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

Olivier Bertrand, Alexandru Vlad, Richard Hoogenboom and Jean-François Gohy*

Research on stimuli responsive polymers builds momentum as nature-inspired applications using man-made materials are increasingly sought.

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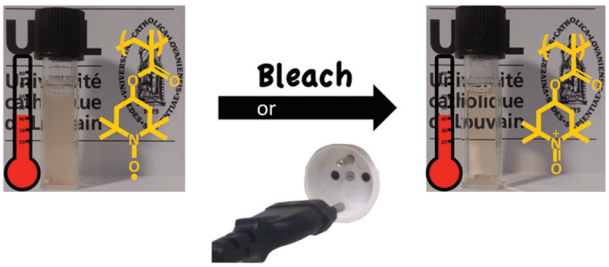

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Polymer Chemistry

PAPER

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

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Research on stimuli responsive polymers builds momentum as nature-inspired applications using man-made materials are increasingly sought. Here, we show for the first time the thermo-responsive upper critical solution temperature (UCST) behaviour of a nitroxide containing polymer based on (2,6,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO). It is demonstrated that poly(TEMPO methacrylate) (PTMA) exhibits a UCST-type cloud point temperature in alcohol–water mixtures that can be tuned by external electrical stimuli. To exemplify this, we studied the UCST behaviour of this polymer in alcohol–water mixtures. The reversible redox response of PTMA is used to tune the thermo-responsive behaviour of the solvated polymer. The effect of the oxidation extent in PTMA on UCST is demonstrated and a correlation between the chemical and electrochemical oxidation routes is presented.

Introduction

Over the years, interest in stimuli responsive polymers has grown to a large extent. By definition, stimuli-responsive polymers display a change in their physical and/or chemical properties when exposed to a chemical of physical stimuli, such as pH,[1,2] temperature,[3–6] and light illumination.[7–10] In solution, thermo-responsive polymers can display two antagonistic behaviours. The polymer may reversibly transit from the soluble to the insoluble state when the temperature is either increased or decreased, referred to as lower critical solution temperature (LCST) and upper critical solution temperature (UCST) behaviours, respectively. The cloud point temperature (Tcp) of the polymer solution can be modulated by different factors, such as the polymer chain length, the polymer concentration, the solvent composition, *etc*.[1,3–6]

LCST behaviour is commonly observed for most water-soluble polymers and is driven by the entropy loss upon hydration of the polymer chains.[4,6] At the Tcp, the enthalpy gain of hydration equals the entropy loss and further heating leads to dehydration of the polymer. The reverse behaviour is less commonly observed and can be based either on strong interpolymer interactions that are weakened upon heating or on a decrease in solvent polarity upon heating.[3,5] The latter is an intrinsic property of alcohol–water mixtures and has recently gained significant interest to develop UCST type polymer solutions.[11–15]

The UCST (or LCST) can be tuned by chemical modification of the polymer chains. To cite, the introduction of hydrophilic/hydrophobic units in the polymer backbone has been shown to increase or decrease the UCST of the copolymer compared to the parent homopolymer.[16–18] According to this idea, multi-responsive copolymer systems were developed *via* the introduction of monomers able to respond to other types of stimuli.[19] The introduction of pH sensitive monomers, such as methacrylic acid (MAA) or dimethylaminoethyl methacrylate (DMAEMA), into the thermo-responsive polymer backbone allows us to modulate the LCST or UCST of the copolymer depending on the solution pH.[17,20] Tuning the thermo-responsive properties with a light stimulus was also achieved by the introduction of azobenzene, *o*-nitrobenzyl or spiropyran groups in the polymer structure.[21–26] The modulation of the thermo-responsive properties of copolymers *via* a redox process was achieved by the introduction of monomers bearing ferrocene or TEMPO derivatives.[27–30] Importantly, these dual responsive polymers also enable isothermal switching of the polymer phase transition based on the second

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†Electronic supplementary information (ESI) available: Polymer synthesis conditions and polymer characterisation, tables containing the numerical values of Tcp and Tcph and other relevant information. See DOI: 10.1039/c5py01864a

response mechanism.[31] To date, there are only very few reports on dual responsive polymers that exhibit UCST behaviour in alcohol–water mixtures.[21,32]

Although, multi stimuli-responsive systems can be obtained by mixing the properties of two stimuli-responsive polymers *via* a copolymerisation process, only a small number of homopolymers are known to display a response to two or more stimuli. PDMAEMA is a trivial example since its LCST can be directly modulated by the pH of the solution.[33,34] Moreover, PDMAEMA is particularly interesting since it can display either a LCST behaviour or a UCST behaviour depending on the presence of trivalent metal hexacyano anions.[35–38]

Here we report on the redox tunable thermo-responsive behaviour of a nitroxide containing homopolymer, poly(TEMPO methacrylate) (PTMA), which was found to exhibit a UCST behaviour in alcohol–water mixtures. First, the synthesis of PTMA *via* a two-step approach is detailed. The thermal properties of the homopolymer are studied next in different alcohol–water mixtures. The critical parameters that influence the phase transition temperature of the polymer are detailed. Next, the reversible redox reaction of the nitroxide group within PTMA is exploited to fine-tune the Tcp of the polymer–solvent system. The chemical or electrochemical oxidation of the nitroxide function of PTMA into its oxoammonium derivative influences the solvation of the polymer and leads to the decrease of the Tcp in the considered alcohol–water mixture. Since the extent of both chemical and electrochemical redox reactions can be precisely controlled, a unique control over the thermo-responsive properties of the system is obtained.

Experimental

Materials

Copper wire (diameter = 0.25 mm) was pre-treated by washing with hydrochloric acid for 15 min and rinsed thoroughly with Milli-Q water, dried under nitrogen and used immediately. $CuBr_2$ (Acros, 99+%), 2,2,6,6-tetramethylpiperidin-4-yl methacrylate (TMPM, TCI), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 98%), 2-propanol (IPA, Acros, 99%) and all other chemicals were used as received.

Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired either on a 300 MHz Bruker Avance II or on a 500 MHz Bruker Avance II in deuterated chloroform. Number average molar masses (M_n), weight average molar masses (M_w), and dispersities ($Đ$) of the polymers were measured on an Agilent size exclusion chromatograph (SEC) system equipped with an Agilent 1100/1200 pump (25 °C; eluent: chloroform/triethylamine/IPA 94 : 4 : 2; flow rate: 1 mL min^{-1}), and an Agilent differential refractometer. UV-visible spectra were recorded on a Varian spectrophotometer (Cary, 50 Conc). Electrochemical experiments were performed using an Arbin Instruments Battery Tester, BT-2043 and a CHI660B instrument. Cyclic voltammetry experiments were realised with a standard three electrode cell: a $Ag|AgNO_3|Bu_4NClO_4$ reference electrode,[43] a Pt mesh counter electrode and a 2 mm Pt working electrode. PTMA oxidations were carried out within a homemade H-type cell consisting of two 50 mL compartments separated by sintered glass with porosity of 40 mm equipped with two glassy carbon electrodes and a $Ag|AgNO_3|Bu_4NClO_4$ reference electrode.

Typical procedure for the synthesis of PTMPM

A Schlenk tube was filled with benzyl-2-bromoisobutyrate (BnBiB, 20.5 mL, 0.112 mmol, 1 eq.), IPA (2.40 mL), TMPM (1.28 g, 5.69 mmol, 51 eq.) and 62.3 mL of a solution of $CuBr_2$/PMDETA in IPA (C_{Cu} = 20 g L^{-1}; $CuBr_2$: 1.25 mg, 5.58 × 10^{-3} mmol, 0.05 eq.; PMDETA: 2.88 mg, 0.013 mmol, 0.12 eq.). This solution was degassed by three freeze–pump–thaw cycles. A magnetic barrel rubbed with 5 cm of activated Cu(0) wire was then introduced under argon flux. The solution was immerged in an oil bath at 40 °C and stirred for 8 h (conv. >99%). The polymerisation was quenched by quickly cooling the tube in a water–ice bath and exposing the reaction mixture to air. The reaction mixture was filtered over basic Al_2O_3 (eluent: CH_2Cl_2). The solvent was removed under reduced pressure. The residue was precipitated in hexane, filtered and dried *in vacuo* at 30 °C overnight, affording a white solid (*m* = 1.24 g, yield = 91%).

M_n (SEC) = 10 870 g mol^{-1}; $Đ$ (SEC) = 1.12; M_n (RMN) = 16 820 g mol^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) $PTMPM_{69}$: 7.45–7.30 (b, 5H, H_{Ar} chain-end), 5.25–4.90 (b, 69H; CH–O), 4.07 (m, 138H; CH_2-O chain end), 2.05–1.51 (b, 1035H; CH_3 + CH_3 backbone), 1.51–0.80 (b, 414H; CH_2 + CH_2 backbone).

Typical procedure for the synthesis of PTMA

A round-bottom flask equipped with a condenser was filled with $PTMPM_{69}$ (232 mg, 1.03 mmol of amine functions, 1 eq.), $Na_2WO_4{\cdot}2H_2O$ (84.9 mg, 0.26 mmol, 0.25 eq.), EDTA (34.7 mg, 0.15 mmol, 0.15 eq.) and methanol (12 mL). The solution was stirred at 60 °C for 5 minutes and H_2O_2 (1.17 mL, 10.3 mmol, 10 eq.) was added dropwise over 60 minutes. The solution was stirred at 60 °C for 24 h. The polymer was extracted with CH_2Cl_2. The organic phase was dried with $MgSO_4$. The solvent was removed under reduced pressure. The residue was precipitated in hexane, filtered and dried *in vacuo* at 30 °C overnight, affording an orange solid (*m* = 174 mg, yield = 75%).

M_n (SEC) = 10 840 g mol^{-1}; $Đ$ (SEC) = 1.12; Dox = 95%.

Typical procedure for the determination of Tcp and Tcph

A quartz cuvette was filled with a solution of PTMA in an EtOH–Milli-Q water mixture (C_{PTMA} = 5 g L^{-1}). The solution was heated to 70 °C for 10 minutes under stirring to dissolve PTMA. The solution was cooled by 1 °C steps and the UV-Vis spectra were recorded at every step after 1 minute equilibration (λ = 350 to 800 nm). The solution was cooled until the transmittance of the solution reached less than 3%. The solution was subsequently heated by 1 °C steps and the UV-Vis spectra were recorded at every step after equilibration for 1 minute. The Tcp was determined by plotting the transmittance of the solution at λ = 790 nm *versus* the temperature and recording

the temperature at 50% transmittance during cooling. The clearance point temperature upon heating (Tcph) was taken as the temperature at 50% transmittance during heating.

Typical procedure for the chemical oxidation of PTMA

A sealed quartz cuvette was filled with a solution of PTMA (15 mg, 6.16×10^{-5} mol of TEMPO functions, 1 eq.) and NaClO (8.2 μL, 1.23×10^{-4} mol, 2 eq.) in an EtOH–Milli-Q water mixture (3 mL, 60–40 vol%). The solution was heated at 75 °C for 24 h.

Cyclic voltammetry (CV)

CV was recorded in a solution of PTMA (100 mg; C_{TEMPO} = 0.08 M), $LiClO_4$ (53.2 mg, C = 0.1 M) and acetonitrile (5 mL) in a 10 mL beaker at 50 mV s^{-1} at 25 °C using a Pt disk working electrode, a Pt wire counter electrode and a $Ag|AgNO_3|Bu_4NClO_4$ reference electrode in acetonitrile.

Typical conditions for electrochemical oxidation of PTMA

A H-type cell was equipped with a glassy carbon working electrode, a $Ag|AgNO_3|Bu_4NClO_4$ reference electrode and a glassy carbon counter electrode. The cell was filled with a $LiClO_4$ solution in acetonitrile (0.01 M). PTMA (135 mg; C_{TEMPO} = 0.02 M) was added to the H-type cell compartment containing the working and the reference electrodes. The electrochemical oxidation was carried out by applying a constant potential of 0.8 V (*vs.* $Ag/AgNO_3$) to the glassy carbon working electrode and ensuring continuous stirring for 5 h.

Results and discussion

Polymer synthesis

The investigated nitroxide-containing polymer was synthesised *via* a two-step methodology as shown in Scheme 1. A poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMPM) precursor polymer was synthesised by copper(0) mediated reversible-deactivation radical polymerisation (RDRP, see Table S1 in the ESI†),[40–42] followed by the oxidation of the PTMPM with H_2O_2 in methanol to obtain poly(TEMPO methacrylate) (PTMA).[43] Table 1 presents the characteristics of the PTMA investigated in this contribution, clearly demonstrating that well-defined polymers are obtained and that the oxidation of PTMPM to PTMA is efficient, leading to PTMA with more than 93% of oxidation yield (Dox).

Table 1 Characteristics of the investigated PTMA

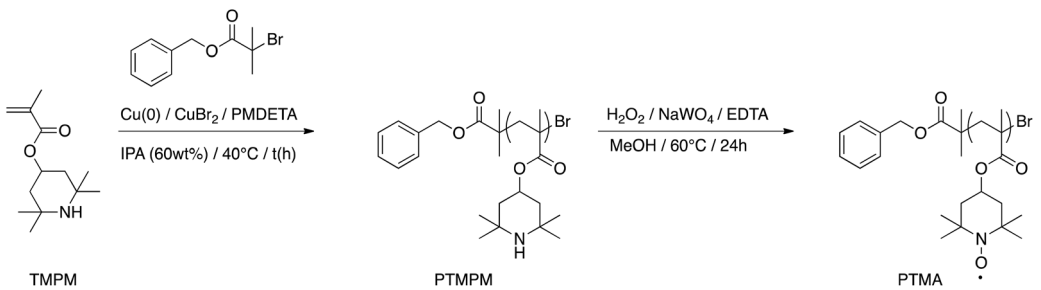
Sample	DP[a]	M_n [a] (g mol^{-1})	$Đ$[b]	Dox[c] (%)
P1	69	16 820	1.12	95
P2	139	33 650	1.12	95
P3	215	51 900	1.11	93

[a] The degree of polymerisation (DP) and molar mass (M_n) were determined by ^{1}H NMR spectroscopy in $CDCl_3$ of PTMPM. [b] Determined by SEC with PMMA standards. [c] Determined by UV-Vis spectroscopy using a TEMPO-*tert*-butyrate calibration.

The oxidation yield was determined using TEMPO-*tert*-butyrate (a PTMA isomorphic organic molecule). The calibration curve was obtained by recording the absorbance at λ = 466 nm of TEMPO-*tert*-butyrate in CH_2Cl_2 *versus* the concentration. The absorbance of solutions of PTMA in CH_2Cl_2 was recorded and compared to the calibration using the Lambert–Beer law.

Thermo-responsive properties of PTMA in alcohol/water mixtures

The UCST behaviour of PTMA in alcohol/water mixtures was first noticed during the purification process after the oxidation step transforming PTMPM into PTMA. We observed the precipitation of the polymer in a methanol/water mixture and that the solubility of the polymer could be restored by increasing the temperature. This phenomenon is consistent with the previously observed UCST behaviour of, amongst other polymers, poly(methyl methacrylate) (PMMA) in ethanol/water mixtures.[3] Inspired by this serendipitous finding, an in-depth analysis of the thermo-responsive behaviour of PTMA in different alcohol/water mixtures was undertaken. This behaviour was studied by UV-Vis spectroscopy by plotting the transmittance (λ = 790 nm) of the solution *versus* the temperature. Fig. 1a presents the evolution of the transmittance with temperature of a PTMA solution in a methanol/water mixture (C_{P1} = 5 g L^{-1}; methanol–water = 80–20 vol%). When the solution is cooled (●), the transmittance of the solution decreases indicating the phase separation of PTMA. An increase of the solution transmittance is observed upon heating (○), indicating the dissolution of PTMA in the mixture and thus demonstrating the reversible



Scheme 1 Two-step synthesis of PTMA.

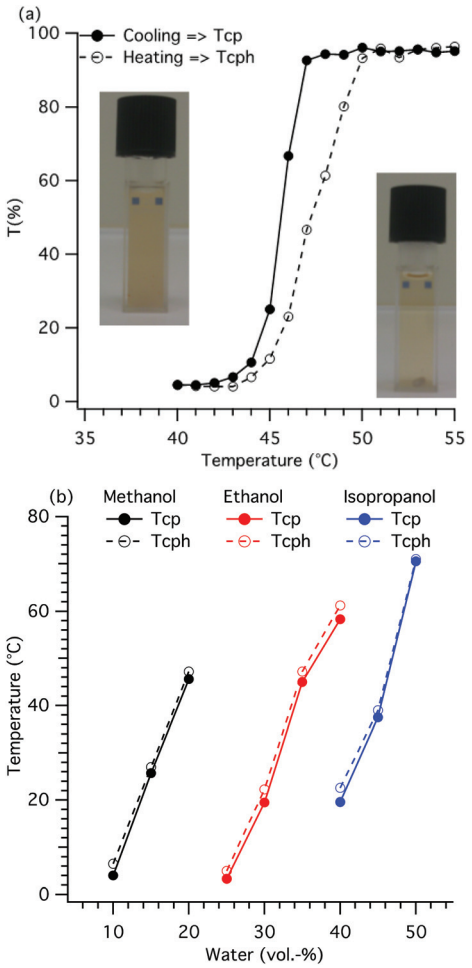


Fig. 1 Phase transition of PTMA (C_{P1} = 5 g L^{-1}) in alcohol–water mixtures: (a) typical evolution of the transmittance with temperature in a methanol–water (80–20 vol%) mixture and (b) evolution of the Tcp and Tcph with the content of water in mixtures with methanol (black), ethanol (red) and isopropanol (blue). Dashed and full lines represent the data recorded upon heating and cooling, respectively.

nature of the observed phase transition. The Tcp and Tcph are taken as the temperatures where the transmittance passes through 50% during cooling and heating, respectively. A minor hysteresis is observed in the phase transition temperature between cooling and heating. This indicates that it is more difficult to hydrate the hydrophobic PTMA clusters upon heating, whereas the polymer chains are already hydrated during the cooling process.[3] This experiment was reproduced with different volume ratios of alcohol to water using different alcohols: methanol, ethanol and isopropanol. Fig. 1b presents the evolution of Tcp and Tcph with the water content of the solution (vol%) for methanol (black), ethanol (red) and isopropanol (blue).

We observed that increasing the water content of the solution leads to the increase of Tcp and Tcph indicating that the phase transition is mostly governed by the polarity of the solvent mixture and that there is no co-solvency effect, as previously observed for PMMA and several poly(2-oxazoline)s.[3,44] Moreover, the polarity of the alcohol drastically influences the Tcp and Tcph further demonstrating that the phase transition temperature decreases by decreasing the solvent polarity. Indeed, the water content in the mixture needs to be increased from 15 to 30 to 40 vol% to observe transitions in the same range, when the polarity of the alcohol is shifted from methanol to ethanol and to isopropanol, respectively.

The phase transition temperatures of PTMA in alcohol–water mixtures can also be modulated by the variation of the concentration and the polymer chain length. The variation of the PTMA cloud point temperature with the concentration in an ethanol–water mixture (P1 in 70–30 vol%) is presented in Fig. 2a. Increasing the polymer concentration leads to the increase of the Tcp, which is typical for polymers displaying thermo-responsive behaviour due to enhanced intermolecular polymer–polymer interactions at higher concentrations that compete with polymer–solvent interactions. Fig. 2b presents the effect of the polymer chain length on the phase transition

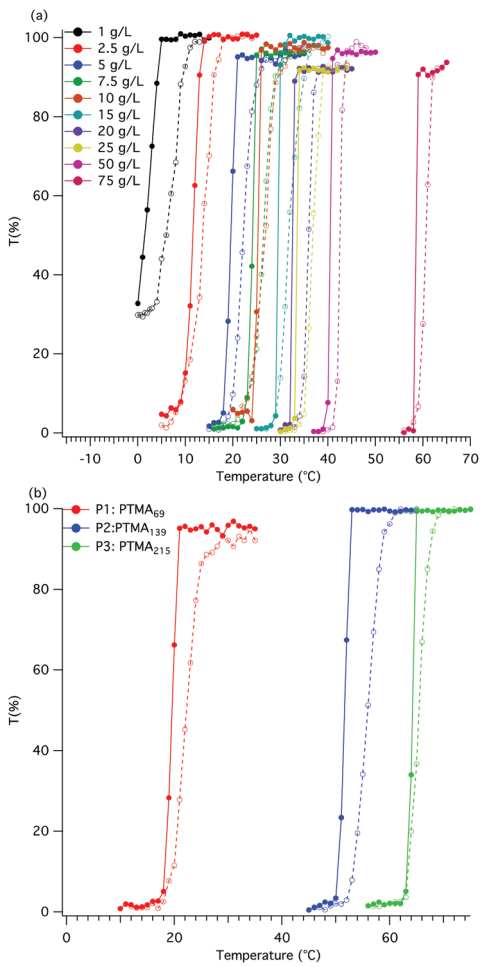


Fig. 2 Evolution of the phase transition diagram of a solution of PTMA in an ethanol–water mixture (70–30 vol%) with (a) the polymer concentration and (b) polymer chain length (C = 5 g L^{-1}). Dashed and full lines represent the data recorded upon heating and cooling, respectively.

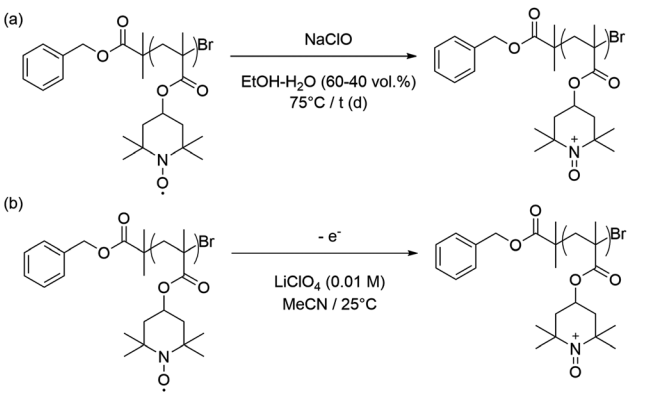
temperature. An increase of the Tcp is also observed when the length of the polymer chains is increased. This is consistent with the Flory–Huggins theory and related to enhanced intramolecular polymer–polymer interactions (see Fig. S3†).[33,45]

Redox tuning of the UCST

The nitroxide radical of PTMA can be reversibly oxidised to an oxoammonium cation. This redox property of the nitroxide radical is vastly used for the (electro)catalytic oxidation of alcohols[46,47] and for energy storage applications.[48–50] This is also expected to induce solvation changes since the polarity of the positively charged oxidized form is significantly higher compared to the starting nitroxide radical, *i.e.* the polymer displays more hydrophilic character that should increase the solubility in the alcohol–water mixture and, thus, decrease Tcp. This hypothesis was investigated by analysing whether a change in the oxidation state of PTMA would impact the UCST phase transition temperature.

The oxidation of the nitroxide radical of the TEMPO side groups can be achieved *via* a chemical or an electrochemical process (Scheme 2). The chemical oxidation of PTMA was performed with sodium hypochloride as the oxidant in an ethanol–water mixture (C_{P1} = 5 g L^{-1} in 60–40 vol% of EtOH–H_2O).[46] PTMA displays Tcp = 58.1 °C under these conditions, and the chemical oxidation was thus performed in a sealed quartz cuvette at a temperature above the cloud point temperature (T = 75 °C).

Before investigating the effect of the oxidation degree on the Tcp, the effect of the addition of NaClO into the solution has to be studied. Indeed, it is well known that the addition of salt in the medium can increase or decrease the phase transition temperature as shown by several studies on polymers displaying LCST or UCST.[51–53] To this end, a solution of PTMA in EtOH–H_2O was filled with sodium hypochloride (TEMPO/NaClO = 1/2 molar ratio, 1.23 × 10^{-4} M in the solution) and the phase transition temperature of the solution was immediately measured. Fig. 3a presents the transition curves observed for



Scheme 2 Oxidation of the nitroxide radical into the oxoammonium cation: (a) chemical oxidation with sodium hypochloride, and (b) electrochemical oxidation.

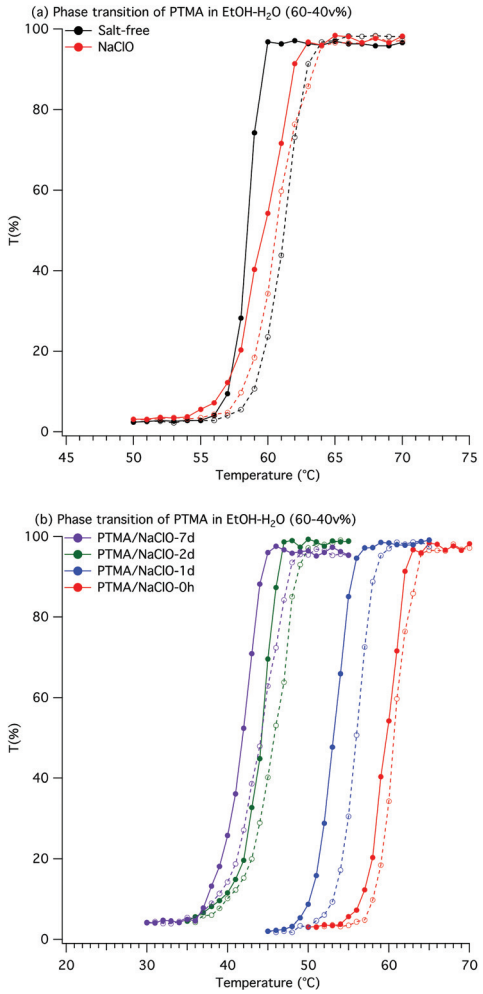


Fig. 3 Evolution of phase transition temperatures with the oxidation of PTMA in an ethanol–water mixture (C_{P1} = 5 g L^{-1}; 60–40 vol%): (a) the effect of NaClO, and (b) the effect of the oxidation time. Dashed and full lines represent the data recorded upon heating and cooling, respectively.

PTMA in a salt-free solution (black curve) and in a solution containing NaClO (red curve). A negligible effect of salt on the Tcp and Tcph is observed at this concentration, namely an increase of 1.6 °C for Tcp (from 58.1 °C to 59.7 °C), this negligible effect was attributed to the high dilution of the salt in the medium, which is not concentrated enough to disturb the solvation of PTMA in the ethanol–water solution. As far as Tcph is concerned, a decrease of 0.6 °C is measured when NaClO is added (from 61.2 °C to 60.6 °C).

The chemical oxidation was performed with different reaction times. Fig. 3b presents the effect of the oxidation time, *i.e.* the oxidation degree, on the phase transition temperatures. The red curve presents the Tcp and Tcph of a fresh unheated solution of PTMA in the presence of NaClO and will serve as the reference (Tcp = 59.7 °C and Tcph = 60.6 °C). The oxidation reaction was performed at 75 °C in a sealed quartz cuvette filled with PTMA and NaClO in EtOH–H_2O (C_{P1} = 5 g L^{-1};

TEMPO/NaClO = 1/2 molar ratio EtOH–H_2O = 60–40 vol%) for 1, 2 and 7 days. The blue, green and purple curves display the phase transition temperatures observed after 1, 2 and 7 days of oxidation respectively. A decrease of Tcp from 59.7 to 53.1, 44.2 and 41.7 °C is observed when the oxidation time is increased, indicating the formation of a more hydrophilic polymer, *e.g.* the oxidised PTMA (referred to as $PTMA^+$ later on). Indeed, the presence of polar oxoammonium groups in the $PTMA^+$ deeply changes the nature of the interaction of the polymer with the surrounding water molecules.

These results demonstrate the possibility to tune the Tcp of the PTMA–alcohol–water solution by changing the oxidation extent of PTMA *via* control of the oxidation time. Although, we monitored a change in the UV-Vis absorption spectra of $PTMA^+$ *versus* PTMA, we were not able to precisely quantify the oxidation extent of these experiments by UV-Vis spectroscopy. Unfortunately, the absorption band of $PTMA^+$ strongly overlaps with the nitroxide absorption band corresponding to the nitroxide function of PTMA, completely impeding deconvolution of the bands (see Fig. S4†).

The oxidation was also realised by means of electrochemistry (Scheme 2b). From a practical point of view, this could be more convenient as the reverse effect can be accessed using the same set-up/configuration. The electrochemical oxidation of PTMA was realised in a good solvent of PTMA and $PTMA^+$ to ensure fully dissolved polymer chains during the reaction. However, cyclic voltammetry on a solution of electrolyte ($LiClO_4$ 0.1 M) in ethanol displayed an irreversible anodic process, which was attributed to the electrolytic oxidation of ethanol at high voltage (see Fig. S5†). Since this irreversible anodic process was not observed in acetonitrile, we used it as a carrier solvent for the electrochemical oxidation reaction. Fig. 4a presents the cyclic voltammetry of PTMA at 50 mV s^{-1} in acetonitrile with $LiClO_4$ (0.1 M). We can observe a reversible redox process around 0.5 V (*vs.* Ag/Ag^+) corresponding to the reversible oxidation of the nitroxide function to the oxoammonium cation. The electrochemical conversion was realised in potentiostatic mode. A constant voltage of 0.8 V was applied to a solution of PTMA (C_{P1} = 5 g L^{-1}) and $LiClO_4$ (0.01 M) in acetonitrile for 5 h under continuous stirring. The solution of $PTMA^+$ was then concentrated under vacuum and dried in a vacuum oven at 35 °C for 24 h to remove all traces of acetonitrile that could interfere with the phase transition temperature.

Fig. 4b presents the evolution of the phase transition temperature with the electrochemical oxidation of PTMA. Similarly to the chemical oxidation, we first monitored the effect of the electrolyte ($LiClO_4$) on the thermo-responsive behaviour of PTMA; the black curve displays the behaviour of PTMA in a salt-free solution of EtOH–H_2O (C_{P1} = 5 g L^{-1}; 60–40 vol%) and the red curve plots the behaviour observed for a solution of PTMA in a solution of EtOH–H_2O containing 0.02 M of $LiClO_4$. A decrease of the cloud point temperature is observed from 58.1 °C to 55.5 °C when $LiClO_4$ is added to the ethanol–water mixture. This phenomenon is consistent with the effect of perchlorate salt on the cloud point temperature of polymer displaying UCST behaviour. It was indeed demonstrated that the addition of chaotropes (*e.g.* ClO_4^-) to a solution of PNIPAm in an ethanol–water mixture led to the decrease of the cloud point temperature compared to the salt-free solution.[52]

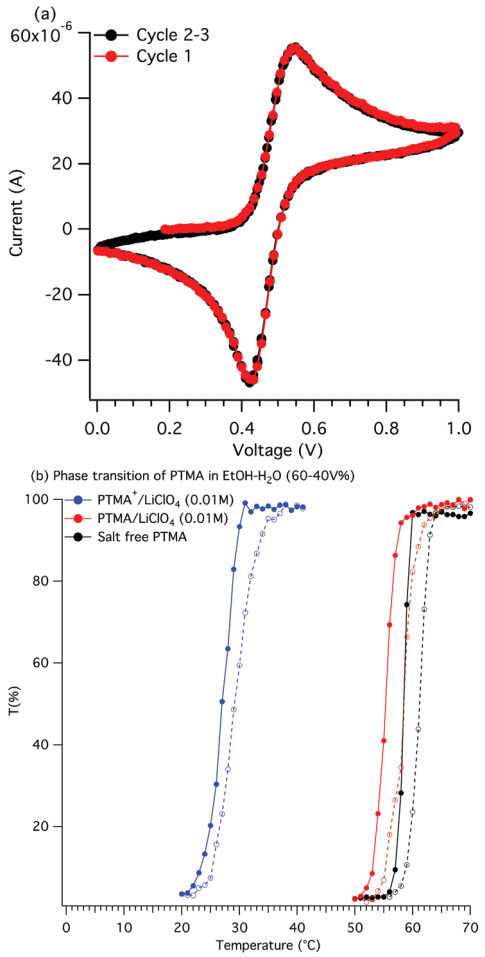


Fig. 4 Electrochemical oxidation of PTMA: (a) cyclic voltammetry of PTMA at 50 mV s^{-1}(P1; first 3 cycles; 0.1 M $LiClO_4$ in MeCN) and (b) evolution of the phase transition diagram of a solution of PTMA in an ethanol–water mixture (C_{P1} = 5 g L^{-1}; 60–40 vol%) with the electrochemical oxidation. Dashed and full lines represent the data recorded upon heating and cooling, respectively.

The thermo-responsive properties of the $PTMA^+$ were studied by dissolving the oxidised sample in an ethanol–water mixture (60–40 vol%). The blue curve of Fig. 4b presents the behaviour observed for $PTMA^+$ (Tcp = 26 °C). A large 29.4 °C decrease of the Tcp is observed compared to a solution of PTMA in solution containing 0.01 M of $LiClO_4$. This large decrease in Tcp clearly demonstrates that the large variation of the Tcp of $PTMA^+$ compared to PTMA is a direct consequence of the increased hydrophilic character of the polymer due to the formation of oxoammonium functions (similarly to the chemical oxidation experiments).

Since the transformation from nitroxide to oxoammonium is a reversible redox process, we can hope to recover the behav-

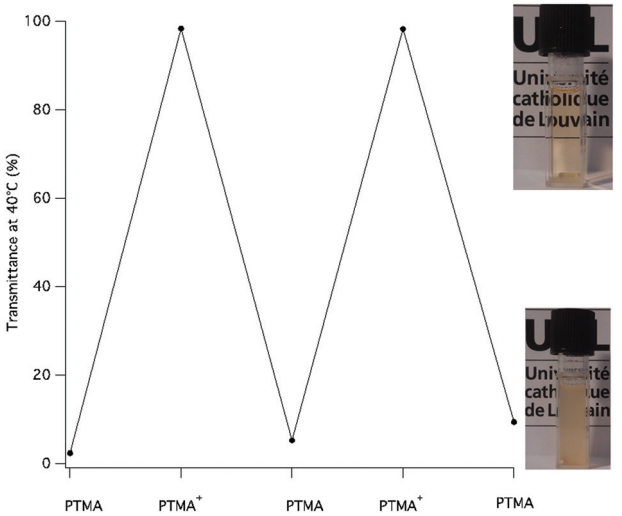


Fig. 5 Reversibility of the redox tuning of UCST: isothermal evolution of the solution transmittance *versus* the oxidation state of PTMA.

iour of PTMA after an oxidation/reduction cycle. The reversibility of the redox tuning of the UCST was realised in potentiostatic mode in a solution of PTMA (C_{P1} = 5 g L^{-1}) and $LiClO_4$ (0.01 M) in acetonitrile. The oxidation reactions were carried out under the conditions detailed previously and the reduction reactions were realised by applying a constant voltage of 0.1 V to the solution under continuous stirring until the current reached a plateau at a low value (similar to the current measured for a 0.01 M solution of $LiClO_4$ in acetonitrile). Samples were withdrawn from the solution after each of the oxidation and reduction reactions. Acetonitrile was removed under vacuum and the polymer samples were dissolved in an ethanol–water mixture (60–40 vol%) before measuring the evolution of the transmittance with temperature. Fig. 5 presents the evolution of the solution transmittance *versus* the oxidation/reduction cycles in isothermal mode (T = 40 °C). This experiment demonstrates the reversibility of the redox tuning of the UCST since the polymer can reversibly transit from its soluble ($T \approx$ 100%) to the insoluble ($T \approx$ 0%) state depending on the amount of oxoammonium functions.

Conclusions

This contribution reports on a homopolymer, PTMA, displaying redox-tunable UCST behaviour in alcohol–water mixtures. The thermo-responsive properties of PTMA were characterised by a full set of experiments including the variation of the PTMA chain length, the polymer concentration and the solvent composition. We have shown that the thermo-responsive behaviour of PTMA is essentially influenced by the polarity of the solvent mixture, either by changing the alcohol or the water content in the alcohol–water mixture. In addition to these common factors to tune the thermo-responsive behaviour of polymers, we have demonstrated that the redox process involving the TEMPO side groups could be used to modify the Tcp of PTMA. Indeed, the oxidation of the nitroxide function of the PTMA into an oxoammonium group increases the hydrophilic character of the polymer chains and thus decreases the UCST phase transition temperature of the PTMA. In this respect, we have monitored a decrease of the Tcp of PTMA *via* chemical and electrochemical oxidation. The precise control of Tcp *via* the extent of the chemical or electrochemical reactions opens possibilities of using PTMA solutions in alcohol–water mixtures as a sensoring system.

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