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研究課題名（和文）Evolution of hierarchically structured ion conducting porous polymers with designable morphology for ionotronic sensors

研究課題名（英文）Evolution of hierarchically structured ion conducting porous polymers with designable morphology for ionotronic sensors

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研究成果の概要（和文）：イオン液体ベースのゲルと多孔質ポリマーを作成するために、PIは、ワンステップ重合プロセスを介して、チオールベースの多機能モノマーとアクリレート架橋剤のチオール-エンネットワークにイオン液体を溶媒として組み込みました。このアプローチにより、重合条件と溶媒を正確に操作できるようになり、カスタマイズされた特性を持つゲルと多孔質ポリマーを慎重に設計できました。PIは、熱溶解フィラメント製造（FFF）技術を利用して、優れた寸法精度を備えた精密で複雑な金型を作成する機能を改善しました。開発された材料は、優れた圧電容量センシング特性を示し、機械的圧力を検出して電気信号に変換することができます。

研究成果の学術的意義や社会的意義
Ion conductive polymers have garnered significant global attention due to their multifunctionality in diverse applications, such as batteries, electroactive soft robotics, and sensors. Overall, this approach has significant potential to improve the functionality of sensors in various applications.

研究成果の概要（英文）：To create ionic liquid-based gels and porous polymers, the PI incorporated an ionic liquid as a solvent into the thiol-ene network of thiol-based multifunctional monomers and acrylate crosslinkers via a one-step polymerization process. This approach enabled precise manipulation of polymerization conditions and solvents, resulting in the careful design of gels and porous polymers with tailored properties. Utilizing fused filament fabrication (FFF) technology, the PI improved capabilities in creating precise and intricate molds with excellent dimensional accuracy. Diversifying the printing methods underscores our commitment to innovation and continuous improvement.Overall, this plan aligns with our objective of advancing manufacturing processes through innovation. The developed materials exhibited excellent piezo-capacitive sensing characteristics, allowing them to detect mechanical pressure and convert it into electrical signals.

研究分野：Polymer Materials/ Engineering Materials

キーワード：Polymer　sensor

１．研究開始当初の背景 Research Background

Network polymers have achieved a significant integration of concepts from physics, chemistry, and materials science, leading to substantial advancements in the properties of gels and functional materials. A diverse array of polymeric materials, including physical gels, ionogels/ionic gels, and aerogels, have been developed for various applications across numerous fields. Notably, porous polymers incorporating ionic groups within their polymer networks hold considerable potential for applications in electrochemistry and the energy sector. One of the most promising methods for imparting ionic conductivity to polymers involves the inclusion of an ionic liquid (IL)-based solvent during the reaction process or the use of a polymerizable IL as a monomeric unit. ILs are salts composed of weakly coordinated ions, which enables these solvents to remain in a liquid state below 100 °C or even at room temperature. These ILs exhibit several desirable properties, including non-volatility, non-flammability, a wide electrochemical window, high thermal stability, and high ionic conductivity, making them attractive candidates for use in gel polymer electrolytes and batteries. In previous study, we have developed various types of cross-linked gels and porous polymers with different reaction mechanisms and molecular designs, demonstrating the feasibility of synthesizing gels with uniform, controlled mesh sizes and tailored internal network structures. The thiol-ene reaction, in particular, allows for such customizable chemistry through a robust yet straightforward, rapid, and facile technique that is applicable to both fundamental research and practical implementation in polymer chemistry. Thiol-ene radical reactions have recently been expanded to a variety of synthetic processes, encompassing basic chemical synthesis, polymeric material modification, and the fabrication of a wide range of polymeric materials. We have explored the developments of conducting porous polymers for ionotronic sensors.

２．研究の目的 Research objectives

The utilization of ionic liquids (ILs) in thiol-ene polymerization has been demonstrated to be highly effective and feasible in recent studies. However, there remains a significant opportunity to develop a diverse range of polymeric materials with tailored properties .
In our previous research, we synthesized and fabricated a series of ionic gels via a thiol-ene reaction within an IL-based solvent system, and characterized their mechanical, conductive, and thermal properties . Building on this foundation, we aim to develop a novel ion-conducting polymeric structure utilizing the thiol-ene reaction. Our approach involves using a diallyl compound with an IL structure as a linker molecule, combined with a multifunctional thiol compound as a joint molecule, within a solvent system containing lithium ions. The selected multifunctional thiol monomers, including tris[(3-mercaptopropionyloxy)-ethyl]-isocyanurate (TEMPIC), pentaerythritol tetrakis(3-mercaptopropionate) (PEMP), and dipentaerythritol hexakis(3-mercaptopionate) (DPMP), are employed to introduce structural variations in the polymer network. This allows us to investigate how these structural differences impact the mechanical and conductive behaviors of the polymers.
The objective of this research is to develop 3D printable, ion-conducting sensors. This involves the systematic synthesis and characterization of the physicochemical properties of the joint-linker type porous polymers, focusing on understanding their mechanical, conductive, thermal and morphological behaviors. Our goal is to create a new class of polymeric materials that are not only ionically conductive but also suitable for 3D printing applications, thus paving the way for advanced sensor technologies.

３．研究の方法 Experimental Methods

Infrared spectra were acquired using a Jasco FTIR (Fourier transform infrared) 410 Plus Spectrometer in transmission mode over the wavenumber range of 400-3500 cm-1..
Mechanical characterization of the ionic gels was performed using a STA-1150 testing machine (Orientec Co., Ltd., Japan). The sample gels for the compression tests were shaped into a cube with a side length of 10 mm, and the crosshead speed during

compression was kept constant at 0.50 mm min−1. All tests were carried out at room temperature.
Thermogravimetric analysis (TGA) of the samples were conducted using open aluminum pans on a thermogravimetry/differential thermal analyzer, TG-DTA2020SA, from room temperature to 500 ° C at a heating rate of 10 ° C min−1 under argon atmosphere.
The conductivity of the ionic porous polymers was measured within the frequency range 4 Hz-1 MHz and determined by using a HIOKI 3532-80 chemical impedance analyzer. The ionic gels were prepared in a constant volume cylindrical cell with stainless steel blocking electrodes and a Teflon spacer. Gel samples were sandwiched between mirror-finish stainless-steel electrodes, sealed in a Teflon container, and subjected to impedance measurements. The measurements were taken at controlled temperatures from 20 to 80 ° C in an Espec SU-220 temperature-controlled chamber three times. The samples were thermally equilibrated at each temperature for at least 1 h prior to the measurements.
The sensing characteristics the porous polymers were studied under compression mode and capacitance was measured to investigate the piezoresistive sensing characteristics.

４．研究成果 Result and Discussion

Porous polymers synthesized in IL showed distinct morphology having interconnected globular networks in three dimensions. Although their morphological stucttr did not depend on the monomer types significantly. Figure 1 shows the morphology of porous polymers containing TEMPIC and DPMP monomers in EMI TFSI ionic liquids.

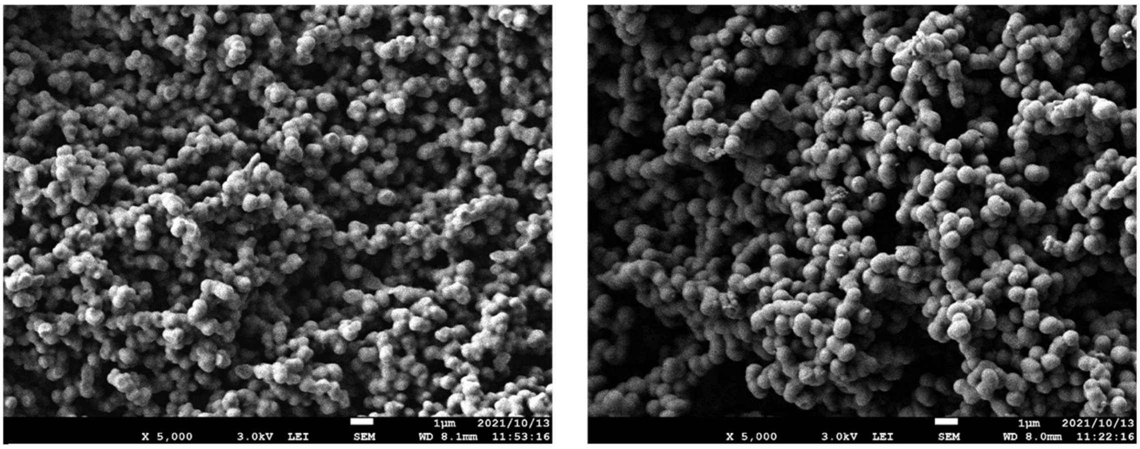

Figure 1 SEM images of porous polymers TEMPIC-NDDA and DPMP-NDDA (right) in 80% EMI TFSI IL medium

The thermal and mechanical properties of the synthesized gels showed high thermal stability and favorable mechanical stiffness with 20-40% stretchability under 50N force. In order to investigate the piezo-capacitive sensing characteristics the porous polymers TEMPIC-NDDA-EMITFSI (80% IL)were placed under the compression gauge and using a LCR meter and mechanical analyzer their force-dependent capacitance was determined (Figure 2).

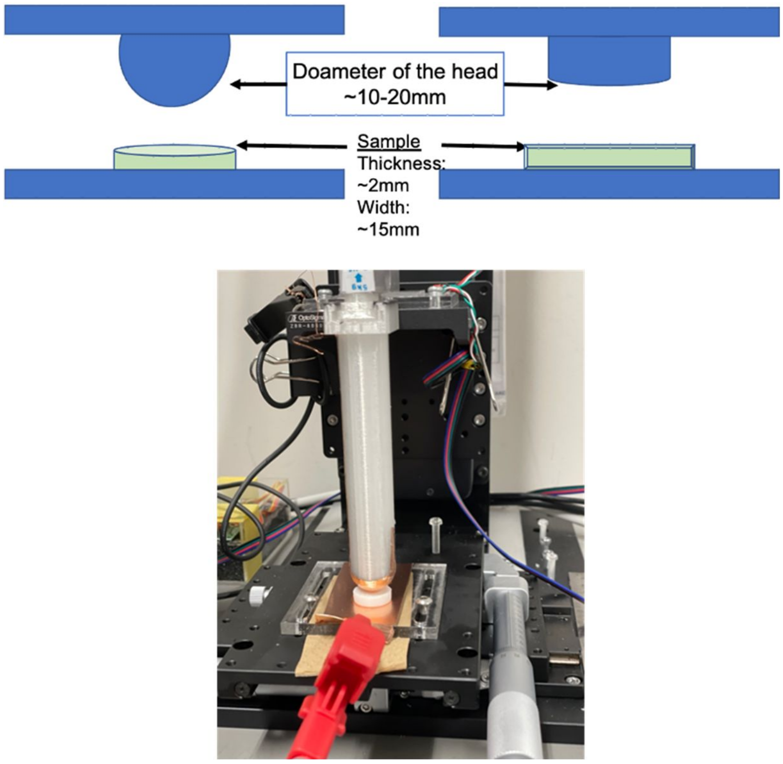

Figure 2 Force dependent capacitance measurement set up

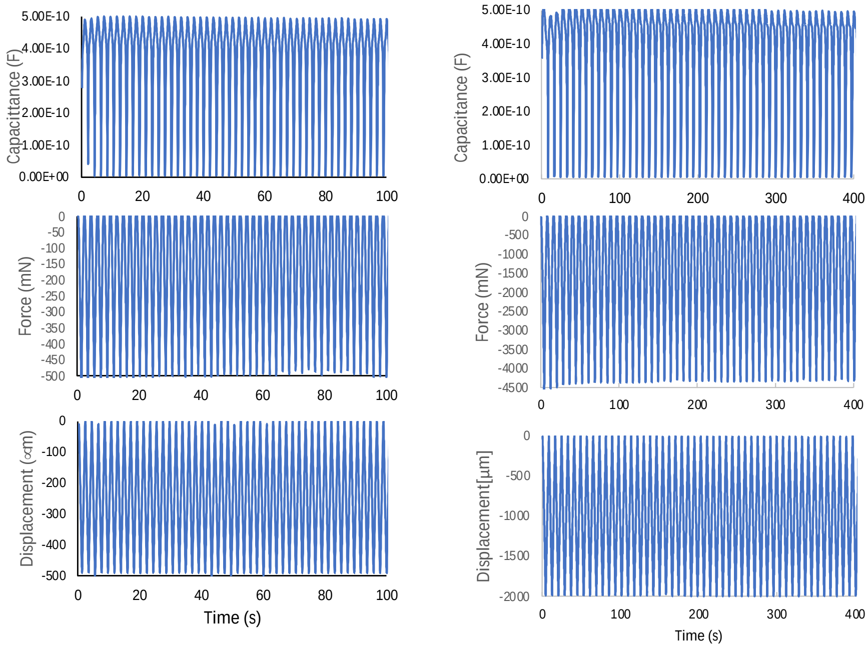

Figure 3 Piezo-capacitive sensing test (left under 0.5/s and right 2mm/s compression rate)

The Ionic liquid incorporated porous polymers TEMPIC-NDDA showed showed highly stable piezo-capacitive sensing characteristics after 50 cycles without any noticeable distortion. These gels were 3D printed using LCD resin 3D printer with good resolution. Thus the synthesized porous polymers showed potential application in the field of designable ionotronic sensors

５．主な発表論文等

〔雑誌論文〕　計2件（うち査読付論文　2件／うち国際共著　2件／うちオープンアクセス　0件）

１．著者名 Muhammad Hisyam Rosle , Zhongkui Wang , MD Nahin Islam Shiblee, Kumkum Ahmed4, Hidemitsu Furukawa Shinichi Hirai	４．巻 60
２．論文標題 Soft Resistive Tactile Sensor Based on CNT-PDMS-Gel to Estimate Contact Force	５．発行年 2022年
３．雑誌名 IEEE Sensors letters	６．最初と最後の頁 1-4
掲載論文のDOI（デジタルオブジェクト識別子） 10.1109/LSENS.2022.3151659	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Naofumi Naga, Riku Arai, Yutaka Naruse, Kumkum Ahmed, Hassan Nageh, Tamaki Nakano	４．巻 6
２．論文標題 Synthesis of porous polymers by polymerization-induced phase separation in the addition reaction of multifunctional isocyanates and dithiol compounds	５．発行年 2022年
３．雑誌名 journal of polymer science	６．最初と最後の頁 3212-3215
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/pol.20220326 Read the full text PDFPDF	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕　計2件（うち招待講演　0件／うち国際学会　2件）

１．発表者名 Kumkum Ahmed
２．発表標題 Facile fabrication of network polymers via thiol-ene click reaction for sensing applications
３．学会等名 SPIE NDE 2023（国際学会）
４．発表年 2022年～2023年

１．発表者名 Kumkum Ahmed
２．発表標題 Facile Synthesis and 3D Printing of Soft Materials and Their Applications in Sensors
３．学会等名 MRS Fall 2022（国際学会）
４．発表年 2022年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

8．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関