Supplementary Material (ESI) for Polymer Chemistry

ELECTRONIC SUPPORTING INFORMATION

Investigation on thiol-(meth)acrylate Michael addition reactions using various amine and phosphine catalysts

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Additional characterization data for MMA and HEMA dimers

Characterisation data for methacrylic dimers.

MMA DIMER

^{1}H NMR (400 MHz, Acetone-d_6), δ = 6.15 (d, J = 1.6 Hz, 1H, 1/2 CH_2=), 5.57 (d, J = 1.3 Hz, 1H, 1/2 CH_2=), 3.69 (s, 3H, =C-$COOCH_3$), 3.59 (s, 3H, C-$COOCH_3$), 2.59 (s, 2H, =C-CH_2), 1.12 (s, 6H, 2*CH_3)

^{13}C NMR (400 MHz, Acetone-d_6), δ = 177.44 (C-*C*=O), 168.26 (=C-*C*=O), 138.74 (=C), 128.25 (CH_2=), 52.36 (COO*C*H_3), 52.06 (COO*C*H_3), 43.46 (CH_2), 42.02 (*C*(CH_3)$_2$), 25.40 (2*CH_3).

ESI-MS Calcd. for $C_{10}H_{16}NaO_4^+$ ($M+Na^+$)=223.09, Found 223.09.

HEMA DIMER

^{1}H NMR (400 MHz, D_2O)

δ = 6.33 (d, J = 0.9 Hz, 1H, 1/2 CH_2=), 5.75 (d, J = 0.5 Hz, 1H, 1/2 CH_2=), 4.25-4.27 (m, 2H, $COOCH_2$), 4.14-4.16 (m, 2H, $COOCH_2$), 3.85-3.87 (m, 2H, C*H*$_2$OH), 3.81-3.83 (m, 2H, C*H*$_2$OH), 2.67 (s, 2H, =C-CH_2), 1.21 (s, 6H, 2*CH_3)

ESI-MS Calcd. for $C_{12}H_{20}NaO_6^+$ ($M+Na^+$)=283.12, Found 283.12.

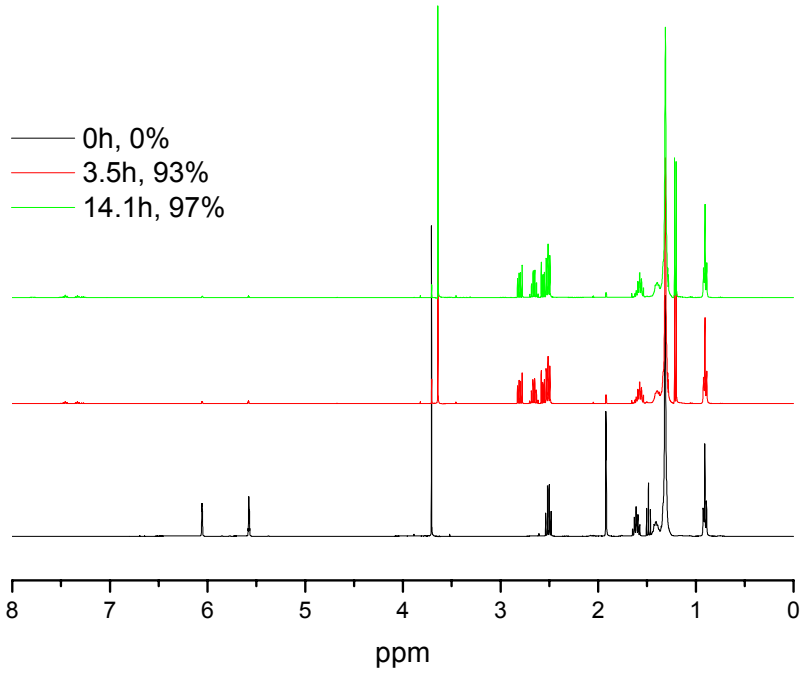


Figure S1. ^{1}H NMR spectra of thiol-Michael addition of MMA with 1-dodecanethiol using 0.05 eq of DMPP in d_6-acetone **P4**.

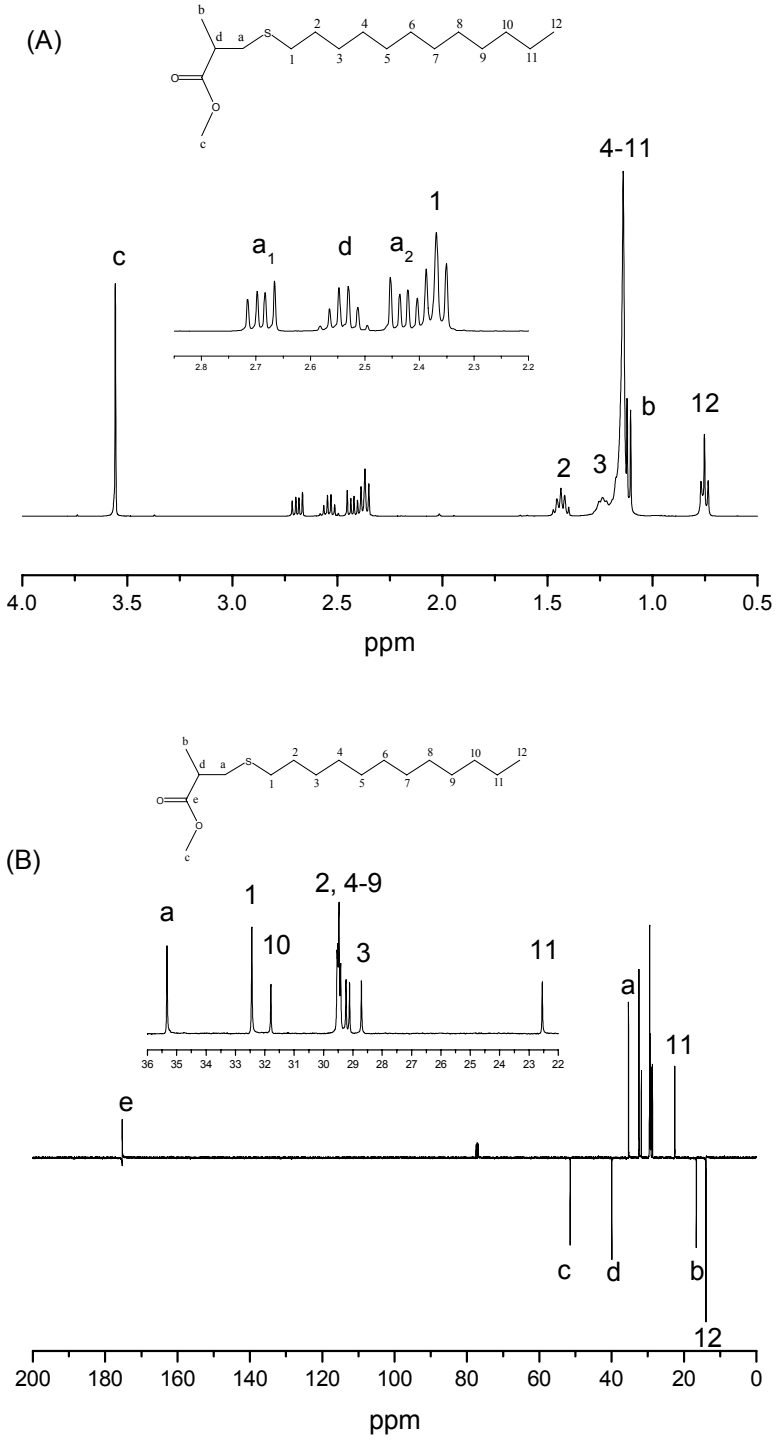


Figure S2. ^{1}H NMR (*top*) and ^{13}C NMR (*bottom*) ($CDCl_3$, 25 °C, 400 MHz) spectra of MMA-DT (**P4**).

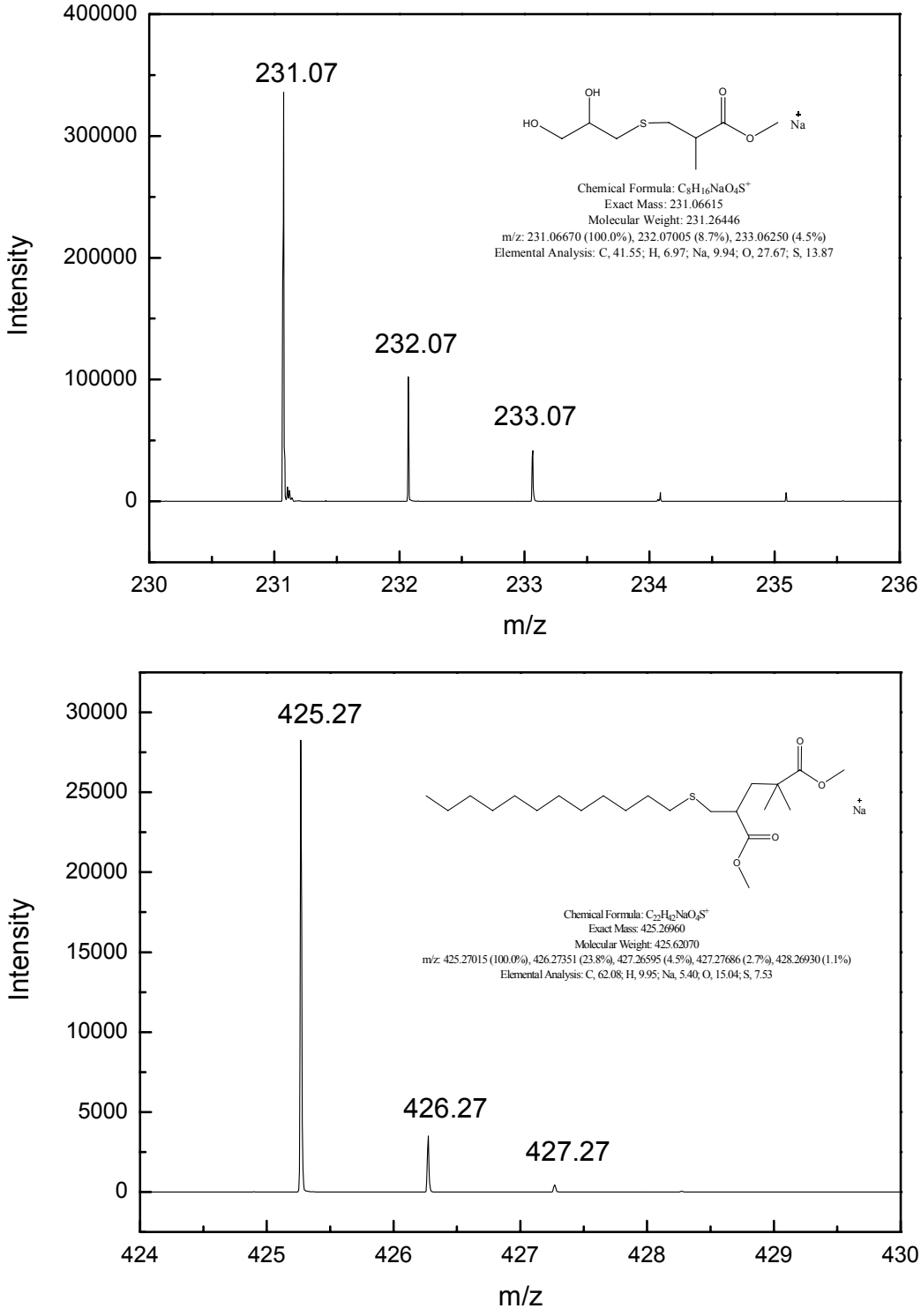


Figure S3. ESI-Mass spectrum of **P3** (left), **P5** (right).

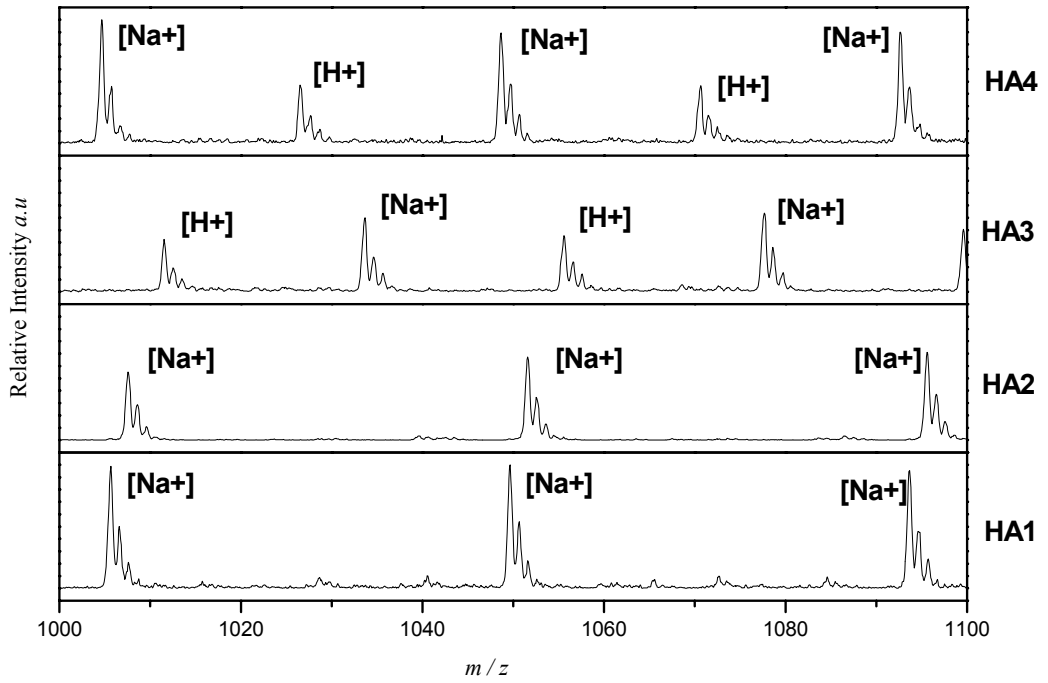


Figure S4. ESI-Mass spectrum from 1000 to 1100 Da of poly(OEG-MA) after modification with different thiols (HA1 to HA4, see Table 3).

Note: all the populations are attributed to expected compounds quaternized with Na^+ and H^+ in the case of HA4 and HA3, and quaternized with Na^+ for HA1 and HA2. The populations were spaced by 44 Da corresponding to ethylene glycol unit.

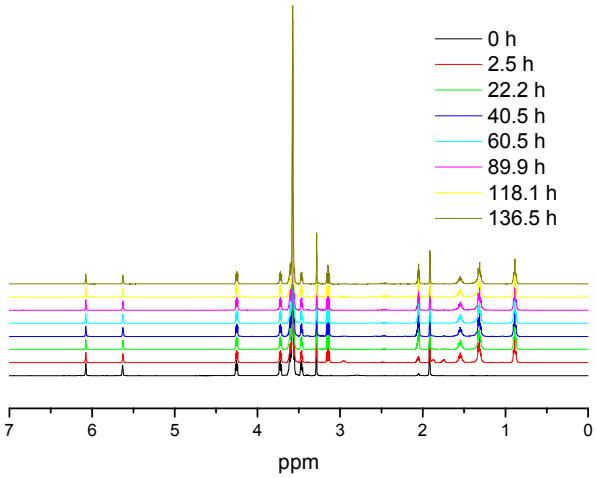


Figure S5. Effect of adding 1.4 equivalents of pentyl amine to PEGMEMA, Lgz137 PEGMEMA475/PA=1/1.4 in acetone as followed by ^{1}H NMR.

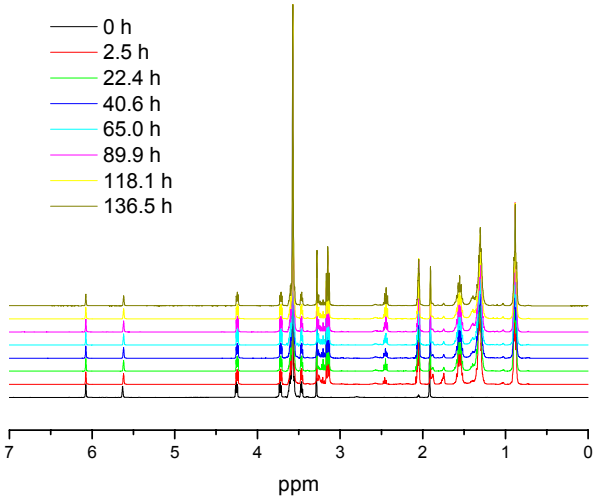


Figure S6. Effect of adding 5.4 equivalents of pentyl amine to PEGMEMA, , Lgz138 PEGMEMA475/PA=1/5.4 in acetone as followed by ^{1}H NMR.

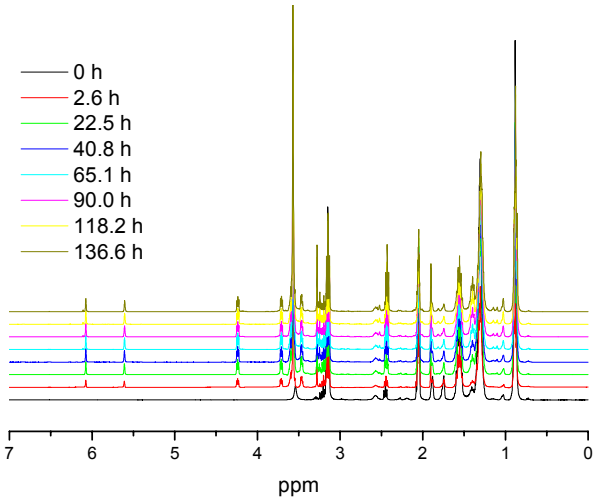


Figure S7. Effect of adding 10.8 equivalents of pentyl amine to PEGMEMA, Lgz138 PEGMEMA475/PA=1/10.8 in acetone acetone as followed by ^{1}H NMR.

Table S1.

Additional data using TCEP as nucleophilic catalyst.

acrylic	**thiol**	**nucleophile**	**Molar ratios**	solvent	Reaction time	% conversion
HEMA	2-ME	TCEP	1:1.5:0.1	D_2O	44.1	22
dMMA	PT	TCEP	1:1.5:0.05	DMSO	95.9	3
dHEMA	2-ME	TCEP	1:1.5:0.1	D_2O	15.8	4
dHEMA	2-ME	TCEP	1:1.5:0.1	D_2O	26.2	85

Table S1. Identified Peaks in the ESI-MS of Products of Thiol-PEGMEMA$_{475}$ dimer reaction showing all mass agreements with the desired product. Error is within the instrumentation error of 0.3 amu for LCQ-Deca.

Compound	m/z experimental	m/z theoretical	m/z error

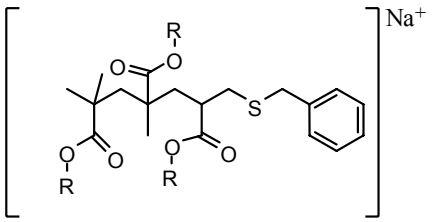
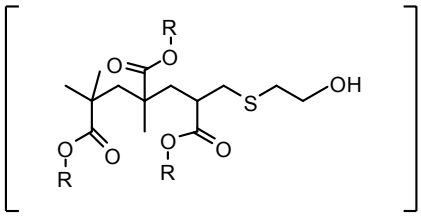
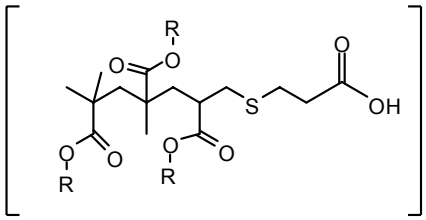
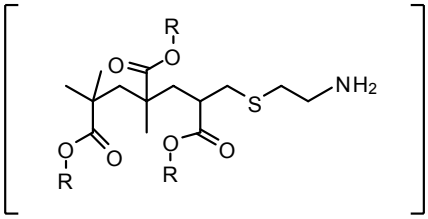
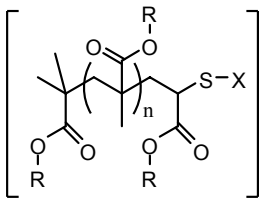
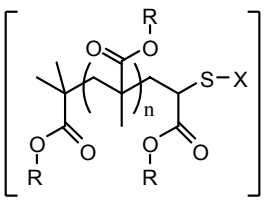
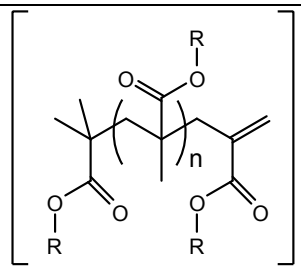
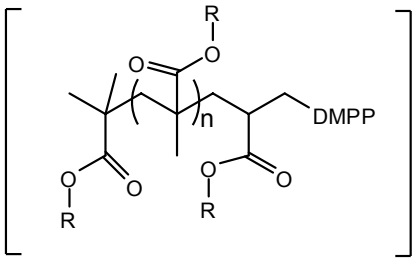
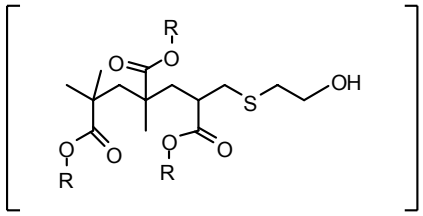
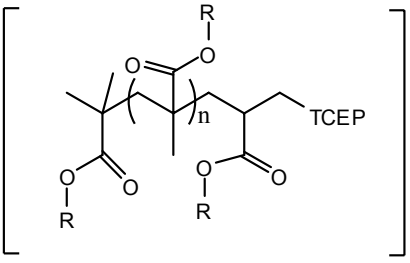
	1095.6	1095.6	0
	1049.7 or 1027.7*	1049.5 or 1027.5*	0.2 or 0.2*
	1077.7 or 1055.6*	1077.5 or 1055.6*	0.2 or 0*
	1048.7 or 1026.5*	1048.6 or 1026.5*	0.1
 X : Glutathione	1278.7 or 1256.5*	1278.6 or 1256.6*	0.1
 X : Glucose	1167.7 or 1145.7*	1167.7 or 1145.7*	0.1

Table S3. Mass identified in the Mass Spectrum showed in Figure 8 in the manuscript with the error is fall well within the error of the instrument of ± 0.3 Da.

Compound	m/z experimental	m/z theoretical	m/z error
	1059.6	1059.6	0
	1087.7	1087.6	0.1
	1049.7 or 1027.7*	1049.5 or 1027.5*	0.2 or 0.2*
	1068.6	1068.5	0.1