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Water swelling, brine soluble imidazole based zwitterionic polymers – synthesis and study of reversible UCST behaviour and gel–sol transitions

Zwitterionic polymers with higher hydrophobic characteristics and enhanced secondary interactions were designed and synthesized. The unique UCST characteristics exhibited by these polymers in brine solution make them suitable for applications in enhanced oil recovery, low-temperature precipitation of proteins, as membrane materials and a variety of other applications.

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Water swelling, brine soluble imidazole based zwitterionic polymers – synthesis and study of reversible UCST behaviour and gel-sol transitions[†]

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New vinylbenzene substituted imidazole based zwitterionic polymers with unique characteristics like swelling in water and solubility in concentrated brine solution in which they exhibited a reversible upper critical solution temperature (UCST) and gel-sol transitions are reported herein.

Zwitterionic polymers,^{1–3} such as polybetaines, have gained much importance of late due to their wide applications in antifouling,^{4–6} membranes,⁷ biotechnology,^{8–15} enhanced oil recovery (EOR),¹⁶ as coatings,^{4,17} *etc.* The three main classes of zwitterionic polymers developed so far include carboxy betaines, phosphobetaines and sulfobetaines. Among these three classes, sulfobetaines are the most convenient to synthesize^{3,18} and thus employed widely.¹⁹ Sulfobetaines derived from acrylamide and methacrylates (Scheme 1) are two of the prominently used monomers for making zwitterionic polymers which are also commercially available.^{20–22} However, these monomers are hydrolytically unstable. These monomers undergo hydrolysis to varying degrees even during polymerization of the zwitterionic monomers resulting in the formation of poly(acrylic acid) along with the zwitterionic polymer. For example, the ester based zwitterionic monomer (Scheme 1a) undergoes hydrolysis



With the aim of synthesizing polysulfobetaines free from hydrolyzable linkages we recently designed and synthesized imidazole based sulfobetaine monomers (Scheme 2 and Scheme S2, ESI[†]).

As reported herein, these imidazole based polysulfobetaines exhibited many unusual solubility characteristics. Unlike the acrylate and acrylamide derived polysulfobetaines which are soluble in water, the benzimidazole based polysulfobetaines are only soluble in concentrated brine solution (22.6 wt% NaCl) and also swell in deionized water. We believe such solubility characteristics are potentially useful for applications like EOR which is gaining significance due to depleting petroleum reserves. These imidazole



Scheme 1 Chemical structure of zwitterionic (a) poly(methyl methacrylate) and (b) poly(methyl methacrylamide).

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Scheme 2 Chemical structures and polymerization of newly synthesized zwitterionic monomers (ZIMs).

Table 1 Summary of free-radical polymerization of ZIM 1 and 2 $\,$

Monomer/initiator (mmol)	Time	Yield ^a	$M_{\rm n,GPC} \left({ m g mol}^{-1}\right)$	PDI	Elemental analysis
ZIM 1 (3.29)/ACVA (0.0165)	1.5 h	98%	6500	2.02	Calc. N, 8.13; S, 9.31; Exp. N, 7.78; S, 9.00
ZIM 2 (2.81)/ACVA (0.0189)	24 h	>98%	10600	1.40	Calc. N, 5.29; S, 6.05; Exp. N, 5.14; S, 6.04

 a Determined by gravimetry after drying the polymer at 50 $^\circ \mathrm{C}$ in vacuo.

derived polymeric zwitterions are unique in that quite apart from the ionic nature they also exhibit other interactions like donoracceptor as well as comparatively more hydrophobicity than the conventional sulfobetaines. This characteristic is the source of the difference in solubility as described below.

The precursors ZIM **1** and **2** were synthesized by reacting vinylbenzylchloride with imidazole and benzimidazole, respectively, followed by a nucleophilic addition reaction with **1**,3 propane sultone in good yield (65–74%). To the best of our knowledge, ZIM **1** and **2** have not been reported before. The monomers ZIM **1** and **2** were obtained as hygroscopic powders, which were characterized by NMR, FTIR, ESI-MS, and elemental analysis (Fig. S1, ESI†). The characterization results are summarized in Table S1 (ESI†).

ZIMs were polymerized at 90 °C using 4,4'-azobis(4-cyanovaleric acid) (ACVA) as the initiator in aqueous sodium bromide solution (25 wt%) as shown in Scheme 2. The polymerization results are summarized in Table 1. The polymeric zwitterions, PZIs, were characterized using ¹H NMR, FTIR, GPC, and UV-Vis spectroscopy (Fig. S2–S5, ESI†). These studies have confirmed that the zwitterionic nature is unaffected during polymerization. The solubility of PZIs was tested in various solvents as detailed in Table S2 (ESI†).

PZI **1** and **2** behaved like hydrogels and the equilibrium swelling ratio measured in deionized water is shown in Fig. S6 (ESI[†]). The swelling tendency and the lack of solubility in deionized water in spite of their zwitterionic character are due to the comparatively higher hydrophobic nature as well as due to strong donor-acceptor type interactions. The hydration studies of PZIs are summarized in Table 2.

The addition of salt readily enhances the solubility of PZIs in water, mainly due to the "anti polyelectrolyte" effect.² The effect of the amount of salt on the solubility of these polymers, *i.e.* the minimum (critical) salt concentration (CSC) necessary to dissolve the polymers, was determined by volumetric titration, transmittance and dynamic light scattering (DLS) studies as shown in Fig. S7 (ESI†). The presence of an additional benzene ring in PZI **2** induces a significant solubility difference as shown in Table 2. The CSC for PZI **2** is higher than that for the other sulfobetaines reported in the literature.^{26–28} In comparison, the acrylamide based sulfobetaine polymer formed a clear solution at 0.25 wt% of NaCl

Table 2	Solution	hehaviour	of P7I	1 and	2 ^a
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	Swelling ratio	Critical salt concentration (CSC, wt%)			
Sample	ple (SR, %)	Titration	Transmittance	DLS	
PZI 1 PZI 2	$\begin{array}{c} 85.23 \pm 4.26 \\ 134.76 \pm 6.74 \end{array}$	$\begin{array}{c} 1.71 \pm 0.2 \; (0.17 \; \text{M}) \\ 7.67 \pm 0.2 \; (1.31 \; \text{M}) \end{array}$	1.52 7.82	1.74 8.20	

 a SR = [(weight of swollen polymer – weight of dry polymer)/weight of dry polymer] \times 100. For CSC, 0.9 wt% of polymers were dissolved in 22.62 wt% of NaCl solution and titrated with deionized water at 25 °C (Fig. S6, ESI).

solution and formed an opaque gel in NaCl solution at a concentration of 27.8 wt% at 20 °C.²⁹ A combination of factors such as rigid structures, which could shorten the Debye length, additional donor-acceptor interactions, increased hydrophobicity, *etc.* are responsible for this change. The unusual solubility behaviour at high concentrations of salt solution and a lower pK_a (Table S3, ESI†) of PZIs could be indicative of a more stable sulfonate anion.³⁰ The stability towards pH 2 to pH 13 makes PZIs potentially applicable for EOR¹⁶ and antifouling.³¹

Aqueous salt solution also promoted the temperaturedependent phase separation of PZIs. Both PZIs exhibited reversible UCST phase transition^{32,33} behaviour between 5 °C and 95 °C in NaCl solution (12.13–5.1 wt% NaCl solution for PZI 2). As illustrated in Fig. 1, the polyzwitterions reached a maximum UCST > 95 °C at low salt concentrations (5.1 wt% NaCl). Fig. S7 (ESI†) shows the phase transition (UCST) of PZI 1 and 2 as a function of NaCl concentration with respect to transmittance observed visually by the cloudy appearance of the solution. The UCST of PZIs was tuneable by changing the salt and polymer concentration. The reversible thermal responsive behaviour of zwitterionic polymers during heating and cooling was also evidenced by DLS (Fig. 1b) and viscosity studies.

Above the UCST, a transparent solution was formed, and no aggregate was detected by DLS (Fig. S8 and S9, ESI†). The mono modal peak observed at high temperatures indicates that the polymer may exist as a coil of globular conformation^{1,33} or may



Fig. 1 UCST of PZIs (a) PZI **1** and PZI **2** in NaCl solution during heating; (b) temperature dependence of the *Z* average diameter of PZI **1** and **2** in NaCl solution during heating and cooling cycles. •: PZI **1** (0.07 wt% of PZI **1** in 1.62 wt% NaCl) is 39.14 ± 0.097 nm at $40 \,^{\circ}$ C and 3986 ± 559 nm at $20 \,^{\circ}$ C; • PZI **2** (0.31 wt% of PZI **2** in 7.89 wt% NaCl) is 63.39 ± 2.44 nm at $40 \,^{\circ}$ C and 514 ± 38.2 nm at $20 \,^{\circ}$ C. Each data point was obtained after equilibrating for 10 min (Fig. S8, ESI†); (c) photographs of PZIs **1** and **2** at variable temperatures and (d) schematic representation of reversible UCST thermal phase transitions.



Fig. 2 Gel-sol transition behaviour of PZI 2 in 22.6 wt% NaCl (a) and schematic representation of sol-gel behaviour (b).

exhibit micelle behaviour.³⁴ In the micelles, the backbone of PZIs made up of hydrophobic polystyrene may act as a core and the hydrophilic zwitterionic moiety could function as a shell. The interaction between the zwitterionic polymer and the salt at UCST was reversible during heating and cooling cycles. Upon heating the solution to 40 °C the turbidity disappeared completely, which reappeared upon cooling to 20 °C due to the formation of aggregates as illustrated in Fig. 1c. Furthermore, the experiment confirmed the reversible thermo responsive behaviour of PZIs.

The viscosity was studied at UCST of PZI 1 and 2 as shown in Fig. S10 and S11 (ESI[†]). Both PZI 1 and 2 exhibited non-Newtonian behaviour. The intermolecular association between charged species of the zwitterionic polymer is assumed to be responsible for the shear thickening behaviour (dilatancy). With increasing temperature, the viscosity of the solution dropped rapidly, though the rate of change was different with a larger change observed for PZI 1 which may be because of less interaction between polymer chains as well as lower rigidity of the polymer backbone combined with its low molecular weight.

Zwitterionic polymers (PZI 1 and 2) acted as reversible, temperature-sensitive gels in brine solution. Similar to agarose and gelatin, the polymer gels flow upon heating above the critical temperature ($T_{c,gel}$). This has been attributed to the disruption of the equilibrium existing among salt, water and zwitterions. Upon cooling, the equilibrium reverted back to the more stable configuration. This gel–sol and sol–gel cycle was repeated several times without any hysteresis. PZI 2 displayed superior gelation properties in that a transparent gel formed at a low concentration of the polymer (3 wt% vs. 42.34 wt% for PZI 1). Fig. 2 shows the thermoreversibility (gel–sol) of PZI 2 gel. The gel window became wider and shifted to a higher temperature when the polymer concentration was increased from 9 to 16 wt%. The PZI 1 also showed similar gel–sol phase transition behaviour, and a detailed study is in progress.

In summary, new hydrolytically stable imidazole based sulfobetaine zwitterionic polymers were synthesized. The PZIs exhibited reversible phase transitions due to the formation of expanded chains at elevated temperature and aggregates below the UCST as studied by DLS, transmittance and viscosity measurements. The unique thermoreversible gelling properties as well as unusual solubility characteristics make them interesting materials for a wide range of applications. Work is in progress to make polymer brushes from these novel vinylbenzene substituted imidazole based sulfobetaines. This work was funded by Agency for Science, Technology and Research (A*STAR), Singapore under Innovative Marine Antifouling Solutions (IMAS) for high value applications programme. The authors thank Dr R. Krishnan, Ms Chen Junhui and Ms Foo Ming Choo for assisting in GPC and DLS studies.

Notes and references

- 1 S. E. Kudaibergenov, Polymer Latexes Epoxide Resins Polyampholytes, 1999, vol. 144, pp. 115–197.
- 2 A. B. Lowe and C. L. McCormick, Chem. Rev., 2002, 102, 4177-4189.
- 3 M. Mertoglu, S. Garnier, A. Laschewsky, K. Skrabania and J. Storsberg, *Polymer*, 2005, **46**, 7726–7740.
- M. Lejars, A. Margaillan and C. Bressy, *Chem. Rev.*, 2012, **112**, 4347–4390.
 A. B. Lowe, M. Vamvakaki, M. A. Wassall, L. Wong, N. C. Billingham,
- S. P. Armes and A. W. Lloyd, *J. Biomed. Mater. Res.*, 2000, 52, 88–94. 6 Z. Zhang, J. A. Finlay, L. Wang, Y. Gao, J. A. Callow, M. E. Callow and
- S. Jiang, Langmuir, 2009, 25, 13516–13521.
- 7 F. Q. Xuan and J. S. Liu, Polym. Int., 2009, 58, 1350-1361.
- 8 H. Jiang, X. B. Wang, C. Y. Li, J. S. Li, F. J. Xu, C. Mao, W. T. Yang and J. Shen, *Langmuir*, 2011, **27**, 11575–11581.
- 9 Y. J. Shih, Y. Chang, A. Deratani and D. Quemener, *Biomacromolecules*, 2012, **13**, 2849–2858.
- 10 S. H. Ye, C. A. Johnson Jr., J. R. Woolley, H. Murata, L. J. Gamble, K. Ishihara and W. R. Wagner, *Colloids Surf.*, B, 2010, 79, 357–364.
- 11 J. Zhang, J. Yuan, Y. L. Yuan, J. Shen and S. C. Lin, *Colloids Surf.*, *B*, 2003, **30**, 249–257.
- 12 S. L. West, J. P. Salvage, E. J. Lobb, S. P. Armes, N. C. Billingham, A. L. Lewis, G. W. Hanlon and A. W. Lloyd, *Biomaterials*, 2004, 25, 1195–1204.
- 13 P. S. Liu, Q. Chen, X. Liu, B. Yuan, S. S. Wu, J. Shen and S. C. Lin, *Biomacromolecules*, 2009, **10**, 2809–2816.
- 14 W. H. Kuo, M. J. Wang, H. W. Chien, T. C. Wei, C. Lee and W. B. Tsai, *Biomacromolecules*, 2011, 12, 4348–4356.
- 15 Z. Cao, L. Zhang and S. Jiang, Langmuir, 2012, 28, 11625-11632.
- 16 D. A. Z. Wever, F. Picchioni and A. A. Broekhuis, Prog. Polym. Sci., 2011, 36, 1558–1628.
- 17 T. Mérian and J. M. Goddard, J. Agric. Food Chem., 2012, 60, 2943-2957.
- 18 L. Sonnenschein and A. Seubert, Tetrahedron Lett., 2011, 52, 1101-1104.
- 19 S. Y. Jiang and Z. Q. Cao, Adv. Mater., 2010, 22, 920-932.
- 20 C. L. McCormick and L. C. Salazar, Polymer, 1992, 33, 4617-4624.
- 21 A. T. Nguyen, J. Baggerman, J. M. J. Paulusse, C. J. M. van Rijn and H. Zuilhof, *Langmuir*, 2011, 27, 2587–2594.
- 22 H. Kitano, M. Imai, K. Sudo and M. Ide, *J. Phys. Chem. B*, 2002, **106**, 11391–11396.
- 23 P. Mary, D. D. Bendejacq, M.-P. Labeau and P. Dupuis, *J. Phys. Chem. B*, 2007, **111**, 7767–7777.
- 24 C. J. Huang, Y. T. Li, J. B. Krause, N. D. Brault and S. Y. Jiang, Macromol. Rapid Commun., 2012, 33, 1003–1007.
- 25 Y. K. Jhon, S. Arifuzzaman, A. E. Ozcam, D. J. Kiserow and J. Genzer, Langmuir, 2012, 28, 872–882.
- 26 J. C. Salamone, W. Volksen, A. P. Olson and S. C. Israel, *Polymer*, 1978, **19**, 1157–1162.
- 27 T. A. Wielema and J. B. F. N. Engberts, Eur. Polym. J., 1990, 26, 639-642.
- 28 V. M. Monroy Soto and J. C. Galin, Polymer, 1984, 25, 254-262.
- 29 J. Ning, K. Kubota, G. Li and K. Haraguchi, *React. Funct. Polym.*, 2013, 73, 969–978.
- 30 L. Wu, J. Jasinski and S. Krishnan, J. Appl. Polym. Sci., 2012, 124, 2154-2170.
- 31 D. M. Yebra, S. Kiil and K. Dam-Johansen, *Prog. Org. Coat.*, 2004, **50**, 75–104.
- 32 D. N. Schulz, D. G. Peiffer, P. K. Agarwal, J. Larabee, J. J. Kaladas, L. Soni, B. Handwerker and R. T. Garner, *Polymer*, 1986, 27, 1734-1742.
- 33 J. Seuring and S. Agarwal, *Macromol. Rapid Commun.*, 2012, 33, 1898-1920.
- 34 A. B. Lowe, N. C. Billingham and S. P. Armes, *Macromolecules*, 1999, 32, 2141–2148.