

Photoresponsive ionic gels as microvalves in microfluidic systems



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Introduction

Photo-responsive gels have attracted interest as functional materials within microfluidic systems 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 pNIPAAm and spirobenzopyran (Fig 1.) has shown significant photo-induced volume change in 0.5mM HCl aqueous solution using blue light.¹

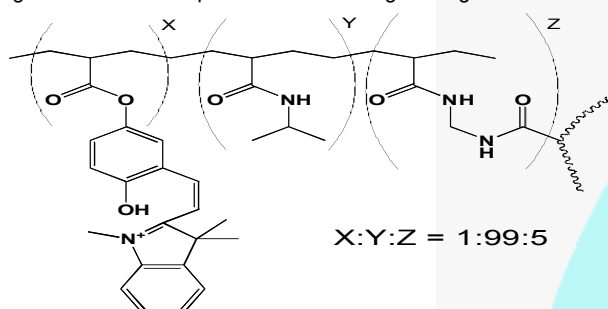


Figure 1: Structure of photo-responsive polymer.

We have polymerized the photo-responsive polymer within various phosphonium based ionic liquids (ILs). Impregnating photoresponsive 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

Benzospiropyran monomer unit synthesized as reported. Monomers dissolved within phosphonium IL containing the anion [NTf₂]⁻. 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. Visible irradiation was applied at a distance of 15 cm, temperature was monitored using a thermostat.

Results and Discussion

UV-vis analysis of ionogel (Fig 2.) 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 ionogel. Ring closing kinetic rate constant calculated to be $2.5 \times 10^{-2} \text{ s}^{-1}$, (Fig 2. inset).

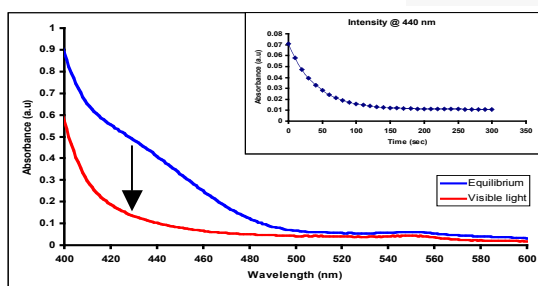


Figure 2: UV-vis of ionogel at equilibrium and after 60 sec of visible light. (Inset) First order kinetic plot of absorbance decay at 440 nm with visible light irradiation.

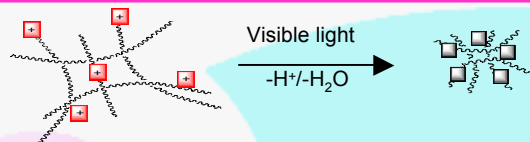


Figure 3: Proposed mechanism of photo-induced ionogel shrinkage.

Photo-induced dehydration results in a physical shrinkage of the ionogel, as seen in the images within Fig 4. After 150 seconds of visible light, there is a 100 μm difference. This photo-effect was monitored using a physical contact profilometer, the kinetic rate of shrinkage was calculated to be 0.457 s^{-1} .

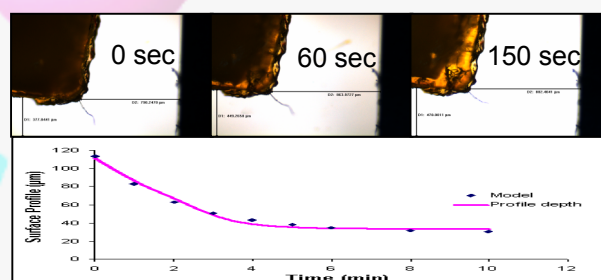


Figure 4: Images of photo-induced ionogel physical change (above) ionogel first order decay calculated using physical contact profilometer (below).

The micro-reactor shown in Fig 5. (4 x 4 cm) is easily fabricated in PMMA and pressure sensitive adhesive (PSA) in four layers using CO₂ ablation laser. 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. In this case microvalves are physically independent of the channel and can be relocated simply by varying the layer.

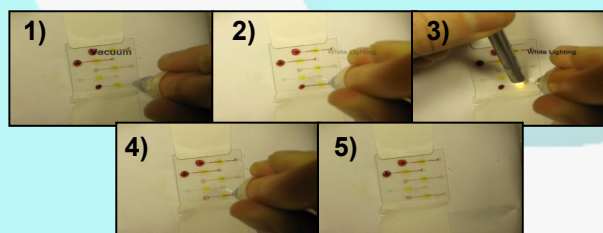


Figure 5: Performance of the ionogel within a microfluidic chip.

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.

Conclusions

Photo-responsive phosphonium based ionic gels were prepared and characterized. It was found that upon visible light irradiation the ionic gels 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

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