Polymerization of vinyl fluoride in ionic liquid and ionic solutions

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ABSTRACT

Poly(vinyl fluoride) films are extensively used as protective, easy-clean materials in the photovoltaic and aerospace industries. However, polymerization of vinyl fluoride (VF) monomer typically requires high pressures (>5000 psi) due to the low solubility of VF monomer in the aqueous polymerization medium. VF was found to exhibit high solubilities in fluorinated ionic liquids and concentrated aqueous ionic salt solutions at low pressures (<1000 psi). Polymerization of vinyl fluoride in the presence of ionic liquids or ionic salt solutions was pursued as a means of reducing the pressure needed to achieve high monomer conversion and molecular weight. The use of traditional ionic liquids possessing alkylimidazolium cations paired with fluorinated anions as solvents for VF polymerization resulted in poor conversion of vinyl fluoride, likely due to hydrogen atom abstraction from the alkyl substituents on the imidazolium cations. Polymerization of VF in the presence of lithium salts of the ionic liquid anions (trifluoromethylsulfonyl imide [Tf$_2$N], triflate, and trifluoroacetate), on the other hand, resulted in high VF conversion and production of high molecular weight polymer at low VF pressures. The morphology of the resultant polymer consisted of fractal-like aggregates, and mixtures of the polymer with the aqueous ionic salt solutions formed viscous pastes.

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1. Introduction

Poly(vinyl fluoride) (PVF) possesses excellent weatherability, chemical resistance and mechanical properties that enable a range of protective film coating applications [1,2]. In particular, PVF films under the brand name Tedlar® find applications in photovoltaic panels as a protective backsheet, where long term protection from the environment is critical to device function. In addition, Tedlar® is used in aerospace and architectural applications where it serves as a protective, easily cleaned layer.

Traditionally, poly(vinyl fluoride) is synthesized in aqueous emulsion at elevated pressures [1–3]. The need for elevated pressures is driven by the poor solubility of vinyl fluoride in aqueous solution. Past efforts to reduce the pressure of vinyl fluoride polymerizations have included low temperature initiation methods, including use of redox systems [3]. Polymerization at lower temperatures allows lower VF pressures to be used, as VF solubility in water increases with decreasing temperature.

Ionic liquids have increasingly been employed as reaction media in recent years, due to their unique solvation capabilities and ease of separation from reactants, products and byproducts [4,5]. For example, ionic liquids have been successfully used as solvents for radical polymerizations of methacrylate and styrenic monomers [6]. Enhanced polymerization rates and reduced termination rates have been observed, resulting in formation of higher molecular weight polymers. This has been attributed to a reduction in activation energy for polymerization, possibly via stabilization of the transition state via charge transfer complexes [6]. Another hypothesis is that ionic liquids might form a solvation sphere around propagating radicals, creating a "protected radical" [7]. Ionic liquids containing polymerizable groups have also been introduced as monomers in controlled radical polymerization [8], and polymerized ionic liquids have been shown to possess high ionic conductivities [9]. Ionic liquids have also been introduced into block copolymers to produce ion gels with high capacitance for applications in electronics [10].

In the work described here, vinyl fluoride polymerization in the presence of ionic liquids or ionic salt solutions was pursued as a means of reducing the pressure needed to achieve high monomer conversion and generate high molecular weight PVF polymer. Vapor-liquid equilibrium studies showed that VF monomer exhibited high solubility at low pressures in traditional ionic liquids possessing alkylimidazolium cations paired with fluorinated anions. However, use of these ionic liquids as solvents for VF

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polymerization resulted in poor monomer conversion, likely due to hydrogen atom abstraction from the alkyl substituents on the imidazolium cations by radicals present in the polymerization reaction mixture. Therefore, VF polymerization in the presence of lithium salts of the ionic liquid anions (trifluoromethylsulfonyl imide [Tf$_2$N], triflate, and trifluoroacetate) was also explored. The use of Li rather than alkylimidazolium cations in these salts eliminated the abstractable hydrogen atoms, so that VF polymerization in concentrated aqueous solutions of the salts resulted in high VF conversion and production of high molecular weight polymer at low VF pressures. The morphology of the resultant polymer differed from that of PVF synthesized in pure water; fractal-like aggregates were formed, and mixtures of the polymer with the aqueous ionic salt solutions formed viscous pastes.
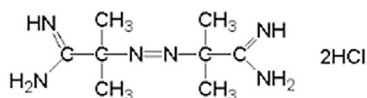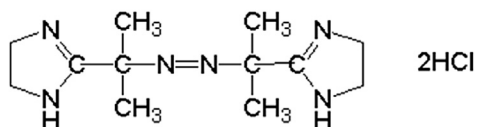
2. Experimental

2.1. Materials

Vinyl fluoride (VF, H$_2$C=CHF, R-1141, molecular weight 46.044 g mol-1, CAS no. 75-02-5) with a minimum purity of 99.9% was obtained from DuPont Fluorochemicals (Wilmington, DE). D-limonene is added to VF as stabilizer during storage and was removed via passage over silica prior to reactions. Initiators VA-044 and V-50 were obtained from Wako Pure Chemical Industries, Ltd. and the chemical structures are shown in Fig. 1. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim] [Tf$_2$N], C$_8$H$_{11}$F$_6$N$_3$O$_4$S$_2$, molecular weight 391.31 g mol^{-1}, CAS no. 174899-82-2, Lot and Catalog no. 259095 IL-201-20-E) with a minimum purity of ≥99.5% (electrochemical grade) was purchased from Covalent Associates Inc. (Corvallis, OR). 1-butyl-4-methylpyridinium tetrafluoroborate ([bmpy][BF$_4$], C$_{10}$H$_{16}$BF$_4$N, molecular weight 237.05 g mol^{-1}, CAS no. 343952-33-0, Lot code H00223-2) with a minimum purity of ≥99% was purchased from IoLiTec, Inc. (Tuscaloosa, AL). 1-butyl-3-methylimidazolium 1,1,2,3,3,3-hexafluoropropanesulfonate ([bmim][HFPS], C$_{11}$H$_{16}$F$_6$N$_2$O$_3$S, molecular weight 370.31 g mol^{-1}) with a minimum purity of ≥99% was synthesized at DuPont [11]. 1-octyl-3-methylimidazolium 1,1,2,2-tetrafluoroethanesulfonate ([omim] [TFES], C$_{14}$H$_{24}$F$_4$N$_2$O$_3$S, molecular weight 376.41 g mol^{-1}) with a minimum purity of ≥99% was also synthesized at DuPont [11]. Lithium bis(trifluoromethylsulfonyl)imide (LiTf$_2$N, LiC$_2$F$_6$NO$_4$S$_2$, molecular weight 287.09 g mol^{-1}, CAS no. 90076-65-6, Lot no. J00520.4 and Catalog no. K1-0001-HP-25) with a minimum purity of ≥99.0% was purchased from IoLiTec (Ionic Liquid Technologies GmbH, Heilbronn, Germany).

2.2. Safety note

VF is highly reactive, flammable, and toxic and should be

V-50 initiator:

VA-044 initiator:

Fig. 1. Structures of initiators V-50 and VA-044 used in this work.

handled with EXTREME CAUTION! Only highly trained professionals with proper facilities and safety procedures should work with VF. All experiments with VF were conducted in an explosion-proof barricade with proper personal protective equipment. Samples were disposed of by incineration.

2.3. Binary VLE measurements

The gas solubility or vapor–liquid equilibria (VLE) of VF in [emim][Tf$_2$N], in aqueous solutions containing LiTf$_2$N, and in water was measured using a glass equilibrium cell [12]. The glass equilibrium cell has a known volume and is agitated so that the upper phase (gas or liquid) mixes into the lower liquid phase. A known amount of [emim][Tf$_2$N], LiTf$_2$N + H$_2$O, or H$_2$O was loaded into the cell and evacuated to degas the head space. Using the density of the fluid, the volume of the liquid-phase was calculated, and the difference from the initial glass cell volume was used to calculate the vapor space volume. A known amount of VF was then fed into the cell while the temperature was held constant with a circulating oil bath. The pressure in the cell was measured and recorded over time. When the pressure stopped changing, the cell was taken to be at equilibrium and the amount of VF absorbed by the fluid in the cell was calculated by taking into account the amount of VF in the equilibrium cell vapor space. When VF was mixed with [emim] [Tf$_2$N], the vapor space was assumed to contain only VF because ionic liquids have extremely low vapor pressure. When VF was mixed with water or LiTf$_2$N + H2O, the vapor pressure of water was taken into account in the calculations. The liquid composition was determined from the total amounts of the components added minus the small amount of VF present in the vapor phase. The instrumental uncertainties in T and P were within ±0.2 °C and ±0.8%, respectively [13]. The absolute error in the mole fractions was therefore less than 0.003 at any given T and P [13]. Details of the experimental equipment and procedures have been published [12–15].

2.4. Polymerizations

VF polymerizations were conducted under semi-batch conditions in a 1 L autoclave. The autoclave was bullet-shaped, 9 inches (22.86 cm) high by 3 inches (7.62 cm) in diameter and was constructed from Hastelloy C. The volume of the autoclave and piping directly above it was measured at 1015 mL. The autoclave was heated resistively, by heating tape wrapped around it, and cooled by water flowing through a small (single loop) cooling coil inserted into the reactor. Stirring was achieved with a large ribbon agitator. Besides the agitator and the cooling coil, the autoclave was equipped with a baffle, a thermowell into which a thermocouple was inserted to measure internal reaction temperature, a VF feed line, an initiator solution feed line, and a dip tube used to empty the reactor. If the reaction mixture was a liquid or fluid emulsion, nitrogen pressure was applied to the reactor to push the reaction mixture out through the dip tube after the run into a collection vessel. VF was fed to the reactor from a chilled 500 mL Isco pump, while aqueous initiator solution was fed to the reactor from a 260 mL Isco pump. Initiator was added at a set flow rate, while VF was fed on demand to maintain the set pressure, until a predetermined amount of VF had been fed (typically 25 or 50 g).

A "boil-out" was conducted before runs to scavenge impurities that might react with and quench PVF radicals. 3 g of V-50 initiator dissolved in 500 mL of degassed, deionized water was added to the autoclave, purged with nitrogen gas, and then heated to 90 °C for 3 h. After the boil-out, the reactor was cooled to 30 °C, and the spent V-50 solution was forced out of the reactor through the dip tube with nitrogen pressure, without opening the reactor or