



Short communication

# Styrene polymerization efficiently catalyzed by iron-containing imidazolium-based ionic liquids: Reaction mechanism and enhanced ionic liquid effect


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## ABSTRACT

Iron-containing imidazolium-based ionic liquids were successfully applied as catalysts in the styrene polymerization. Solventless conditions, organic solvents and different imidazolium-based ionic liquid catalysts were tested to evaluate the best reaction conditions. The ionic liquids BMI.FeCl<sub>4</sub> and BMI.Fe<sub>2</sub>Cl<sub>7</sub> showed very distinct catalytic activities. Schulz–Flory distributions indicate two or three active catalytic species in different distributions. Via on-line direct infusion electrospray (tandem) mass spectrometry (ESI-MS(/MS)) reaction monitoring, both active catalytic species in accordance with the Schulz–Flory distributions were intercepted and characterized, providing important mechanistic insights that allowed us to propose a rationale for the origin of the superior catalytic efficiency.

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## 1. Introduction

Without doubt, polymers are crucial materials of increasing demand in modern society life. It is therefore mandatory for us chemists to develop highly active catalysts for key polymerization reactions. The finding of new and highly efficient catalysts for polymerization reactions has been, however, a great challenge in modern chemistry [1]. Due to safety and ecological reasons, this search has been also focused on non-toxic and more active and selective catalysts [2]. Non-toxic and environmentally bearable metals have also been tested as a viable alternative to other more expensive metal-containing catalysts [3]. For instance, catalysts containing metals such as scandium, molybdenum, copper, nickel, manganese, and others have been successfully employed. Catalysts based on one of the earth most abundant and cheapest metal, that is iron, have been also tested to overcome safety, ecological and toxicity drawbacks associated with this polymerization reaction [4], especially for the radical polymerization processes [5]. But the search still continues for more active iron-based catalysts able to operate under more sustainable conditions.

Styrene is a versatile monomer that undergoes free radical, anionic, cationic or metal-catalyzed polymerization processes. Polystyrene homopolymer, generally known as general-purpose polystyrene (GPPS), is one of the most important thermoplastic polymer commodity widely produced all over the world. As main features, GPPS commonly exhibits high glass transition temperature, stiffness, brilliance, gloss, hardness and high refractive index. Another important class of polystyrene, commonly named as high-impact polystyrenes (HIPS) (or simply impact-modified polystyrene, IPS), has been developed in order to overcome the undesirable brittleness of traditional GPPS by the incorporation of an elastomer polymeric phase into the polystyrene thermoplastic phase. HIPS polymers, as for instance, acrylonitrile–butadiene–styrene (ABS), acrylonitrile–styrene–acrylate (ASA), styrene–acrylonitrile (SAN) copolymers, MABS (methyl methacrylate–acrylonitrile–butadiene–styrene) and MBS (methyl methacrylate–butadiene–styrene) deserve more attention. Nowadays, most GPPS and HIPS commodities are produced using free radical initiators in homogeneous phase (bulk or solution) or in heterogeneous phase (suspension or emulsion) polymerizations systems, carried out in a continuous (homogeneous system) or batch mode (heterogeneous system).

Ionic liquids (ILs), mainly those based on 1,3-dialkylimidazolium cation are regarded as environmentally acceptable reaction media [6]. Indeed, ILs are already successfully applied in the chemical industry, as reviewed elsewhere [7]. ILs derived from the imidazolium cation, such

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as BMI.PF<sub>6</sub> (1-*n*-butyl-3-methylimidazolium hexafluorophosphate), BMI.BF<sub>4</sub> (1-*n*-butyl-3-methylimidazolium tetrafluoroborate) and BMI.NTF<sub>2</sub> (1-*n*-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide), are commonly used as effective reaction media in catalysis [8].

ILs are also successfully applied as reaction media for catalytic polymerization reactions [9], and radical and cationic polymerizations of styrene have been reported in these ionic fluids [10,11]. We have already demonstrated the advantages of combining Lewis acid properties of transition metals (such as indium) with imidazolium derivatives in a single structure. For instance, we have shown that BMI.InCl<sub>4</sub> is capable of promoting the tetrahydropyranlation of alcohols [12], in situ generation and stabilization of iminium ions [13] and to co-promote the formation and stabilization of charged-intermediates during transesterification reactions [14]. We have also recently investigated iron-based ILs as catalysts for oxidation [15], reduction [16] and multicomponent reactions [17–19]. In this sense, we have therefore envisaged that the iron-containing ILs could also work as efficient catalysts for the styrene polymerization. Herein, we disclose the catalytic properties of two of such ILs (named BMI.FeCl<sub>4</sub> and BMI.Fe<sub>2</sub>Cl<sub>7</sub>) for the styrene polymerization, proposing a plausible mechanism for their catalytic action and the importance of the IL effect on this key polymerization reaction.

## 2. Experimental

Polymerization reactions were carried out in sealed assay tubes, organized in two main groups: (i) bulk polymerization reactions performed with 44 μmol of catalyst (14 mg BMI.FeCl<sub>4</sub> or 20 mg of BMI.Fe<sub>2</sub>Cl<sub>7</sub>), 5 mL of vacuum fresh distilled styrene (44 mmol) and temperatures ranging from 30 °C to 85 °C under an inert nitrogen atmosphere (to keep the reaction environment free of oxygen) and constant magnetic agitation; (ii) homogeneous phase reactions carried out in BMI.NTF<sub>2</sub> employed as reactional supports, 44 μmol of catalyst (BMI.FeCl<sub>4</sub> or BMI.Fe<sub>2</sub>Cl<sub>7</sub>), 5 mL of vacuum fresh distilled styrene monomer and reaction temperature between 30 °C and 85 °C under nitrogen gas and constant magnetic agitation. Additional polymerization were also carried out with the different molar ratio of catalyst:monomer in the range from 1:1000 to 1:10,000; in common solvents such as toluene or water.

Average molar masses ( $\overline{M}_w$  and  $\overline{M}_n$ ), molar mass dispersity ( $\mathcal{D}_M$ ) and molar mass distributions (MMDs) of the polymer samples were determined through gel permeation chromatography (GPC) on a Viscotek GPCmax™ (Malvern Instruments Ltd, Worcestershire, United Kingdom) equipped with a refractometer detector, an injection loop of 200 μL, four linear separation columns presenting gel porosity in the range of 10<sup>3</sup> Å to 10<sup>6</sup> Å, inline degasser, a pump, and an autosampler. Polystyrene solutions of concentration ranging from 1.0 g/L to 1.5 g/L were prepared with dry samples. The GPC analyses were carried out in THF as a mobile phase with a flow rate of 1 mL min<sup>-1</sup> at 40 °C. The calibration curve was built using standard polystyrene samples with molar-mass dispersity close to 1 and mass-average molar masses in the range from 3 × 10<sup>3</sup> to 1.85 × 10<sup>6</sup> g mol<sup>-1</sup>.

The surface morphology of polystyrenes was characterized by scanning electron microscopy (SEM) on a FEI Quanta 200 Scanning Electron Microscope (FEI Company, Oregon, USA).

Thermal transitions of the polystyrene samples were characterized by differential scanning calorimetry (DSC) on a Shimadzu DSC-60 calorimeter (Shimadzu Scientific Instruments, Maryland, USA) at heating rates of 10 °C min<sup>-1</sup> under helium atmosphere with a flow rate of 30 mL min<sup>-1</sup>. The DSC analyses were performed using polystyrene samples ranging from 8.0 mg to 10.0 mg, sealed into aluminum crucibles.

ESI-MS and ESI-MS/MS measurements were performed in the positive ion mode (*m/z* 50–2000 range) on a HDMS Synapt G1 instrument. This instrument has a hybrid quadrupole/ion mobility/orthogonal acceleration time-of-flight (oa-TOF) geometry and was used in the TOF V+ mode. All samples (reaction monitoring) were dissolved in

methanol and were directly infused into the ESI source at a flow rate of 15–20 μL min<sup>-1</sup>. ESI source conditions were as follows: capillary voltage 3.0 kV, sample cone 20 V, extraction cone 3 V. Collision energies were optimized to get the most comprehensive set of fragments for all MS/MS analyses.

## 3. Results and discussion

The syntheses of the known BMI.FeCl<sub>4</sub> and BMI.Fe<sub>2</sub>Cl<sub>7</sub> ILs [20] were carried out as depicted in Scheme 1. Both BMI.FeCl<sub>4</sub> and BMI.Fe<sub>2</sub>Cl<sub>7</sub> were obtained in quantitative yields.

Initially, both BMI.FeCl<sub>4</sub> and BMI.Fe<sub>2</sub>Cl<sub>7</sub> were tested as the catalyst for the styrene polymerization reaction. However, when BMI.FeCl<sub>4</sub> was used as the reaction media (2 mL – not catalytic), no styrene polymerization could be noted at 85 °C. The reaction was also conducted using BMI.FeCl<sub>4</sub> as catalyst and benzoyl peroxide (10 mol%) as an initiator, but only a poor polystyrene yield was obtained. We concluded therefore that BMI.FeCl<sub>4</sub> failed to act as an efficient catalyst for styrene polymerization.

Fortunately, BMI.Fe<sub>2</sub>Cl<sub>7</sub> proved to be a very active catalyst, as Table 1 summarizes.

Noted that, even at low molar ratio concentration of 1:1000 (catalyst:monomer), the yield of the polymer is 71% in only 15 min of reaction (Table 1, Entry 1). Using the ratio of 1:10,000, the catalyst still displays a good activity (Table 1, Entry 10) yielding the polymer in 40%, but in a longer reaction time (120 min), but many catalysts currently used for such polymerization require many hours of reaction to yield polystyrene yields above 80% (see the cited reviews).

The possibility of an IL effect in the polymer formation and the best temperature to promote the reaction were also investigated (Table 2). The temperature effect was also investigated under solventless conditions to check for a positive IL effect (Fig. 1). Reactions performed in BMI.BF<sub>4</sub> were also carried out and gave poor yields. Therefore, we decided to keep the study using BMI.PF<sub>6</sub> and BMI.NTF<sub>2</sub> as the ionic media, which showed excellent results (Table 2 and Fig. 1).

Fig. 1 shows that the higher the reaction temperature, the higher the polymerization yield, as a likely result of the higher efficiency of the catalyst. Clearly therefore, the IL effect plays an important role in the formation and stabilization of the reaction intermediates, as discussed below.

The effect of the IL as reactional media also should be considered regarding its high capacity of heat removal from the reaction system during polymerization. BMI.PF<sub>6</sub> and the BMI.NTF<sub>2</sub> provided better stability of the reaction medium likely via the aid of their ion pairs (and larger supra-molecular aggregates), reducing the medium viscosity (which naturally increases as a consequence of the growing polymer chains), contributing to the minimization of undesirable viscosity (gel and glass) effects as the mobility of the monomer [21]; therefore the growing polymer chains are enhanced, resulting in higher styrene conversions.

Comparatively, BMI.NTF<sub>2</sub> displayed better performance than BMI.PF<sub>6</sub>. The anion effect is therefore a possible reason for this difference. [NTf<sub>2</sub>]<sup>-</sup> is known to be much less coordinating than [PF<sub>6</sub>]<sup>-</sup> [22], and therefore, it is maintained more available for the stabilization of cationic intermediates.

As Table 2 summarizes in Entries 8 and 9, polymerizations were also performed in toluene and water. Toluene is commonly employed as a solvent in the solution polymerization of styrene and aqueous media are generally used as continuous phase in heterogeneous suspension styrene polymerizations. Very low conversions of styrene were attained in solution polymerizations carried out in toluene and water at 70 °C and 80 °C after 15 min of reaction, exhibiting only traces of polystyrene. Although high styrene conversions were achieved, the reaction times were considerably larger, that is, 77 h for toluene with a conversion of 96% and 22 h for water with a conversion of 90%. The significance of the IL effect on the styrene polymerization and for the catalyst performance is therefore evident.

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