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# Poly(ionic liquid) prepared by photopolymerization of ionic liquid monomers as quasi-solid-state electrolytes for dye-sensitized solar cells

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ABSTRACT

Vinylimidazolium-typed poly(ionic liquids) (PILs) are prepared by photo-polymerization of ionic liquid monomers. Vinylimidazolium-based ionic liquid monomers with C4 and C8 alkyl tail length were synthesized via quaternization of 1-vinylimidazole with corresponding *n*-alkyl bromides. Polymerization was conducted at a 3 wt.% of photoinitiators in these monomers using illumination of 36 W LED light. In the same procedure, preparation of cross-linked PILs was performed in the presence of 15 mol% of divinylimidazolium-based cross-linker. These PILs are characterized by using chemical structure, physical characteristics, and electrical conductivity. Electrical conductivity of $C_4$-based PILs is greater than that of $C_8$-based PILs, whereas linear PILs are higher than crosslinked PILs. Crosslinked PILs have higher glass transition and thermal decomposition temperatures as compared linear PILs. PILs consist of the repeating units of anion and cation pair. Its nature has moderate electronic conductivity, which is suitable use in gel-type or quasi-solid-state dye-sensitized solar cells (DSSCs). The linear PILs were incorporated in DSSCs obtaining an efficient quasi-solid-state cell to solve the leakage of liquid electrolyte in a liquid-type DSSC.



## 1. Introduction

Ionic liquids (ILs) are composed of an organic cation and an anion, existing fluid state over a wide temperature range with low melting point below 100 °C. PILs have attracted attention to study their creating characteristics of properties and functions, such as excellent ionic conductivity, strong polarity, high heat capacity, outstanding solubility, superior thermal and chemical stability [1–6]. Some ionic liquids are especially suitable for applications in electrochemical systems from which moisture must be excluded over long-term operation. And, some ionic liquid derivatives present plastic solid state having reasonable conductivity at room temperature [7], or other some can be altered into soft, elastomeric solids at room temperature by adding small amounts (~5%) of a suitable polymer [8].

Polymeric ILs (PILs) belong to a special kind of polyelectrolytes, connecting an IL species in each of the repeating units. The rapid development in the related field can be confirmed by recent many publications [9–11]. From the point of view of macromolecular design, the superiority of a PIL has the enhanced mechanical stability, processability, durability, and spatial controllability over an IL. Promising applications of PILs involve energy harvesting and storage [12–20], thermoresponsive materials [21–24], catalysts [25–28], optical materials [29].

Imidazolium-based PILs are the most studied materials such as poly(1-vinylimidazolium) [30–34], which were generally prepared by free radical polymerization of the corresponding IL monomers. Photopolymerization is similar to the free radical polymerization instead of no solvent addition. Other polymerization techniques have also been proposed to synthesize PILs for further particular features [35].

In this work, we report a simple method to prepare linear PILs via photopolymerization of vinylimidazolium-based ionic liquid monomers. Crosslinked PILs were also produced in the same steps with adding 15 mol% of di-vinylimidazolium-based crosslinker. The electrical conductivity of these PIL films was measured as a function of temperature. It is worth noticed that the potential application of linear PILs as quasi-solid-state electrolytes was demonstrated in DSSC devices.

## 2. Experimental

### 2.1. Materials

1-Vinylimidazole (Alfa Aesar 99%), 1-bromooctane (Across 99%), 1-bromobutane (Alfa Aesar 98%), 1,4-dibromobutane (Alfa Aesar 99%), and photoinitiators: diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide (TPO, Darocur), 1-hydroxy-cyclohexyl-phenyl-ketone (Irgacure

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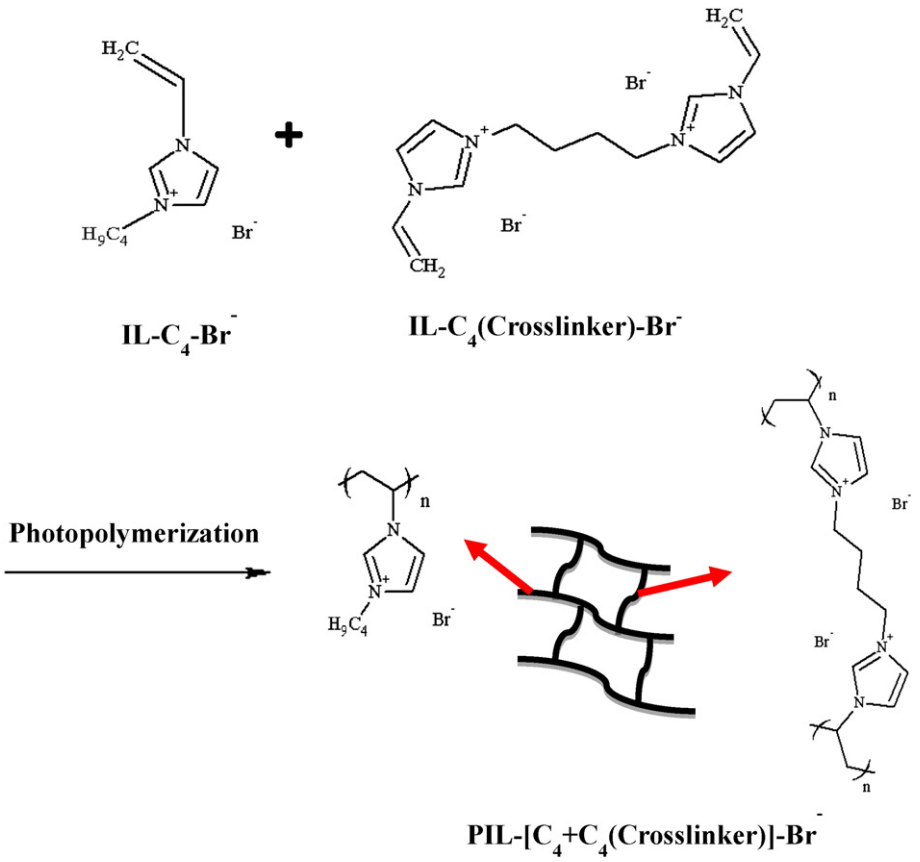
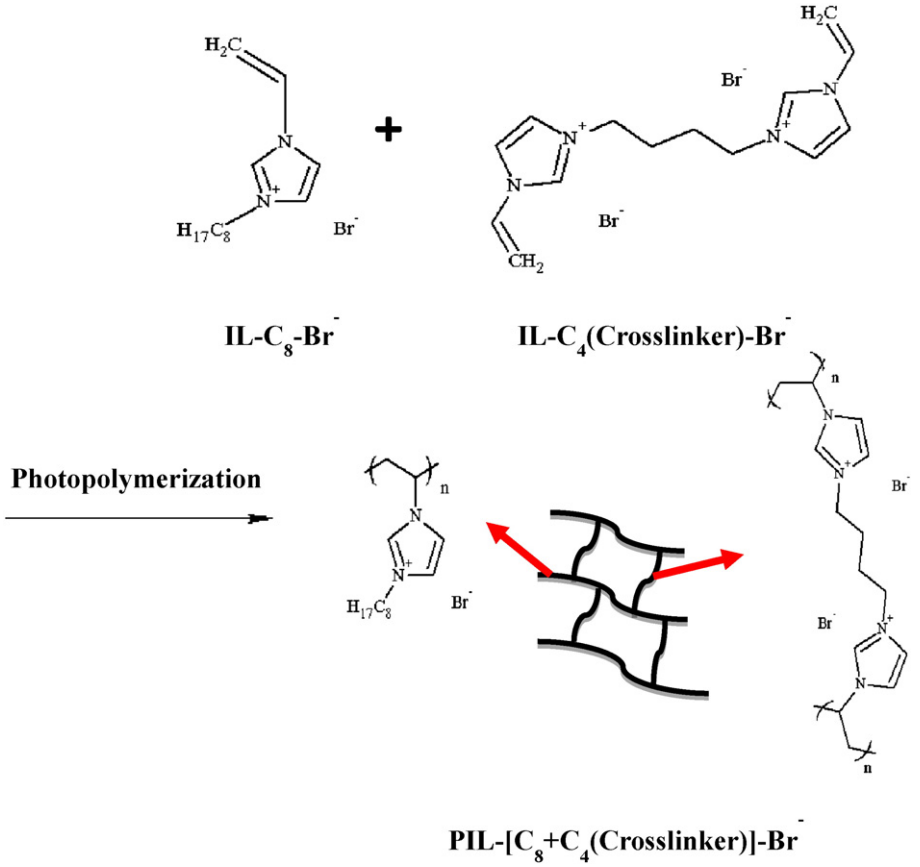



**Scheme 1.** Preparation of crosslinked PIL of PIL-[$C_4$ + $C_4$(Crosslinker)]-$Br^-$.




**Scheme 2.** Preparation of crosslinked PIL of PIL-[$C_8$ + $C_4$(Crosslinker)]-$Br^-$.