

EWA ANDRZEJEWSKA<sup>\*)</sup>, IZABELA STĘPNIAK

Politechnika Poznańska  
Wydział Technologii Chemicznej  
Pl. M. Skłodowskiej-Curie 2, 60-965 Poznań

## Highly conductive solid polymer-(ionic liquid) electrolytes prepared by *in situ* photopolymerization

### RAPID COMMUNICATION

**Summary** — Solid polymer electrolytes containing ionic liquids (ILs) were prepared by the photopolymerization of monomer-IL homogenous mixtures. This method enables the preparation of solid polymer electrolytes in reaction carried out at room temperature in the time of about 10 min. The appropriate selection of the substrate allowed to obtain the high ionic conductivity of the solid polymer electrolytes (of the order of  $10^{-3} - 2 \cdot 10^{-2}$  S/cm), in some cases exceeding the conductivity of the ionic liquid used.

**Key words:** polymer electrolytes, ionic liquids, photopolymerization, electrolytic conductivity.

STAŁE ELEKTROLITY TYPU POLIMER-CIECZ JONOWA O DUŻYM PRZEWODNICTWIE JONOWYM OTZYMYWANE METODĄ POLIMERYZACJI *IN SITU*

**Streszczenie** — W pracy zaproponowano metodę otrzymywania stałych elektrolitów polimerowych polegającą na fotopolimeryzacji mieszanin monomer-ciecz jonowa. Metoda ta pozwala na uzyskanie stałych elektrolitów polimerowych w wyniku reakcji przebiegającej w temperaturze pokojowej w stosunkowo krótkim czasie rzędu 10 min. Do wytworzenia matrycy polimerowej wybrano monomery oraz żywice (met)akrylowe. Stosowane cieczy jonowe podano w tabeli 1. Dzięki odpowiedniemu doborowi substratów uzyskano stałe elektrolity polimerowe o dużym przewodnictwie jonowym, rzędu  $10^{-3} - 2 \cdot 10^{-2}$  S/cm (tabela 2), w niektórych przypadkach przekraczającym przewodnictwo zastosowanej cieczy jonowej.

**Słowa kluczowe:** elektrolity polimerowe, cieczy jonowe, fotopolimeryzacja, przewodnictwo właściwe.

Traditional polymer electrolytes are the solutions of electrolyte salts in polymers. Ionic liquids (ILs), also known as room-temperature molten salts, due to their immeasurably low vapor pressure, high ionic conductivity, and great thermal and electrochemical stability are considered to be suitable electrolyte salts for polymer-in-salt systems [1]. New class of solid electrolytes of the polymer-ionic liquids type can be applied in electrochemical devices, especially batteries and chemical capacitors.

One of the methods of their preparation is dissolution of a polymer and IL in a volatile solvent and then evaporation of the latter. Another possibility is the usage of two solvents — volatile and non-volatile one — what after the evaporation of the latter leads to the formation of so called gel polymer electrolytes [2—4]. The usage of solvents (increasing costs) and the need of their evapora-

tion (not friendly to the environment) are the disadvantages of the process.

A very promising method seems to be the direct polymerization of a solution of homogenous mixture of a monomer and IL. This method has been applied in a limited number of papers [5—13], using thermal initiators. The monomers tested were methyl methacrylate (MMA), acrylonitrile, vinyl acetate, styrene and 2-hydroxyethyl methacrylate (HEMA), but only MMA and HEMA gave satisfactory results [11, 12]. The reaction had to be carried out at elevated temperatures (70—80 °C) during a long time (2—24 h). Such reaction conditions favor the thermal degradation of the product and the polymer — IL phase separation. The ionic conductivity of so-obtained electrolytes was of the order on  $10^{-5} - 10^{-2}$  S/cm.

A very attractive method of initiation of the polymerization is the photochemical initiation. It enables the polymerization to occur at the room temperature and to shorten the polymerization time to minutes. In this work we report on the possibility of preparation of highly con-

<sup>\*)</sup> Author for correspondence; ewa.andrzejewska@put.poznan.pl

ductive polymer-IL solid electrolytes ( $10^{-3}$ – $10^{-2}$  S/cm) in a short time using the photopolymerization method. The work presents the preliminary results of our investigations [14].

## EXPERIMENTAL

### Materials

The following monomers were chosen to form the polymer matrix:

- polyethylene glycol monomethacrylate (PM, Aldrich);
- dipropylenglycol diacrylate (DPGDA, Actilane 422, Akzo Nobel);
- dianol diacrylate (DDA, Actilane 420, Akzo Nobel);
- aliphatic urethane acrylate (AU, Ebecryl 270, Surface Specialties).

The photoinitiator 2,2'-dimethoxy-2-phenylacetophenone (Irgacure 651) was purchased from Ciba—Geigy and sulfolane (purified before use [15]) from Merck.

### Polymerization

The homogeneous mixture containing the monomer, IL and the photoinitiator (in amount of 1 wt. %) was spread between two polyethylene terephthalate films and irradiated by 366 nm light for 10 min at room temperature in Ar atmosphere giving the solid electrolyte layer (thickness *ca.* 0.03 cm). In the case of DDA, sulfolane was introduced to the composition to achieve the homogeneity of the mixture.

### Methods of testing

The ionic conductivity of ionic liquids and polymer electrolytes was measured by impedance method using an impedance analyzer (Atlas-Sollych, Poland) over the frequency range from 0.01 to 99 kHz. Polymer electrolytes were sandwiched between two platinum electrodes (blocking electrodes); a surface of working platinum electrode was 0.01 cm<sup>2</sup>. Ionic conductivity of ionic liquids was measured between two platinum electrodes in the glass conductivity cell. Measurements were made at 25 °C.

Table 1. Ionic liquids used in this work

Abbreviation	Chemical name
[BMIm][BF <sub>4</sub> ]	1-butyl-3-methylimidazolium tetrafluoroborate
[BMIm][NTf <sub>2</sub> ]	1-butyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide
[BMPy][NTf <sub>2</sub> ]	<i>N</i> -butyl- <i>N</i> -methylpyrrolidinium bis(trifluoromethane sulfonyl)imide
[EMIm][BF <sub>4</sub> ]	1-ethyl-3-methylimidazolium tetrafluoroborate
[EMIm][NTf <sub>2</sub> ]	1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide

The ionic liquids used are shown in Table 1. They were prepared in two-step synthesis from the appropriate imidazolium halide and a salt containing the desired anion according to the general reaction scheme presented in ref. [16–20] and after introduction of necessary modifications.

## RESULTS AND DISCUSSION

Eight samples of solid polymer electrolytes with compositions of initial mixtures specified in Table 2 were prepared.

The selection of the monomers was based on the properties of the polymerized monomer-IL mixture — the film obtained had to be soft, very flexible, with a good mechanical strength. The base monomers formed linear (PM) or crosslinked (DPGDA, AU, DDA) polymers. The results of conductivity measurements of synthesized polymers are given in Table 2.

The data presented indicate that the conductivity values of the obtained solid electrolytes were high and comparable to or even higher than the conductivity of ILs used as the electrolytes. This behavior seems not to be associated with the formation of the linear or crosslinked polymer or with the presence or absence of the

Table 2. Compositions of initial mixtures and conductivity of solid electrolytes and corresponding ionic liquids

Monomer	Solvent	Ionic liquid	Monomer-solvent-ionic liquid weight ratio	Solid electrolyte conductivity · 10 <sup>3</sup> S/cm	Ionic liquid conductivity · 10 <sup>3</sup> S/cm
PM	—	[EMIm][BF <sub>4</sub> ]	3:0:7	16.54	21.2
PM	—	[EMIm][NTf <sub>2</sub> ]	3:0:7	4.14	11.0
DPGDA	—	[BMIm][BF <sub>4</sub> ]	3:0:7	1.75 <sup>)</sup>	3.3
DPGDA	—	[EMIm][NTf <sub>2</sub> ]	3:0:7	1.88 <sup>)</sup>	11.0
UA	—	[EMIm][NTf <sub>2</sub> ]	2:0:8	9.63	11.0
UA	—	[BMIm][NTf <sub>2</sub> ]	2:0:8	3.12	3.51
DDA	sulfolane	[EMIm][BF <sub>4</sub> ]	2:3:5	18.00 <sup>)</sup>	21.2
DDA	sulfolane	[BMPy][NTf <sub>2</sub> ]	2:2:6	6.87 <sup>)</sup>	3.0

<sup>)</sup> the electrolyte film obtained was translucent.

inert solvent. Specific interaction of the polymer matrix with the anion of the ionic liquid can play a role [1].

Concluding we can say that the photopolymerization is a very efficient, fast and simple method of preparation of IL-containing solid electrolytes. The fact of obtaining of the solid electrolytes showing high ionic conductivity should also be stressed. The key role to achieve the high ionic conductivity seems to play the appropriate selection of the monomers and ILs.

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