

## Synthesis of Polymerizable Ionic Liquid Monomer and Its Characterization

Jagannath Sardar<sup>1</sup>, Uno Mäeorg<sup>2</sup>, Illia Krasnou<sup>1</sup>, Vikram Baddam<sup>1</sup>, Viktoria Gudkova<sup>1</sup>, Andres Krumme<sup>1\*</sup>, Natalja Savest<sup>1</sup>, Elvira Tarasova<sup>1</sup> and Mihkel Viirsalu<sup>1</sup>

<sup>1</sup> Tallinn University of Technology, Department of Polymer Materials, 19086 Tallinn, Estonia.

<sup>2</sup> University of Tartu, Institute of Chemistry, 50411 Tartu, Estonia.

\*Any correspondence to be made: Andres.Krumme@ttu.ee, Phone: +372 6202907

### Abstract:

The polymerizable monomer of 1-(6-hydroxyhexyl)-3-methylimidazolium bromide ionic liquid (IL) was synthesized. The thin layer chromatography tests were conducted at each step to verify the reactions. It was observed that the ionic liquid compound formed after 48 hours though confirmed the presence of starting materials. A high viscous transparent liquid was extracted and believed to be formed of 99% yielding of ionic liquid. Apart from that, the synthesis of ionic liquid was also performed using microwave treatment and heating to stimulate the reaction. Surprisingly, it was observed that the reaction was taking place within a fraction of second when the synthesis process was conducted with microwave treatment. In the second step, esterification IL with methacryloyl chloride was done to obtain monomer of polymerizable ionic liquid (m-PIL). The final product was a high viscous yellowish liquid.

**Keywords:** Synthesis, polymerization, ionic liquid, polyionic liquid

### 1. Introduction

The synthesis of polymerizable ionic liquids (PILs) is a challenging objective and has drawn an intense attraction for its uniqueness such as mechanical durability, excellent ionic conductivity and low glass transition temperature ( $T_g$ ) which make suitable to employ in electrospinning process and other emerging technology [1-2]. Over the fifteen years, researches going on to polymerize the ionic liquids in various methods. It is observed that the ionic conductivity drops repeatedly after polymerisation due to decrease of mobility of ions in the medium [1]. Owing to enhance the electrical conductivity, preliminary IL can be blended with PILs monomer [3]. The PILs can be classified into several events by their polymerization manner such as polyanion and polycation type ILs, polyzwitterion type IL, copolymer type IL, cross-linked PILs etc. PILs can be synthesized via two basic strategies direct polymerization of IL monomers and chemical modification of existing polymers. A polymerizable unit can be located in an ILs monomer conjugated either with cation or with anion, solely depending on the architecture of desired polymeric constituents [4]. These processes can be employed by several methods such as free radical polymerization to homopolymer or cross-linkable ILs, copolymerization, in-situ polymerization/post-processing polymerization and other polymerization methods [4-6].

We made synthesis of imidazolium-bromide based PIL, introducing an effective functional group of the methacrylate into synthesized IL backbone capable for next polymerization [2]. The higher alkyl chain lengths between imidazolium cation and polymerizable entity the higher the spacer length which enhance electrical conductivity of the polymerized material [2, 7]. The main objective of the work has been specified by two steps: (a) synthesis of IL using 1-methyl imidazole by alkylation with 6-bromo-1-hexanol and (b) synthesis of PIL monomers using methacryloyl chloride followed by esterification of the alkylimidazole ionic liquid of the previous step.



## 2. Materials and Methods

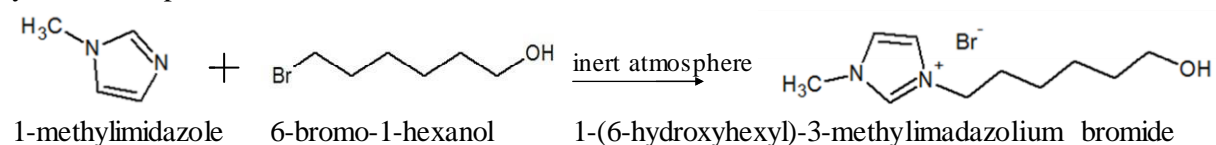
### 2.1. Synthesis of IL (1-(6-hydroxyhexyl)-3-methylimidazolium)

In accordance to the initial step to synthesis ionic liquids, 1-methylimidazole (Sigma-Aldrich) and 6-bromo-1-hexanol (Aldrich) were used as received. The detailed procedure formulated to synthesis the ILs can be found in the following statements:

Initially, 6-bromo-1-hexanol was taken in a round bottom flask. The weight of the chemical was noted as 4.79 g equivalent to 0.0264 moles, calculated according to molecular weight (Mw: 181.07 g/mole). To keep the molar ratio of 1:1, methylimidazole was measured as 2.166 g equivalent to 0.0264 moles (Mw: 82.10 g/mole). Methylimidazole was added to bromohexanol dropwise. The mixture flask was kept at room temperature filled with Argon gas and stirred mechanically using magnetic stirrer in order to synthesis the alkylated IL. This step takes 48 hours.

To control the reaction mixture the thin layer chromatography was conducted time after time in a predefined time span. The chromatographic tests were also done for the starting materials.

The possible reaction between bromohexanol and imidazole has shown in the Figure 1 the reaction yielded transparent viscous solution.



**Figure 1:** Synthesis of alkylated IL: Chemical reaction and yielded transparent compound

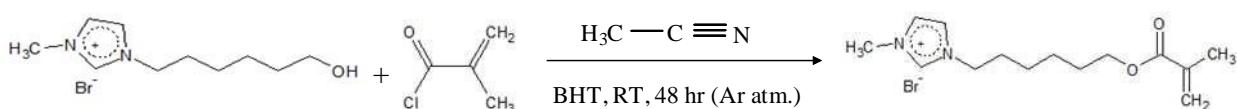
In the next step the IL compound was kept in vacuum for 12 hours at 1.1 mbar pressure in order to remove the unwanted substrates. The final IL was washed out thoroughly with toluene for three times in order to remove the starting materials (imidazole and bromohexanol) and hence vacuumed at the same pressure for another 12 hours. Final yield of the product after vacuumed was measured approximately 6.46 g.

### 2.2. Synthesis of PIL (1-[(6-methacryloyloxy) hexyl]-3-methylimidazolium bromide)

All next described processes were done under Argon atmosphere. Synthesized 1-(6-hydroxyhexyl)-3-methylimidazolium bromide was taken into the round bottomed flask (6.41g) and suspended into 37.66 ml of acetonitrile. In order to stabilize and prevent localized oxidation 1.25 mg of BHT (2,6-di-tert-butyl-p-cresol) was added into the mixture. The mixture was set on ice bath to prevent uncontrolled exothermal reaction during mixing of components.

Methacryloyl chloride (5.11 g) was taken in another round bottom flask and 5 ml of acetonitrile was added. This solution was added dropwise into the reaction flask with IL. After mixing of components the reaction mixture was leaved to warm up to room temperature and stirred for 48 hr.

**Figure 2.** Synthesis of PIL: chemical reaction and yielded compound (1-(6-hydroxyhexyl)-3-



methacryloyl chloride, 1-[(6-methacryloyloxy) hexyl]-3-methylimidazolium bromide and methylimidazolium bromide).

After 48 h the solution was dried out using condenser reflux in order to remove unreacted chemicals and gases. In order to remove excess of methacryloyl chloride, BHT and acetonitrile, product was washed for three times with diethyl ether ( $3 \times 10$  ml) and kept 12 hours at vacuum. The yielded m-PIL was extracted as high viscous yellowish liquid. The probable reaction was shown in the Figure 2.

### 3. Thin Layer Chromatography

Thin layer chromatography (TLC) is an advanced technique to identify the chemicals and compounds. Nevertheless, this technique gives bold information about the nature of the substrates as well as highlights the stability of the chemical structure. It also separates non-volatile mixtures and determines the purity of the chemicals [8-11]. This technique boosts the idea in order to determine the polarity of the applied substrates [12].

In the present work, the TLC analyses were carried out on aluminium-backed  $65 \times 25 \times 0.2$  mm plate of improved resolution silica sheets (Alugram®Sil G/UV254, Macherey-Nagel). Development was performed in a developer glass chamber with glass lid. The chamber dimensions of 70 mm tall and 40 mm inner diameter, containing only a minimal volume of the eluent solvent.

Initially the substance was dissolved with suitable solvent in 2 ml Eppendorf tube. For this study, specifically, methanol was used to dissolve IL compound and ethyl acetate for starting chemicals, imidazole and bromohexanol. The detailed of suitable dissolved solvent and eluent solvents have been listed in the Table 1.

**Table 1.** Relevant solvents for dissolution and eluent solvents for TLC

Compound	Solvent used for dissolve	Solvent taken in TLC chamber
1-methylimidazole	ethyl acetate	90% ethyl acetate + 10% methanol
6-bromo-1-hexanol	ethyl acetate	90% ethyl acetate + 10% methanol
1-(6-hydroxyhexyl)-3-methylimidazolium bromide	methanol	90% ethyl acetate + 10% methanol
AIBN (azobisisobutyronitrile)	methanol	85% hexane + 15% methanol
2-hydroxyl-2-methyl propiophenone (Mw: 164.20 g/mole)	methanol	85% hexane + 15% methanol

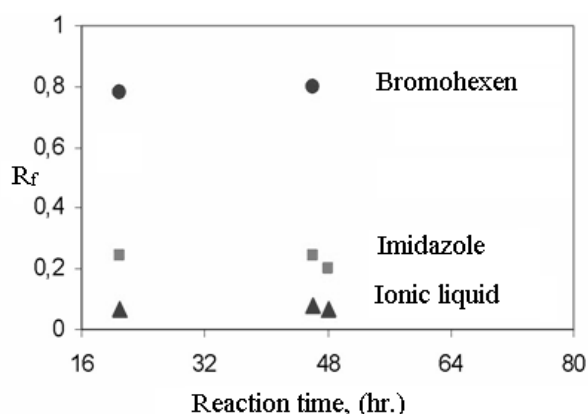
In the developer chamber, the eluent solvent 90% ethyl acetate + 10% methanol was taken for 1-methylimidazole, 6-bromo-1-hexanol and 1-(6-hydroxyhexyl)-3-methylimidazolium bromide (IL), whereas, 85% Hexane + 15% methanol was taken as solvent for AIBN (Azobisisobutyronitrile) 2-hydroxyl-2-methyl propiophenone.

At the first step of TLC, the compound or the starting substances of 2-4  $\mu\text{L}$  were applied using capillary tube to the TLC plate at marked starting line. The TLC plate was placed vertically with slight inclination in the developer chamber in such a way so that the starting line should not be immersed into eluent solvent. The solvent, thus, allowed to elute through Silica gel contained TLC.

After a certain time, the TLC plate was taken out from the chamber and marked the finishing line of the eluent and examined under fluorescent light. If the spot unidentified under fluorescent light, the TLC plate was plunged into potassium di-chromate ( $\text{KMnO}_4$ ) or Phosphomolybdenum acid solution to identify the resultant spots.

### 4. Results and discussion

In the preliminary experiment, imidazole and bromohexanol were tested with TLC. The mixed solvent contained 90% of Ethyl acetate and 10% of Methanol. Further, the spot was contrasted by exposure in  $\text{KMnO}_4$  solution. The samples of IL were also tested by TLC to identify the starting materials residues. The presence of starting materials in final product proved that the reaction yielding less than 100%. The starting materials removed from the compound after three times wash with toluene.



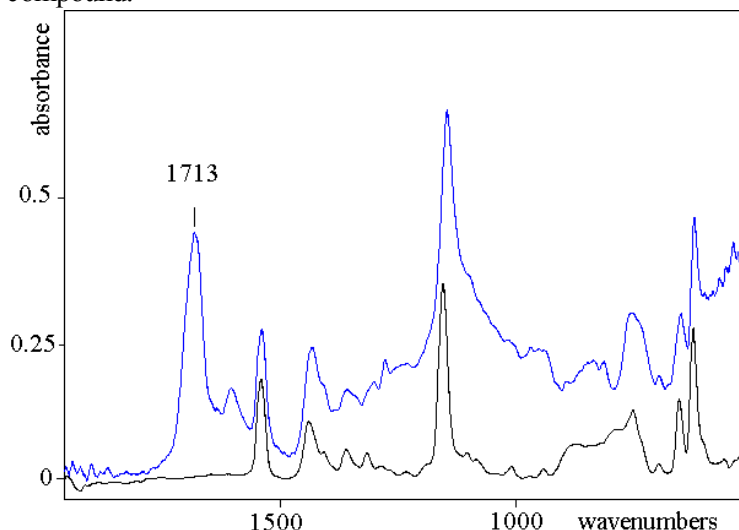
**Figure 2.** Variation of Rf of starting materials and the synthesized ionic liquid.

In order to predict the polarity behaviour of the chemicals, it was observed that the bromohexanol has the less polar nature as compared to imidazole and the reaction compound i.e. IL has the highest polarity than imidazole as well as bromohexanol. Similarly, the initiator for polymerization, hydroxy propeophenon and AIBN were also used to predict polarity. One can notice that the hydroxy propeophenon has high polarity as compared to AIBN.

From the TLC results the retention factor (Rf) was calculated and plotted in the Figure 2. From the figure, it was observed that the bromohexanol is less polar, as compared to imidazole, whereas ionic liquid shows the highest polarity.

The above mentioned process, in order to synthesize of ILs was also conducted using microwave treatment to reduce the duration of reaction. Eventually, it was observed that the reaction was taking place a fraction of second when microwave was used. The yield compound was extracted as light brown viscous liquid which could evidence decomposition of reaction substances. The TLC tests were also conducted in the similar manner and the results are demonstrated that the starting chemicals are present in the yield compound of ILs in a significant amount. It is to be believed that the starting materials can be removed by washing of the reaction compound using toluene.

The heat induced synthesis of IL was done temperature at 80 °C. In this process the time was predefined for 24 hours. The mixture of the starting chemicals, imidazole and bromoethanol were taken in a round bottom flask and kept in an oil bath in order to maintain exact temperature. The IL compound was turned to a solid salt when it contacted the air, presuming the oxidation of the compound.



**Figure 3.** FT-IR of synthesized PIL.

The TLC tests were also conducted for the yielded PIL as well. Surprisingly it was observed that the IL (1-(6-hydroxyhexyl)-3-methylimidazolium bromide) and PIL (1-[(6-methacryloyloxy)hexyl]3-methylimidazolium bromide) showed the same polarity. It was also observed that PIL and IL cannot be separated in TLC. In the Figure 3, the FT-IR spectra is represented to verify the polymerizable group formed in the synthesized PIL. The peak at 1713 cm<sup>-1</sup> for PIL was assigned to the C=O stretching mode of the methacrylate group.

## 5. Conclusions

Synthesis the polymerizable ionic liquid 1-[(6-methacryloyloxy)hexyl]3-methylimidazolium bromide were successfully conducted. The reaction compound was yielded as transparent viscous liquid. To identify the nature of reaction compound and prove its structural evidence, several chromatographic tests were conducted followed by the principle of thin layer chromatography (TLC) and the results were discussed with relevant features and probable reasons. From the TLC results, it could be anticipated that the IL compound is polar, whereas, the starting materials are nonpolar.

The synthesis of IL was also conducted in microwave irradiation in order to reduce the reaction time. Unfortunately the reaction went not fully and side reactions were observed, thus microwave treatment necessitate individual investigation. The synthesis process was also conducted with heat treatment for 24 hours at 80 °C. The yield compound was observed as solid salt structure when the liquid comes in contact with air. The probable reason is as the oxidation of the ILs under heat.

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