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Thermoresponsive poly(ionic liquid) hydrogels†

Bartosz Ziółkowski and Dermot Diamond*

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A new series of LCST ILs have been copolymerised with crosslinkers of varying length to afford the first ever thermoresponsive poly(ionic liquid)-based hydrogels. These hydrogels exhibit surprisingly broad LCST and volume transition behaviour compared to standard thermoresponsive gels and linear ILs.

Ionic liquids (ILs) – organic salts that exhibit melting points below *ca.* 100 °C are a widely known and continuously developing class of materials.[1] The main advantages of these materials include low vapour pressure and the possibility to tune the properties of the IL by alternating the structures of the constituent cations and anions. These features make them particularly useful for synthesis of ionogels[1] and stimuli responsive materials.[2]

Gel materials (in which a crosslinked polymeric network is filled with an IL phase) combine the characteristics of the polymer with those of the IL, often resulting in new hybrid materials with interesting properties.[1–3] These include appearance of Lower Critical Solution Temperature (LCST) of the gel network that allows shrinkage of the gel when the temperature is raised above the LCST.[3] Also the ability to tune mechanical,[4] photoresponsive,[16] and magnetic[5] ionogel properties has been reported.

Moreover a subgroup of ILs wherein either the cation or anion is also a monomer and can be polymerised to form macromolecular ILs is also rapidly growing.[6] These monomeric and polymeric ILs have also attracted significant attention due to the possibility of having the properties of macromolecules and ILs integrated in one network. These include polyIL electrolytes and sorbents, and electroactive materials.[7]

Recently a new and fascinating class of thermo-responsive ILs has been reported.[8,9] These ILs are miscible with water at room temperatures but when heated, they phase separate, much like thermoresponsive polymers such as *N*-isopropylacrylamide.[10] Such temperature-sensitive behaviour opens up new possibilities for using these ILs as functional fluids *e.g.* for reversible protein extraction.[9,11] Interestingly, out of many different cation–anion combinations, the majority of the thermo-responsive ILs reported are based on variations of phosphonium cations, such as tetrabutyl or tributyl-hexyl phosphonium[9,11,12] The most common anions employed to make LCST ILs thus far have been derivatives of benzenesulfonic acid. A particularly interesting development was to use 4-styrene sulfonate as an anion.[13] This combination of cation and anion produced a monomeric IL that displayed LCST behaviour.[13] This IL was then polymerised to form the first ever thermo responsive poly IL. This polyIL when dissolved in water precipitated when heated above the LCST and re-dissolved when cooled below the LCST. Consequently, other monomeric ILs based on sulfopropylmethacrylate anion and tributyl-hexyl phosphonium cation[12] or C3–C6 sulfoalkyl anion and tributyl-4-vinylbenzyl phosphonium cation[14] have been reported.

A common property of these LCST polymeric ILs is that their LCST depends on the concentration of the polyIL in water.[12,14,15] This phenomenon allows easy tuning of the LCST of these materials. As the concentration of the IL in water increases the LCST decreases. Moreover, addition of salts such as KBr[15] or phosphate buffer[12] can alter the LCST higher or lower, respectively, behaviour that is attributed to the salt's cosmotropicity.[12] The LCST of these materials can also be tuned using the standard route which involves copolymerisation of the responsive monomer with a hydrophobic comonomer. For example, when tetrabutylphosphonium 4-vinylsulfonate was copolymerised with 30% tributyl-hexyl phosphonium 4-vinylsulfonate, the LCST was shown to decrease from 60 to 40 °C (at the same polymer concentration).[13] This thermoresponsive behaviour make these ILs and poly(ILs) very promising candidates for a new group of stimulus responsive polyionic materials such as, for example, reversible graphene solution stabilisers.[15]

Therefore, it has been proposed that these thermoresponsive monomeric ILs can be polymerised into a hydrogel to form thermoresponsive poly IL hydrogels. Ideally these materials should behave similarly to the well known thermoresponsive poly(*N*-isopropylacrylamide) (NIPAAm) hydrogels, but with modification of properties due to the presence of the IL component. These materials could open new approaches to the production of polyIL-based stimulus responsive gels, with potential applications as,

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CLARITY, The Centre for Sensor Web Technologies, National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland. E-mail: dermot.diamond@dcu.ie; Tel: +353 17005405

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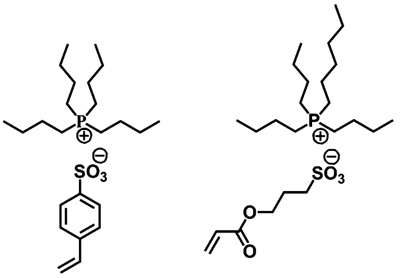


P-SS **P-SPA**

Scheme 1 Structures and abbreviations of the monomeric ILs used in this study.

for example, microfluidic flow controllers and actuators, controlled absorb, release and delivery materials *etc.*

The following work investigates the preparation and the thermal and actuation properties of crosslinked thermoresponsive polyILs using two monomeric LCST ILs. We have synthesised the known tetrabutylphosphonium styrenesulfonate (**P-SS**)[13] and the new tributyl-hexyl phosphonium 3-sulfopropylacrylate (**P-SPA**) (Scheme 1) with the aim of photopolymerising these monomers with various crosslinkers such as *N,N′*-methylenebisacrylamide (MBAAm), poly(ethylene glycol) diacrylate Mn = 256 (PEG256), poly(ethylene glycol) diacrylate Mn = 700 (PEG700) and poly(propylene glycol) diacrylate Mn = 800 (PPO800) to form thermoresponsive gels. Since these monomeric ILs are liquid at room temperature and, like most ILs, have high solvating ability, they are miscible with organic initiators and crosslinkers, allowing easy handling of the mixtures, *via* moulding and subsequent photopolymerisation.

Initial gels were prepared with **P-SS** and 5 mol% of MBAAm as the crosslinker (details of IL and gel synthesis found in the ESI†). These gels when placed in DI water at room temperature swelled enormously (more than ~400% in diameter) in less than 2 hours and the material disintegrated into small fragments (*ca.* 1 mm) in the process (Fig. S1a, ESI†). The same swelling behaviour occurred with 10% MBAAm. Therefore, 5% PEG256 was used as another type of crosslinker but yielded same excessive swelling and cracking as occurred with MBAAm. From our experience with standard poly(NIPAAm) hydrogels, generally speaking at 10 mol% MBAAm and PEG256 crosslinker, the material is very tightly crosslinked and can swell in water not more than 20% in diameter. Bearing this in mind it was suspected that, in the case of our monomeric ILs, the crosslinking was not efficient. Conversion of vinyl groups during polymerisation was confirmed by the disappearance of characteristic vinyl bands at ~1630 cm^{-1} in Fig. S2 and S3, ESI.† Given this, it was hypothesised that steric hindrance might have been responsible for the ineffective crosslinking. Due to the bulky nature of the monomers and the small size of the MBAAm and PEG256 the alkyl chains of the phosphonium cations might be shielding the approach of subsequent monomers to the side arm of the crosslinker or resulting in a rigid side branch. Therefore, longer chain crosslinkers were used. When both **P-SS** and **P-SPA** were crosslinked with 5% of PPO800 and the gel placed in DI water observable swelling occurred but stopped after 60 minutes reaching ~146% of the initial diameter. These gels were quite stiff in their hydrated forms but did not crack during swelling and were relatively easy to handle (Fig. S1b, ESI†). Similar behaviour was observed when PEG700 was used with **P-SS** and **P-SPA**. The only difference between PEG256 and PEG700 crosslinkers is the PEG unit length. Therefore, the difference in the stability of these gels cannot be associated to the styrene + acrylate copolymerisation reactivity issues. A summary of the outcomes of these experiments can be found in Table 1. It must be noted that PPO800 is hydrophobic in nature and immiscible with water. It is miscible in the monomeric IL but above 9 mol% of this crosslinker the resulting gel becomes opaque during the swelling process. Thermal analysis was performed on the water-swollen gels to determine their LCST behaviour. DSC scans were conducted on the poly(IL) gels to observe the LCST endothermic peak during heating.

As previously mentioned, polyILs have been reported to manifest concentration dependant LCST behaviour.[12,14] Therefore, it was hypothesised that the LCST of the gel could be controlled *via* the amount of crosslinker used. Increasing crosslinker content prevents the polymer chains from drifting apart during swelling and therefore the gels with more crosslinker swell less. It was assumed that if the polyILs retain their LCST dependence on concentration in the gels then in our case higher crosslinker concentrations should produce a lower LCST for the water swollen gel. Consequently, the **P-SS** monomeric IL was polymerised with 3 different concentrations of crosslinker. It was found that gels prepared with 5% PPO800 displayed the highest LCST (53 °C) compared to 7 and 8% PPO800 (46 and 43 °C) respectively (Table 2). The swelling of these gels (in diameter and weight) is also lower for the higher crosslinker content which further confirms previous assumptions.

What is striking about the DSC results of the crosslinked gels (Fig. S4, ESI†) is the broadness of the LCST peaks (~40 °C). When **P-SPA** gel (5% PPO800) is compared to a linear poly(**P-SPA**)

Table 1 Monomeric ILs and crosslinkers used to produce hydrogels with their respective appearances after swelling for 4 hours in DI water at room temperature

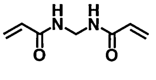
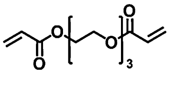
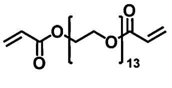
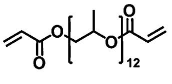
		P-SS	**P-SPA**
	MBAAm	Cracks, no stable shape, excessive swelling	Cracks, no stable shape, excessive swelling
	PEG256 diacrylate	Cracks, no stable shape	Cracks, no stable shape
	PEG700 diacrylate	Stable, transparent gel	Stable, transparent gel
	PEG800 diacrylate	Stable, transparent gel (up to 9% mol)	Stable, transparent gel (up to 9% mol)

Table 2 Crosslinker content used for the **P-SS** gels and the resulting gel swelling and LCST characteristics

PPO800 content [mol%]	Swollen gel polymer concentration [wt%]	Swelling [% initial diam.]	Gel DSC LCST peak [°C]
5	26	46	53
7	32	39	46
8	34	34	43

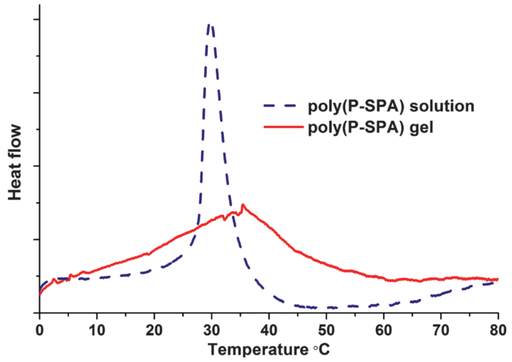


Fig. 1 DSC scans of **P-SPA** gel crosslinked with 5 mol% PPO800 and **P-SPA** linear polymer solution in DI water 1 : 1 weight%.

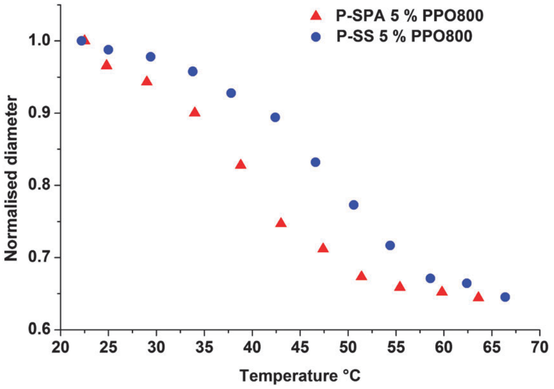


Fig. 2 Temperature induced shrinking profiles of **P-SS** and **P-SPA** both crosslinked with 5 mol% of PPO800.

solution in water (1 : 1 by weight, Fig. 1) one can see that the LCST of the linear polymer solution is much sharper (10 °C) and that the LCST DSC peak becomes broad once the polyIL is crosslinked.

Therefore, in light of these results, this broadening of the LCST peak after crosslinking the polyIL is suspected to be caused by the decreased level of freedom the bulky polyIL has in the gel. This DSC thermal response broadening after crosslinking also manifests itself in the temperature induced volume transition of the gels. Fig. 2 shows the temperature induced shrinking behaviour of two gels with the highest swelling (and presumably highest shrinking degree): **P-SPA** and **P-SS** both crosslinked with 5% of PPO800 diacrylate.

When these gels are subjected to heating in 5 °C equilibrium steps, they do not shrink as is typical with thermoresponsive gels *e.g.* poly(*N*-isopropylacrylamide). This means that the shrinking behaviour does not take place suddenly at one particular temperature. Rather, these polyIL gels shrink gradually over ∼40 °C as the temperature increases (Fig. 2). At the same crosslinker concentration, the **P-SPA** gel appears to be slightly more hydrophobic than **P-SS**, which results in the former shrinking to a greater extent at lower temperatures.

This unusual thermal shrinking behaviour renders these gels unsuitable for fast actuation applications. However, this behaviour could have interesting applications in scenarios that demand a continuous change in the material volume over a temperature range, rather than an abrupt phase change. For example, in drug delivery systems where one requires a slow release of substance over a long period of time and wide window of stimuli rather than a rapid bust of the drug as it is with standard thermoresponsive gels. Of course having the actuation distributed across a wider temperature range causes the volume change per unit temperature change to be smaller. Another potential application is the area of microfluidic temperature controlled flow regulators, since their volume can be varied over a temperature range in order to control the extent by which flow in a microfluidic channel is impeded.

To conclude, a new and fascinating family of thermoresponsive monomeric ILs have been used to synthesise first ever thermoresponsive polyIL hydrogels. These monomeric ILs have been photopolymerised with crosslinkers of varying length to show that only long chain crosslinkers allow the material to swell in water without cracking and disintegrating. The LCST of these gels decreases with increasing gel crosslinker concentration, which is in accordance with previously reported LCST concentration dependence of these materials. However, the thermal behaviour of these materials did not mirror the similar linear systems reported. Instead, the crosslinked polyILs display a significant broadening of the temperature range over which the LCST behaviour occurs. Consequently, the gels shrink over a wide temperature range compared to typical thermoresponsive polymeric gels. This is attributed to the lack of freedom that the bulky and highly charged polymer backbone experiences in the crosslinked hydrogel state.

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