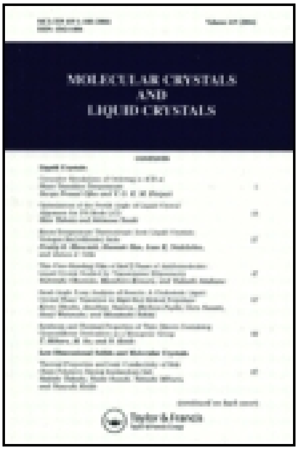

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Dry Type Conducting Polymer Actuator Based on Polypyrrole-NBR/Ionic Liquid System

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Version of record first published: 20 Aug 2006

To cite this article: M. S. Cho, J. D. Nam, Y. Lee, H. R. Choi & J. C. Koo (2006): Dry Type Conducting Polymer Actuator Based on Polypyrrole-NBR/Ionic Liquid System, Molecular Crystals and Liquid Crystals, 444:1, 241-246

To link to this article: http://dx.doi.org/10.1080/15421400500365052

Mol. Cryst. Liq. Cryst., Vol. 444, pp. 241–246, 2006
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500365052

Dry Type Conducting Polymer Actuator Based on Polypyrrole–NBR/Ionic Liquid System

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The fabrication of dry type conducting polymer actuator was presented. In the preparation of actuator system, nitrile rubber (NBR) was used as a base material of the solid polymer electrolyte. Thin films of NBR (150 ~ 200 μm) were prepared by compression molding process. The conducting polymer, polypyrrole(PPy) was synthesized on the surface of NBR by chemical oxidation polymerization technique, and the room temperature ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide (BMITFSI) was introduced into the composite film. The cyclic voltammetry responses and the redox switching dynamics of PPy in NBR/ionic liquid solid polymer electrolyte were studied. The displacement of actuator was measured by laser beam.

Keywords: electro-active polymer; ionic liquid; NBR; polypyrrole

INTRODUCTION

Recently, Baughman [1] has reviewed the use of conducting polymers as artificial muscles and described potential applications including robotics and prosthetics. Many other workers have demonstrated

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This research (article) was performed for the Intelligent Robotics Development Program, one of the 21st Century Frontier R&D Programs funded by the Ministry of Science and Technology of Korea.

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simple actuator devices using conducting polymers and solid type actuators in which the liquid was replaced with a solid polymer electrolyte (SPE) [2,3].

The actuators working in air are generally built in a configuration where SPE is sandwiched between two conducting polymer [4,5]. Such type of actuators has several problems. A delaminating process, which is due to the poor cohesion between the conducting polymer film, the layer of metal and the flexible SPE, limits the lifetime of actuator [6]. In order to solve the delaminating, the conducting polymer is embedded in an elastomeric and conducting matrix. And then the matrix is immersed in liquid electrolyte [7]. The system is a one-piece device instead of being a conventional multi-layered device. Here, the matrix is composed of poly (butadiene-co-acrylonitrile), a synthetic rubber (NBR) as the SPE. The conducting polymer, polypyrrole (PPy) was synthesized on the surface of NBR by chemical oxidation polymerization technique.

In order to build solid-state devices that perform as effectively as demonstrated in liquid electrolytes, Room-Temperature Ionic Liquids (RTIL) is chosen in our system. RTIL as electrolyte systems should have an impact on many areas of application in π–conjugated polymer electrochemical devices. The RTIL offer high ionic conductivity and a large electrochemical window and are especially resistant against oxidation, which explain the considerable attention given to electrochemical studies [8–10].

The present article reports on some issues and our approach to the design of practical PPy–NBR actuators in RTIL environment.

EXPERIMENTAL SECTION

Material

The NBR is a copolymer composed of butadiene and acrylonitrile with a relative 40/60 wt. proportion. The NMR is supported by Kumho Chem. Ltd. and thin films ($150 \sim 200\,\mu m$) were prepared by compression molding process. The dielectric constant of NBR is measured to be 4.8 at 10^6 Hz. The monomer pyrrole was offered by Aldrich Chemical Co. and was purified by passing through an activated neutral aluminum oxide column. 40 wt.% ferrictoluenesulfonate (FTS)-solution from Bayer Chemical Co. was used as received.

Preparation of Conducting Polymer Based NBR

NBR films were soaked into pure pyrrole for 10 minutes after which their surface was wiped off with a filter paper. The swollen films were then immersed into the FTS solution for 24 hours for oxidative polymerization. The film is washed several times with methanol. The PPy–NBR film is dried at 25°C under vacuum for 24 hours. After the edges were cut out, the PPy–NBR film ($5 \times 10 \times 0.200$ mm) were immersed in 50/50 CH_2Cl_2/BMITFSI solution or in 0.5 M $LiClO_4$/propylene carbonate (PC) for 24 hours at room temperature. After CH_2Cl_2 evaporation, the incorporated BMITFSI and $LiClO_4$ caused the $10 \sim 15\%$ of weight increase. The composite film is kept in air.

Synthesis of the Room Temperature Ionic Liquid (RTIL)

The synthesis of 1-butyl-3-methyl imidazoliumbis(trifluoromethylsulfonyl)imide (BMITFSI), was carried out according to the procedure described by Bonhote *et al.* [11].

Ionic Conductivity Measurements

The ionic conductivity of BMITFSI swollen NBR film was determined by AC impedance spectroscopy. Cells equipped with two blocking, stainless steel electrodes were used to hold the film. A Teflon spacer was included to fix the sample dimension. The impedance tests were carried out in the 10 mHz $\sim$ 100 kHz frequency range using Impedance/Gain phase analyzer, Solatron SI model 1260.

Displacement Measurements

The displacement of actuator was measured by laser beam radiation, KEYENCE LK-081 (KEYENCE Co., Japan): semiconductor laser 670 nm, maximum out put 0.95 mV, pulsed radiation. The point of laser radiation is focused on the bottom of film (15 mm long, 8 mm wide 200 μm thick).

RESULTS AND DISCUSSION

We presented herein electrochemical characterizations performed on polypyrrole synthesized in 40 wt.% FTS-solution and activated in BMITFSI ionic liquid. The NBR film activated in BMITFSI was ca. 10^{-3} S/cm in the conductivity at room temperature (15 wt.% ionic liquid uptake). Cyclic voltammograms in the ranges of –6 to 6 V at the scan rate of 400 mV/s (two electrode system) were recorded for actuators swollen by BMITFSI in Figure 1. PPy is oxidized with a main anodic peak centered at +2.1 V. On the cathodic scan, one

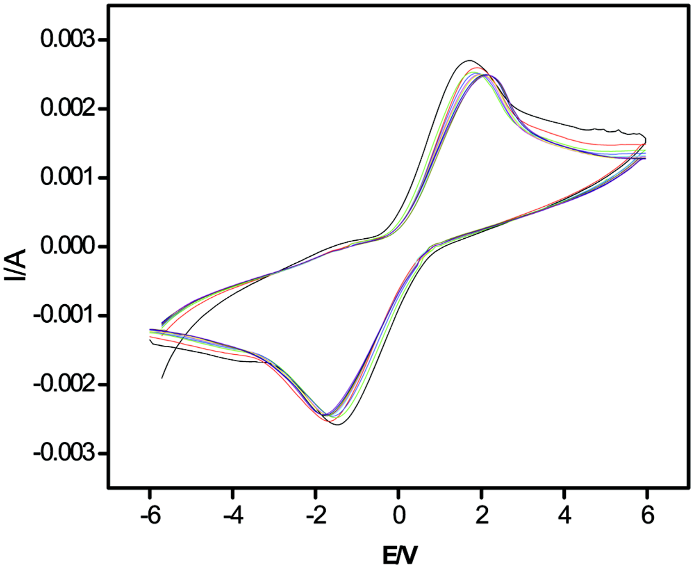

FIGURE 1 Cycle voltammograms of BMITFSI swollen PPy–NBR actuator in between –6 and + 6V. Scan rate: 400 mV/s. 100th cycle.

well-defined reduction peak at –1.8 V is observed. The actuator displayed distinct oxidation and reduction peaks. The electrical stability is satisfactory even after 100 scans.

As shown in Figure 2, activation of PPy–NBR in BMITFSI resulted into very active displacement (4–5 mm) while 2–3 mm displacement in $LiClO_4$/PC. Both the bending and bending rates observed in ionic liquids were greater than those observed in convention electrolyte systems. The reason for improved performance in ionic liquids is not fully understood at this time. In the consideration of enhanced actuating function of ionic liquids, the mobility and the concentration might be two key factors. The ionic liquids do not require any solvent molecules, the concentration of ions at the PPy and rubber interface is much higher than that of conventional $LiClO_4$/PC system. The ionic liquids present a much higher concentration of ions at the double layer on the surface of the polymer, which could account for some of the improved performance. An observation that has also been noted in other conducting polymers [12,13]. We measured a cycle life in excess of 200 cycles for PPy–NBR activated in BMITFSI. Neither chemical degradation nor any declination in the bending-displacement (bending-amplitude) was observed even after 200 cycles.

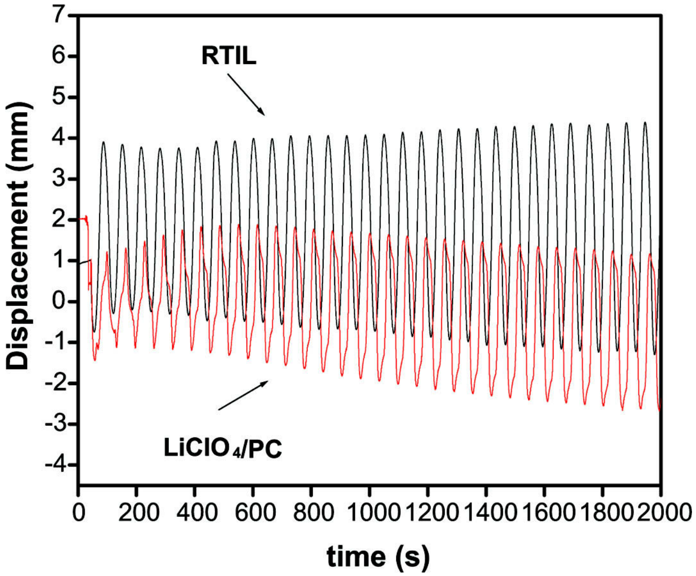

FIGURE 2 Bending displacement of the PPy–NBR activated in BMITFSI ionic liquid and $LiClO_4$/PC monitored by laser radiation: –6 and +6V. Scan rate: 400 mV/s.

CONCLUSION

New type solid actuator, PPy–NBR was synthesized and its bending actuation in ionic liquid environment was studied. This work represents a significant improvement of polypyrrole bending actuation through the introduction of ionic liquid and novel solid polymer electrolyte NBR and presents the possibility of greater improvements in the field of conducting polymer actuation working in air.

REFERENCES

[1] Baughmann, R. H. (1996). *Synth. Met.*, *78*, 339.
[2] Wallace, G. G., Spinks, G. M., & Teasdale, P. R. (1997). *Electoactive Polymers: Intelligent Materials Systems*, Technomic: Lancaster, UK.
[3] Stero, T. F. (1997). In: *Conductive Polymers: Transport, Photophysics, and Applications*, Nalwa, H. S. (Ed.), Chapter 1–2, John Wiley & Sons: New York.
[4] Chiarelli, P., Santa, A. D., DeRossi, D., & Mazzolidic, A. (1995). *J. Intell. Mater. Syst. Struct.*, *6*, 32.
[5] Smela, E., Jnganas, O., Pei, Q., & Lundstrom, I. (1993). *Adv. Mater.*, *5*, 630.
[6] Kaneto, K., Knaeko, M., Min, Y., & MacDiarmid, A. G. (1995). *Synth. Met.*, *71*, 2211.

[7] Beebe, D. J., Moore, J. S., Bauer, J. M., Yu, Q., Liu, R. H., Devadoss, C., & Jo, B. H. (2000). *Nature*, *404*, 588.

[8] Ohno, H. & Yoshizawa, M. (2002). *Solid State Ionics*, *303* 154–155.

[9] Ue, M., Takeda, M., Toriumi, A., Kominato, A., Hagiwara, R., & Ito, Y. (2003). *J. Electrochem. Soc.*, *150*, A499.

[10] Nanjundiah, C., McDevitt, S. F., & Koch, V. R. (1997). *J. Electrochem. Soc.*, *144*, 3392.

[11] Bonhote, P., Dias, A. P., Papageorgious, N., Kalyanasundaran, K., & Graetzel, M. (1996). *Inorganic Chemistry*, *35*, 1168.

[12] Vandesteeg, N., Anquetil, P. A., & Hunter, I. W. (2003). *Proc. of SPIE*, 183, 5385.

[13] Lu, W., Fadeev, A. G., Qi, B., Smela, E., Mattes, B. R., Ding, J., Spinks, G. M., Mazurkiewicz, J., Zhou, D., Wallace, G. G., MacFarlane, D. R., Forsyth, S. A., & Forsyth, M. (2002). *Science*, *297*, 983.