Poly(ionic liquid) Based Thermo Responsive Hydrogels

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Introduction:

Stimuli-responsive materials have been the subject of increasing research interest due to their many potential applications, including their use as fluid handling actuators [1,2,3]. Materials research in this area has been mostly based on poly(*N*-isopropylacrylamide), a thermo-responsive polymer with a lower critical solution temperature (LCST) at ~30 ˚C. However, recently polymerisable ionic liquids that manifest LCST behaviour have been reported[4]. Therefore, these materials may be interesting candidates for a new class of poly-ionic liquid responsive gels.

Herein we report tetrabutyl-phosphonium-4-vinylbenzenesulfonate and tributyl-hexyl-3-sulfopropyl acrylate ionic liquids that have been polymerised with a crosslinker. When placed in water, these materials quickly swell, and form hydrogels within one hour. The amount of crosslinker used determines the rate at which the gel swells, and the amount of water uptake. Since the LCST of these ILs is concentration dependant, we show that it can be controlled by varying the amount of crosslinker used.

Aim:

- To investigate the possibility of producing thermoresponsive hydrogels through polymerisation of thermoresponsive monomeric phosphonium based ionic liquids
- Analysis of the LCST behaviour of the resulting gels

Experimental:

Monomeric ILs used

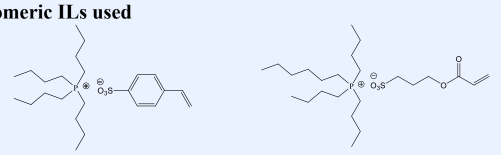


Fig. 1. Structures of ionic liquid monomers tested. Left: [$P_{4,4,4,4}$][SS]; Right: [$P_{4,4,4,6}$][SPA]

Gel synthesis

- The monomeric IL was mixed with a crosslinker, UV photoinitiator and polymerised under UV light in circular PDMS moulds for 1h
- Crosslinkers used:

N,N'-methylenebis acrylamide Mn = 154 (MBIS)

Poly(ethyleneglycol) diacrylate Mn = 256 (PEG256)

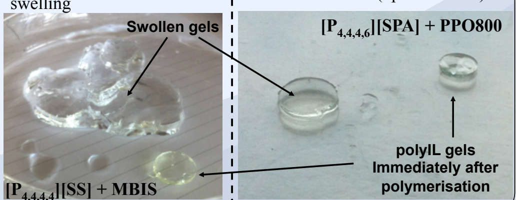
Poly(ethyleneglycol) diacrylate Mn = 700 (PEG700)

Poly(propyleneglycol) diacrylate Mn = 800 (PPO800)

Results:

Table 1. Characteristics of poly([$P_{4,4,4,4}$][SS]) gels obtained using crosslinkers of varying molecular weight.

	MBIS	PEG 256	PEG 700	PPO 800
[$P_{4,4,4,4}$][SS]	Cracks, no stable shape, excessive swelling	Cracks, no stable shape	Stable, transparent gel	Stable, transparent gel (up to 9 %mol)
[$P_{4,4,4,6}$][SPA]	Cracks, no stable shape, excessive swelling	Cracks, no stable shape	Stable, transparent gel	Stable, transparent gel (up to 9 %mol)



- Longer chain crosslinkers (PEG700, PPO800) are required to produce stable gels with satisfactory mechanical properties

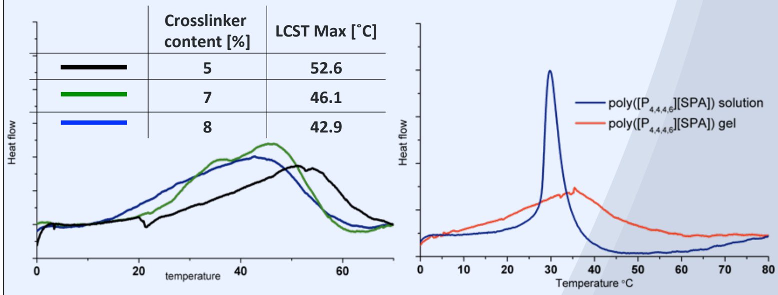


Fig. 2. Left: DSC scans of poly([P4,4,4,4][SS]) gels crosslinked with varying amounts of PPO800. Right: DSC scans of poly([P4,4,4,4][SPA]) gel crosslinked with 5 % PPO and poly([P4,4,4,4][SPA]) 50 %wt water solution

- DSC scans reveal that the polyIL gels exhibit a very broad LCST peaks (Fig.2: left) compared to the linear polyIL solutions in water (Fig 2: right), and the maximum depends on the crosslinker content (decreases as crosslinker % increases).

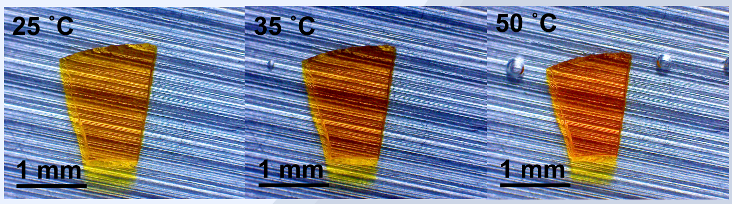


Fig. 3. poly([$P_{4,4,4,4}$][SS]) gel with 8 % PPO800 as crosslinker shrinking as the temperature is increased from 25 ˚C to 50 ˚C. Orange coloration is due to spiropyran acrylate copolymersied with the gel at 2 mol%

Conclusions:

- Thermoresponsive poly(ionic liquid) hydrogels can be produced from monomeric ILs that have LCST properties
- These gels shrink when heated and expand after cooling
- Only longer-chain crosslinkers such as PEG700 and PPO800 produce polymeric gels that are mechanically stable
- Crosslinking these ILs results in a significant broadening of the LCST peak
- LCST max and related actuation behaviour can be tuned by changing the crosslinker concentration

References

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