

Hybrid Materials Based on Photo-responsive Ionogels

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Introduction

Photo-responsive gels have attracted interest as functional materials as valves and actuators. Light irradiation is an attractive means of control as it can be applied instantaneously and with high resolution, without physical contact. The co-polymer of isopropylacrylamide, methylene-bis-acrylamide and acryloyl spirobenzopyran (Fig 1.) has shown significant photo-induced volume change in 0.5mM HCl aqueous solution using blue light.¹

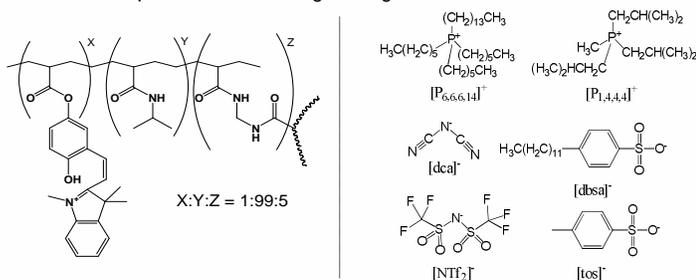


Figure 1: (A) Structure of photo-responsive polymer. (B) Structure of ILs used in ion gels.

We have photo-polymerized these monomers within various phosphonium based ionic liquids (ILs). Impregnating photo-responsive gels with ILs offers certain advantages for example, through the tailoring of chemical and physical properties of ILs (acid/ base character, viscosity etc.). These ionogels were characterized by optical and physical analysis and incorporated into a micro-fluidic platform as micro valves.

Experimental

Monomers dissolved within phosphonium ILs containing the anions [NTf₂]⁻, [dca]⁻, [tos]⁻ and [dbsa]⁻. Ionogel prepared by photo-polymerization with DMPA. After washing, ionogel immersed in 1mMol aqueous HCl for 24hrs in dark. All measurements recorded at 20 °C. For comparison, a gel was prepared containing no IL.

Characterisation

Hybrid material of polymer and phosphonium ILs were analysed by Raman and IR spectroscopy. Figure 2(a) shows FT-IR spectra of [P66614][dbsa] ionogel. It can be clearly seen that polymer chain vibrations are clearly affected by the presence of the [P66614][dbsa]. Raman spectra of [P66614][dca] ionogel shows new vibration contributions, Figure 2(b).

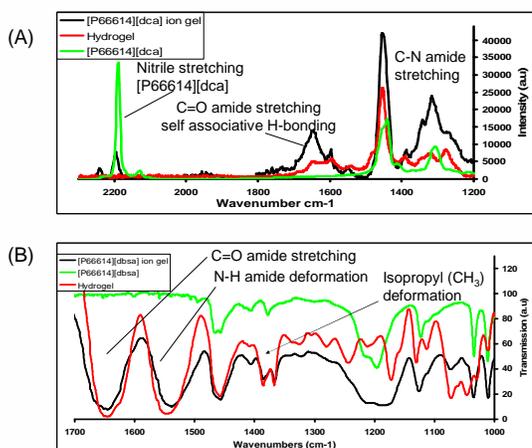
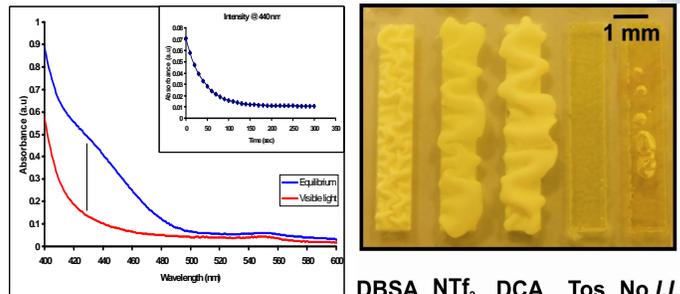


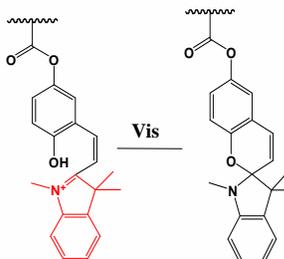
Figure 2: (A) FT-IR spectra of [P66614][dbsa] ionogel, IL and hydrogel. (B) Raman spectra of [P66614][dca] ionogel, IL and hydrogel.



DBSA NTf₂ DCA Tos No I.L.

Figure 3: UV-vis of [P66614][dca] ionogel at equilibrium and after 60 sec of visible light. (Inset) First order kinetic plot of absorbance decay at 440 nm with visible light irradiation (left) and photograph of ion gels in 1mMol aqueous HCl (right).

UV-vis analysis of the ionogel containing [P66614][dca] (Fig 3.) at equilibrium indicates the protonated form of the merocyanine, band at 440 nm. Upon exposure to visible light the band at 440 nm decreases in intensity due to the ring closing of the merocyanine (hydrophilic) to the spirobenzopyran (hydrophobic).



This ring closing induces a dehydration of the [P66614][dca] ionogel. Ring closing kinetic rate constant calculated to be $2.5 \times 10^{-2} \text{ s}^{-1}$, (Fig 3. inset). Photo-induced dehydration results in a physical shrinkage of the ionogel. After 150 seconds of visible light, there is a 73% physical deformation. The kinetic rate of physical shrinkage was calculated to be 0.457 s^{-1} .

Figure 4: Proposed mechanism of photoinduced deformation of ionogel.

Application

This impressive functionality of the ionogel was applied as a microvalve in a micro-reactor to control the movement of fluids. The micro-reactor shown in Fig 5. (4 x 4 cm) is easily fabricated in PMMA and pressure sensitive adhesive (PSA). The ionogel valve is placed within the PMMA and PSA layer (80 µm deep, 300 µm width/length), this is then covered with a thin and flexible PDMS layer.

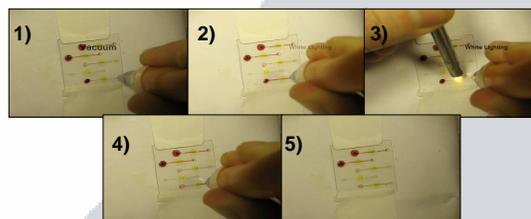


Figure 5: Performance of the ionogel within a microfluidic chip.

The micro-reactor valve was successfully tested using vacuum as driving force in the outlet and a colorant in the inlet. When light is applied to the valve the ionogel decreases in volume and so the valve opens letting the colorant pass through the channel.

Conclusion

Photo-responsive phosphonium based ionic gels were prepared and characterized. It was found that upon visible light irradiation the ionogels decreased in volume due to the photo-isomerization of spirobenzopyran. These gels were then successfully incorporated into a microfluidic manifold as photo-actuated micro valves.

Reference

1) Shinji Sugiura, Sensors and Actuators A 140 (2007) 176–184

Acknowledgements

The project has been carried out with the support of Science Foundation Ireland under CLARITY grant (07/CE/L1147). FBL would like to thank IRCSET fellowship number 2089.