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Electrical Conductivity and Interactions in Poly(Methyl Methacrylate)–1-Butyl-3-methylimidazolium Hexafluorophosphate Microheterogeneous System

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Abstract—Microheterogeneous composite films of varied composition based on poly(methyl methacrylate) and 1-butyl-3-methylimidazoluim hexafluorophosphate have been prepared. The introduction of *N*-vinylpyrrolidone into the polymer matrix has been shown to deteriorate the electrical conductivity of the composite. Specific ionic conductivity of the composites has been measured as a function of the alternate current frequency and the material composition. Hydrogen bonding between the polymer electrolyte components as well as additional interaction between cation and anion of the ionic liquid encapsulated in the polymer matrix have been confirmed by IR spectroscopy studies.

Keywords: polymer electrolyte, composite, ionic liquid, electrical conductivity
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Conductive polymer materials (polymer electrolytes) have been recently applied as substitutes of conventional liquid electrolytes for lithium batteries, fuel cells, electrolytic capacitors, photogalvanic cells, and other electrotechnical devices. Polymer electrolytes can be prepared in the forms of bulk solid, gel, or thin film, thus enabling development of compact, durable, and safe items [1, 2].

Polymer electrolytes are generally produced via introduction of various plasticizers and conductive fillers into the matrix of poly(ethylene oxide), poly(methyl methacrylate), polyacrylonitrile, and other polymers. In particular, ionic liquids (IL), the low-melting (<100°C) salts containing certain sterically hindered ions [3], have been recognized as promising conductive fillers. The salts of asymmetric 1-butyl-3-methylimidazolium cation are among the most important ionic liquids. Such compounds are known for the low melting (devitrification) point, high ionic conductivity, wide electrochemical stability window, and good thermal stability; the polymer materials containing 1-butyl-3-methylimidazolium salts have recently attracted considerable attention [4–8].

The development of polymer electrolytes based on ionic liquids aims to attain the highest electrical conductivity preserving the good mechanical properties of the polymer matrix: strength and elasticity. The material conductivity is usually enhanced with the growing content of the IL; however, the mechanical properties are simultaneously deteriorated, and the problem of leakage of the excess of IL appears. The optimization of the material composition has been recently addressed by using various copolymers (including block copolymers) as the polymer matrix [9, 10]. In view of this, it is important to gain the information about the interactions between the polymer and the ionic liquid as well as between the ions constituting the IL. Such interactions determine the compatibility of the components and the ions mobility (i.e., the polymer electrolyte conductivity).

Physicochemical properties of the imidazole-containing ionic liquids as well as the intra- and intermolecular interactions in such systems have been well studied up to now [11–14]. The interaction of poly(ethylene oxide), poly(methyl methacrylate), and cellulose hydrate with imidazoluim cation has been

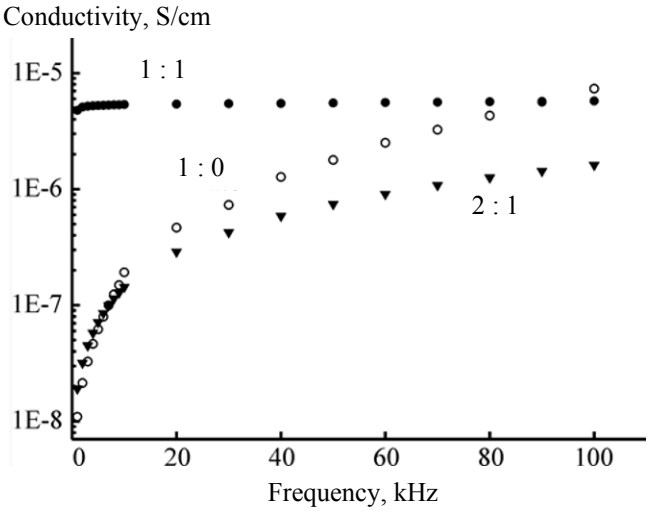


Fig. 1. Specific conductivity of the PMMA–$BMImPF_6$ films as a function of the current frequency. Mass ratios of the polymer and the ionic liquid are given near to the corresponding curves.

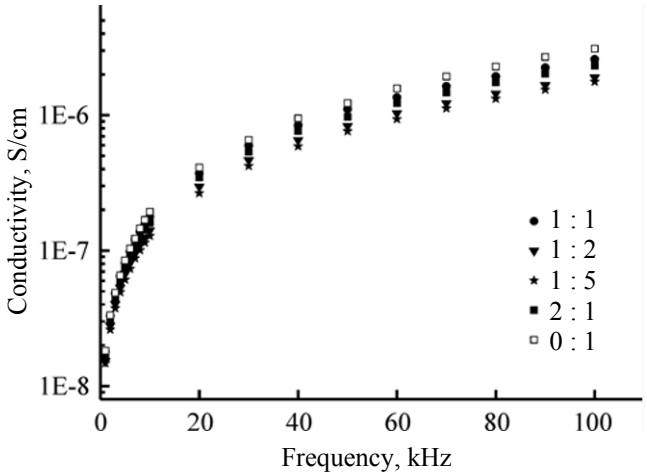


Fig. 2. Specific conductivity of the 3 : 1 films of PMMA–$BMImPF_6$ and P(NVP-*co*-MMA)–$BMImPF_6$ at different ratios of NVP to MMA as a function of the current frequency.

studied by means of IR, Raman, and NMR spectroscopy [4, 15–17].

This work aimed to prepare film polymer electrolytes consisting of poly(methyl methacrylate) PMMA and 1-butyl-3-methylimidazolium hexafluorophosphate $BMImPF_6$, to study the conductivity of the prepared materials and the interactions in the PMMA–$BMImPF_6$ system, and to investigate the effect of *N*-vinylpyrrolidone NVP introduction in the polymer matrix on the composite conductivity. PMMA is a known film-forming polymer well compatible with the $BMImPF_6$ ionic liquid. The choice of NVP as the comonomer was inspired by the suggestion that its carbonyl oxygen can bind to the proton-donor groups and additionally favor the IL retention in the material.

The following polymer-to-IL mass ratios were tested: 1 : 1, 2 : 1, 3 : 1, and 4 : 1. In the case of PMMA homopolymer, the resulting films were rigid and non-conductive at c_{IL} < 20 wt %, whereas at c_{IL} > 50 wt % the ionic liquid leakage was observed. The materials based on the copolymers were poorer in the IL retention (<30 wt %); in that case the 3 : 1 and 4 : 1 film compositions were studied. All the prepared composite films were semi-opaque (microheterogeneous).

Frequency dependences of specific ionic conductivity (σ) of pure PMMA and its composites with $BMImPF_6$ of varied compositions are shown in Fig. 1. As seen, the films with c_{IL} < 50 wt % (the 2 : 1 ratio) were dielectrics, similar to the pure polymer (the 1 : 0 ratio): the conductivity was low (~10^{-8} S/cm) at low frequency, was only slightly dependent on the IL concentration and increased with the current frequency over the whole studied range. At c_{IL} of 50 wt % (the 1 : 1 ratio), the low-frequency σ value was two orders of magnitude higher than that of the pure polymer, and remained practically constant with frequency; such behavior was typical of polymer electrolytes. The data pointed at significant changes in the polymer material structure. The highest conductivity value was (0.57±0.01) × 10^{-5} S/cm (25°C). The conductivity of such heterogeneous systems is generally realized via the ions motion through the connected droplets of ionic liquid forming the extended conductive network [8, 16].

Frequency dependences of the σ values of the 3 : 1 composites of the P(MMA-*co*-NVP) copolymers with $BMImPF_6$ are shown in Fig. 2; the curve for the PMMA homopolymer composite is shown for comparison. It is to be seen that the conductivity was practically independent of the monomers ratio in the matrix, ranging between (1.47±0.05) × 10^{-8} and (1.79±0.06) × 10^{-8} S/cm at 1 kHz. The copolymers composites conductivity was 5–6 times lower than that of the composite based on PMMA homopolymer,

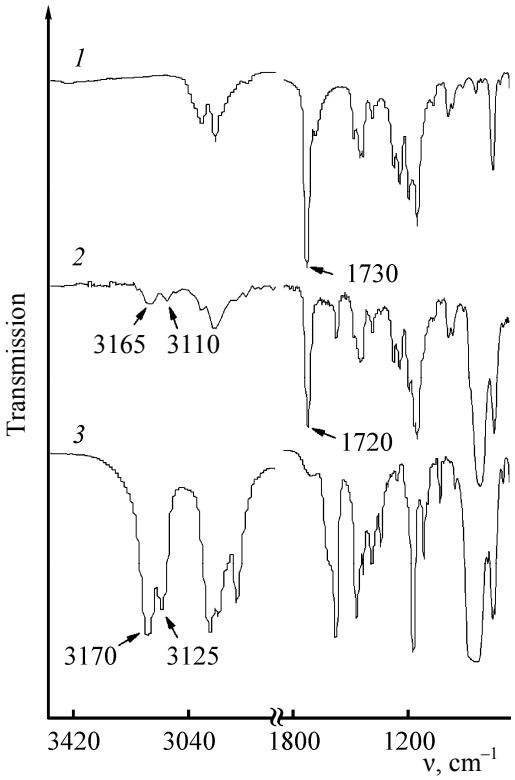


Fig. 3. IR spectra of (*1*) PMMA, (*2*) the 1 : 1 PMMA–$BMImPF_6$ film, and (*3*) $BMImPF_6$.

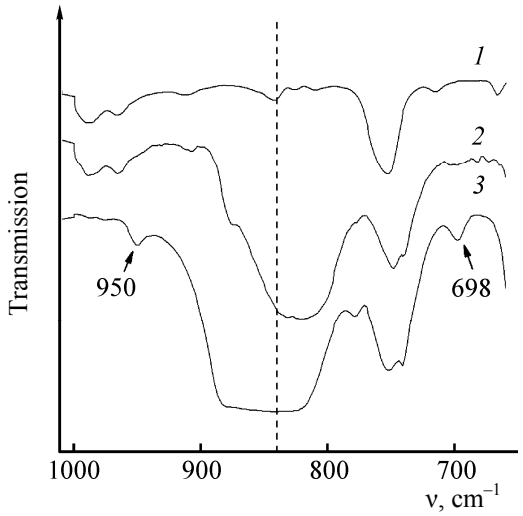
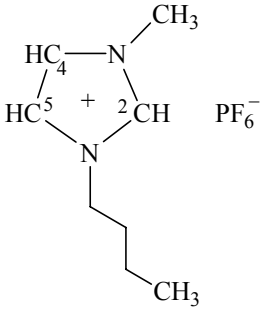


Fig. 4. Enlarged view of fragments of IR spectra of (*1*) PMMA, (*2*) the 1 : 1 PMMA–$BMImPF_6$ film, and (*3*) $BMImPF_6$.

$(9.1\pm0.2) \times 10^{-8}$ S/cm. Seemingly, the introduction of the NVP units changed the polymer matrix structure and prevented the formation of the continuous IL phase, therefore deteriorating the ion transport.

IR spectra of PMMA, $BMImPF_6$, and their composite of the optimal 1 : 1 composition are shown in Fig. 3. The pure polymer spectrum (curve *1*) contained the absorption bands at 3000–2900 cm^{-1} (assigned to CH_3 and CH_2 groups stretching vibrations), 1730 cm^{-1} (C=O stretching vibrations), 1500–1400 cm^{-1} (CH_3 and CH_2 bending vibrations), and 1300–990 cm^{-1} (C–O–C stretching vibrations) [4, 18–20]. The spectrum of the pure ionic liquid (curve *3*) contained the overlapped bands at 3200–3000 and 3000–2800 cm^{-1} (aromatic and aliphatic C–H stretching vibrations, respectively), whereas the broad band at 840 cm^{-1} was assigned to the ν_{as}(P–F) vibrations in the PF_6^- anion [4, 21–23].

The cation and the anion of $BMImPF_6$ are bound via the electrostatic forces, practically not forming hydrogen bonds. It is known that the formation of hydrogen bonds involving BMImCl or BMImBr occurs predominantly via the hydrogen C^2H atom and results in the red shift of the absorption band of aromatic C–H stretching vibrations [23, 24].



The spectrum of the PMMA–$BMImPF_6$ composite film (Fig. 3, curve *2*) contained the characteristic bands of PMMA and $BMImPF_6$ (cf. curves *1* and *3*) showing the following changes: the ν_s(C=O) band of the polymer experienced the red shift by 10 cm^{-1}, and the $\nu_s(C^{4,5}H)$, $\nu_{as}(C^{4,5}H)$, and $\nu_s(C^2H)$ bands of the ionic liquid cation suffered the red shifts by 5–15 cm^{-1}.

The spectral range containing the absorption band of the ionic liquid anion is shown extended in Fig. 4. It is seen that the shape of the broad band at 840 cm^{-1} was significantly changed upon the composite formation: its half-width decreased from 93 to 70 cm^{-1}, and the maximum experienced a blue shift by 10 cm^{-1} (cf. curves *2* and *3*).

Fig. 4 shows certain changed in the bands assigned to bending vibrations of C–H bonds of the imidazole ring. In particular, the band observed at 698 cm^{-1} in the spectrum of the pure IL {δ(CH) [4]} almost disappeared in the spectrum of the composite, and the band at 950 cm^{-1} {δNC(H)CN [21]} was transformed

into a shoulder. Deconvolution of the spectra into the Gaussian peaks demonstrated that the absorption band corresponding to that shoulder had a maximum at 947 cm^{-1}, 3 cm^{-1} lower than the respective band in the pure IL spectrum.

In general, the analysis of the IR spectra showed that the characteristic bands of PMMA and $BMImPF_6$ were shifted towards lower frequency range in the composite spectrum evidencing the interaction of the corresponding groups. The strongest shifts were observed in the cases of the C^2–H vibration of the IL cation, the P–F vibration of the IL anion, and the C=O vibration of the polymer. Evidently, the interaction of PMMA with $BMImPF_6$ occurred via the C^2–H···O=C hydrogen bonds, whereas the cation and the anion of the IL trapped inside the polymer matrix formed the C^2–H···F–P and $C^{4,5}$–H···F–P hydrogen bonds.

To summarize, the specific ionic conductivity of heterogeneous films of poly(methyl methacrylate) and poly(methyl methacrylate–*co*–*N*-vinylpyrrolidone) containing up to 50 wt % of 1-butyl-3-methylimidazolium hexafluorophosphate was determined by the contact conductometry method. The optimal ratio of PMMA and $BMImPF_6$ giving the highest ionic conductivity of the composite was determined. It was found that introduction of *N*-vinylpyrrolidone units worsened the polymer–IL compatibility and deteriorated the formed composite conductivity. IR studies of the interactions between the components in the composite of the optimal composition revealed that PMMA and $BMImPF_6$ formed hydrogen bonds, whereas the cation and the anion of IL dispersed in the composite interacted stronger than in the IL bulk phase.

EXPERIMENTAL

Poly(methyl methacrylate) (M_w = 46500 g/mol) and copolymers of *N*-vinylpyrrolidone with methyl methacrylate (2 : 1, 1 : 1, 1 : 2, and 1 : 5) were prepared via radical suspension polymerization under conditions of microwave irradiation. Synthesis, analysis, and properties of the polymers have been reported earlier [8].

The ionic liquid $BMImPF_6$ (M = 284.18 g/mol, d = 1.38 g/cm^3, Merck) was dried in vacuum at 120°C during 2 h prior to use.

In order to prepare the film, about 0.35 g of the polymer was dissolved in chloroform ("chemically pure" grade); the required amount of the ionic liquid was dissolved separately in the same solvent. Homogeneous solutions of the polymer and the ionic liquid were combined, stirred during 2 h, and poured onto a Petri dish; the solvent was removed first under normal conditions and then in a vacuum at 30°C during 24 h. The so formed semi-transparent films were 0.23–0.5 mm thick. IL-free polymer films were prepared similarly. The samples showing no liquid leakage were further studied by conductometry and IR spectroscopy.

Electrical conductivity of the films was determined by means of the alternating current contact conductometry using an E7-20 immitance measuring device. The total resistance of the film (R) was determined in a cell equipped with two planar platinum electrodes at 25°C (1–100 kHz, 0.04 V). The specific electrical conductivity (σ) was calculated as $\sigma = \delta/RS$, with δ being the film thickness (cm) and S being the electrodes surface area (cm^2).

IR spectra were recorded using an AVATAR E.S.P spectrometer. The IL specimens were prepared in the form of films at the KRS-5 (the mixed TlBr–TlI crystal) support.

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