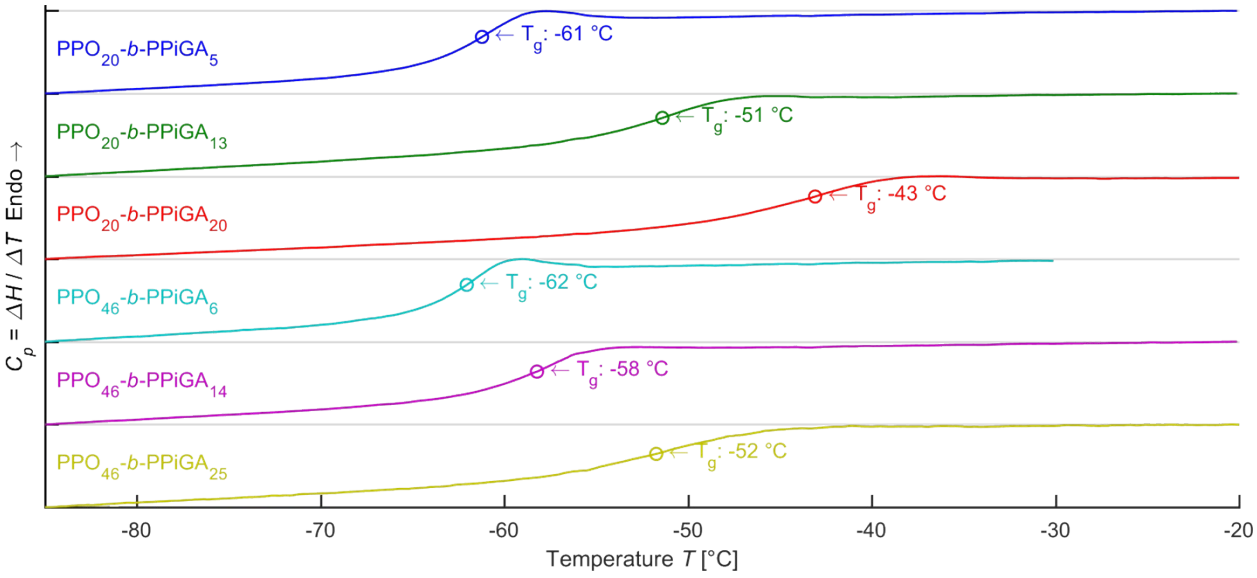

Fig. S8 DSC diagrams of PPO-*b*-PPiGA block copolymers.

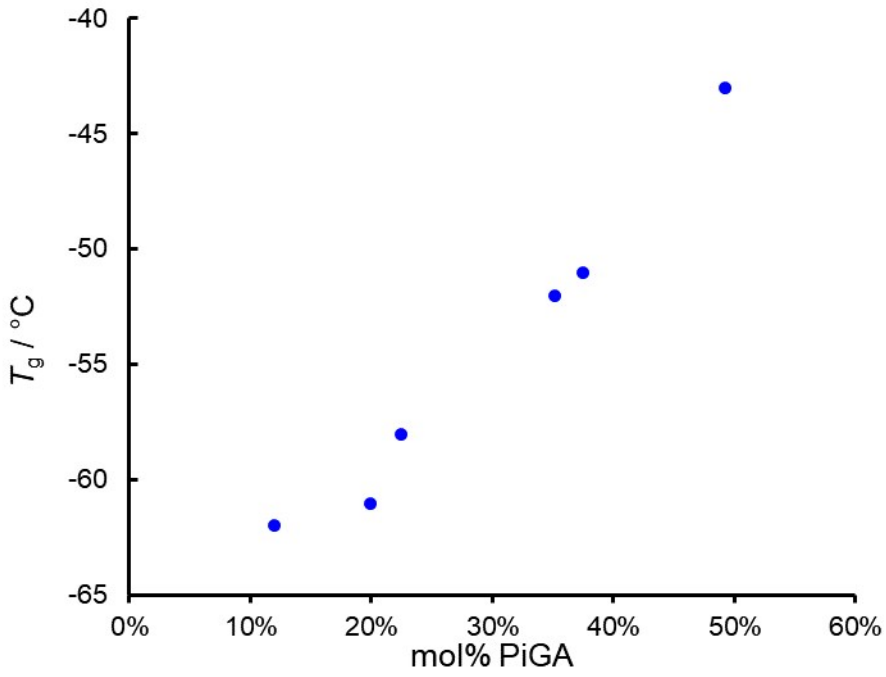

Fig. S9 Dependence of glass transition temperatures of PPO-*b*-PPiGA on composition.

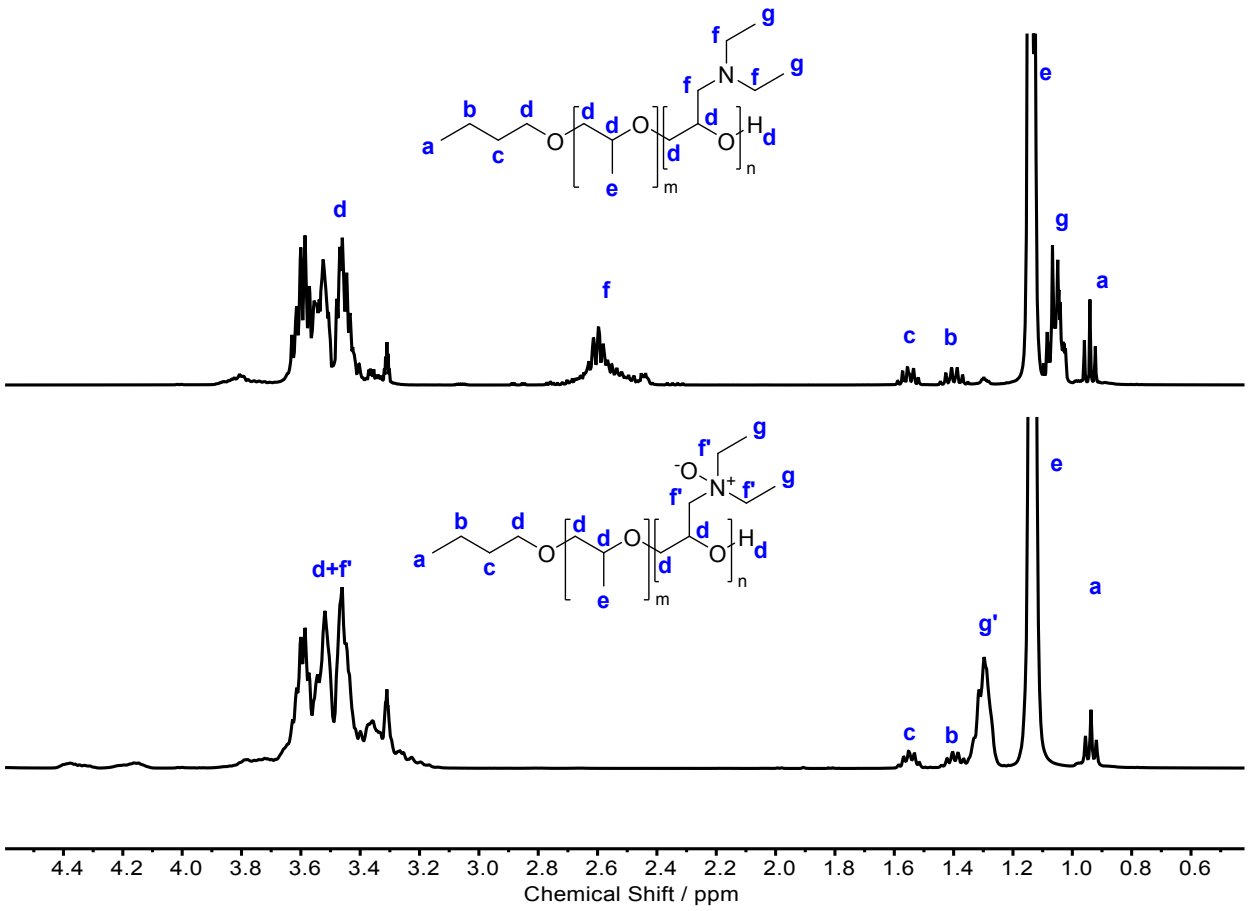

Fig. S10 ^{1}H NMR spectra (400 MHz, C*D*$_3$O*D*) of PPO_{21}-*b*-$PDEGA_6$ (top) and the corresponding oxidized PPO_{21}-*b*-$PDEGAO_6$ (bottom) block copolymer.

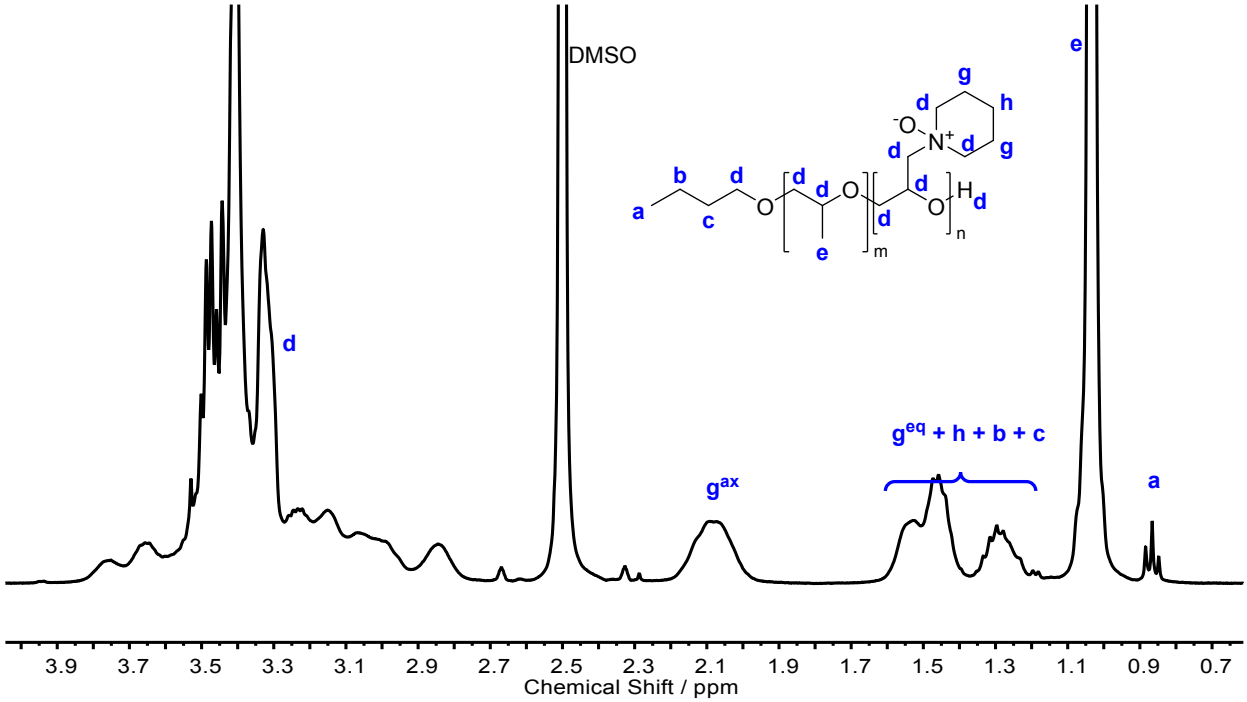

Fig. S11 ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of the oxidized PPO_{47}-*b*-$PPiGAO_{25}$ (the axial (ax) and equatorial (eq) protons g are split).

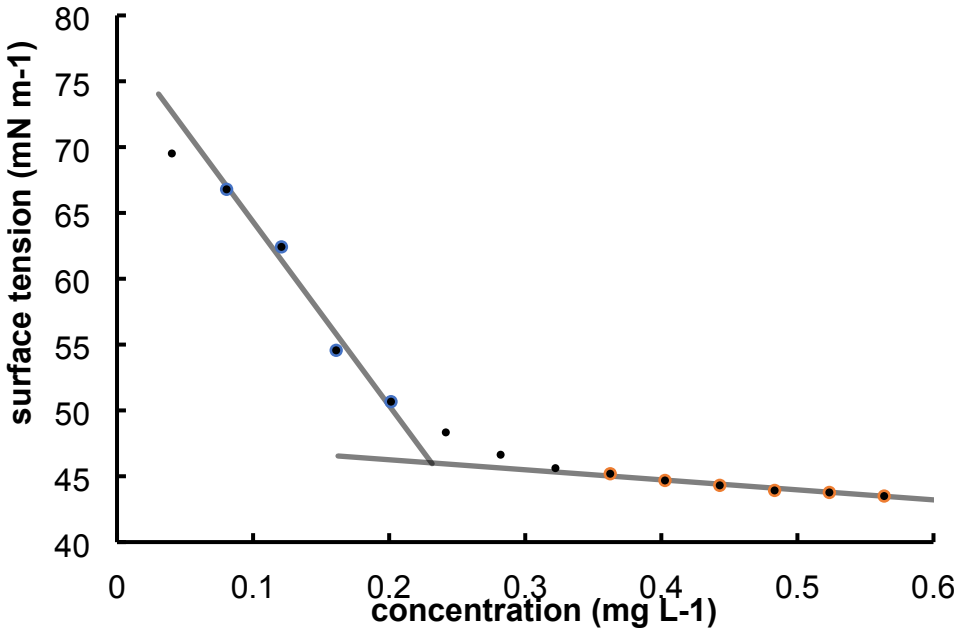

Fig. S12 Determination of the CMC by surface tension measurement (25 °C) for PPO_{47}-*b*-$PDEGAO_6$.

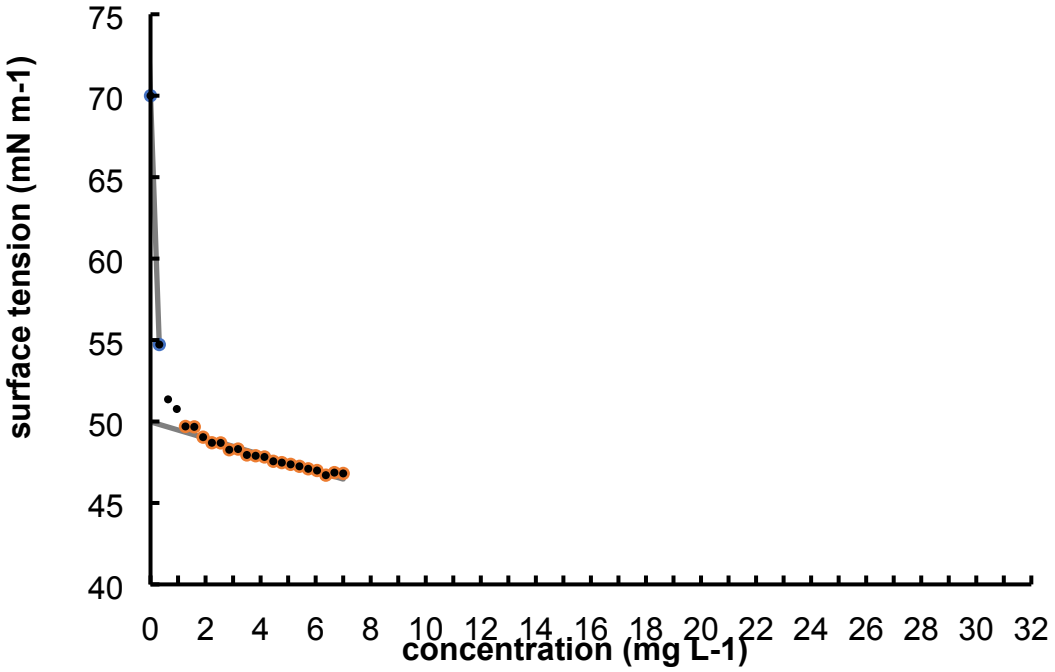

Fig. S13 Determination of the CMC by surface tension measurement (25 °C) for PPO_{21}-*b*-$PPiGAO_5$.

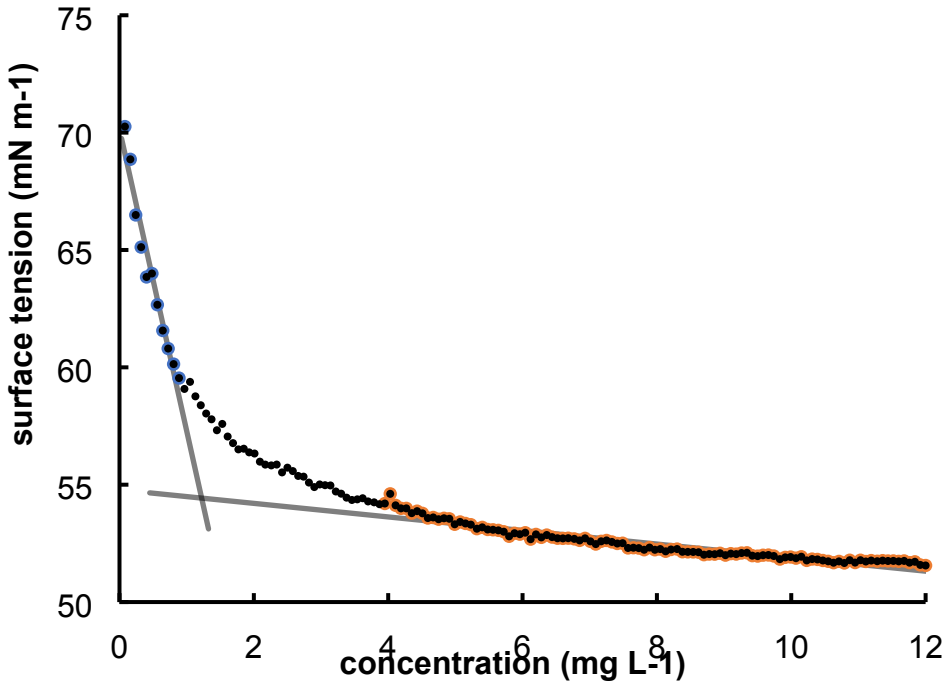

Fig. S14 Determination of the CMC by surface tension measurement (25 °C) for PPO_{21}-*b*-$PPiGA_{20}$.

Table S1. Determined particle sizes by distribution fits.

Sample	r_H / nm (smaller aggregate)	r_H / nm (larger aggregate)
PPO_{21}-*b*-$PDEGAO_6$	18	118
PPO_{21}-*b*-$PDEGAO_{12}$	26	104
PPO_{21}-*b*-$PDEGAO_{21}$	/	143
PPO_{47}-*b*-$PDEGAO_6$	16	/
PPO_{47}-*b*-$PDEGAO_{11}$	11	505
PPO_{47}-*b*-$PDEGAO_{20}$	/	149
PPO_{21}-*b*-$PPiGAO_5$	12	152
PPO_{21}-*b*-$PPiGAO_{13}$	10	148
PPO_{21}-*b*-$PPiGAO_{20}$	9	131
PPO_{47}-*b*-$PPiGAO_6$	15	360
PPO_{47}-*b*-$PPiGAO_{14}$	16	188
PPO_{47}-*b*-$PPiGAO_{25}$	12	113

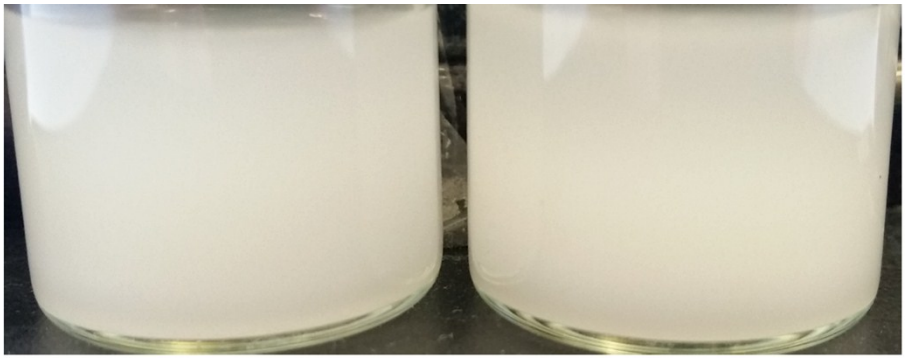

Fig. S15. Formation of a stable emulsion of ethyl acetate/water mixture (3:1) upon addition of PPO_{47}-*b*-$PDEGAO_6$ (left) and PPO_{47}-*b*-$PiGAO_6$ (right).