ROYAL SOCIETY OF CHEMISTRY

PAPER

Thermoresponsive ureido-derivatized polymers: the effect of quaternization on UCST properties

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A series of thermoresponsive ureido-derivatized polymers were synthesized *via* atom transfer radical polymerization (ATRP) and a post-modification process. All of the polymers were designed to exhibit an upper critical solution temperature (UCST) in aqueous solution, which was mainly dependent on (i) the presence of ureido moieties, (ii) the chain length of the side groups, and (iii) the degree of quaternization (DQ) on a triazole ring. Side group modification of PHEMA was carried out by DCC coupling with 4-pentynoic acid to prepare PHEMA-alkyne (PHA). 2-Azidoethylurea and 3-azidopropylurea were combined with the PHA backbone *via* click reaction, resulting in triazole-ring containing ureido-derivatized polymers. Quaternization reactions with methyl iodide were conducted on the triazole ring of each polymer to further control the UCSTs. Results showed that the UCST could be precisely tuned by the level of DQ.

Introduction

Thermoresponsive polymers exhibit a volume phase transition at a certain temperature that causes a sudden change in the solvation state.[1-6] Thermoresponsive polymers have either a lower critical solution temperature (LCST) above which the polymer becomes insoluble upon heating, or an upper critical solution temperature (UCST)[7-11] above which the polymer becomes soluble. LCST and UCST systems are not restricted to an aqueous solvent environment, but aqueous systems are primarily of interest for biomedical applications such as cell patterning,[12-14] smart drug release,[15,16] and DNA sequencing.[17]

Thermoresponsive polymers are based on the amphiphilic character of its functional groups, which encourage changes in the extent of hydrogen bonding. In contrast to LCST polymers, only a small number of polymeric materials with an UCST in aqueous media are known.[7,8,18-21] UCST behavior has mainly been observed in organic and water/organic solvent mixtures,[22-26] where inter-polymer interactions weakened upon heating. The UCST of polymers is based on either electrostatic (ionic) interactions like polybetaines[27,28] and poly(dimethylaminoethyl methacrylate)[29,30] or hydrogen bonding between hydrogen bond donors (N–H) and acceptors (C=O) like poly(allylurea).[11] The structure of chain ends[21,31-33] and the presence of ionic impurities in aqueous medium can also influence the UCST transitions. The best studied examples of UCST polymers are poly(allylurea),[11] poly(6-(acryl-oyloxymethyl)uracil),[18] and poly(N-acryloylasparaginamide)

(NAAAM)),[7] in water. There are several other copolymers like poly(p-dioxanone)-grafted poly(vinyl alcohol).[34] Despite recent progress in the field, only a few UCST-type polymers have been reported. In the present study, we report the synthesis and thermoresponsive behavior of a series of ureido-derivatized polymers with different degrees of quaternization (DQ) of their triazole rings. This work is very promising for water-stable functional coatings, controlled release and for various biomedical applications. To the best of our knowledge, this work represents the first example of UCST tuning of ureido-derivatized polymers simply by the DQ.

Experimental

Materials

2-Hydroxyethyl methacrylate (HEMA, 95%, Tokyo Chemical Industry; TCI) was purified by passing it through a column filled with basic alumina (Acros) so as to remove inhibitors. Sodium azide (99.5%), 4-pentynoic acid, N,N-dimethylformamide (DMF, 99.8%), 2-chloro-1-ethylamine hydrochloride, 3-chloro-1-pro-pylamine hydrochloride, potassium isocyanate (KOCN), CuCl₂ (99.9%), CuBr (98%), 4-dimethylaminopyridine (DMAP), ethyl α-bromoisobutyrate (EBiB), KOH, tetrahydrofuran (THF, 99.9%), dichloromethane (DCM, 99.9%), diethyl ether, MgSO₄, and N,N'-dicyclohexylcarbodiimide (DCC, 99%) were purchased from Aldrich with the highest purity and used as received without further purification. Anisole (99%), methyl alcohol (99.9%) and N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) were purchased from TCI and used as received.

Instrumentation

¹H NMR spectra were recorded in CDCl₃, DMSO-d_6, or DMF-d_7 using a Bruker Avance 300 MHz NMR spectrometer. The apparent molecular weight and molecular weight distribution

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were measured by gel permeation chromatography (GPC) (Agilent Technologies 1200 series) using a PMMA standard with DMF as the eluent at a flow rate of 1.00 mL min^{-1} at 30 °C. The cloud point of polymer solution in deionized water was measured using a Thermo Scientific Evolution 600 UV-Vis spectrophotometer equipped with a digital temperature controller at a wavelength of 650 nm. Sample cells (1 cm) were thermostatted with a water jacket ranging from 10 to 99 °C with a heating and cooling rate of 1 °C min^{-1}. The cloud point was defined as the middle point of the transmittance change. The hydrodynamic diameter was measured by dynamic light scattering (DLS, Nano ZS 90, Malvern, UK) with zetasizer software 7.01.

Syntheses

2-Azido-1-ethylamine (1). 2-Azido-1-ethylamine was prepared as previously reported.[35] In brief, NaN$_3$ (16.8 g, 0.258 mol) was added to a solution of 2-chloro-1-ethylamine hydrochloride (10 g, 0.086 mol) in water (100 mL), and the reaction mixture was heated to 80 °C for 15 h. The solution was basified with KOH (50 g) and extracted with diethyl ether. The organic layer was dried over MgSO$_4$, filtered, and concentrated to give a volatile colorless oil (4.5 g, 0.1 mol, 50%).

^{1}H NMR (300 MHz, DMSO-d_6, δ in ppm): 3.24 (2H, t, J = 5.9 Hz, N$_3$CH$_2$CH$_2$); 2.71 (2H, t, J = 5.9 Hz, N$_3$CH$_2$CH$_2$); 1.92 (2H, s, NH$_2$).

3-Azido-1-propylamine (2). NaN$_3$ (7.5 g, 0.115 mol) was added to a solution of 3-chloro-1-propylamine hydrochloride (5 g, 0.038 mol) in water (100 mL), and followed the same procedure as described for **1** to give a volatile colorless oil (3 mL, 0.03 mol, 80%).

^{1}H NMR (300 MHz, DMSO-d_6, δ): 3.98 (2H, br, s, NH_2); 3.74 (2H, s, −N−CH_2−); 3.20 (2H, s, −C−CH_2−C−); 1.55 (2H, d, J = 4.4 Hz, −N$_3$−CH_2−).

2-Azido-1-ethylcarbamide (3). Concentrated HCl (2.07 mL, 23.88 mmol) was added to 2-azido-1-ethylamine (2 g, 19.9 mmol) at 0 °C, and the mixture was dissolved in hot ethanol (10 mL). This solution was added to a solution of KOCN (2.498 g, 23.88 mmol) dissolved in distilled water (10 mL), and the reaction mixture was stirred for 15 h at room temperature. The reaction mixture was then concentrated under reduced pressure, and 2.3 g of 2-azido-1-ethylcarbamide (19.9 mmol, 92% yield) crystallized from the remaining solution.

^{1}H NMR (300 MHz, DMSO-d_6, δ): 5.18 (1H, br, NH); 4.67 (2H, br, NH$_2$); 3.45−3.25 (4H, t, CH$_2$CH$_2$).

3-Azido-1-propylcarbamide (4). 3-Azido-1-propylcarbamide was prepared using the same procedure as described for **3** (92% yield).

^{1}H NMR (300 MHz, DMSO-d_6, δ): 5.18 (1H, br, NH); 4.89 (2H, br, NH$_2$); 3.47 (2H, q, −N$_3$−CH$_2$−); 3.20 (2H, s, −NH−CH$_2$−); 1.81 (2H, d, J = 4.4 Hz, −C−CH$_2$−C−).

PHEMA. PHEMA (M_n = 48 700 g mol^{-1}, M_w/M_n = 1.18) was prepared as previously reported.[36]

^{1}H NMR (300 MHz, DMSO-d_6, δ in ppm): 5.01 (s, H^e); 4.09 (s, H^c); 3.78 (s, H^d); 2.05−1.88 (d, H^a); 0.86 (s, H^b).

PHEMA-alkyne (PHA). PHA (M_n = 69 500 g mol^{-1}, M_w/M_n = 1.26) was prepared as previously reported.[35] ^{1}H NMR (300 MHz, DMF-d_7, δ in ppm): 4.44−4.36 (d, H^f); 3.64 (s, H^g); 2.93−2.73 (m, H^{a,h}); 2.10 (s, H^i); 1.03−0.88 (d, H^b).

PEU (PHA-click-3). The ratio of reagents [PHA]$_0$/[3]$_0$/[CuBr]$_0$/[PMDETA]$_0$ was 1/2/0.1/0.1. The click reaction between PHA (0.2 g, 0.95 mmol) and **3** (163 µL, 1.9 mmol) was conducted in 3 mL of DMF using CuBr/PMDETA as a catalyst. After 10 h, the polymer solution was exposed to air, diluted with DMF, and passed through neutral alumina to remove the copper catalyst. The resulting polymer was precipitated in diethyl ether and dried in a vacuum oven for 24 h. PEU (M_n = 96 800 g mol^{-1}; M_w/M_n = 1.30).

^{1}H NMR (300 MHz, DMF-d_7, δ in ppm): 7.79 (s, H^j); 6.10 (s, H^k); 5.60 (s, H^l); 4.30−4.17 (t, H^m); 3.41−3.34 (t, H^g); 2.73−2.66 (br, H^a); 1.16−0.77 (br, H^b).

PPU (PHA-click-4). PPU (M_n = 99 400 g mol^{-1}; M_w/M_n = 1.31) was prepared as described above for PEU. ^{1}H NMR (300 MHz, DMF-d_7, δ in ppm): 7.83 (s, H^j); 6.11 (s, H^k); 5.51 (s, H^l); 4.28−4.17 (t, H^m); 3.42−3.27 (m, H^g); 2.95−2.73 (br, H^a); 1.88−1.84 (t, H^n); 1.16−0.77 (br, H^b).

Quaternization of PEU (PEU–MI). A typical procedure for quaternization of PEU with methyl iodide (1 : 1 molar ratio) was as follows. A solution of PEU (0.5 g; 2.0 mmol of triazole groups) and methyl iodide (0.284 g; 2.0 mmol) in DMF (20 mL) was stirred for 16 h at 45 °C. Quaternized PEU was precipitated in diethyl ether, filtered, and dried under vacuum. Reactions with four different molar ratios (1 : 1, 1 : 1.5, 1 : 2, 1 : 5) of PEU to methyl iodide were carried out, and the degree of quaternization (DQ) was 4%, 5%, 7%, and 18%, respectively.

^{1}H NMR (300 MHz, DMF-d_7): d = 8.73 (s, H$^{j'}$); 7.80 (s, H^j); 6.21 (s, H$^{k'}$); 6.11 (s, H^k); 5.68 (s, H$^{l'}$); 5.60 (s, H^l); 4.58 (s, Ho), 4.31−4.25 (d, H^m); 3.47−2.96 (m, H^g); 2.89−2.57 (br, H^a); 1.11−0.77 (br, H^b).

Quaternization of PPU (PPU–MI). The same procedure as described for quaternization of PEU was applied. Reactions with three different molar ratios (1 : 1, 1 : 2, 1 : 5) of PPU to methyl iodide were carried out. The degree of quaternization (DQ) was 4%, 10%, and 18%, respectively.

^{1}H NMR (300 MHz, DMF-d_7): d = 8.79 (s, H$^{j'}$); 7.85 (s, H^j); 6.12 (s, H$^{k,k'}$); 5.52 (s, H$^{l'}$); 5.51 (s, H^l); 4.57 (s, Ho); 4.28−4.24 (d, H^m); 3.42−2.89 (m, H^g); 2.73−2.55 (br, H^a); 1.88−1.84 (t, H^p); 1.11−0.78 (br, H^b).

Results and discussion

The ureido azides, 2-azido-1-ethylcarbamide (**3**) and 3-azido-1-propylcarbamide (**4**), were synthesized by reacting 2-azido ethylamine (**1**) and 3-azido propylamine (**2**) in conc. HCl with aqueous KOCN. ^{1}H NMR spectra confirmed the successful synthesis of compounds **3** and **4** (Fig. 1). The strategy employed in this study is illustrated in Scheme 1.

In the next step, DCC coupling of PHEMA with 4-pentynoic acid yielded PHA (M_n = 69 500 g mol^{-1}, M_w/M_n = 1.26) as the polymer backbone. ^{1}H NMR spectra confirmed the successful synthesis of PHA by monitoring the disappearance of peak (e) and the appearance of peaks (i, g, and h) at 2.10, 3.64, and 2.73 ppm, respectively (Fig. 2). Compounds **3** and **4** were successfully added to the PHA backbone in DMF with a CuBr/PMDETA complex at room temperature using click chemistry, resulting in PEU and PPU, respectively. The ^{1}H NMR spectra provided
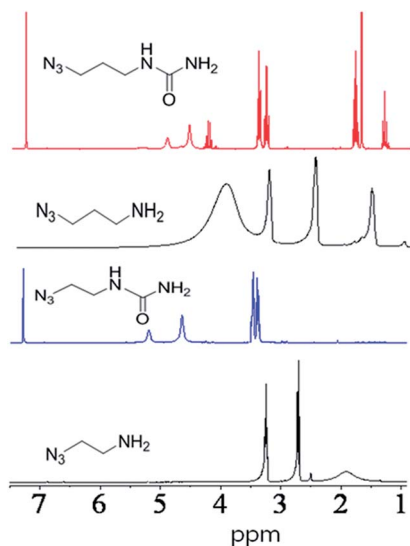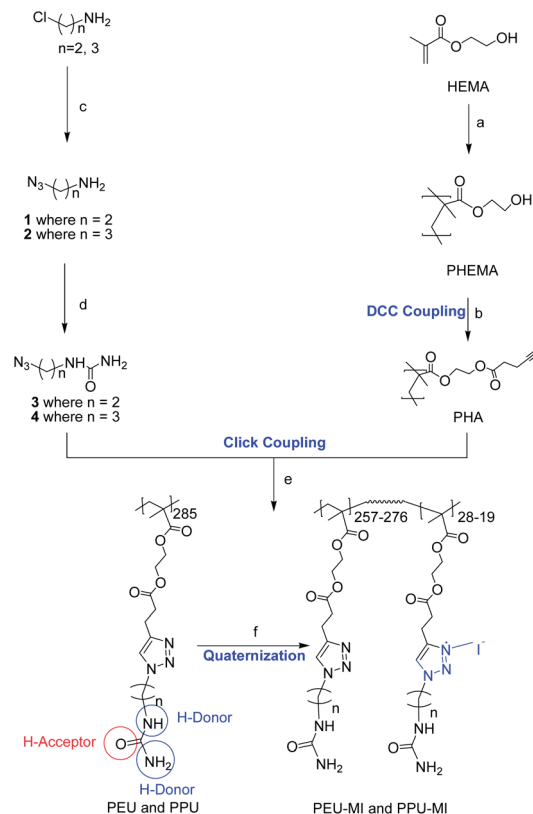
Fig. 1 ^{1}H NMR of 2-azido ethylamine (**1**), 3-azido propylamine (**2**), and ureido azide derivatives (**3** and **4**).

Scheme 1 Synthesis of ureido functionalized polymers and their quarternized analogues synthesized by a combination of ATRP, click reaction, and quaternization of triazole rings. *Reaction conditions*: (a) Bpy, CuBr, CuCl$_2$, EBiB, methanol, anisole, argon atmosphere, RT, 24 h; (b) DCC, pentynoic acid, DMF, 0–4 °C; DMAP in DMF, RT, 48 h; (c) NaN$_3$, water, 80 °C, 15 h, KOH; (d) conc. HCl, 0 °C, hot ethanol, KOCN, distilled water, RT, 15 h; (e) CuBr/PMDETA, DMF, 10 h, RT. (f) CH$_3$I, DMF, 45 °C, 16 h.

evidence of the successful synthesis of the ureido-functionalized polymers by click reaction (Fig. 2). The addition of compound **3** to PHA was confirmed by clearly visible peaks (j, k, l, and m) at 7.83–7.79, 6.11–6.10, 5.60–5.51, 4.30–4.17 ppm, respectively. For PPU, an extra peak (n) for the –CH$_2$– group appeared at 1.88–1.84 ppm.

In the final polymer modification step, the ureido polymers were quarternized with methyl iodide to prepare various levels of the quarternized polymers, PEU–MI and PPU–MI. Reactions under four different molar feed ratios (1 : 1, 1 : 1.5, 1 : 2, 1 : 5) of PEU to methyl iodide were carried out in DMF at 45 °C. The DQ for the PEU series was 4%, 5%, 7%, and 18%, respectively. It was difficult to predict the DQ since the quaternization reaction was relatively inefficient. For example, a five-fold molar excess of methyl iodide over triazole groups in the repeating units of PEU yielded only an 18% DQ. Partial quaternization was confirmed by ^{1}H NMR spectra (Fig. 2). For PEU–MI-7%, a new peak (j′) representing the proton on the quarternized triazole ring appeared at 8.7 ppm, while the intensity of the proton on the triazole ring without quaternization (j) decreased. The degree of quaternization (DQ) was calculated from the integration areas of peaks j and j′.

Reversible solubility of the series of PEU and PPU polymers was achieved by changing the temperature of the aqueous polymer solutions. The thermoresponsiveness of the polymers in dilute aqueous solution was studied by observing changes in the percent transmission at a fixed wavelength (650 nm) via UV-vis spectroscopy. Percent transmission data were recorded during cooling cycles. The concentration of all aqueous solutions was fixed at 1.0 wt% since the cloud point was easier to detect at a higher concentration.

Unquaternized PEU and PPU were not soluble in aqueous solution at room temperature due the hydrophobic nature and strong polymer–polymer interactions in aqueous media. Upon an increase in the solution temperature, hydrogen bonding between ureido groups was weakened, and PEU exhibited an UCST transition at 76 °C and the more hydrophobic PPU had an UCST transition at 96 °C (Fig. 3).

Additionally, the UCST transitions could be readily tuned by the addition of methyl groups via quaternization of triazole groups of PEU and PPU. As stated in our previous report,[36] there are pi–pi interaction between triazole rings. These interactions also weakened by quaternization and additionally affected the UCST values. The UCST values were found to be dependent on the degree of quaternization (DQ). The hydrophilicity of PEU and PPU increased with the increasing DQ, which in turn caused the UCST to decrease. It was found that the UCST values for the PEU series decreased between 21 and 40 °C as the DQ increased from 3 to 7% (Fig. 4a). PEU–MI-18% did not exhibit an UCST transition and remained soluble below 10 °C since it became completely hydrophilic after 18% of DQ (Fig. 5). Similar trends were observed for the PPU series (Fig. 4b). PPU–MI-10% was chosen to investigate the hysteresis behavior because it exhibited an UCST transition near the physiological
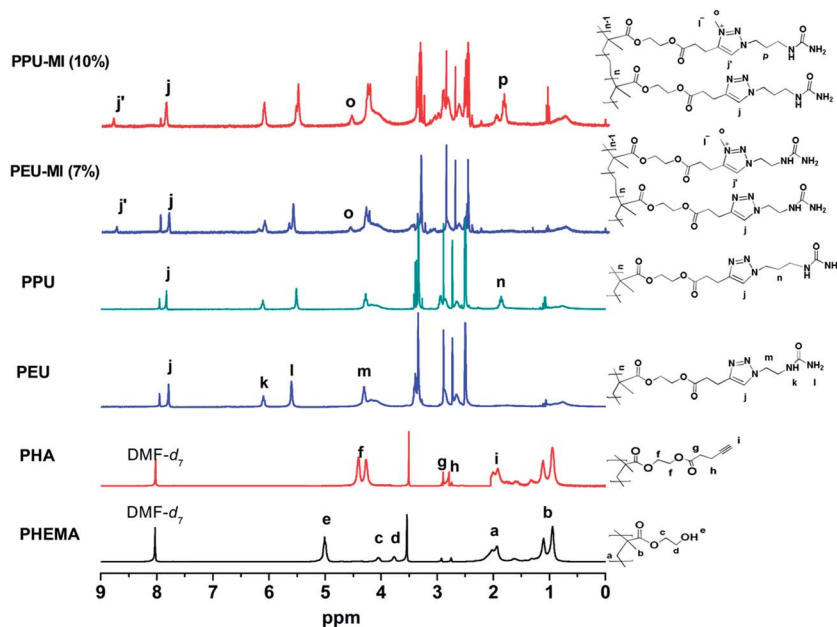
Fig. 2 ¹H NMR spectra of PHEMA, PHA, PEU, PPU, PEU–MI 7% (7% DQ), and PPU–MI 10% (10% DQ).
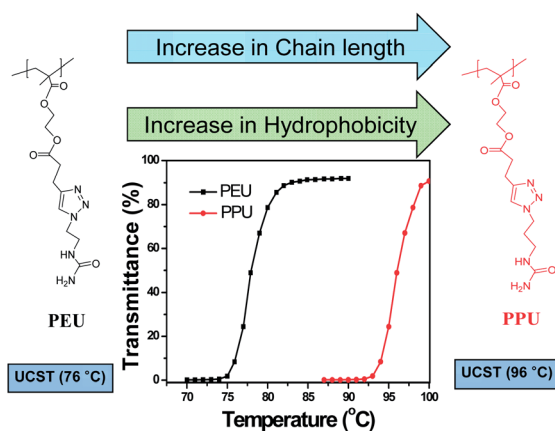

Fig. 3 Thermoresponsiveness of 1.0% aqueous solutions of PEU and PPU measured by percent transmission at 650 nm; the effect of chain length of alkyl urea moieties on UCST behavior.

temperature; however, we found no significant hysteresis for PPU–MI-10% (Fig. 6).

The effect of quaternization on the UCST point was also studied by dynamic light scattering (DLS) with the same aqueous concentration (1.0 wt%) as employed for turbidimetry studies. DLS data were also recorded during cooling cycles. The UCST point was defined as the onset temperature of the increase in particle size. It was expected that the particle size of all of the polymers would increase with decreasing temperature. DLS analysis identified the UCST of an aqueous solution of PEU at 85 °C. As the DQ increased from 0 to 7%, the hydrophilic nature of the polymers gradually increased, resulting in the UCST lowering from 85 to 44 °C. Real hydrodynamic diameters ranged from 20 to 200 nm (Fig. 7a).
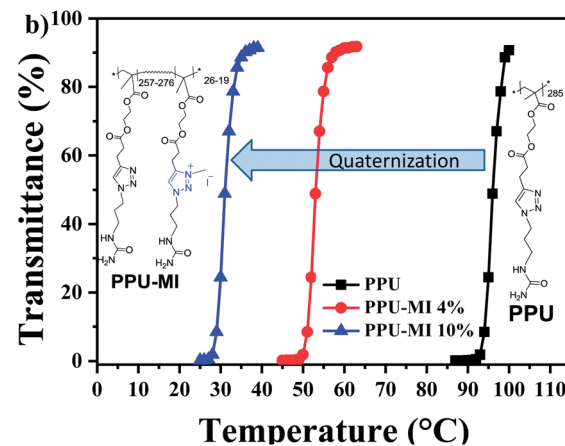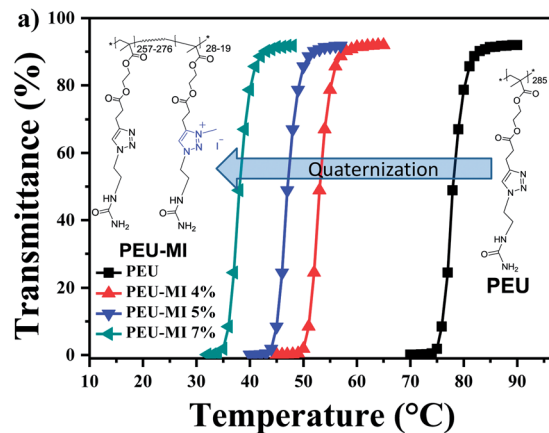

Fig. 4 Effect of quaternization on the thermoresponsiveness of 1% aqueous solution: (a) PEU series and (b) PPU series measured by percent transmission at 650 nm.
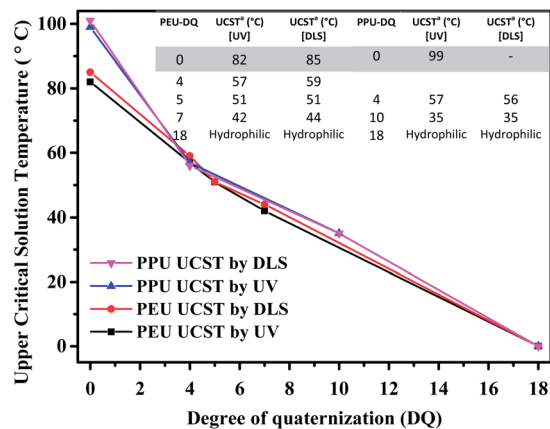
PEU-DQ	UCST^a (°C) [UV]	UCST^a (°C) [DLS]	PPU-DQ	UCST^a (°C) [UV]	UCST^a (°C) [DLS]
0	82	85	0	99	–
4	57	59	4	57	56
5	51	51	10	35	35
7	42	44	18	Hydrophilic	Hydrophilic
18	Hydrophilic	Hydrophilic			

Fig. 5 Degree of quaternization of PEU and PPU (PEU-DQ and PPU-DQ) for UCST studies; ^{a}: c = 1.0 wt%; heating rate = 1.0 °C min^{-1}.
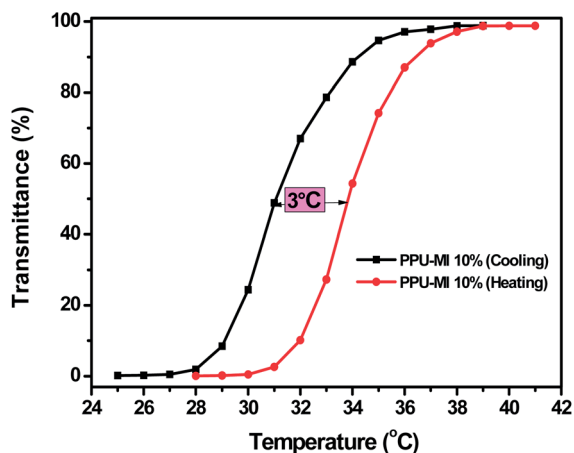

Fig. 6 Hysteresis of PPU–MI-10% with 1.0 wt% aqueous solution; the solution was heated and cooled at a rate of 1 °C min^{-1}.
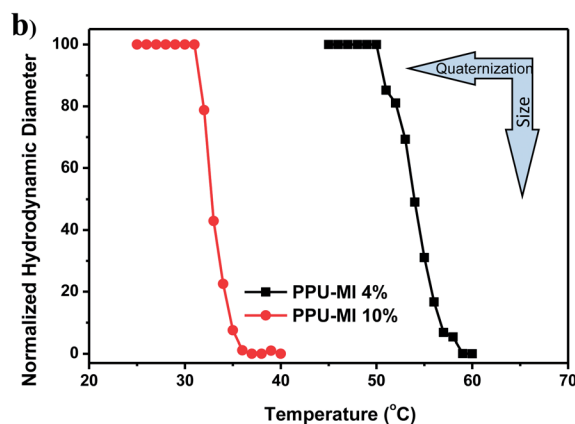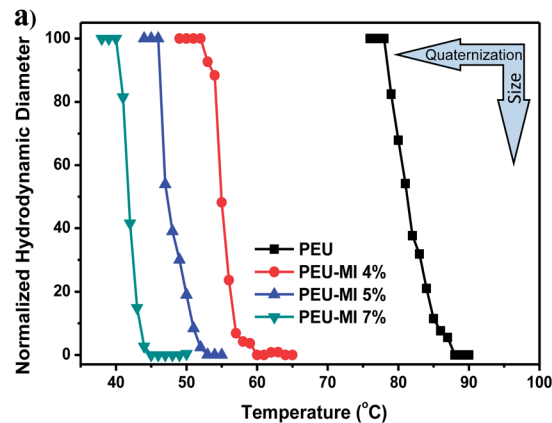

Fig. 7 Effect of quaternization on the thermoresponsiveness of 1% aqueous solution: (a) PEU series and (b) PPU series measured by dynamic light scattering (DLS).

There was no change in the hydrodynamic diameter for PEU–MI-18% since it was too hydrophilic. The time correlation function of scattering intensity for unquaternized PPU could not be obtained since its UCST was too high. Similarly, for the PPU series, the UCST values decreased towards the physiological temperature with increasing DQ (Fig. 7b). The hydrophilic PPU–MI-18% did not exhibit an UCST.

Conclusions

Novel thermoresponsive ureido-derivatized polymers with UCST properties were prepared via ATRP, followed by post-modification using DCC coupling, click coupling, and quaternization. UCSTs of ureido-derivatized polymers were tuned simply by the DQ of the triazole rings. It was demonstrated that the polymer UCST could be affected by the existence of ionic groups as well as ureido moieties. This emerging class of triazole ring containing ureido homopolymer and its quaternized form represent promising materials in the biological and sensor fields.

Acknowledgements

Notes and references

1 I. Dimitrov, B. Trzebicka, A. H. E. Mueller, A. Dworak and C. B. Tsvetanov, Prog. Polym. Sci., 2007, 32, 1275–1343.
2 H.-I. Lee, J. Pietrasik, S. S. Sheiko and K. Matyjaszewski, Prog. Polym. Sci., 2010, 35, 24–44.
3 J.-F. Lutz, Angew. Chem., Int. Ed., 2007, 46, 1018–1025.
4 J. K. Oh, D. J. Siegwart, H.-I. Lee, G. Sherwood, L. Peteanu, J. O. Hollinger, K. Kataoka and K. Matyjaszewski, J. Am. Chem. Soc., 2007, 129, 5939–5945.
5 N. Rapoport, Prog. Polym. Sci., 2007, 32, 962–990.
6 D. Roy, J. N. Cambre and B. S. Sumerlin, Prog. Polym. Sci., 2010, 35, 278–301.
7 S. Glatzel, A. Laschewsky and J. F. Lutz, Macromolecules, 2011, 44, 413–415.
8 J. Seuring and S. Agarwal, Macromol. Rapid Commun., 2012, 33, 1898–1920.

9 J. Seuring and S. Agarwal, *ACS Macro Lett.*, 2013, **2**, 597–600.

10 J. Seuring, F. M. Bayer, K. Huber and S. Agarwal, *Macromolecules*, 2012, **45**, 374–384.

11 N. Shimada, H. Ino, K. Maie, M. Nakayama, A. Kano and A. Maruyama, *Biomacromolecules*, 2011, **12**, 3418–3422.

12 X. Cheng, Y. Wang, Y. Hanein, K. F. Bohringer and B. D. Ratner, *J. Biomed. Mater. Res., Part A*, 2004, **70**, 159–168.

13 I. E. Hannachi, M. Yamato and T. Okano, *Biofabrication*, 2009, **1**, 022002.

14 Y. Tsuda, T. Shimizu, M. Yamato, A. Kikuchi, T. Sasagawa, S. Sekiya, J. Kobayashi, G. Chen and T. Okano, *Biomaterials*, 2007, **28**, 4939–4946.

15 P. De, S. R. Gondi and B. S. Sumerlin, *Biomacromolecules*, 2008, **9**, 1064–1070.

16 J. A. Johnson, Y. Y. Lu, A. O. Burts, Y. Xia, A. C. Durrell, D. A. Tirrell and R. H. Grubbs, *Macromolecules*, 2010, **43**, 10326–10335.

17 V. Barbier, M. Herve, J. Sudor, A. Brulet, D. Hourdet and J. L. Viovy, *Macromolecules*, 2004, **37**, 5682–5691.

18 T. Aoki, K. Nakamura, K. Sanui, A. Kikuchi, T. Okano, Y. Sakurai and N. Ogata, *Polym. J.*, 1999, **31**, 1185–1188.

19 O. Marstokk, B. Nystrom and J. Roots, *Macromolecules*, 1998, **31**, 4205–4212.

20 J. Seuring and S. Agarwal, *Macromol. Chem. Phys.*, 2010, **211**, 2109–2117.

21 H. Yoshimitsu, A. Kanazawa, S. Kanaoka and S. Aoshima, *Macromolecules*, 2012, **45**, 9427–9434.

22 R. O. R. Costa and R. F. S. Freitas, *Polymer*, 2002, **43**, 5879–5885.

23 R. Hoogenboom, C. R. Becer, C. Guerrero-Sanchez, S. Hoeppener and U. S. Schubert, *Aust. J. Chem.*, 2010, **63**, 1173–1178.

24 R. Hoogenboom, H. M. L. Lambermont-Thijs, M. J. H. C. Jochems, S. Hoeppener, C. Guerlain, C. A. Fustin, J. F. Gohy and U. S. Schubert, *Soft Matter*, 2009, **5**, 3590–3592.

25 K. Pagonis and G. Bokias, *Polymer*, 2004, **45**, 2149–2153.

26 Q. L. Zhang, P. Schattling, P. Theato and R. Hoogenboom, *Polym. Chem.*, 2012, **3**, 1418–1426.

27 N. Gonsior and H. Ritter, *Macromol. Chem. Phys.*, 2012, **213**, 382–388.

28 Z. Zhang, T. Chao, S. Chen and S. Jiang, *Langmuir*, 2006, **22**, 10072–10077.

29 F. A. Plamper, A. Schmalz and A. H. E. Müller, *J. Am. Chem. Soc.*, 2007, **129**, 14538–14539.

30 Q. Zhang, J.-D. Hong and R. Hoogenboom, *Polym. Chem.*, 2013, **4**, 4322–4325.

31 G. B. H. Chua, P. J. Roth, H. T. T. Duong, T. P. Davis and A. B. Lowe, *Macromolecules*, 2012, **45**, 1362–1374.

32 E. E. Dormidontova, *Macromolecules*, 2004, **37**, 7747–7761.

33 F. Y. Liu, J. Seuring and S. Agarwal, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 4920–4928.

34 G. Wu, S.-C. Chen, Q. Zhan and Y.-Z. Wang, *Macromolecules*, 2011, **44**, 999–1008.

35 S. H. Jung, H. Y. Song, Y. Lee, H. M. Jeong and H. I. Lee, *Macromolecules*, 2011, **44**, 1628–1634.

36 S.-H. Jung, J. Ryu, D. Sohn and H.-I. Lee, *Polym. Chem.*, 2012, **3**, 1002–1006.

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