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Fabrication of ionic liquid gel beads via sequential deposition

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ABSTRACT

In this paper, we demonstrate the fabrication of gel beads composed of ionic liquid (IL) and polymer. The IL droplets are kept spherical during the deposition process by placement onto chromatography paper coated with fluoropolymer. The deposition process then occurs in two steps. In the first step, the monomer is absorbed into the IL droplet. In the second step, the initiator radicals are introduced. This sequential deposition process allows polymerization to primarily occur within the liquid droplet and therefore the beads are not attached to the underlying substrate and can be easily removed.

1. Introduction

The initiated chemical vapor deposition (iCVD) process is a solventless polymerization process which is typically used to coat solid surfaces [1,2]. We recently demonstrated that we can use the iCVD process to deposit polymer onto liquid substrates with low vapor pressures such as silicone oils and ionic liquids (ILs) [3,4]. The deposition of polymer onto these liquids has complexity due to surface tension effects and solubility effects. The surface tension effects determine whether polymer deposition leads to the formation of films or particles at the surface of the liquid [5]. Monomer solubility in the liquid allows for interesting dynamics due to different polymerization kinetics in the bulk liquid [6]. For example, higher molecular weight polymers and increased propagation rate coefficients have been reported for free radical polymerizations in IL media compared to organic solvents [7–10].

ILs have attracted considerable attention due to such properties as high ionic conductivity [11], wide electrochemical window [12], thermal stability [13], and low vapor pressure [14] making them useful for diverse applications such as energy storage and utilization [15,16], radioactive waste handling [17,18], and carbon capture [19]. Integration of polymers within ILs is important for combining the chemical functionality of ILs with the mechanical properties of polymers [20]. We have previously demonstrated two methods to incorporate polymers with ILs. In the first method, we encapsulated IL droplets within polymer shells composed of poly(1H,1H,2H,2H–perfluorodecyl acrylate) (PPFDA), poly(ethylene glycol diacrylate) (PEGDA), and poly(1H,1H,2H,2H–perfluorodecyl acrylate-co-ethylene glycol diacrylate) (P(PFDA-*co*-EGDA)) [21]. The IL droplets were first stabilized into spherical shapes by rolling them in poly(tetrafluoroethylene) (PTFE) particles and then they were placed on a bed of PTFE particles during deposition in order to prevent bridging between the deposited polymer and the underlying substrate. The PTFE particles that were used to stabilize the droplet shape were incorporated into the polymer shell after deposition. The shells were robust enough to remove the IL inside shell and replace it with another liquid. In the second method, we fabricated thin gel films of thicknesses from 3 to 20 μm via iCVD polymerization of monomer 2-hydroxyethyl methacrylate (HEMA) within 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4] [6]. Since HEMA is soluble in [emim][BF4], the monomer can both adsorb and absorb into the IL and therefore polymerization occurs on both the liquid surface and within the interior liquid. A transition from a viscous liquid to a gel was observed with increasing polymer concentration. Molecular weight analysis of the films by gel permeation chromatography showed the presence of low molecular weight polymer chains which formed on the surface and high molecular weight polymer chains which formed within the interior liquid.

In the above gel fabrication study, the monomer and initiator vapors were introduced simultaneously and therefore polymerization occurred at both the surface and within the interior. In this paper, we fabricate gel beads using a sequential deposition process. Sequential depositions are used in processes such as atomic layer deposition (ALD) and molecular layer depositions (MLD) to fabricate thin films [22,23]. The film thickness can be precisely controlled due to the sequential exposure of the substrate to precursors. The sequential processing also provides conformal films on substrates with complex geometries. In ALD and MLD, the precursors are reacted to the underlying substrate. In a typical iCVD process, there is no reaction with the underlying substrate and therefore sequential processing does not lead to film formation because the monomer or initiator will get pumped out between steps. However, we can use sequential processing on a liquid substrate because the liquid can act as a monomer sink. To fabricate the gel beads, the monomer

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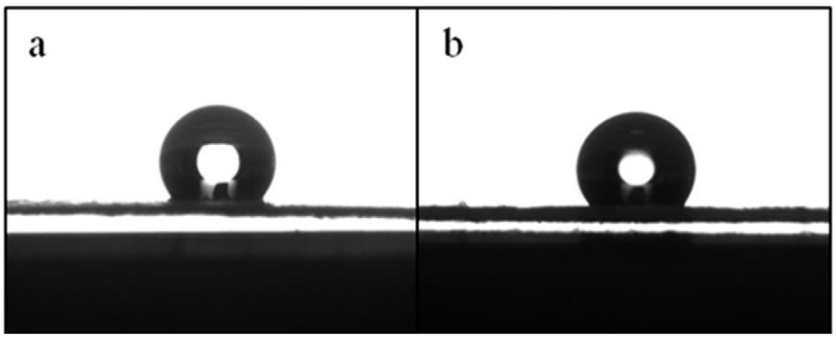

Fig. 1. Contact angle images of a) a water droplet and b) a [emim][BF_4] droplet on chromatography paper coated with PPFDA fluoropolymer.

was first absorbed into the IL and then the initiator was introduced to polymerize the monomer. Since the majority of the polymerization occurs within the liquid, this sequential deposition prevents the formation of a film around the IL and therefore allows the beads to be easily removed from the underlying substrate. Instead of using PTFE particles to stabilize the droplet shape during polymerization, we introduce the concept of using fluorinated chromatography paper as our substrate in order to use surface tension interactions to keep the IL droplets spherical.

2. Experimental

2.1. Polymer deposition

2-Hydroxyethyl methacrylate (HEMA) monomer (98% Aldrich), 1H,1H,2H,2H–perfluorodecyl acrylate (PFDA) monomer (97% Aldrich), 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]), and di-*tert*-butyl peroxide (TBPO) (98% Aldrich) were used as received without further purification. All polymer depositions were performed in a custom built reactor (25 cm diameter, 48 mm height) (GVD Corporation) equipped with a recirculating chiller to adjust the substrate temperature. A nichrome filament array (80% Ni, 20% Cr, Omega Engineering) was placed 3.5 cm above the substrate. Deposition rates were monitored by in situ laser (633 nm helium-neon) interferometry (Industrial Fiber Optics) on a reference silicon wafer. Polymer depositions of poly (1H,1H,2H,2H–perfluorodecyl acrylate) (PPFDA) were performed on a 10 cm × 6 cm piece of chromatography paper (GE Healthcare Life Sciences Whatman™) at a rate of 10 nm/min to alter the wetting properties of the paper. A deposition time of 40 min was chosen to deposit polymer for a total thickness of 400 nm in order to ensure a uniform coating of fluoropolymer over the individual fibers of the porous chromatography paper. The base pressure before starting the deposition was 5.73 Pa. The deposition was performed at a pressure of 10.67 Pa, the PFDA monomer jar was maintained at 50 °C, and the TBPO flowrate was kept at 0.5 sccm using a mass flow controller (Type 1152C MKS). The stage temperature was maintained at 30 °C and the filament array was heated to a temperature of 250 °C.

A two-step process was performed to create the gel beads. 1.5 μl of [emim][BF_4] was pipetted onto a 2 cm × 2 cm square of chromatography paper coated with PPFDA and placed inside the reactor for monomer

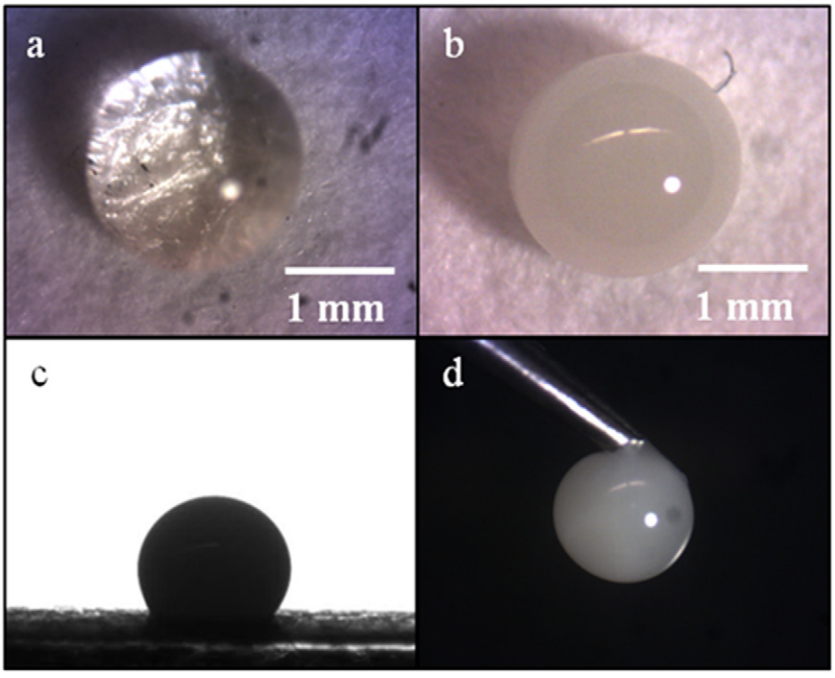

Fig. 2. Top down images of a) a transparent droplet of [emim][BF_4] on PPFDA coated chromatography paper and b) an opaque gel bead composed of PHEMA and [emim][BF_4] after sequential deposition. c) Side view image of the gel bead. d) The gel bead held using a pair of tweezers.