

# MICROFLUIDIC FABRICATION OF POLYMERIZED IONIC LIQUID MICROGELS

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## ABSTRACT

We present a simple capillary-based microfluidic method to fabricate monodisperse microgels composed of polymeric ionic liquids (PILs). We are able to tune the size, hydrophilicity/hydrophobicity and chemical nature of these microgels by selecting an appropriate anion from a diverse pool of anions. Further, these microgels can also stably accommodate organic indicators useful for pH sensing and remove ionic contaminants from water.

**KEYWORDS:** Microfluidics, Ionic liquid, Microgels, Purification, pH Sensing

## INTRODUCTION

Microscale hydrogels or microgels possessing diverse chemistries and geometries have attracted tremendous research and commercial interest over the past decade due to their potential applications in drug delivery, cell encapsulation, as tissue engineering scaffolds, and in chemical sensing [1]. In this paper, we present microfluidic fabrication methods for monodisperse polymerized ionic liquid microgels. Ionic Liquids (ILs) are liquid salts composed of organic cations and organic or inorganic anions. They possess a range of remarkable properties including high electrical conductivity, excellent thermal stability, very low volatility as well as wide range of solvability. Physical properties of ILs such as viscosity, density, hydrophobicity etc. can be altered by the judicious choice of cations or anions [2]. The incorporation of ionic liquids into macromolecular architectures to modulate their intriguing features has recently attracted enormous interest in material science. 'Poly (ionic liquids)' or PILs have enhanced stability, improved processability, durability, in addition to control over their meso- to nano-structure while retaining all the salient features of ionic liquids [3, 4]. PILs are excellent functional materials for carbon dioxide capture, microwave absorption, catalysis processes, chemical separation and sensing applications. However, despite several advances in the application of PILs, there are no robust and reliable methods to fabricate these particles with strict control over structure and monodispersity [5].

In most cases, ionic liquid-based polymers or PILs are produced as bulk polymeric materials, typically by classical emulsion polymerization in stirred tanks [5, 6]. Hence the products do not have well-defined, regular shapes and sizes. In order to fundamentally and quantitatively investigate how the chemical nature of the constituent cations and/or anions of ionic liquids can dictate or alter the structural features of the PILs, at different size-scales (micro-nanometers), there is a need for a reliable way of producing monodisperse PIL-based materials. In addition, ionic liquids can accommodate both polar and nonpolar molecules – a property that can be exploited to use such PIL microgels for chemical separations and sensing. The availability of monodisperse PIL microgels also facilitates quantitative studies in these applications. We present two simple capillary-based microfluidic methods to generate nearly monodisperse PIL microgels over a wide size range (~200-1000  $\mu\text{m}$ ), where we utilize the UV cross-linking of an IL monomer, alkenylimidazolium bromide with poly(ethylene glycol) diacrylate (PEGDA). We leverage the ion-exchange feature of synthesized PIL microgels to controllably tune their sizes and also switch from hydrophilic to hydrophobic behavior. We demonstrate applications of these PIL microgels as *reversible* pH sensors and in heavy metal removal from water.

## EXPERIMENTS AND RESULTS

PIL microgels are prepared using emulsion-based microfluidic co-polymerization of an IL monomer, 1,3-bis(pentenyl)-2-methylimidazolium bromide in the presence of poly(ethylene glycol) diacrylate (PEGDA) as the cross-linking agent and photoinitiator Darocur 1173. Two exemplary capillary-based microfluidic setups employing co-flow (needle-in-tube through a PEEK T-junction) and flow-focusing (simple PEEK cross-junction) are utilized to generate droplets of the IL-PEGDA monomer mixture in silicon oil. This is followed by photopolymerization using a UV lamp leading to PIL microgel formation (Fig. 1 (a,b)), in which the imidazolium cations are cross-linked with

PEG diacrylate, while bromide anions are electrostatically attached with the positively-charged imidazolium backbone. Stereomicroscopic and FESEM images reveal that highly monodisperse and perfectly spherical microparticles are obtained (Fig. 1 (c-g)). The particle surfaces are textured at the sub-micron scale, as seen in the SEMs in Figure 2(a-c).

We investigate the structural and chemical features of PIL microgels. A crucial and unique feature of such microgels is the ability to readily switch physical properties by switching the constituent anions. For example, the as-synthesized hydrophilic PIL microgels (with imidazolium bromide moieties on the surface) are readily and rapidly transformed to hydrophobic microgels by anion exchange with bistriflimide, leading to rapid aggregation and clustering in water, but easy dispersion in an organic solvent. Due to relatively higher hydrophobicity of  $\text{NTf}_2^-$  anions compared to  $\text{Br}^-$  anions, a significant amount of the entrapped water in microgel is extruded, causing the shrinkage of anion-exchanged microgels to about 40% of their original size. We observe varying extents (10-40%) of shrinkage of the PILBr particles when exposed to different anions ( $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{ClO}_4^-$ , etc) indicating the control over the water content of the microgels. Hence, PIL microgel sizes can be manipulated in the hydrated state by creating a particular chemical environment by simply swapping anions. Such anion exchange can not only change the particle size, but can also impart new functionalities to the particles through a suitable choice of task-specific anion. The availability of monodisperse populations of PIL microgel particles is essential to track and quantitatively gauge the affect of anion and the environment on the size and chemistry of such particles. Facile exchange of larger anions with the parent bromide in the synthesized PIL microgels has helped us to employ these microgels as special tools for wastewater treatment and purification. The as-synthesized PIL microgels are capable of reaching 74mg/g adsorption capacity in Chromium (VI) removal (in the form of dichromate) from wastewater.

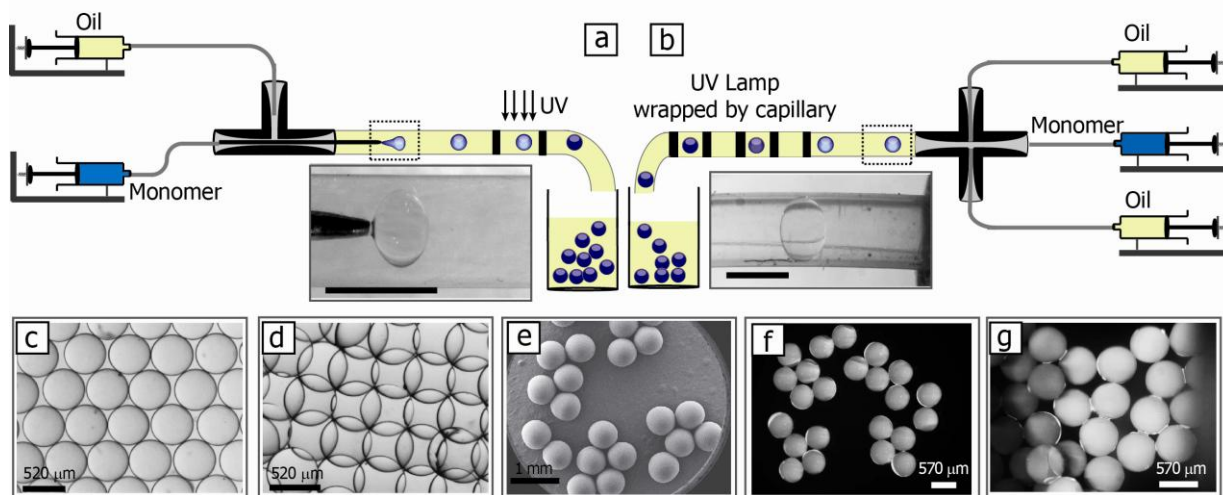


Figure 1: Schematics illustrating microfluidic methods to generate poly (ionic liquid) microgels employing a) co-flow (needle-in-tube through T-junction) b) flow-focused (cross-junction) break-up mechanisms, inset images show the stereomicroscope images of droplets. (c, d) stereomicroscope images of PIL microgels showing their monodispersity and transparency. (e) FESEM and (f, g) stereomicroscope (under UV irradiation) images of PIL microgels.

We also demonstrate an analytical application of such particles in reversible pH sensing, showcasing their ability to selectively entrap and retain probe molecules with little or no leaching. pH-Indicator (Thymol blue)-doped PILs colorimetrically respond to the pH of the surrounding medium in a reversible manner (Fig. 2(d-f)). When the indicator-doped microgels are exposed to acidic environment, the yellow color of the microgels changes rapidly to orange-red. The same beads can revert back to their neutral color in pure water or blue in an alkaline solution. A single set of beads can be repeatedly exposed to varying pH conditions (acid/neutral/base) and can colorimetrically respond to the surrounding pH changes without loss of performance. Such robustly reversible feature of pH sensing using PIL microgels opens up the way for the applications of such microgels as smart pH-monitors in environments where pH fluctuates. Apart from pH sensing, these ionic liquid-based particles can be doped with a wide range of

probe molecules, catalysts and enzymes (either by physical adsorption or ion-exchange) and can potentially enable high throughput, non-interfering, analysis of multiple analytes.

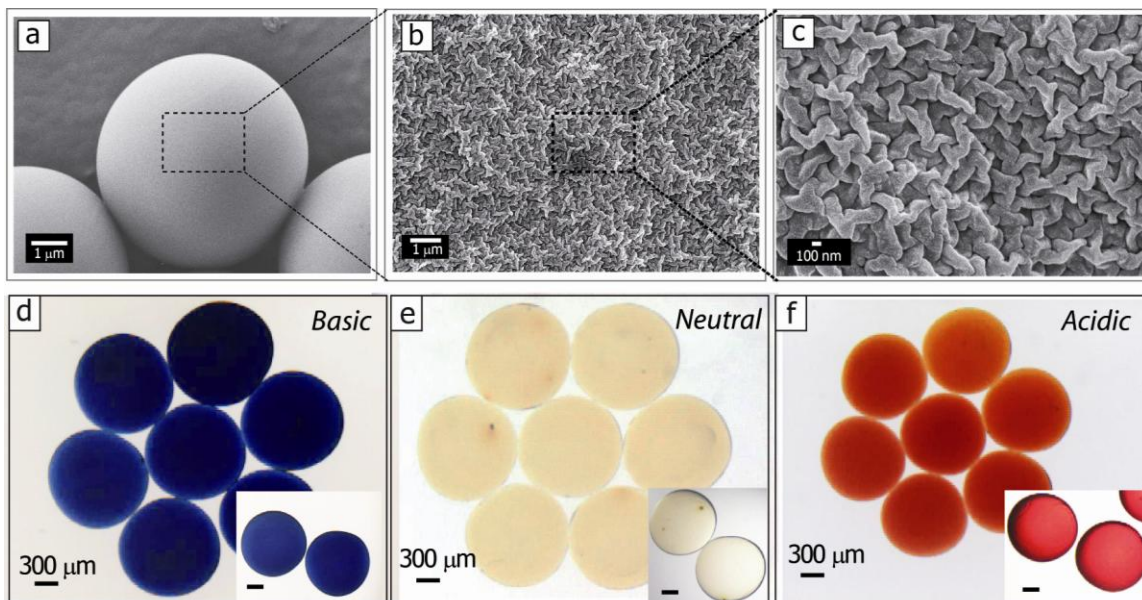


Figure 2: FESEM images showing a) PIL microgel containing bromide anion and b,c) corresponding surface structures with higher resolution showing nanoscale texturing. d-f) stereomicroscope images demonstrating colorimetric response of PIL microgels containing pH indicator in basic (pH 14), neutral (pH 7) and acidic (pH 0.2) aqueous environments; respectively.

## CONCLUSION

In conclusion, we demonstrate simple microfluidic methods to produce ionic liquid-based spherical microgels in a highly monodisperse, robust and scalable manner. These microgels have much potential for the creation of unique advanced functional materials, by incorporation of ionic liquid in their macromolecular structure. The ability to switch the constituent ions of PIL microgels helps us to tune the physical and chemical features of such microgels, thereby enabling applications in chemical separations and sensing.

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