

## Synthesis of New Bromine Ion-Containing Monomers Based on Metacrylic Acid

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**Abstract:** Article is dedicated to the synthesis of ion-liquid monomers (IL) based on methacrylic acid reacting with alkyl halides and diethylaminoethanol. Structure obtained IL monomers confirmed by IR and NMR spectroscopy.

**Key words:** Ionic liquid, ionic liquid monomer, methacrylic acid, synthesis.

### 1. INTRODUCTION

One of the global problems confront humanity in the twenty-first century is the problem of protecting the environment, and in this respect creating new, environmentally efficient production and processing technologies is one of the most promising direction in chemical industry. Meanwhile, due to specific properties inherent to «ionic liquids»: wide interval of liquid state ( $>300^{\circ}\text{C}$ ), low melting temperature ( $M.p < 100^{\circ}\text{C}$ ), low pressure of saturated steams, non-volatility, incombustibility, non-toxicity, non-explosibility, high polarity, good dissolving ability of inorganic, organic and metal-organic compounds, various gases and also easiness and simplicity of technology of production and possibility of multiple use a wide volume and diversity of the area of their application and also creation of ecologically and economically acceptable technologies on this base is provided [1].

Superior properties inherent in them, ionic liquids, used in the separation of various organic compounds and elements [2], as a selective solvents in the treatment of various oil fractions by the extractions method [3], efficient catalytic system or as a component of catalytic system[4]. Along with all, the synthesis of ionic liquid monomers and the synthesis based on its high molecular polymer and co-polymers having practical importance and a new set of properties are in the attention of the researches as a perspective direction of high molecular weight compounds chemistry [5].

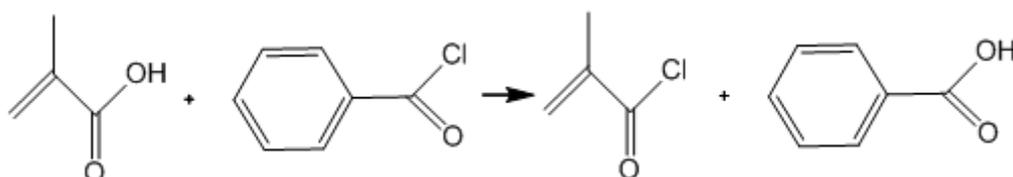
In recent years, ILs have stirred great interest in various fields such as green synthesis [6] catalysts [7] as well as olefin/paraffin separation [8] for its unique properties such as low vapor pressure, nonflammable. Especially, for its high ionic conductivity, ILs have been proposed as promising electrolyte for fuel cells [9] Li ion batteries [10], supercapacitors [11].

Also should noted that the investigations in the field of synthesis of polymer, copolymers on the basis of IL monomers are relatively new direction and are in the stage of intensive development. The polymers on the basis of IL monomers – this is new class of polymers possessing valuable complex of operational properties such as thermostability, high mechanical characteristics, electrochemical activity and ability to absorb  $\text{CO}_2$ . For today in the literature there is some information relatively synthesis of polymers by polymerization of IL monomers. The higher interest to polymers on the basis of IL monomers in the chemistry of high-molecular compounds has been connected both with creation of polymer materials possessing unique properties of the ionic liquids and with creation of new polymer materials possessing new complex of qualities and correspondingly, new area of application. Additionally, poly ionic liquids (PIL) has the potential advantage of defined size, shape and geometry, such as thin films, fibers, coatings, deposition of metals and semiconductors, for catalysis, for separation and crystallization, in nanoscience, and many others [12].

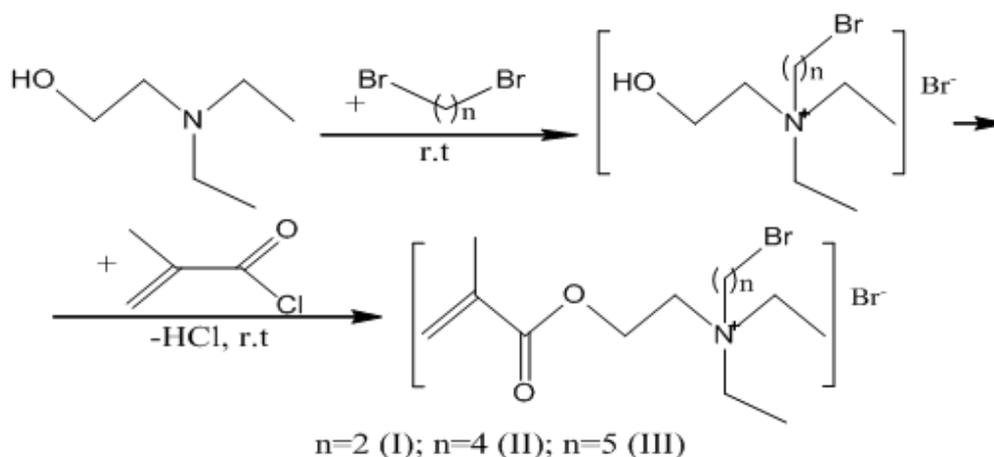
## 2. RESULT AND DISCUSSION

Taking into consideration the number of research works carried out in this area is increasing. From this point of view and from the known fact that the variety of ionic liquids composition, a wide spectrum of properties, also the modification capabilities of anions and cations which includes in ionic liquid composition provides a variety of their specific indications, properties and application area, in this article has been shown the synthesis process of ionic liquids monomers based on methacrylic acid, alkyl dibromides and diethylaminoethanol.

In the synthesis process all of the showing ionic liquid monomers were used methacryloyl chloride which is synthesized by the known method [13]. The scheme of the synthesis of methacryloyl chloride is following:



In the synthesis of brom containing ionic liquid monomers was taken in two stages. In the first stage, alkyl halogenides such as 1,2-dibromoethane; 1,4-dibromobutane and 1,5 dibromopentane are react with a diethylaminoethanol as a aminocomponent in a corresponding mol ratio. Products obtained from this reactions then react with a methacryloyl chloride in a corresponding mol ratio too. The general scheme of the synthesis process of these ionic liquid monomers is following:



## 3. EXPERIMENTAL

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a 300 spectrophotometr using in  $\text{CDCl}_3-d_1$  as the solvent. Chemical shifts values are reported in ppm taking tetramethylsilane as the integral standard and J values are given in hertz. The types of signals are indicated by the following letters: s=singlet, d=doublet, t=triplet, q=quartet. The structure of the synthesized ionic liquid monomers were taken in IR Infrared Spectroscopy apparatus of Bruker firm of German, in the  $600-4000\text{ cm}^{-1}$  of wave frequency range and it was approved that different functional groups of these ionic liquid monomers have different characteristic absorption frequency. Reactions were monitored by thin-layer chromatography (TLC) using precoated silica gel plates, visualized by UV light.

### 3.1. The Synthesis of Methacryloyl Chloride

Synthesis was taken into the round bottomed flask which is fitted with cooling, thermometer and mixer. For this purpose placed in a flask 24g (0,5 mol) of methacrylic acid, 78g (1mol) of benzoyl chloride and 0,15 g hydroquinone was added to the flask. The flask with a mixture was heated under the temperature  $110\text{ }^\circ\text{C}$ . The first fraction boiling up to  $105-106\text{ }^\circ\text{C}$  receiver in the ice-cooled collected which is 0,15g of hydroquinone placed it. In the second distillation process of the fraction, collected distillate under the temperature  $110\text{ }^\circ\text{C}$  repeat expelled from the same height column with the size 25 cm, under the temperature  $95-96\text{ }^\circ\text{C}$ . After the synthesis proceses obtained pink colour liquid, with the yield 70%.

### 3.2. Synthesis N,N-diethyl-N-(2-bromethyl)-N-(2-methacryloxyethyl) Ammonium-bromid (I)

The synthesis ionic liquid monomer- N,N-diethyl-N-(2-bromethyl)-N-(2-methacryloxy-ethyl) ammonium-bromid (I) also was carried out in two stage. Thus, in the first step synthesized N,N-diethyl-N-(2-bromethyl)-N-(2-hydroxyethyl)ammonium-bromid. Synthesis was carried in the two necked round bottom flask which is fitted with the thermometer and mixture. Then, in the molar ratio 1:1, 16.06 g (0, 085 mol) of 1, 2 dibromethane was added into the round flask. After this 10 g (0, 085 mol) of diethylaminoethanol added to the flask to. The mixture was stirred 7 h, and then mixture flask was kept at room temperature 15h. After 15 h the solution was dried out using condenser reflux in order to remove unreacted chemicals and gases and kept 12 hours at vacuum. Obtained yellow liquid compound with the yield 96%. In the second stage of the synthesis process was synthesis of the ionic liquid monomer -N,N-diethyl-N-(2-bromethyl)-N-(2-methacryloxyethyl)ammonium-bromid (I) in 1:1 molar ratio of N,N-diethyl-N-(2-bromethyl)-N-(2-hydroxyethyl)ammonium-bromid and methacryloyl chloride. Into the 3 necked round flask which is fitted with the thermometer and mixture was added 14,5 g (0,047 mol) of N,N-diethyl-N-(2-bromethyl)-N-(2-hydroxyethyl) ammonium-bromid complex salt, then added to the flask 5g (0,047 mol) of methacryloyl chloride by the dropping funnel. The mixture stirred 6h and kept at room temperature. After 6h the solution was dried out using condenser reflux in order to remove unreacted chemicals and gases and kept 12 hours at vacuum. Obtained brown salt with the yield 98%

IR: (KBr) 2979, 2609, 2474, 2449, 1453, 1407, 1358, 1294, 1267, 1246, 1157, 583, 563, 546, 509  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ , m.h.: 1.38-1.43 (t,  $J = 7.5$  Hz, 6H,  $2\text{CH}_3$ ), 1.97 (s, 3H,  $\text{CH}_3$ ), 3.25-3.31 (t,  $J = 6$  Hz, 4H,  $2\text{CH}_2\text{-N}$ ), 3.45-3.50 (t,  $J = 9$  Hz, 2H,  $\text{CH}_2\text{-N}$ ), 4.06-4.15 (tt,  $J = 9$  Hz,  $J = 9$  Hz, 4H,  $\text{CH}_2\text{-CH}_2\text{-Br}$ ), 4.47-4.52 (t,  $J = 7.5$  Hz, 2H,  $\text{CH}_2\text{-O}$ ), 5.93-6.12 (dd,  $J = 3$  Hz,  $J = 3$  Hz, 2H,  $\text{CH}_2\text{=C}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ , m.h.: 9.85 ( $2\text{CH}_3$ ), 17.96 ( $\text{CH}_3$ ), 32.27 ( $\text{CH}_2\text{-Br}$ ), 53.12 ( $2\text{CH}_2\text{-N}$ ), 57.92 ( $\text{CH}_2\text{-O}$ ), 59.56 ( $\text{CH}_2\text{-N}$ ), 63.71( $\text{CH}_2\text{-N}$ ), 124.42 ( $\text{CH}_2\text{=C}$ ), 134.21( $\text{CH}_2\text{-C}$ ), 167.91 (CO).

### 3.3. Synthesis N,N-diethyl-N-(2-methacryloxyethyl)-N-(4-brombutyl) Ammonium-bromid (II)

Synthesis was carried out in the two necked round bottom flask which is fitted with the thermometer and mixture. For this purpose in the molar ratio 1:1, 6 g (0, 051 mol) of diethylaminoethanol added to the flask and then 11 g (0,051mol) of 1, 4-dibrombutane added to flask. The mixture was stirred 7 h, and then flask with mixture was kept at room temperature 14h. After 14h the solution was dried out using condenser reflux in order to remove unreacted chemicals and gases and kept 12 hours at vacuum. Obtained white salt with the yield 96%. After into the 3 necked round flask which is fitted with the thermometer and mixture was added 2,013 g (0,006mol) of N,N-diethyl-N-(2-hydroxyethyl)-N-(4-brombutyl) ammonium-bromid suspended with 2 ml ethanol as a solvent. Then 0.627 g (0, 006 mol) of methacryloyl chloride was added to the mixture very slowly by the dropping funnel. The mixture stirred 6h and the was kept at room temperature. After 6h the solution was dried out using condenser reflux in order to remove unreacted chemicals and gases and kept 12 hours at vacuum. Obtained white salt with the yield 98%

IR: (KBr) 2986, 2883, 2655, 1987, 1721, 1483, 1381, 1144, 469, 644  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ , m.h.: 1.39-1.44 (t,  $J = 7.5$  Hz, 6H,  $2\text{CH}_3$ ), 2.00 (s, 3H,  $\text{CH}_3$ ), 2.17-2.43 (qq,  $J = 6$  Hz,  $J = 7.5$  Hz, 2H,  $\text{CH}_2$ ), 3.54-3.59 (t,  $J = 7.5$  Hz, 6H,  $3\text{CH}_2\text{-N}$ ), 3.71-3.78 (t,  $J = 10.5$  Hz, 2H,  $\text{CH}_2\text{-Br}$ ), 4.05-4.12 (t,  $J = 12$  Hz, 2H,  $\text{CH}_2\text{-N}$ ), 4.58-4.62 (t,  $J = 6$  Hz, 2H,  $\text{CH}_2\text{-O}$ ), 5.90-6.09 (dd,  $J = 3$  Hz,  $J = 3$  Hz, 2H,  $\text{CH}_2\text{=C}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ , m.h.: 10.43 ( $2\text{CH}_3$ ), 18.04 ( $\text{CH}_3$ ), 25.11-34.42 ( $3\text{CH}_2$ ), 52.12 ( $2\text{CH}_2\text{-N}$ ), 56.98 ( $\text{CH}_2\text{-O}$ ), 60.07 ( $\text{CH}_2\text{-N}$ ), 61.24 ( $\text{CH}_2\text{-N}$ ), 124.21 ( $\text{CH}_2\text{=C}$ ), 134.96 ( $\text{CH}_2\text{-C}$ ), 167.89 (CO).

### 3.4. Synthesis N,N-diethyl-N-(2-methacryloxyethyl)-N-(5-brompentyl) ammonium-bromid (III)

Synthesis was carried out in the two necked round bottom flask which is fitted with the thermometer and mixture. Then, in the molar ratio 1:1, 19,65 g (0,085 mol) of 1,2 dibromopentane was added into the round flask. After this 10g (0,085 mol) diethylaminoethanol added to the flask to. The mixture was stirred 7 h, and then flask with mixture was kept at room temperature 15h. Obtained yellow liquid compound with the yield 96%. After into the 3 necked round flask which is fitted with the thermometer and mixture was added 4,4 g (0.0126 mol) of N,N-diethyl-N-(2-hydroxyethyl)-N-(5-

brombpentyl) ammonium-bromid and suspended with 2 ml ethanol. Then 1,32 g (0.0126 mol) of methacryloyl chloride was added into the flask by the dropping funnel. The mixture stirred 6h. and the was kept at room temperature. After 6h the solution was dried out using condenser reflux in order to remove unreacted chemicals and gases and kept 12 hours at vacuum. Obtained cream colour salt with the yield 98%.

IR: (KBr) 2973, 2934, 2898, 2655, 1987, 1715, 1636, 1448, 1379, 1176, 1160, 735  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ , m.h.; 1.38-1.45 (t,  $J = 9$  Hz, 6H,  $2\text{CH}_3$ ), 1.67-1.82 (qqq,  $J = 6$  Hz,  $J = 6$  Hz,  $J = 7.5$  Hz, 6H,  $3\text{CH}_2$ ), 1.99 (s, 3H,  $\text{CH}_3$ ), 3.50-3.55 (t,  $J = 7.5$  Hz, 6H,  $3\text{CH}_2\text{-N}$ ), 3.69-3.75 (t,  $J = 9$  Hz, 2H,  $\text{CH}_2\text{-Br}$ ), 4.02-4.06 (t,  $J = 6$  Hz, 2H,  $\text{CH}_2\text{-N}$ ), 4.51-4.57 (t,  $J = 6$  Hz, 2H,  $\text{CH}_2\text{-O}$ ), 5.93-6.13 (dd,  $J = 3$  Hz,  $J = 3$  Hz, 2H,  $\text{CH}_2=\text{C}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ , m.h.; 10.43 ( $2\text{CH}_3$ ), 18.04 ( $\text{CH}_3$ ), 25.67-34.91 ( $4\text{CH}_2$ ), 51.96 ( $2\text{CH}_2\text{-N}$ ), 56.73 ( $\text{CH}_2\text{-O}$ ), 61.16 ( $\text{CH}_2\text{-N}$ ), 61.89 ( $\text{CH}_2\text{-N}$ ), 124.73 ( $\text{CH}_2=\text{C}$ ), 134.75 ( $\text{CH}_2\text{-C}$ ), 167.54 (CO).

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