Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Polyurethane based organic macromolecular contrast agent (PU-ORCA) for magnetic resonance imaging

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1. Nomenclature and Abbreviations

Table S1. Nomenclature and Abbreviations

Abbreviation	Description
DBU	1,8 Diazabicyclo[5.4.0]undéc-7ène
HDI	hexamethylene diisocyanate
DMSO	dimethyl sulfoxide
Mn	number-average molecular weight
MPA	methylpropanoate
Mw	weight-average molecular weight
NMR	nuclear magnetic resonance spectroscopy
PDI	polydispersity index
PEG	poly(ethylene glycol)
SEC	size exclusion chromatography
PU-ORCA	Polyurethane based organic contrast agent
TEM	transmission electron microscopy
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl

2. NMRs

All the NMRs presented in this section have been performed in DMSO-d_6. Monomers and polymers containing radicals have been previously quenched by 1.2 equivalent of phenyl-hydrazine in order to do not perturb the recording. (Figure S1)

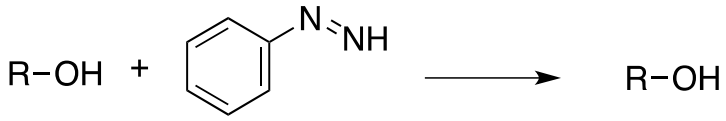

Figure S1. Reduction of the nitroxide-containing compounds by phenyl-hydrazine.

2.1 Synthesis of (bis-MPA-TEMPO)

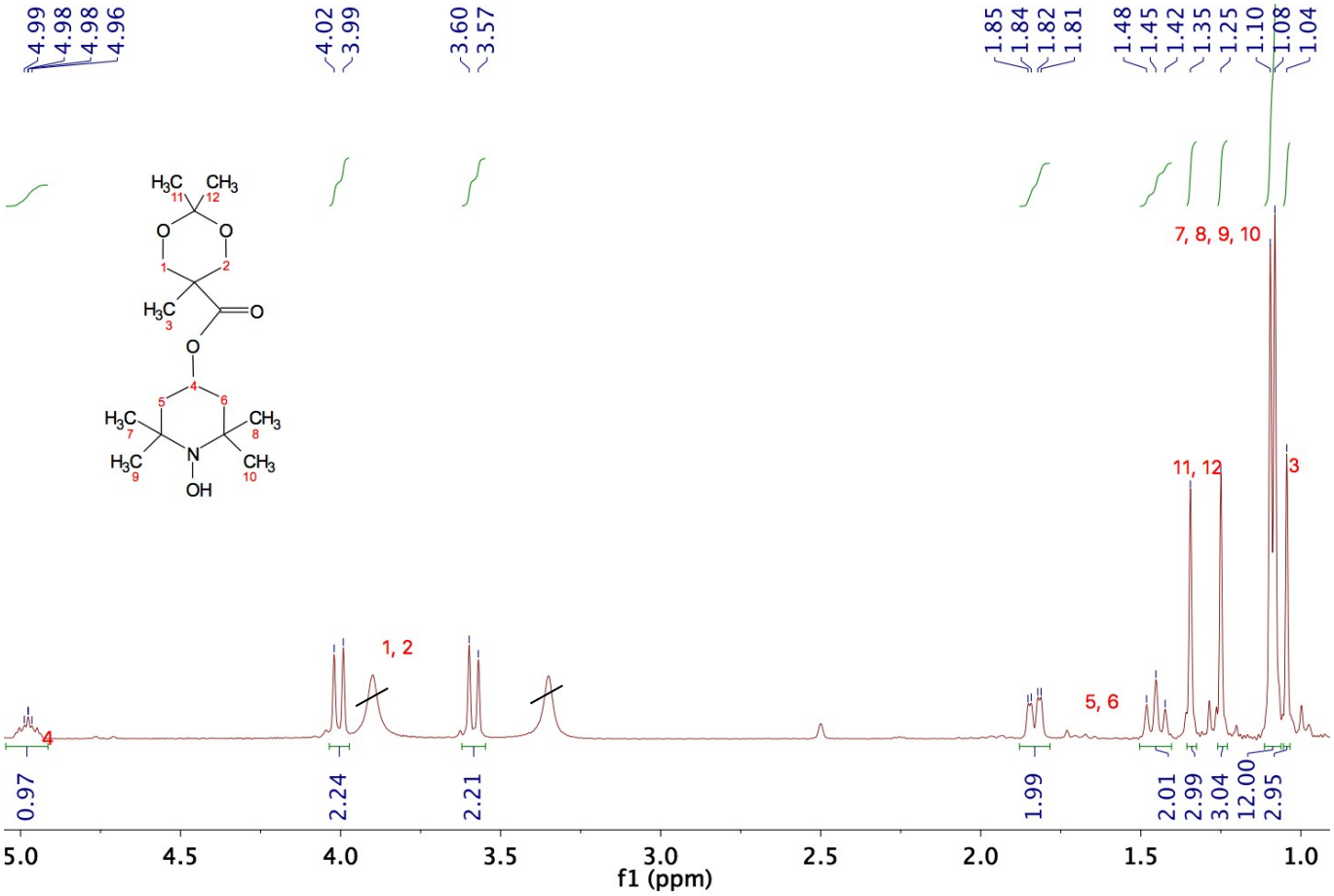

Figure S2. ^{1}H NMR of the protected bis-MPA-TEMPO monomer

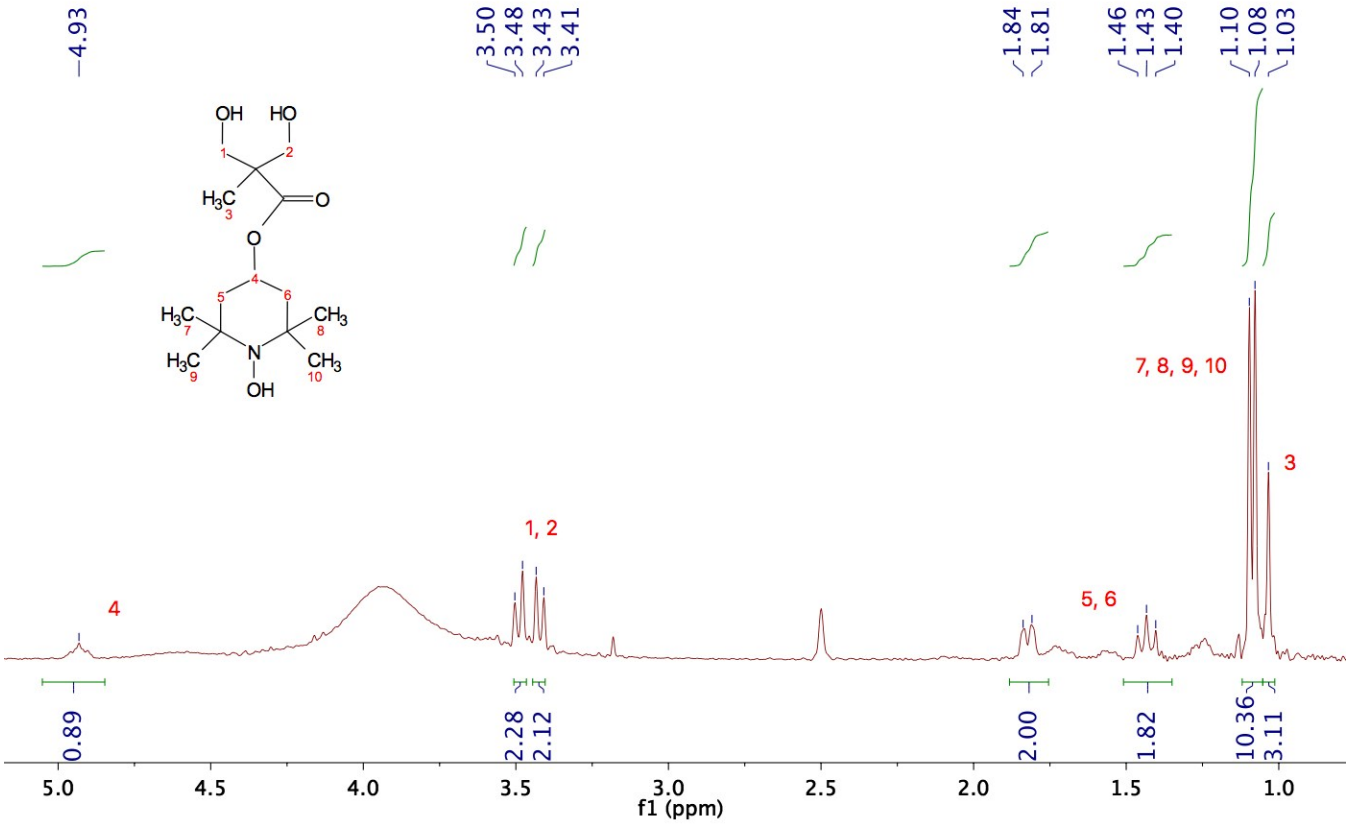

Figure S3. ^{1}H NMR of the bis-MPA-TEMPO monomer

2.2. Homopolymer: poly(MPA-TEMPO-HDI)urethane

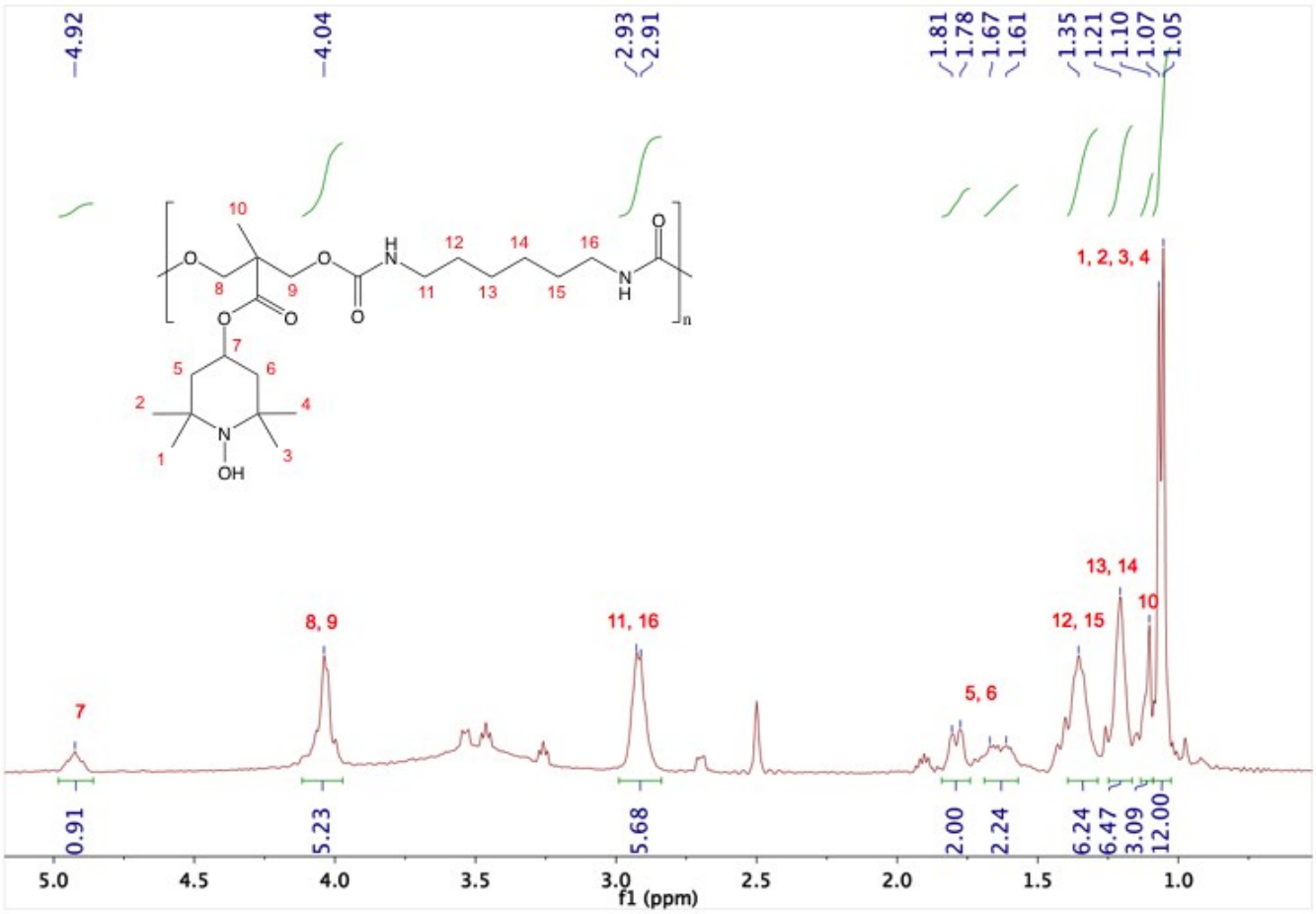

Figure S4. ^{1}H NMR of poly(MPA-TEMPO-HDI)urethane

2.3. Segmented polyurethane: poly(MPA-TEMPO-HDI-PEG)urethane (PU-ORCA)

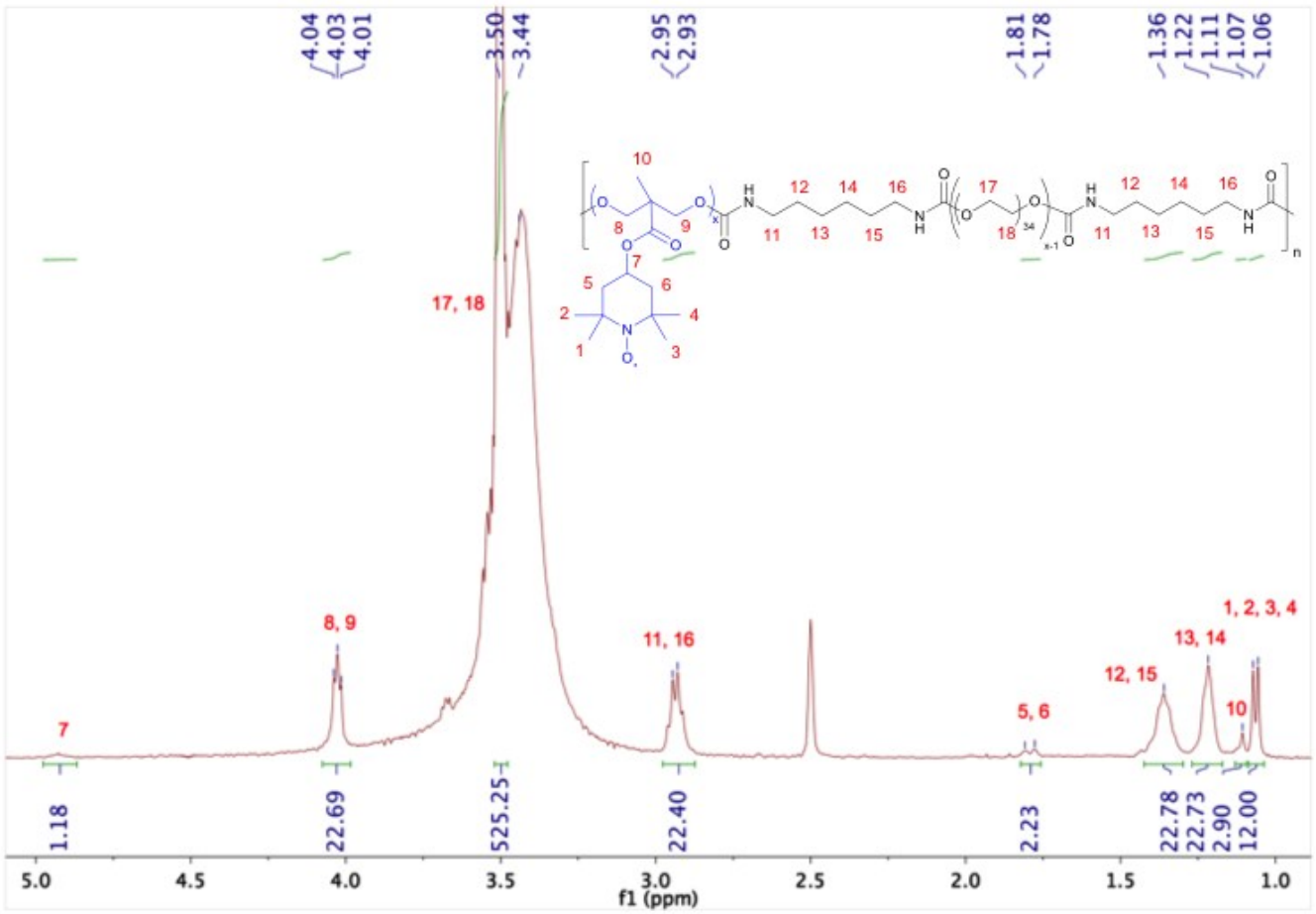

Figure S5. ^{1}H NMR of poly(MPA-TEMPO-HDI-PEG)urethane (PU-4)

3. SEC

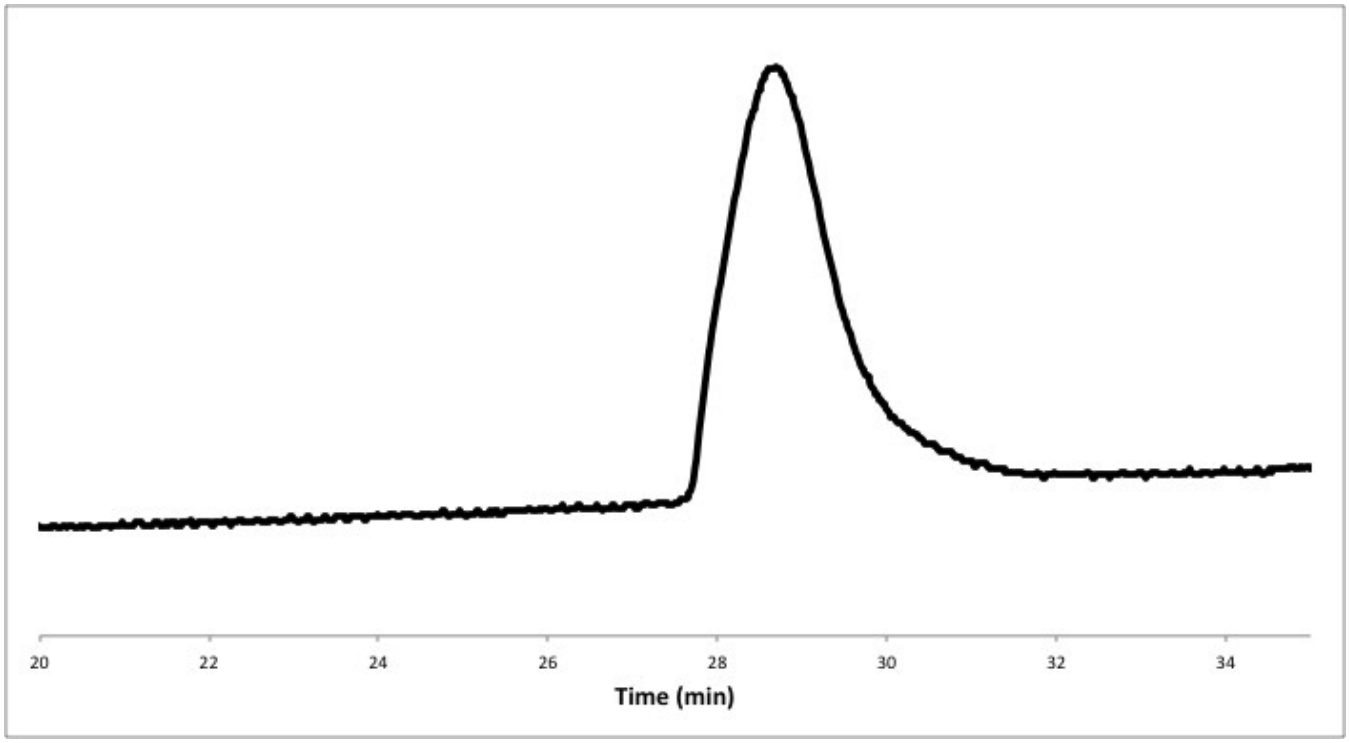

Figure S6. SEC of poly(MPA-TEMPO-HDI-PEG)urethane (PU-4) PU-6.

4. Infrared spectra

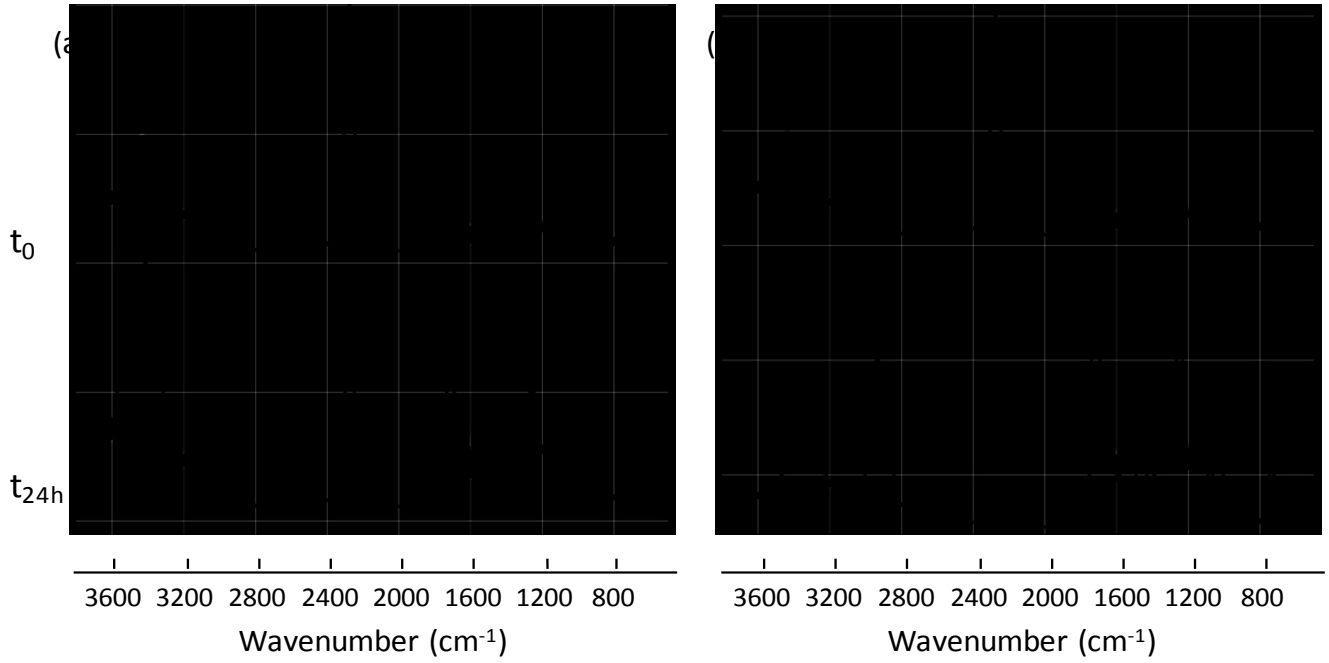

Figure S7. (a) Infrared spectra recorded at 0 and 24h in the presence of triflic acid catalyst (b) Infrared spectra recorded at 0 and 24h in the presence of DBU catalyst.

5. Cyclic voltametry

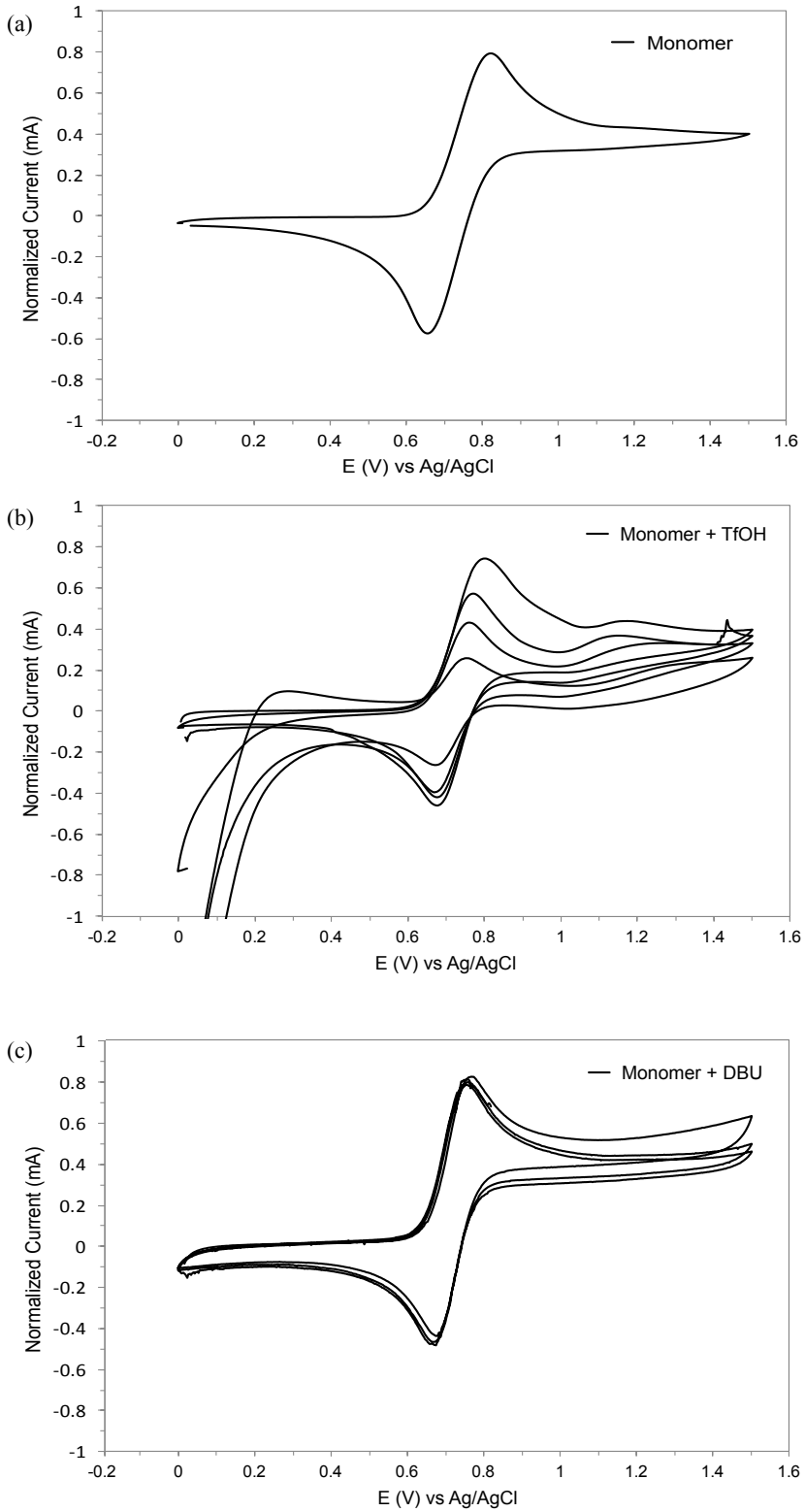

Figure S8. Cyclic voltammetry of (a) bis-MPA-TEMPO and (b) bis-MPA-TEMPO with triflic acid added dropwise and bis-MPA-TEMPO with DBU added dropwise.

6. UV-visible spectra

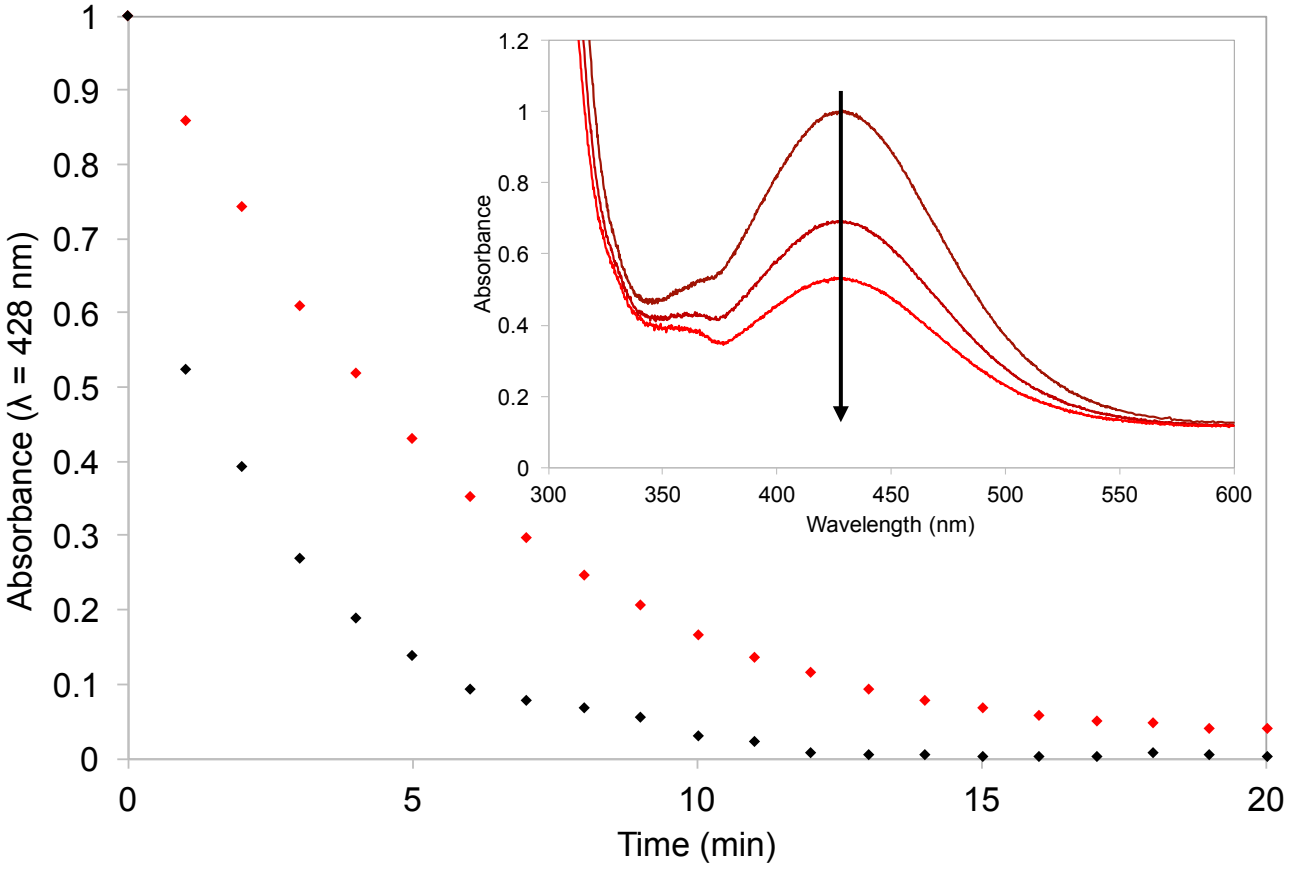

Figure S9. Reduction of bis-MPA-TEMPO (black line) and PU-6 (red line) in the presence of ascorbic acid monitored by disappearance of the nitroxide signal in the UV-visible spectroscopy recorded at 428 nm (internal plot).

7. Relaxivity

Table S2. Relaxivity values (r_1 and r_2) and r_2/r_1 ratio for **PU-5**, **PU-6** and **PU-7** nitroxide-containing polyurethane in water (37 °C, 1.5 T).

	PU-5	**PU-6**	**PU-7**
r_1 ($mM^{-1}\cdot s^{-1}$)	0.66	0.45	0.16
r_2 ($mM^{-1}\cdot s^{-1}$)	0.98	0.60	0.30
r_2/r_1	1.47	1.34	1.88

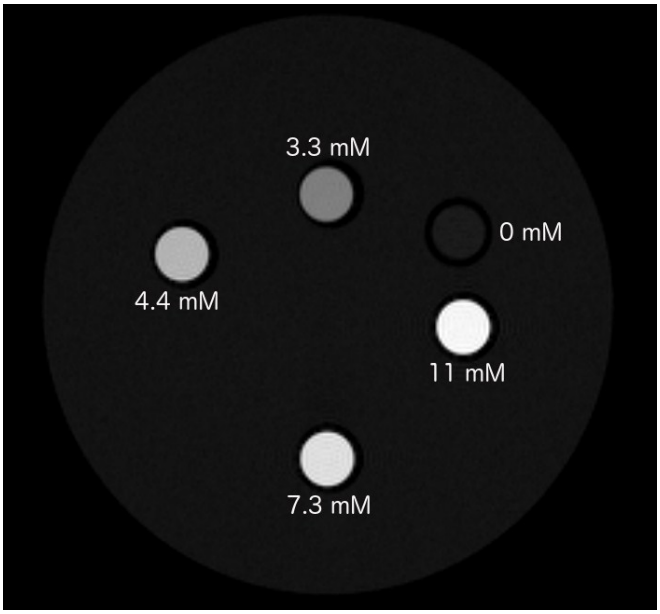

Figure S10. T_1-weighted phantom MR images of increasing concentration of Gadovist (0, 3.3, 4.4, 7.3 and 11 mM) dissolved in human serum.

8. Dynamic Light Scattering (DLS)

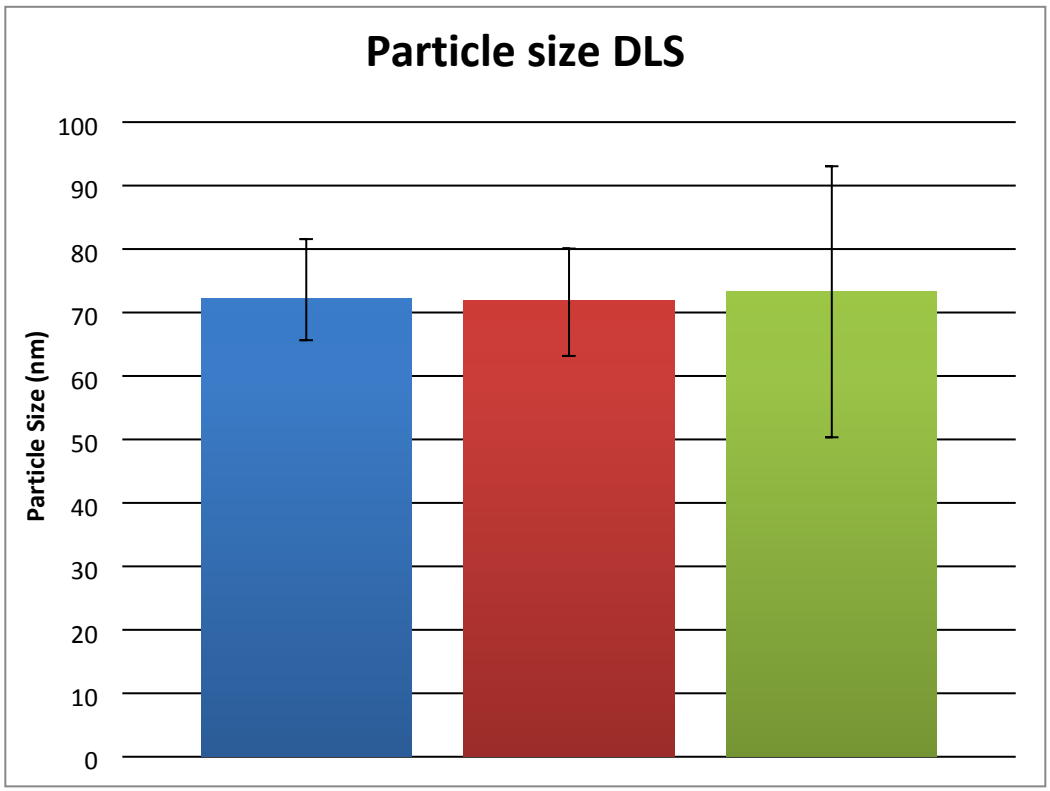

Figure S11. Average particle sizes (nm) determined by dynamic light scattering corresponding to PU-5 (green), PU-6 (red) and PU-7 (blue) in pure water.

8. EPR

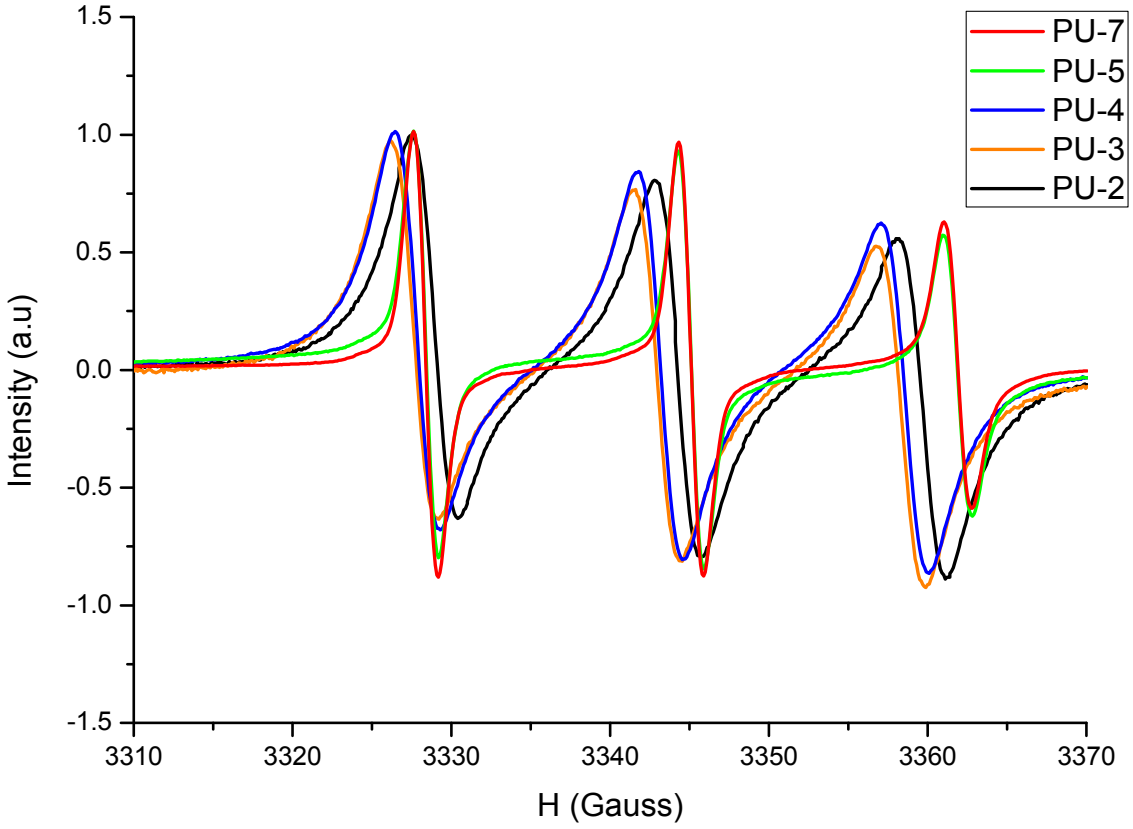

Figure S12. X-band EPR spectra of PU-2,PU-3, PU-4, PU-5 and PU-7.