Journal Name

ARTICLE

Redox-controlled upper critical solution temperature behaviour of a nitroxide containing polymer in alcohol-water mixtures Supplementary Information

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Olivier Bertrand[a], Alexandru Vlad[b], Richard Hoogenboom[c], Jean-François Gohy[a]*

Result and discussion

Polymer synthesis

Table S1: Conditions and results for the polymerisation of TMPM by zero-valent metal mediated RDRP.

exp[a]	BnBiB/ TMPM (eq.)	t (h)	conv[b] (%)	*Mn*[b] (g/mol)	*Đ*[c]
P1	1/51	17	>99.9	16,820	1.12
P2	1/100	22	>99.9	31,550	1.12
P3	1/150	22	99.5	48,720	1.12

[a] reaction conditions: BnBiB/$CuBr_2$/PMDETA = 1/0.05/0.12; Cu(0) wire = 5cm; IPA = 60wt%; T = 40°C.

[b] determined by ^{1}H NMR spectroscopy in $CDCl_3$ of the PTMPM

[c] determined by SEC with PMMA standards

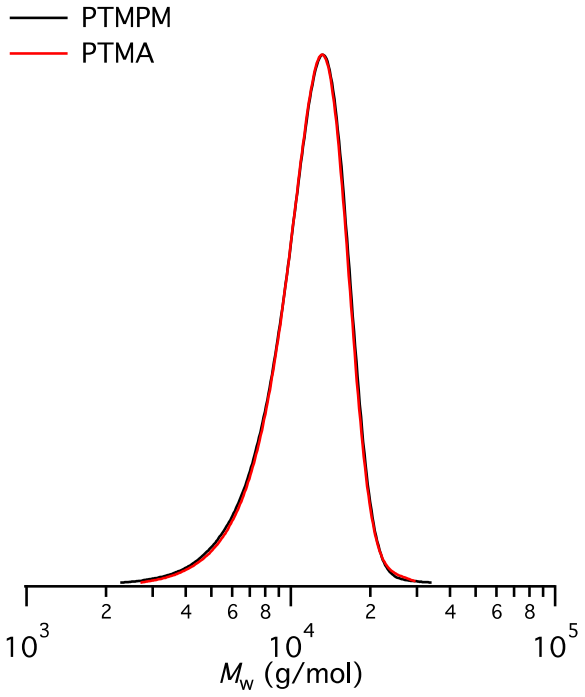

Figure S1: Overlay of the SEC chromatograms of $PTMPM_{69}$ (black curve) and $PTMA_{69}$ (red curve)

Thermo-responsive properties of PTMA in alcohol/water mixtures

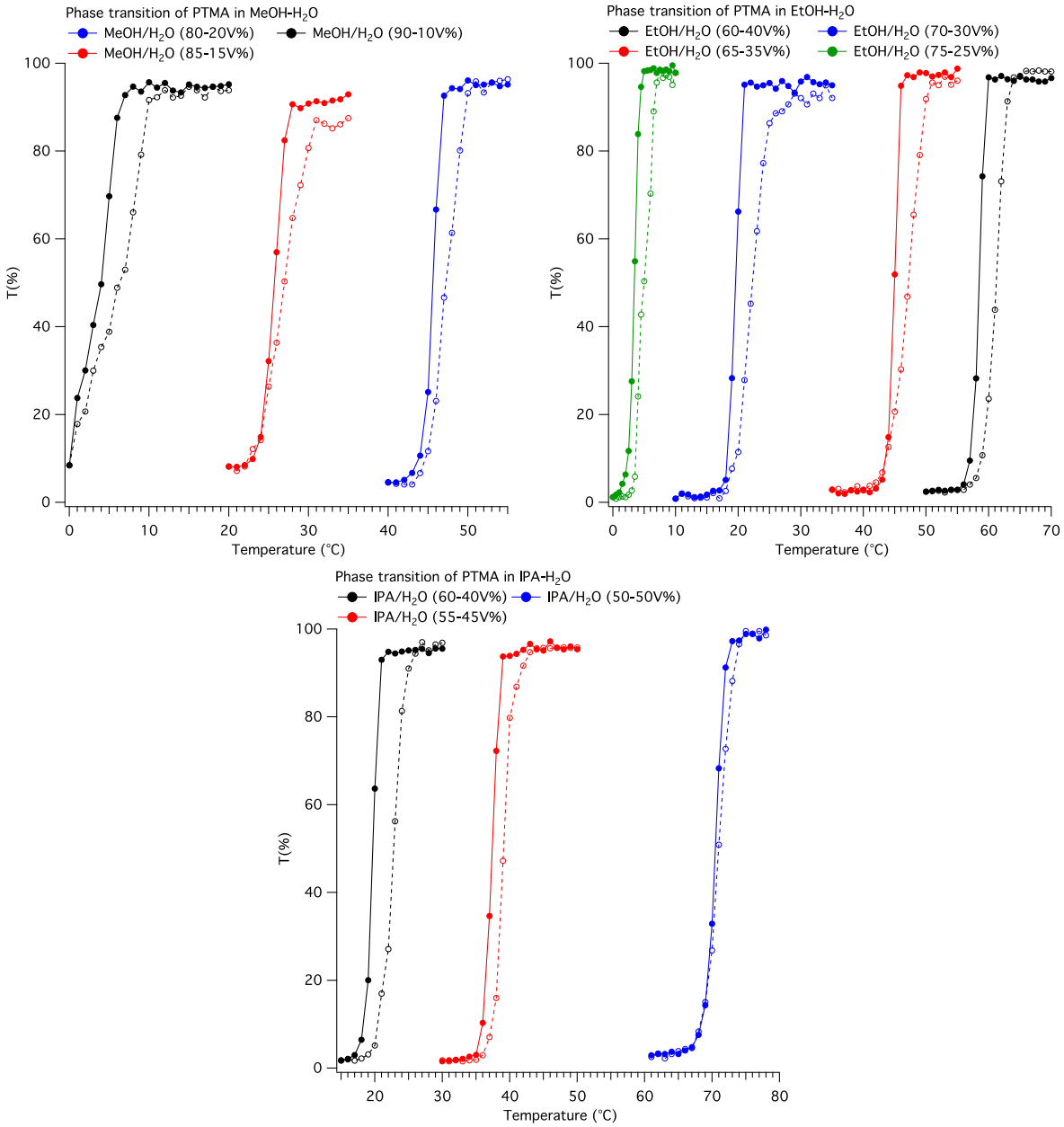

Figure S2: Effect of the alcohol nature and water content on the phase transition of PTMA: (a) methanol, (b) ethanol and (c) isopropanol.

Table S2: Effect of the alcohol nature on the Tcp and Tcph of PTMA in alcohol water mixture (C_{P1} = 5g/L).

Solvent	water (vol.-%)	Tcph (°C)	Tcp (°C)
MeOH	10	7	4
MeOH	15	27	25.4
MeOH	20	47.1	45.6
EtOH	25	4.4	2.8
EtOH	30	21	19
EtOH	35	47.2	45
EtOH	40	61.2	58.1
IPA	40	22.6	19.6
IPA	45	39	36.5
IPA	50	71	70.5

Table S3: Effect of the concentration on the Tcp and Tcph of PTMA in ethanol-water mixture (P1 in 70-30 vol.-%).

C_{P1} (g/L)	Tcph (°C)	Tcp (°C)
1	7.4	2.6
2.5	13.8	11.8
5	21.3	19
7.5	26.4	24.2
10	27	25.4
15	31.8	27.6
20	35.9	32.7
25	38.8	33.6
50	42.6	40.5
75	60.6	58.6

Table S4: Effect of the PTMA chain length on the Tcp and Tcph of PTMA in ethanol-water mixture (C = 5g/L in 70-30 vol.-%).

Sample	DP	Tcph (°C)	Tcp (°C)
P1	69	22.4	19.5
P2	139	55.9	51.6
P3	215	65.4	64.2

Equation 1 presents the evolution of the critical temperature (Tcp) as a function of the polymer chain length (DP), ϑ is the theta temperature, and ψ accounts for the sign of the temperature dependence of the Flory-Huggins parameter χ:

$$\frac{1}{T_{cp}} = \frac{1}{\theta} + \frac{1}{\theta\psi}\left(\frac{1}{2DP} + \frac{1}{\sqrt{DP}}\right) \quad \text{(equ1)}$$

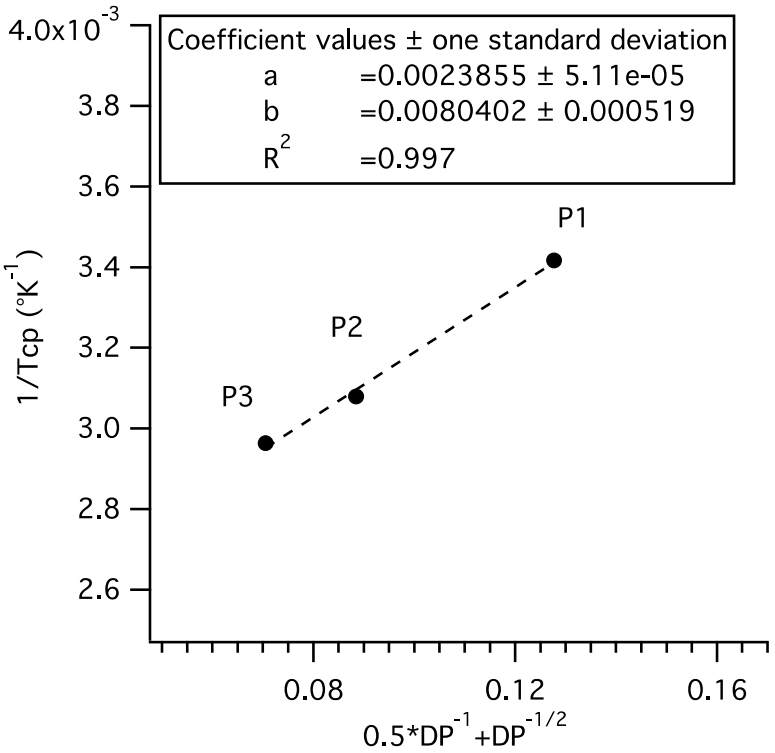

Figure S3: Plot of inverse cloud points according to Flory-Huggins theory (eq 1) using the number-average degree of polymerization DP.

Redox tuning of the UCST

Table S5: Effect of the chemical oxidation of the PTMA in ethanol-water mixture (C_{P1} = 5g/L; 60-40 vol.-%; T = 70°C).

TEMPO/NaClO (eq.)	t (d)	Tcph (°C)	Tcp (°C)
1/0	0	61.2	58.1
1/2	0	60.6	59.7
1/2	1	56	53.1
1/2	2	45.7	44.2
1/2	7	44.2	41.7

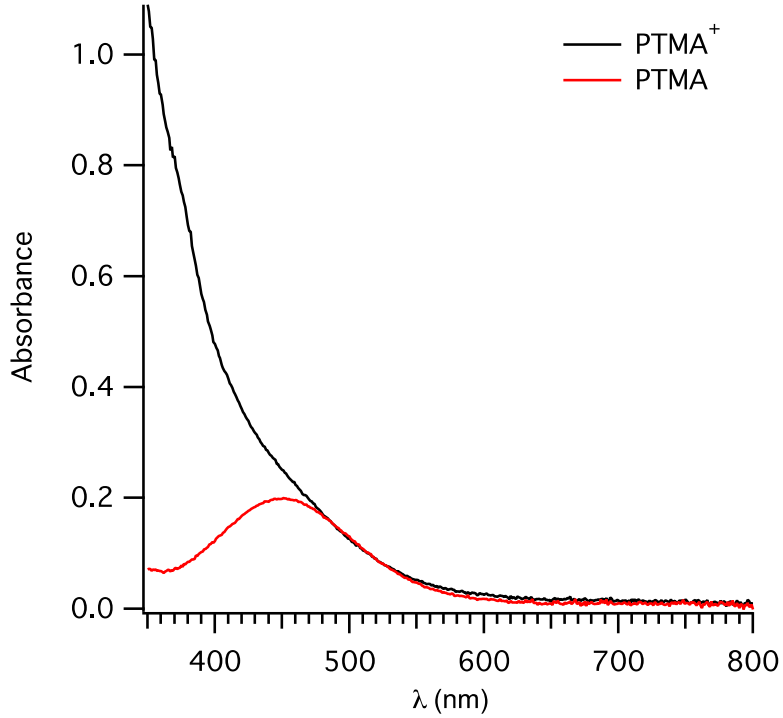

Figure S4: overlay of the UV-Vis spectra of a solution of PTMA (red curve) and oxidised PTMA (black curve) in ethanol-water mixture at 70°C (CPTMA = 5g/L; in 60-40 vol.-%).

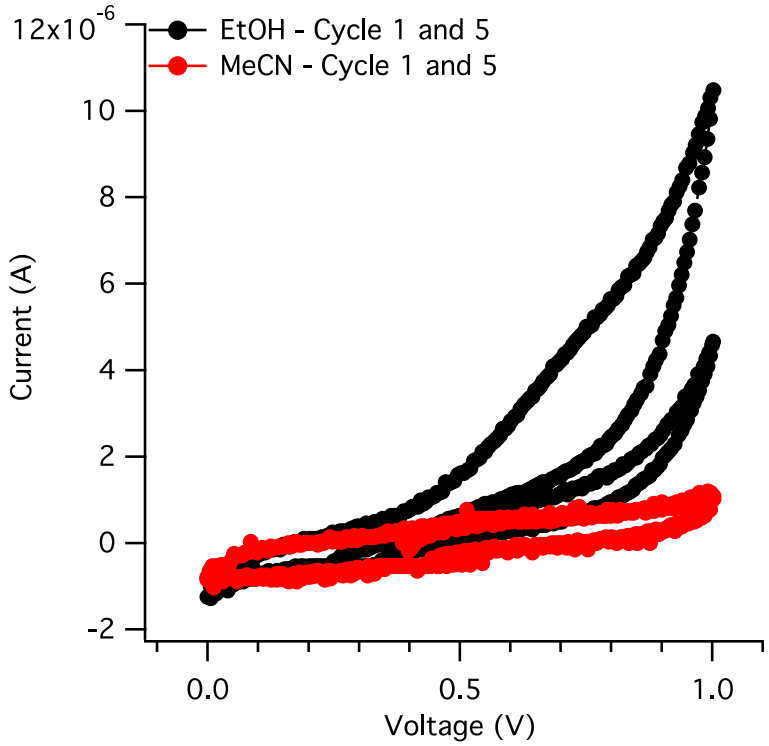

Figure S5: Cyclic voltammetry of a solution of $LiClO_4$ in acetonitrile (red curve) and ethanol (black curve) at 50 mV s^{-1} (cycles 1 and 5; 0.1M $LiClO_4$).

Table S6: Effect of the electrochemical oxidation of the PTMA in ethanol-water mixture (C_{PI}= 5g/L; 0.01M of $LiClO_4$ in 60-40 vol.-%).

Nature of the PTMA	Cycle	Applied voltage (V)	t (h)	Tcph (°C)	Tcp (°C)
PTMA		0	0	58.5	55.4
$PTMA^+$	Oxidation C1	0.8	5	27.4	25.2
PTMA	Reduction C1	0.1	5	45.3	44.1
$PTMA^+$	Oxidation C2	0.8	4	29.1	27
PTMA	Reduction C2	0.1	5	45.1	43.3