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Yong Zhong, Giao Nguyen, Cedric Plesse, Frédéric Vidal, Edwin Jager. Highly Conductive, Photolithographically Patternable Ionogels for Flexible and Stretchable Electrochemical Devices. ACS Applied Materials & Interfaces, 2018, 10 (25), pp.21601-21611. 10.1021/acsami.8b03537 . hal-03287119

HAL Id: hal-03287119

<https://hal.science/hal-03287119>

Submitted on 2 Feb 2024

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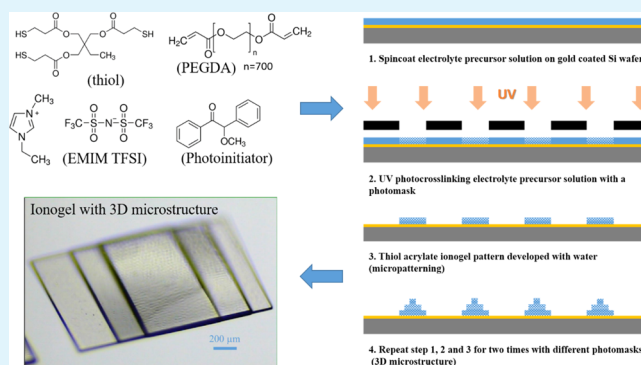
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Highly Conductive, Photolithographically Patternable Ionogels for Flexible and Stretchable Electrochemical Devices

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ABSTRACT: An ionic conducting membrane is an essential part in various electrochemical devices including ionic actuators. To miniaturize these devices, micropatterns of ionic conducting membrane are desired. Here, we present a novel type of ionogel that can be patterned using standard photolithography and soft imprinting lithography. The ionogel is prepared in situ by UV-initiated free-radical polymerization of thiol acrylate precursors in the presence of ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The resultant ionogel is very flexible with a low Young's modulus (as low as 0.23 MPa) and shows a very high ionic conductivity (up to 2.4×10^{-3} S/cm with 75 wt % ionic liquid incorporated) and has a reactive surface due to the excess thiol groups. Micropatterns of ionogel are obtained by using the thiol acrylate ionogel solution as an ionic conducting photoresist with standard photolithography. Water, a solvent immiscible with ionic liquid, is used as the photoresist developer to avoid complete removal of ionic liquid from thin micropatterns of the ionogel. By taking advantage of the reactive surface of ionogels and the photopatternability, ionogels with complex three-dimensional microstructure are developed. The surface of the ionogels can also be easily patterned using UV-assisted soft imprinting lithography. This new type of ionogels may open up for building high-performance flexible electrochemical microdevices.

KEYWORDS: micropatterning, ionogel, reactive surface, thiol acrylate photochemistry, electrochemical devices, photolithography



1. INTRODUCTION

The increasing demand for wearable and flexible electrochemical devices has emphasized a need for soft and flexible ionic conducting membranes with high ionic conductivities.^{1–5} An ionic conducting membrane such as a solid polymer electrolyte and an ionogel is a type of material that has been widely used as an ion reservoir and electronic insulator in numerous applications, including supercapacitors,⁶ ionic actuators,⁷ electrolyte-gated transistors,⁸ electrochromic devices,⁹ solar cells,¹⁰ and electrochemical sensors.¹¹ Usually the ionic conducting membrane is prepared by confining solid or liquid electrolytes in a polymer system. Recently, room-temperature ionic liquids emerged as a promising class of electrolytes among the various liquid electrolytes because of their many excellent physicochemical properties, such as wide electrochemical window, high ionic conductivities, low melting points, chemical and thermal stability, nonflammability, and negligible vapor pressure.^{11,12} When the ionic liquid is loaded within a polymer gel network, the resultant ionic conducting membrane has been termed in the literature as ionogel in which the ionic liquid enables ionic conduction while the polymer network provides a solid supporting structure.¹³

Micropatterning and microstructuring of an ionic conducting membrane is an important aspect for the development and fabrication of arrays of flexible microelectrochemical components on large substrates.¹⁴ There are several micropatterning techniques that can be used to pattern the ionic conducting membrane, and one interesting technique is conventional photolithography as it enables a single-step process for precise micropatterning. As such, photolithography has been widely used for mass production of silicon-based microelectronics in the semiconductor industry.¹⁵ To use this micropatterning technique for microelectrochemical device fabrication, an ionic conducting membrane photopatternable like a commercial photoresist has to be developed. Recently, several groups have demonstrated the micropatterning of poly(ethylene glycol) diacrylate (PEGDA)-based ionic conducting membrane using a photolithographic process. PEGDA-based electrolyte patterns were then integrated in transistors^{16–18} and micro-supercapacitors.¹⁹ An ABA-triblock copolymer-based ionogel was also utilized to prepare high-capacitance thin ionic conducting

Received: March 1, 2018

Accepted: June 1, 2018

Published: June 1, 2018

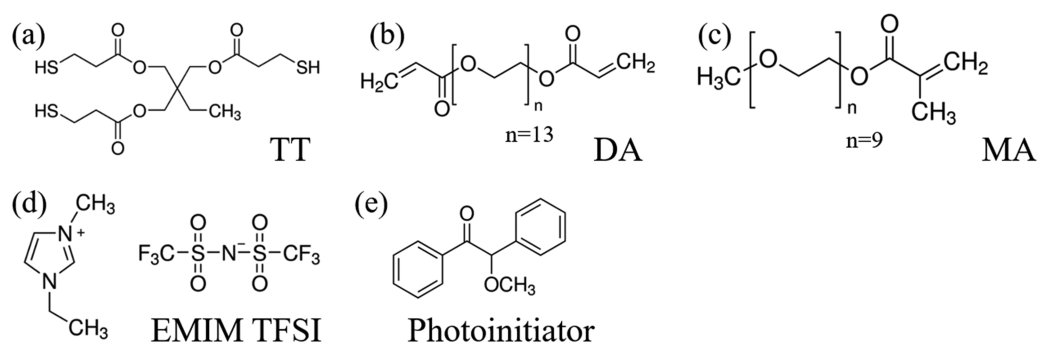


Figure 1. Chemical structures of materials used in this study: (a) Trimethylolpropane tris(3-mercaptopropionate) (TT), (b) poly(ethylene glycol) diacrylate (PEGDA, average $M_n = 700$ g/mol) (DA), (c) poly(ethylene glycol) methyl ether methacrylate (PEGMA, average $M_n = 500$ g/mol) (MA), (d) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI), and (e) benzoin methyl ether (Photoinitiator).

micropatterns for electrolyte-gated transistors.⁸ These studies show that conventional standard photolithography is a convenient technique to obtain micropatterns of ionic conducting membrane and incorporate them into various microdevices. In addition to photolithography, a microscale patterned ionic conducting membrane is also possible by using soft imprinting lithographic or micromoulding techniques.²⁰

It is essential that these microfabricated ionic conducting membranes exhibit a low Young's modulus and high ionic conductivity for applications in flexible electrochemical devices. A high ionic conductivity of the ionic conducting membrane leads to fast ion intercalation or deintercalation and thus fast operation of the electrochemical devices, such as soft actuators and electrochromic pixels. The low Young's modulus of the ionic conducting membrane is especially important in soft actuators, as softer ionic conducting membranes give a larger bending movement or stroke of the actuator, but also essential in other flexible electrochemical devices, such as flexible electrochromic displays.

Beyond its mechanical and conductive properties, adhesion between the ionic conducting membrane layer and other functional layers is also very important in these flexible electrochemical devices that usually have a multilayered structure.^{21,22} Delamination between the layers may occur upon temperature change or repeated mechanical bending due to a mismatch of the thermal expansion coefficient or Young's modulus, respectively, especially if only weak physical bonding exists.¹⁷ This poor interfacial adhesion issue severely affects the long-term performance of these devices. A possible solution is to create permanent chemical bonding between the layers. As demonstrated by Jeong and co-workers, the adhesion between the ionic conducting membrane layer and the substrate for an organic transistor was greatly improved by using a substrate with a reactive surface through covalent chemical bonding.¹⁷

In this article, we present a novel type of soft and flexible ionogel with a low Young's modulus and a very high ionic conductivity. This new type of ionogel can be micropatterned using both standard photolithography and soft imprinting lithography. The ionogel is prepared in situ by UV-initiated free-radical polymerization of thiol acrylate precursors in the presence of an ionic liquid: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI). These ionogels also have a reactive surface with excess of thiol groups. By taking advantage of the reactive surface and the photopatternability of the ionogels, complex three-dimensional (3D) microstructures are developed. This new type of ionogel may

open up pathway for building high-performance flexible electrochemical microdevices.

2. MATERIALS AND METHODS

2.1. Materials. Trimethylolpropane tris(3-mercaptopropionate) (TT), poly(ethylene glycol) diacrylate (PEGDA, $M_n = 700$ g/mol) (DA), poly(ethylene glycol) methyl ether methacrylate (PEGMA, $M_n = 500$ g/mol) (MA), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI), and benzoin methyl ether (Photoinitiator) were purchased from Sigma-Aldrich and used without further purification. The chemical structures of these materials are shown in Figure 1.

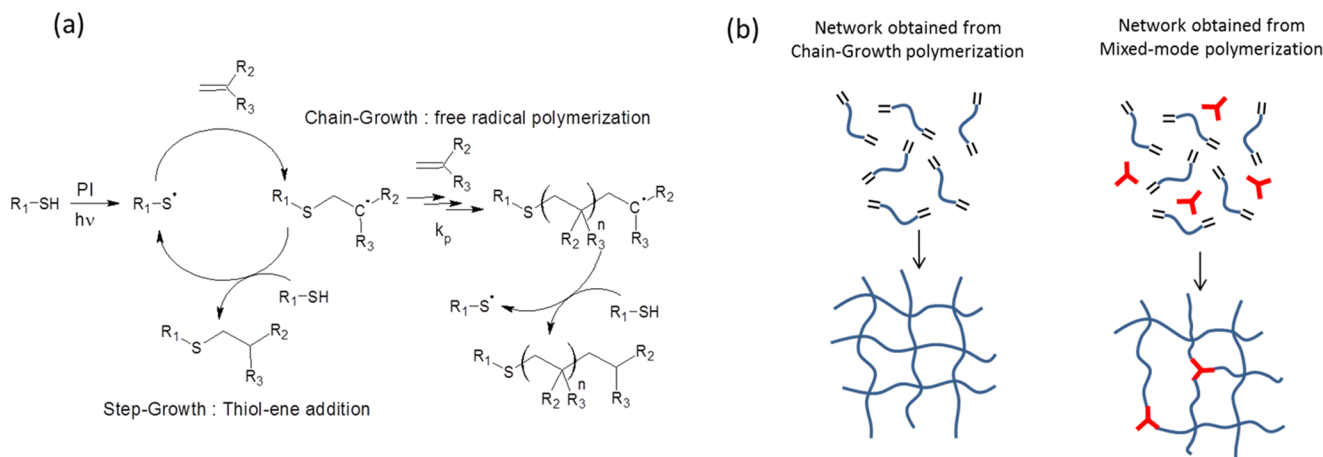
2.2. Preparation of Ionogel Films. The following general procedure was used for the preparation of ionogel films. The precursor mixture was first prepared by mixing thiol (TT), (meth)acrylate precursors (PEGDA and PEGMA) and photoinitiator (1 wt % of the total weight of TT, PEGDA and PEGMA) under a light-protected condition. A stoichiometric balance between total thiol groups and (meth)acrylate groups was maintained for all samples. The methacrylate groups accounts for 0, 12.5, or 25% of the total (meth)acrylate functional groups in the precursor mixture. Ionic liquid was added in the precursor mixture to obtain a final electrolyte precursor solution with ionic liquid weight percentage of 25, 50, or 75 wt % versus the total weight of the final electrolyte precursor solution. Details of all sample compositions are listed in Table 1. The electrolyte precursor solution was then encased between two glass plates and the thickness was

Table 1. Composition of Each Ionogel Sample^a

sample name	composition			
	TT (mol)	PEGDA (mol)	PEGMA (mol)	EMIM TFSI (wt %)
DA100MA0	2	3		
DA87.5MA12.5	2	2.625	0.75	
DA75MA25	2	2.25	1.5	
DA100MA0IL25	2	3		25
DA87.5MA12.5IL25	2	2.625	0.75	25
DA75MA25IL25	2	2.25	1.5	25
DA100MA0IL50	2	3		50
DA87.5MA12.5IL50	2	2.625	0.75	50
DA75MA25IL50	2	2.25	1.5	50
DA100MA0IL75	2	3		75
DA87.5MA12.5IL75	2	2.625	0.75	75
DA75MA25IL75	2	2.25	1.5	75

^aEach sample is named by the ratio of PEGDA, PEGMA, and ionic liquid. For example, DA75MA25IL50 denotes 75% molar percent of the acrylate groups from PEGDA, 25% methacrylate groups from PEGMA, and 50 wt % ionic liquid in the mixture while maintaining 1:1 thiol (meth)acrylate stoichiometry.

Scheme 1. (a) General Scheme for Mixed-Mode Photopolymerization with a Combination of Chain-Growth Polymerization of (Meth)acrylate and Thiol-(meth)acrylate Addition Reaction in a Mixture of Thiol-(meth)acrylate with Radicals; (b) Illustration of Polymer Network Obtained from Chain-Growth Polymerization and Mixed-Mode Polymerization



controlled by a 0.5 mm thick silicon wafer spacer. Freestanding ionogel films were obtained by curing the electrolyte precursor solution in normal atmosphere with a UV curing conveyor system (Primarc UV Technology, Minicure, Mercury vapor Lamp, UV intensity 100 W/cm², duration of each scan 4 s). Functional group conversion monitored by Fourier-transform infrared (FT-IR) was used to determine the minimum number of UV scans for full curing. Polymer films without the ionic liquid and PEGDA films without thiols from pure acrylate homopolymerization were also prepared in the same way.

2.3. Micropatterning of Ionogels. Micropatterns and microstructures of the ionogels were prepared using standard lithographic processes. The electrolyte precursor solution was spun onto a gold-coated silicon wafer at 800 rpm with an acceleration of 300 rpm/s for 30 s. Patterned UV illumination was performed by using a mask aligner (MJB-3 SUSS MicroTec) with UV intensity of 3 mW/cm² for 60 s. The uncured materials in the unexposed areas were removed using two different solvents (deionized water and acetone) as the development solvent. Thereafter, samples were dried with compressed nitrogen. To obtain 3D microstructures of ionogels, these lithographic steps were repeated two more times and an alignment step was performed between each layer deposition. The thickness profile for these micropatterns and microstructures was measured with a Veeco Dektak 6 M surface profilometer. The surface of ionogel films was patterned with a soft imprinting lithographic technique. SU-8 2010 negative photoresist was used to make a master template on a silicon wafer using a standard photolithographic process.²³ The polymer electrolyte solution was casted on the SU-8 patterns and cured by UV exposure for 4 min with a portable UV lamp (VL-208.BL, Vilber). Thereafter, the patterned ionogel films were peeled off from the patterned silicon wafer.

2.4. Fourier-Transform Infrared (FT-IR). Attenuated total reflection (ATR)-FT-IR spectroscopy was used to study the polymerization kinetics and to monitor functional group conversion. FT-IR analysis was performed using a Tensor 27 (Bruker) FT-IR instrument equipped with an ATR accessory unit. (Meth)acrylate conversion was monitored at 810 cm⁻¹ (C=C twisting vibration band), whereas thiol conversion was observed at 2560 cm⁻¹ (S-H twisting vibration band).²⁴ Conversions were estimated using the ratio of the peak area after curing to the peak area prior to UV irradiation.

2.5. Mechanical Properties. Mechanical property measurements of ionogel films were performed on a Dynamic Mechanical Analyzer instrument (TA, Q800) in tensile mode. Strips with a typical size of 8 mm × 15 mm cut from the sample films were tightened in the clamps and the strain-ramped at 20%/min to 200%, with initial strain of 0.02% and preload force of 0.01 N.

2.6. Electrical Impedance Spectroscopy. The ionic conductivity of ionogel films and micropatterns was determined by electrochemical impedance spectroscopy with a VSP potentiostat (Biologic SA). The

ionogel films were placed between two electrodes, and the impedance was measured in the frequency range 1 MHz–0.01 Hz, at 10 points/dec, with an oscillation potential of 10 mV around 0 V. To measure the ionic conductivity of micropatterns, thin micropatterns were initially deposited on a gold-coated silicon wafer, which acts as an electrode during the measurement, and then another small electrode with a predetermined surface area was placed on the top of the micropatterns. The ionic conductivity was calculated using the following equation

$$\sigma = \frac{1}{Z} \frac{d}{S}$$

where Z is the real part of the complex impedance (ohms), d is the thickness of the sample, and S is the sample area between the two electrodes (cm²).

2.7. Extractible Content. To study the formation of polymer gel network prepared by thiol acrylate photopolymerization, sample films with known weight (w_0) and ionic liquid weight percentage (X) were extracted in a Soxhlet for at least 72 h using dichloromethane to remove the non-cross-linked material. The extracted samples were dried in a vacuum oven at room temperature to a constant weight (w_1). The extractible content was determined as follows

$$\text{extractible content (\%)} = \left(1 - \frac{w_1}{(1 - X) \times w_0} \right) \times 100$$

2.8. Preparation of Electrochromic Patterns and Electrochemical Trilayer Actuators. To prepare electrochromic patterns, a poly(3,4-ethylenedioxythiophene) (PEDOT)–poly(styrene sulfonate) (PSS) (PH1000, Heraeus)-coated positron emission tomography (PET) film was used as the flexible substrate. The width of the printed PEDOT–PSS lines on the PET film is around 0.9 cm, and two PEDOT–PSS line patterns were separated by 0.1 cm. Patterns of ionogels from formulation DA100MA0IL50 were prepared on top of two adjacent PEDOT–PSS lines by a photolithographic process, as described in Section 2.3. A step potential for 10 s at 1 and –1 V was applied between the two PEDOT–PSS electrodes using a potentiostat (Ivium Technologies). An electrochemical actuator was prepared by drop casting about 1 mL of PEDOT–PSS solutions onto both sides of ionogel films that were patterned using soft imprinting lithography, as explained under Section 2.3. Dimethyl sulfoxide solvent, 5% by volume, was added to the PEDOT–PSS solution to increase the conductivity. Actuator strips were cut out, with the imprinted pattern at 45° relative to the length of the strip. A cycling step potential for 30 s at 3 V and 30 s at –3 V was applied to the PEDOT–PSS electrodes, and the resultant bending movement was recorded with a portable camera.

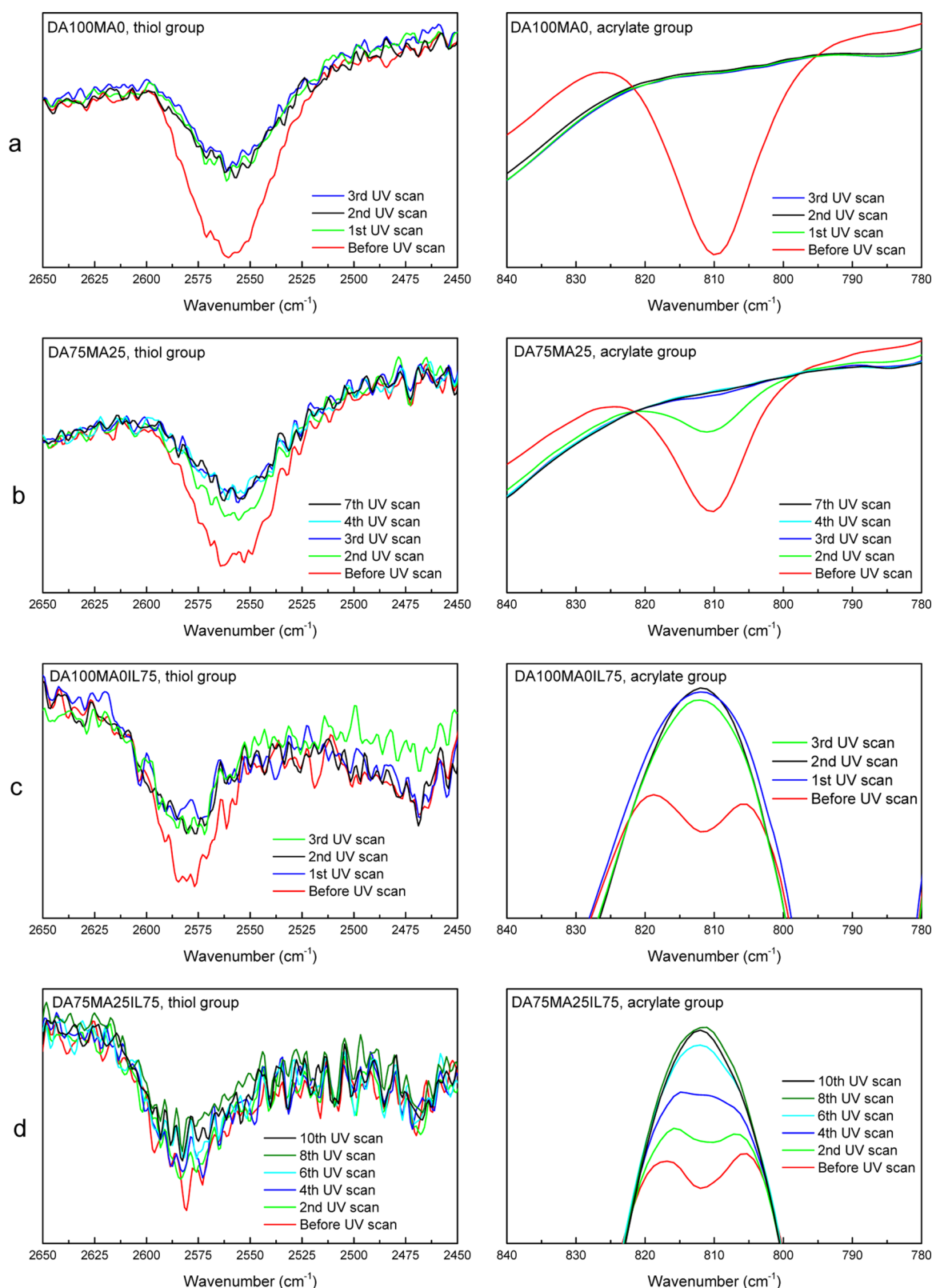


Figure 2. FT-IR spectra for samples: row (a) DA100MA0, (b) DA75MA25, (c) DA100MA0IL75, and (d) DA75MA25IL75 with different numbers of UV scans.

3. RESULTS AND DISCUSSION

3.1. Ionogel Prepared by Thiol Acrylate Photopolymerization. The polymer gel network for ionogel preparation in this study was synthesized by the photopolymerization of a

mixture of trifunctional thiol, PEG diacrylate, and monofunctional PEG methacrylate in the presence of the photoinitiator benzoin methyl ether. The polymerization can be carried out in the presence or in the absence of ionic liquid (EMIM TFSI). The related reaction mechanisms for this thiol (meth)acrylate free-

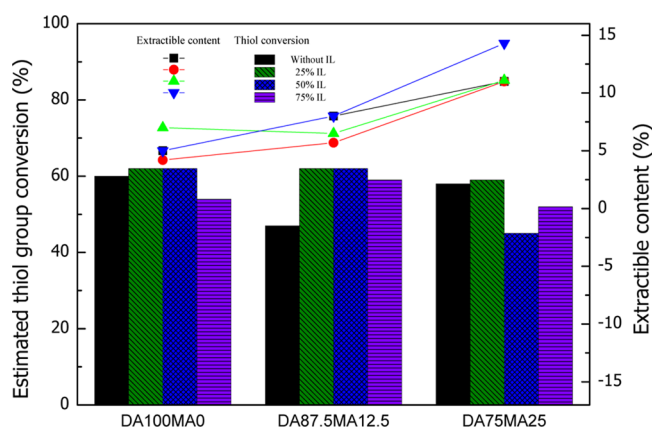


Figure 3. Estimated thiol group conversion (left axis) and extractable content (right axis) for the samples studied.

radical photopolymerization are discussed first to get a better understanding of the experimental results. The scheme for this photopolymerization process is illustrated in Scheme 1 inspired from the mechanism proposed in ref 25.

Upon UV irradiation, the photoinitiator generates radicals for polymerization initiation. The generated radical is transformed into a propagating thiyl radical (R_1-S^\bullet) by abstracting a hydrogen from the thiol functional group. The thiyl radical attacks a carbon–carbon double bond in the (meth)acrylate groups forming the carbon radical. This carbon radical abstracts a hydrogen from a thiol function group for regenerating thiyl radical, which can reinitiate the thiol-ene addition reaction with a step-growth mechanism. In this case, the thiol groups in the mixture act as a chain-transfer agent to regenerate active propagating thiyl radicals. There is another propagation step occurring in thiol acrylate photopolymerizations as these carbon radicals readily react with the (meth)acrylate groups via conventional free-radical chain-growth mechanism. Therefore, in a mixture of (meth)acrylate and thiol monomers, photopolymerization occurs via a radical-mediated mixed-mode mechanism that is a combination of step-growth and chain-growth reactions.^{26–28}

The polymer gel network resulting from this unusual thiol (meth)acrylate mixed-mode photopolymerization has several

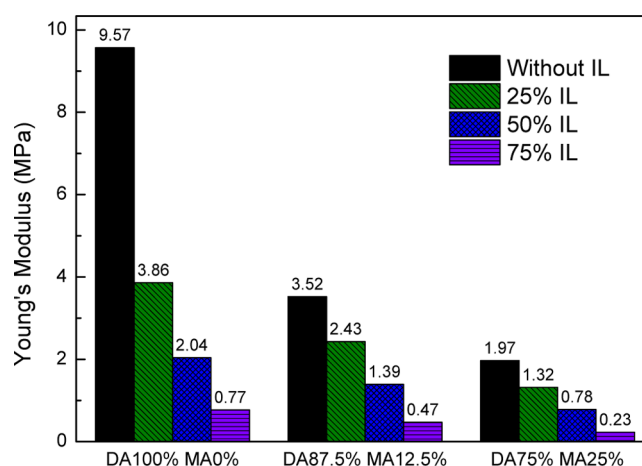


Figure 5. Young's modulus for the samples with varying ionic liquid loading.

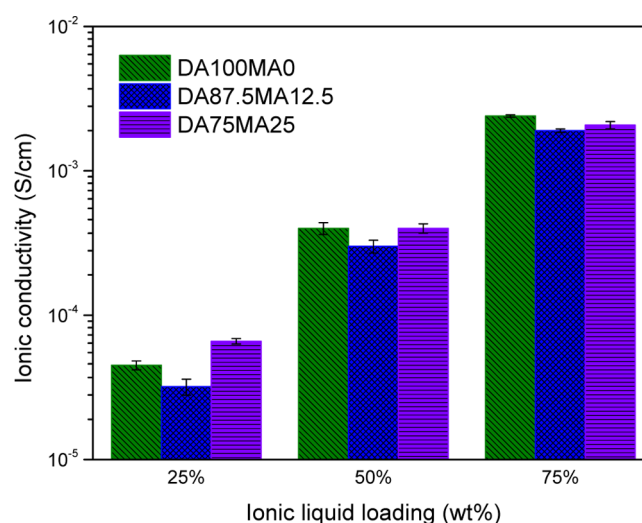


Figure 6. Ionic conductivity at room temperature for the thick-film samples prepared.

unique and attractive properties that cannot be obtained through conventional (meth)acrylate free-radical polymerization. To

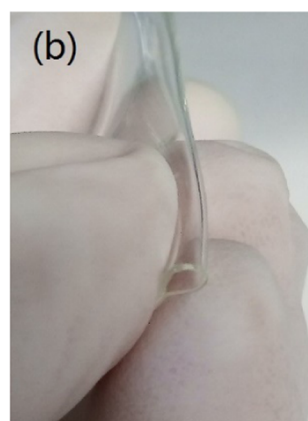
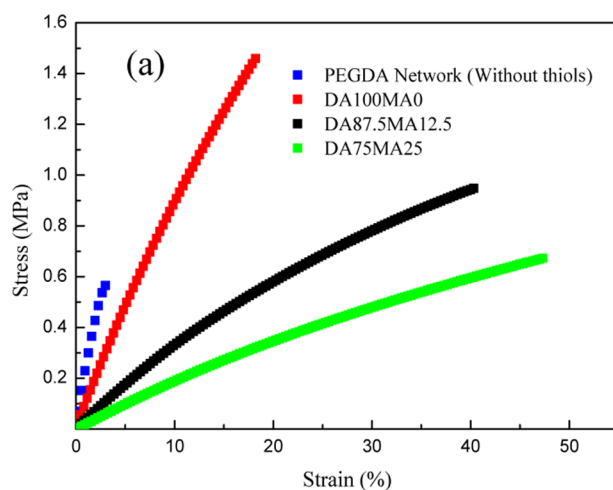


Figure 4. (a) Stress–strain curves for PEGDA network without thiol (as a control sample) and thiol-based PEGDA network samples: DA100MA0, DA87.5MA12.5, and DA75MA25; (b) photograph of folded thiol-based PEGDA gel DA100MA0 showing high flexibility.

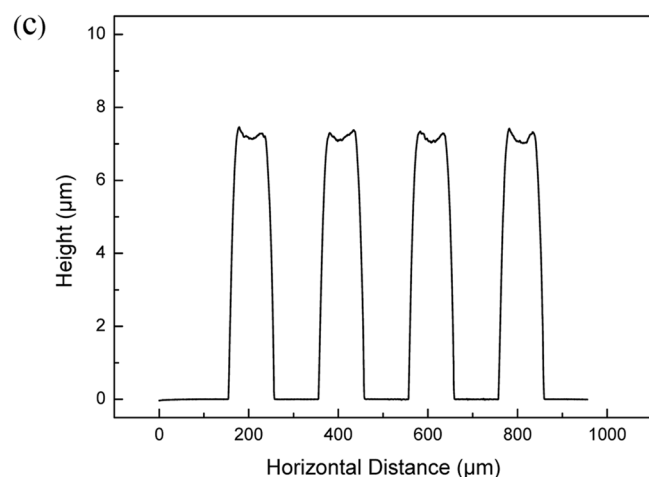
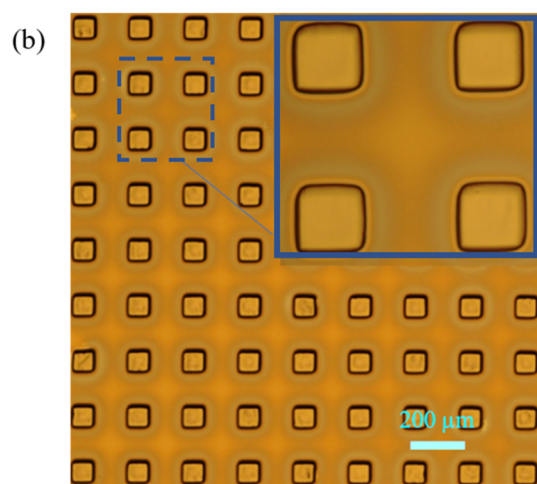
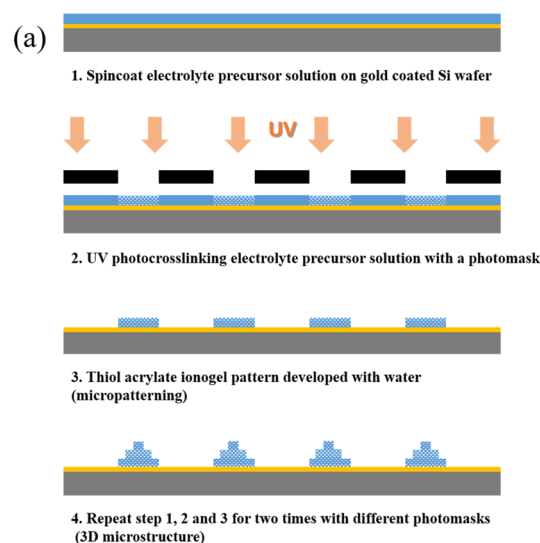


Figure 7. (a) Photolithographic process flow overview; (b) microscope images of the obtained micropatterns of ionogel (DA100MA0IL50) using water as the development solvents, inset shows a higher magnification; and (c) their thickness profile.

begin with, the polymerization kinetics were studied by FT-IR spectroscopy. All samples are synthesized by maintaining 1:1 thiol (meth)acrylate stoichiometry with 1 wt % of photoinitiator. The addition of monofunctional methacrylate is to reduce the

Table 2. Measured Ionic Conductivity for Ionogel Thick Films and Their Micropatterned Thin Films

sample name	thin pattern/thick film	development solvent	ionic conductivity (S/cm)
DA100MA0IL50	thin pattern (10 μm)	water	4.7×10^{-5}
DA100MA0IL50	thin pattern (10 μm)	acetone	1.4×10^{-7}
DA100MA0IL50	thick film (0.5 mm)	N/A	4.0×10^{-4}
DA100MA0	thick film (0.5 mm)	N/A	1.5×10^{-6}

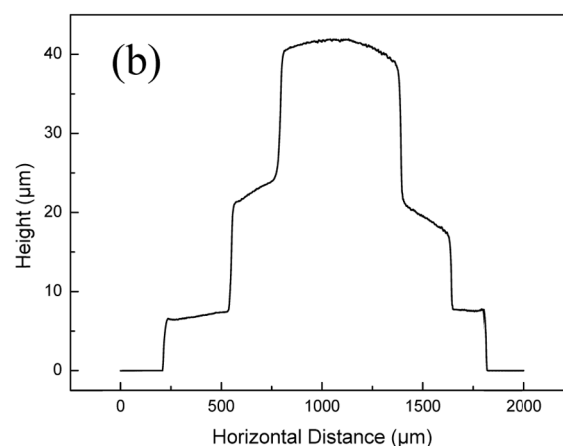
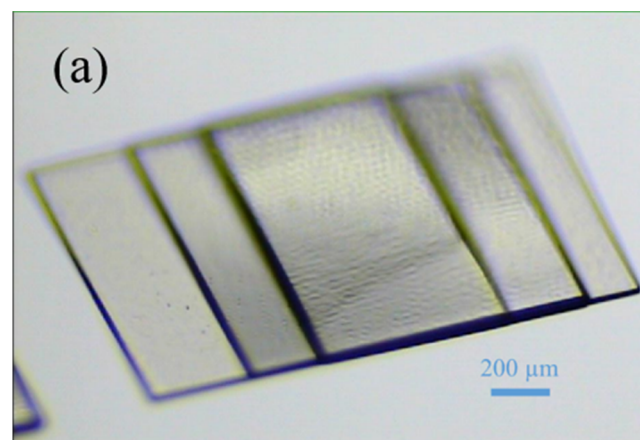


Figure 8. (a) Photograph of the obtained 3D microstructure of ionogel (DA100MA0IL50) using water as the development solvents and (b) its thickness profile.

cross-linking density. The reaction kinetics of DA100MA0 and DA75MA25 are investigated, and their spectra are shown in Figure 2a,b, respectively. The simultaneous decrease in the intensity of both the thiol twisting vibration band at 2570 cm^{-1} and the (meth)acrylate double bond twisting vibration band at 810 cm^{-1} indicates both functional groups are taking part in the reaction. No more variation of the absorbances was observed after just one UV scan for sample DA100MA0 and after four UV scans for sample DA75MA25, indicating the completion of polymerization. A lower reactivity versus thiol-ene addition of the methacrylate group of PEGMA compared to that of the PEGDA acrylate may lead to the extra UV scans needed for full curing of DA75MA25.^{29,30} The IR absorbance for (meth)acrylate group disappears completely after UV exposure, which means a full conversion of (meth)acrylate groups while the thiol groups do not achieve a full conversion. When ionic liquid is added to the reactive mixtures, the same behavior is observed

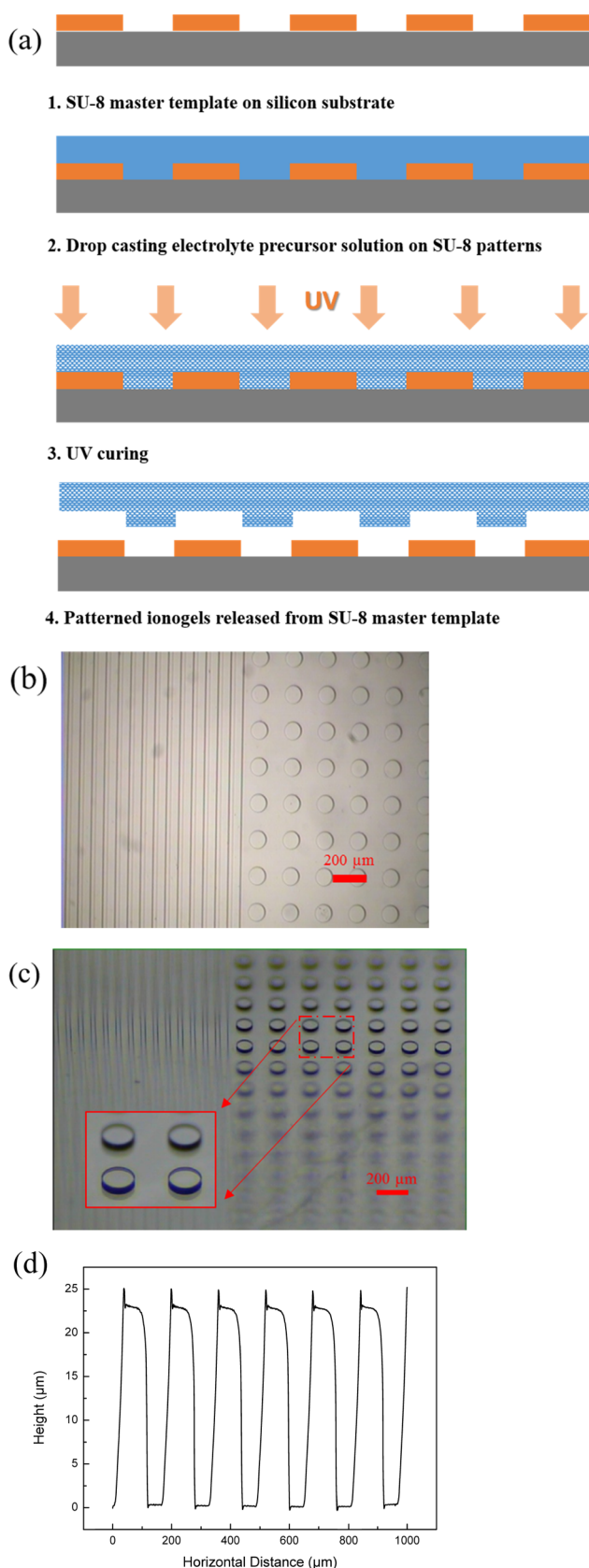


Figure 9. (a) Soft lithographic process flow overview, (b) top view, (c) side view of the obtained micropatterns of DA100MA0IL50 ionogel (micropillar diameter, 100 μm ; line width, 50 μm ; inset with higher magnification photos), and (d) thickness profiles for the micropillar structure (when measuring the line width, the needle from the Dektak distorted the line pattern due to the softness of the material).

(Figure 2c,d). Indeed, the FT-IR spectra for DA100MA0IL75 and DA75MA25IL75 also show that thiol groups are not fully reacted while acrylate/methacrylate groups had a full conversion in the presence of ionic liquid. This shows the addition of ionic liquid did not change the mixed-mode polymerization mechanism. However, the number of UV scans needed to achieve a full polymerization for sample DA75MA25IL75 increased from 3 to 8 UV scans compared to that without ionic liquid loading. The slower polymerization rate is caused by the dilution of the precursor solution with the ionic liquid, which also makes determination of thiol conversions difficult due to a small, relatively noisy thiol absorption absorbance. Nevertheless, there are a large number of unreacted thiol groups remaining not only in the bulk but also on the surface of ionogel film.

The estimated thiol group conversion for all samples according to absorbance area comparison is shown in Figure 3, which shows that around 50–60% percent of the thiol groups remain unreacted. This means the conversion of the (meth)acrylate functional groups can reach twice that of the thiol functional groups. The unequal consumption of thiol and (meth)acrylate groups for starting mixtures having 1:1 ratios of thiol and (meth)acrylate functional groups is due to the unusual mixed-mode polymerization reaction as discussed before, in which the (meth)acrylate monomer participates not only in step-growth polymerization with thiol groups but also in chain-growth free-radical polymerization. Prior studies reported the kinetic constant for the acrylate propagation via homopolymerization to be 1.5 times greater than that of the hydrogen abstraction reaction by thiol groups.²⁴ Using this value, theoretical final thiol conversion for initial thiol acrylate molar ratios of 1:1 is calculated to be 52%.²⁷ This shows that the final thiol conversion in this study was well in accordance with the theoretical value.

Although half of the initial thiol groups remain unreacted after the photopolymerization, low extractable content values were obtained, as measured by the soluble fraction of polymer gel network, summarized in Figure 3. For the sample in DA100MA0, only 5% of the initial weight is extractable from the polymer network. This low extractable content, characterizing a well-formed polymer network, is explained by the use of trifunctional thiol in step-growth polymerization and exclusively difunctional acrylate precursors in chain-growth polymerization. In addition, this low extractable content allows stating that most of unreacted thiol functions are incorporated to the network as pendant thiol groups, despite their low conversion. As the monofunctional methacrylate content increases, the extractable contents increase moderately to 14%, indicating the increase of non-cross-linked polymer chains in the polymer network. The higher extractable content can be ascribed to the increased presence of linear polymer chains formed by monofunctional methacrylate homopolymerization, initiated by a thiol monomer but not incorporated to the polymer network. It is worthy to mention that comparable extractable contents were obtained with or without ionic liquid in the reaction mixture, independent to the mixture composition. The presence of ionic liquid does not seem to influence the photopolymerization. Thus, the polymer membranes generated from thiol acrylate photopolymerization have well-formed polymer networks even with a high amount of unreacted thiol groups, which stay in the bulk and on the surfaces unrestricted by the quantity of ionic liquid present in the mixture.

All in all, the mixed-mode mechanism together with the different propagation rates in two propagation routes for (meth)acrylates are responsible for the presence of unreacted thiol groups in thiol (meth)acrylate photopolymerization. These

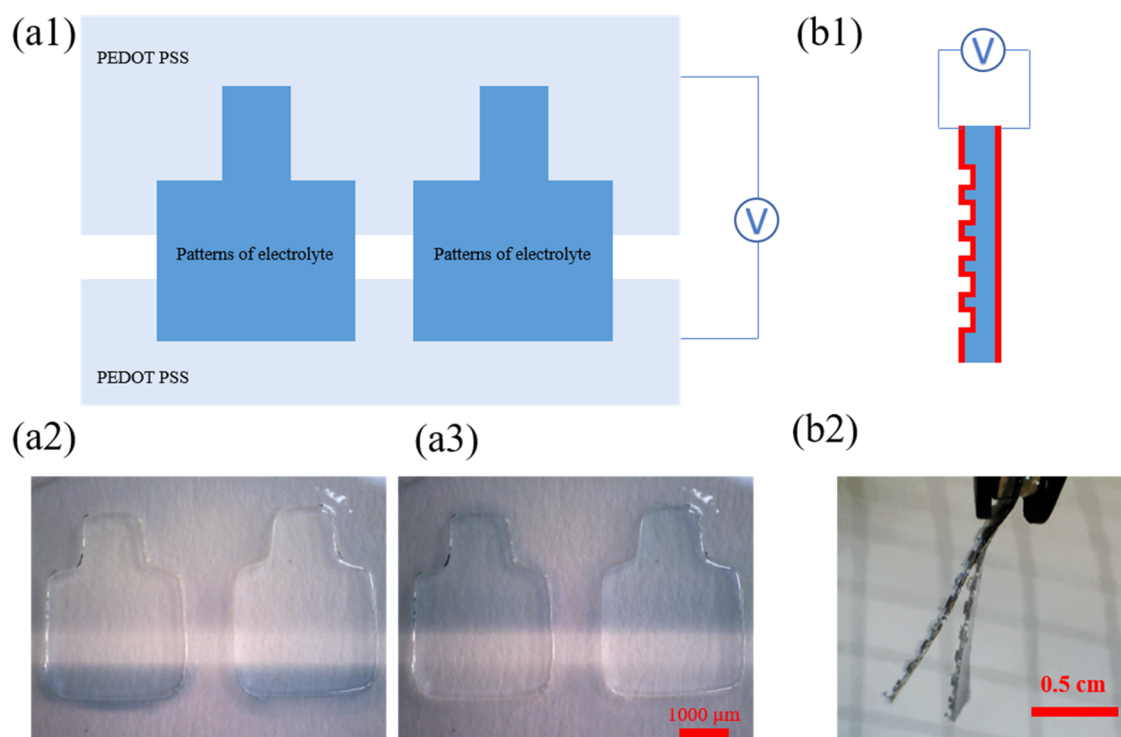


Figure 10. (a1) Schematic of electrochromic patterns in which two UV-micropatterned ionogels are located on two electrically isolated PEDOT–PSS lines on a flexible PET foil, (a2) bottom PEDOT electrode reduced and top oxidized in their two electrochromic states and (a3) vice versa; (b1) schematic of micropatterned ionogel using a soft imprinting in a electrochemical trilayer actuator and (b2) an overlay photograph of the bending movement showing a twisting of the actuator due to the micropattern.

excess thiol groups are still reactive and can still participate in thiol-related chemical reactions. The reactive surface will be demonstrated in the micropatterning process to build a microstructure. Thus, an ionogel with a reactive surface is achieved.

To study the effect of mixed-mode polymerization mechanism on the mechanical properties, polymer films made from thiol acrylate photopolymerization are mechanically tested along with polymer films from pure acrylate homopolymerization as a reference. As shown in Figure 4, PEGDA network prepared without thiols shows a low strain of less than 5%, whereas adding the thiol into PEGDA network leads to a great strain improvement to 20% (DA100MA0). The Young's modulus is also decreased from 23.17 to 9.57 MPa after thiol incorporation, as evidenced by a reduced slope value from the stress–strain curves. Thus, the polymer film with thiol addition is very soft and flexible. It can be folded without breaking, as shown in Figure 4b, whereas PEGDA without thiol addition breaks easily when trying to bend it. The improved mechanical properties after thiol addition are due to the fact that thiol monomers are incorporated into the PEGDA network via a step-growth mechanism, causing a reduction in the cross-linking density, thereby modifying mechanical properties.^{31,32} The mechanical properties are improved by partially replacing difunctional PEGDA with monofunctional methacrylate PEGMA to reduce further the cross-linking density in the polymer network. With methacrylate contents increasing from 0 to 25%, the strain at break for thiol acrylate network increases from 20 to 50% and the Young's modulus decreases from 9.57 to 1.97 MPa, as shown in Figure 5. Soft and flexible polymer gels resulting from the thiol acrylate photopolymerization are advantageous for use as the polymer matrix for flexible ionogel preparation. The incorporation of

ionic liquid had a huge effect on the Young modulus of the ionogel film. With increasing ionic liquid loading from 0 to 75%, the Young modulus decreased from 9.57 to 0.77 MPa. The lowest Young's modulus of polymer electrolytes films was obtained when 75% of ionic liquid was incorporated into 25% methacrylate. This made the obtained ionogel film soft and flexible.

The ionic conductivity of the ionogel with ionic liquid incorporated is shown in Figure 6. It is noteworthy to mention that the ionic conductivity of neat ionic liquid is 8×10^{-3} S/cm. The conductivity of synthesized solid polymer electrolytes increased with an increase of ionic liquid loading up to 2.4×10^{-3} S/cm at room temperature for DA100MA0IL75, indicating that the presence of polymer network has limited effect on the ionic conductivity. Also, the addition of methacrylate had only a little effect on the ionic conductivity. At the same ionic liquid loading, the conductivity showed very little difference.

3.2. Micropatterns of Ionogels by Standard Photolithography. The thiol acrylate polymerization is initiated by UV light, which allows to control the polymerization spatially and temporally.³³ The thiol acrylate polymerization is not significantly inhibited by oxygen, and therefore does not exhibit an uncured surface even when the reaction is exposed to ambient conditions.³⁴ The reduction of oxygen inhibition also leads to a relatively fast polymerization kinetics compared to that of conventional acrylate-based photopolymers that are significantly inhibited by oxygen.³⁵ Therefore, the ionogels prepared by this photoreaction are suitable for thin-film preparation and were further employed for the preparation of thin micropatterns using standard photolithography techniques, as illustrated in Figure 7.

The starting point was the test of micropatternability of the polymer electrolyte. The sample DA100MA0IL50 with a fast

kinetics was chosen for the micropatterning test due to the low UV intensity of the mask aligner. Precursor solution was first spin-coated on a gold-coated silicon wafer to obtain uncured thin film. UV exposure of the precursor solution was performed through a quartz chromium photomask with a UV intensity of 3 mW/cm² for 60 s. The development of the micropatterns was done by rinsing the irradiated polymer films in water to wash away the non-cross-linked materials on the wafers. The obtained micropatterns were visualized by microscopic techniques, and their thickness profiles are shown in Figure 7b. Without any optimization, polymer patterns with a lateral structure size of 100 μ m and thickness of around 10 μ m were obtained. This clearly demonstrates the excellent micropatternability of the polymer electrolyte solution by thiol acrylate photopolymerization.

Apart from the micropatternability, it is also important to check the ionic conductivity of the micropatterns after the development process. Two different liquids were chosen as development solvent to investigate the effect of development step on the conductivity of ionogel micropatterns. Acetone, a miscible solvent with ionic liquid, and water, an immiscible solvent with ionic liquid, were investigated. The ionic conductivity for the micropatterns was measured with impedance measurement and shown in Table 2, together with the results for thick nonpatterned ionogel films for comparison. Well-developed micropatterns were obtained by both solvents as development solvent. However, the ionic conductivity of these micropatterns differed hugely dependent on the development solvents. The ionic conductivity for micropatterns developed by acetone was extremely low. This means the ionic liquid was probably removed by acetone during the development. The ionic conductivity for micropatterns developed by water was 4.7×10^{-5} S/cm, whereas the value for DA100MA0IL50 thick films without the development process was 4.0×10^{-4} S/cm. The decrease of ionic conductivity indicates some of the ionic liquid may be removed by the water during the development process but they were not completely removed because the ionic liquid is hydrophobic. Thus, by using water as the development solvent, these thin micropatterns had a relatively good ionic conductivity and thiol acrylate-based ionogel solution can be used as a negative-toned ionically conducting photoresist.

As discussed previously, the ionogel film prepared by thiol acrylate photopolymerization has excess thiol groups on the surface due to the mixed-mode photopolymerization mechanism. These thiol groups on the surface were still reactive, and ionogels with 3D microstructure were built by taking advantage of these reactive surfaces. After the first micropatterned layer was formed, the precursor electrolyte solution was then spin-coated again on the substrate. In the exposure area, the precursor electrolyte solution was solidified and the excess thiol groups on the top surface of the micropatterns on the first layer will also participate in the polymerization reaction. Thus, chemical bonds will be formed between the first and second layers at the interface. As an example, an ionogel (DA100MA0IL50) with a three-layered structure was achieved by repeating these photolithographic process three times, as shown in Figure 8. As a result, multilayered, three-dimensional complex microstructures were obtained by a stepwise process from these thiol acrylate materials. This reactive surface may be very interesting for the fabrication of robust flexible electrochemical devices. The adhesion between layers can be easily improved by chemical bonding using versatile thiol-based chemical reactions on these ionogels with reactive surfaces.^{36–38}

3.3. Patterning with Soft Imprint Lithography. UV-assisted soft imprint lithography was employed to pattern the surface of thiol acrylate-based ionogel. Soft lithography is a well-known, versatile technique for fabricating or replicating structures from elastomeric materials, most notably poly-(dimethylsiloxane) using molds.^{39–41} Features measured on the micrometer to nanometer scale for production of diverse micro- and nanostructures are easily obtained by this technique.²⁰ Here, we used SU-8 molds for soft imprinting lithography, formed using the standard photolithographic process with the photoresist SU-8 2010 on a silicon wafer. Round and line template patterns on a silicon wafer were used to investigate the replication process. The ionogel precursor solution DA100MA0IL50 was casted on the patterned silicon wafer, followed by UV exposure, as illustrated in Figure 9. Patterns were then transferred to the polymer materials after the curing and peeling off from the substrate. A microscope image of the obtained patterned ionogel films shows well-defined edge profiles and demonstrates that a high fidelity is achieved in this process from thiol acrylate ionogel solution.

3.4. Application in Flexible Electrochemical Devices.

To demonstrate the potential application of the ionogels fabricated using thiol acrylate photopolymerization in flexible electrochemical devices, electrochromic patterns and electrochemical soft actuators were prepared. Figure 10a shows the schematics of the electrochromic patterns, and their electrochromic color changes when the polarity of the applied potential switches. These electrochromic patterns were composed of two thin PEDOT–PSS electrodes and the ionogel patterns made by photolithographic patterning in a parallel electrode configuration. When 1 V was applied, the color of the bottom electrode area covered by the gel became a darker blue due to the reduction of the PEDOT, while the top area of the PEDOT became a lighter blue due to the oxidation of PEDOT. When the voltage polarity was changed, the electrochromism was reversed; the bottom electrode area turned a lighter blue, while the top electrode area turned a darker blue. These electrochromic patterns show the photolithographic micropatterning ability of ionogel based on thiol acrylate photopolymerization and its high ionic conductivity even after the development process. Figure 10b shows the structure of electrochemical soft actuators, in which the micropatterned ionogel was sandwiched between two PEDOT–PSS electrodes. When potential is applied, one side of the PEDOT–PSS electrode oxidizes and contracts while the other electrode gets reduced and expands. This contraction and expansion due to ion deintercalation/intercalation causes the whole structure to bend. The electrochemical actuators prepared from thiol acrylate photopolymerization show a very fast and large bending movement, which may be ascribed to the fact that the ionogel has a high ionic conductivity and a low Young's modulus. The movement can be further controlled by adding the micropattern on the ionogel.⁴² Here, the pattern was placed at 45° relative to the actuator length, creating a variable bending stiffness that caused the trilayer actuator to twist. All in all, these results show that the developed soft ionogels are highly promising materials in flexible electrochemical devices and will be used in soft microrobotic devices.⁴³

4. CONCLUSIONS

In this manuscript, a thiol acrylate mixed-mode photopolymerization was used to prepare a novel soft and flexible ionogel with a reactive surface and a high ionic conductivity. The ionic conductivity was 2.4×10^{-3} S/cm for the casted films from the

composition DA100MA0IL75 and 4.7×10^{-5} S/cm for the photolithographically patterned films including development from the composition DA100MA0IL50. The developed ionogel materials are well suited to be used with conventional photolithography as a negative-toned ionically conducting photoresist. Lithographic capabilities of the material enable direct fabrication of ionic conductive micropatterns and 3D microstructures using conventional photolithography. We have also successfully utilized thiol acrylate photopolymers in a high-resolution soft imprint lithography process to pattern the surface of the ionogel film. These achievements demonstrate that the developed soft ionogels are highly promising materials and future work will focus on further optimization and its applications in flexible microelectrochemical devices, including soft robotic actuators.

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Notes

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ACKNOWLEDGMENTS

The research was supported by European Union's Horizon 2020 research and innovation program under the Marie Skłodowska Curie grant agreement No. 641822 and the Swedish Research Council (VR-2014-3079).

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