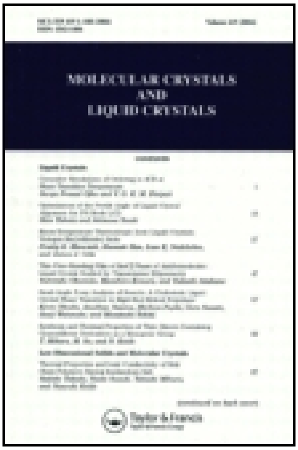

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

A Solid State Actuator Based on the PEDOT/NBR System: Effect of Anion Size of Imidazolium Ionic Liquid

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Version of record first published: 22 Sep 2010

Mol. Cryst. Liq. Cryst., Vol. 464, pp. 51/[633]–56/[638], 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601028492

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The fabrication of a dry type conducting polymer actuator is presented using nitrile rubber (NBR) as the base material for the solid polymer electrolyte. A conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), was synthesized on the surface of the NBR by the chemical oxidation polymerization technique, and room temperature ionic liquids (RTIL) based on imidazolium salts, viz. 1-butyl-3-methyl imidazolium X [where X = BF_4^-, PF_6^-, $(CF_3SO_2)_2N^-$], were introduced onto the composite film. The effects of the anion size of the ionic liquids on the displacement of the actuator were investigated. The displacement increased with increasing anion-size of the ionic liquids. The cyclic voltammetric responses and the redox switching dynamics of the actuators were studied in different ionic liquids.

Keywords: conducting polymer actuator; ionic liquid; nitrile rubber; PEDOT

INTRODUCTION

Poly(3,4-ethylenedixythiophene) (PEDOT) holds a special position due to its exceptional electrochemical stability and provides potential

This work was supported by the Korea Science and Engineering Foundation Grant. (R01-2006-000-10348-0).

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applications in electrical and optical devices, electrolytic capacitors, and electrochemical windows [1]. PEDOT has also shown the ability to support ionic intercalation, which is one proposed mechanism for achieving strain observed against a load in conducting polymers [2]. We previously reported on the preparation and actuation of the dry type actuator, PEDOT/NBR/ionic liquid [3–5]. In the preparation of the actuator system, nitrile rubber (NBR) was used as the base material for the solid polymer electrolyte. The PEDOT/NBR actuator was activated in an ionic liquid, viz. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide (EMITFSI). The findings of this study were that the displacement rate in ionic liquids is greater than that observed in conventional electrolytes systems [5]. From this result it has been a goal to study the effect of the ionic liquids having different anion size on the PEDOT actuation.

The actuators prepared in the present study were activated in several ionic liquids: 1-butyl-3-methyl imidazolium (BMI) X [where $X = BF_4^-$, PF_6^-, $(CF_3SO_2)_2N^-$], and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. The electrochemical actuation of several BMI ionic liquids was determined in our work. We demonstrated that the anion-size of BMIX ionic liquids influenced the displacement of the actuator by examining three ionic liquid couples: BF_4^-, PF_6^-, $(CF_3SO_2)_2N^-$.

EXPERIMENTAL SECTION

Materials

NBR is a copolymer composed of 60 mol% butadiene and 40 mol% acrylonitrile. The NBR is supported by Kumho Chem. Ltd. and thin films (150 $\sim$ 200 μm) were prepared by the compression molding process at 160°C for 20 min under the pressure of 100 kg_f/cm^2 to complete vulcanization process. The dielectric constant of NBR was found to be 4.8 at 10^6 Hz. 3,4-Ethylenedioxythiophene (EDOT) was supplied by Aldrich Chemical Co. and was purified by passing it through an activated neutral aluminum oxide column. $FeCl_3$ was obtained from Aldrich Chemical Co. and was used as received.

Preparation of PEDOT/NBR/BMITFSI Composite Film

The PEDOT/NBR actuators were prepared by the previously reported procedure [3–5].

Synthesis of Ionic Liquid

The ionic liquids were synthesized according to standard procedures and dried before use [6–8]. The following ionic liquids were synthesized:

1-butyl-3-methyl imidazolium tetrafluoroborate ($BMIBF_4$), 1-butyl-3-methyl imidazolium hexafluorophosphate ($BMIPF_6$), 1-butyl-3-methyl imidazolium bis(trifluoromethyl sulfonyl)imide, (BMITFSI), and N-butyl-3-methyl pyrrolidinium bis(trifluoromethyl sulfonyl)imide (BMPTFSI).

Instrumentation

The ionic conductivity of all films was determined by AC impedance spectroscopy. Cells using two blocking, stainless steel electrodes were used to hold the film. A Teflon spacer was included to fix the sample thickness. The impedance tests were carried out in the 10 mHz $\sim$ 100 kHz frequency range using Impedance/Gain phase analyzer, Solarton SI model 1260. The displacement of the actuator was measured by laser beam radiation using an instrument, KEYENCE LK-081 (KEYENCE Co., Japan). The point of the laser radiation was focused on the bottom of the film which was 20 mm long, 5 mm wide, and 200 μm thick. Cyclic voltammetry (CV) was performed by the cyclic scanning of the potential between -10 and 10 V with a sweep rate of 400–500 mVs^{-1} in the solid electrode.

RESULTS AND DISCUSSION

The characteristics of solid electrolyte films produced by the impregnation of the ionic liquid into the NBR matrix films were characterized using a measurement of ionic conductivity. The NBR films were activated for 24 hr in different ionic liquid, $BMIBF_4$, $BMIPF_6$, BMITFSI, respectively. The incorporated ionic liquid in the NBR matrix was found to have caused a 67 $\sim$ 70% increase in weight. The variation of the ionic conductivity as a function of the different ion size for imidazolium salts was examined; 0.524×10^{-4} S/cm for the NBR/$BMIBF_4$, 1.26×10^{-4} S/cm for the NBR/$BMIPF_6$, 2.08×10^{-4} S/cm for BMITFSI.

PEDOT/NBR actuators activated in different ionic liquids were prepared. In general, the mechanism for their actuation primarily involves the reversible transport of ions and solvent molecules between the polymer and the electrolyte during electrochemical oxidation and reduction. Studies of the mobile anions, BF_4^-, PF_6^-, and $(CF_3SO_2)_2N^-$ have suggested that conformational effects of the polymer chains also influence the actuation process. A $(CF_3SO_2)_2N^-$ doped PEDOT actuator was found to exhibit a large displacement, whereas a PEDOT film doped with BF_4^- did not, and the maximum displacement generated electrically was 5.49 mm, which is much higher than that of the PEDOT actuators doped with BF_4^- (1.10 mm) or PF_6^- (3.09 mm). The reason that

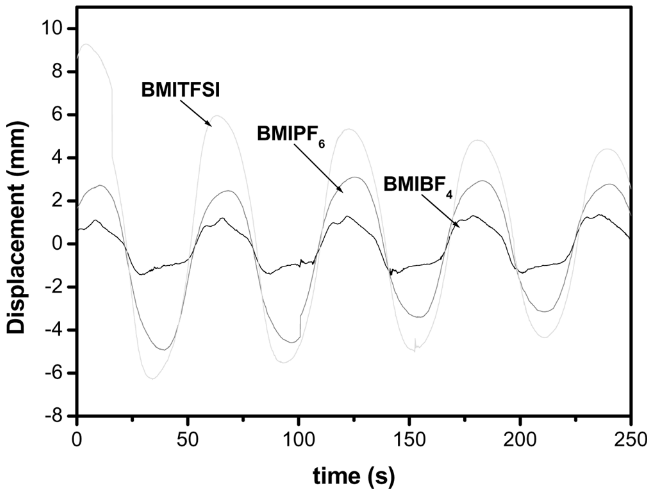

FIGURE 1 Bending displacement of the PEDOT/NBR actuators activated in $BMIBF_4$, $BMIPF_6$, and BMITFSI ionic liquid and monitored by laser radiation: -5 and $+5$ V. Scan rate: 300 mV/s.

$(CF_3SO_2)_2N^-$ endowed the PEDOT films with a higher displacement than did BF_4^- and PF_6^- might be the larger anion size in the PEDOT films. For example, the calculated anion volume is in the following order: BF_4^-, 48 Å^3, PF_6^-, 68 Å^3, TFSI, 189 Å^3 [9].

In Figure 1, it is clearly observed that increasing the anion size increases the displacement. Approximately 7- and 4- fold increases of the displacement in the PEDOT/NBR/BMITFSI actuator were observed compared to those of the PEDOT/NBR/$BMIPF_6$ and PEDOT/NBR/$BMIBF_4$ actuators, respectively. Hara *et al.* [10] reported that the larger displacement was observed with the actuator film using larger anion in the polypyrrole (PPy) bilayer films. The electrochemical strain of the PPy actuators depended on the anions used for the electrochemical stretching and was in the following order: $PF_6^- > BF_4^- > Cl^-$. This order of electrochemical strain strongly supports the proposed mechanism of electrochemical stretching of conducting polymer actuators [10–12], in which expansion and contraction occur upon the doping and dedoping of the anions, respectively. Thus, the PEDOT/NBR films were activated in the ionic liquids, BMITFSI and BMPTFSI, and their displacements were observed. In Figure 2, the role of the different cations in the ionic liquid did not appear to be significant with the imidazolium in ionic liquid giving rise to a slightly higher displacement than the pyrrolidium one.

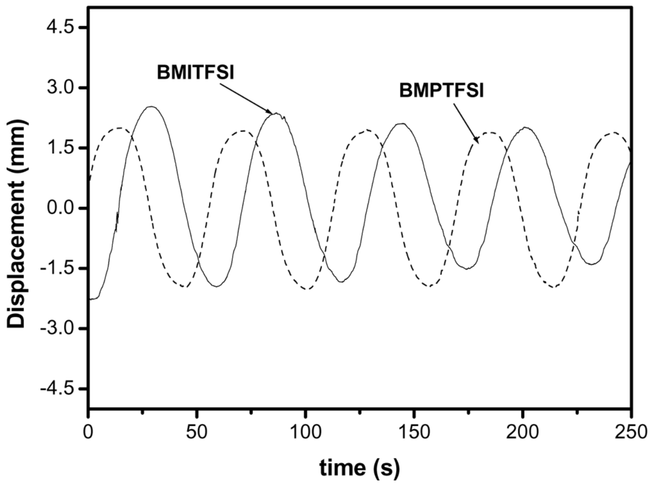

FIGURE 2 Bending displacement of the PEDOT/NBR actuators activated in BMIITFSI and BMP TFSI ionic liquid and monitored by laser radiation: -5 and $+5$ V. Scan rate: 300 mV/s.

CONCLUSION

The PEDOT/NBR films were activated in the different ionic liquids, viz., $BMIBF_4$, $BMIPF_6$, BMITFSI, and BMPTFSI, respectively and their displacements were observed. The $(CF_3SO_2)_2N^-$-doped PEDOT actuator exhibited a large displacement, and the maximum displacement generated electrically was 5.49 mm, which was much higher than that of the films doped with BF_4^- (3.09 mm) or PF_6^- (1.10 mm). The difference in the displacement of the actuators made with the mobile cations, imidazolium and pyrrolidinium, was quite small.

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