High-performance supramolecular ionogel synthesized via click chemistry

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Abstract. The development of high-strength ionogels is of great significance for high-performance flexible sensing and soft robots. However, the introduction of ionic liquids will cause a decrease in the modulus and strength of ionogels and can cause unnecessary leakage problems. This poses a challenge for designing high-strength ionogels. In this work, based on the design concept of click chemistry, a modular polymer is constructed. The polymer self-assembled a phase-separated microstructure between soft phase and hard phase, exhibiting an ionic liquid-free, flexible, high-strength characteristic. By adjusting the molar ratio of the hard segment and the soft segment, it endows ionogels with various mechanical properties. When the content of hard segment increases from 5mol% to 20mol%, the Young's modulus of the ionogel increases from 4.37 MPa, 25.17 MPa to 129.94 MPa, the strength increases from 4.34 MPa, 9.67 MPa to 18.39 MPa, and the elongation at break decreases from 1129%, 1063% to 797%, respectively. Meanwhile, the supramolecular ionogel shows good stress-sensing ability and stability, which has promoted the development of high-performance flexible sensing and soft robots.

Keywords: ionogel, click chemistry, supramolecules, mechnical property, strain-sensing.

1. Introduction

In recent years, scientists have put much effort into smart materials, which are based on the observation of mimics' nature, for the purpose of achieving ideal functionalities such as actuate, complex, and smooth movement.[1-3] Inorganic materials, such as metal oxides, can be applied in gas sensors to identify and measure the concentration of gas in the atmosphere with excellent stability. Nevertheless, inorganic composition limits the selectivity and sensitivity at low concentrations over a broad range[4]. The rigidity also restricts their utilization in many applications including wearables as well as interactive robots as discomfort may be caused by its high modulus. Therefore, research on soft materials have gained great popularity and significant harvest have been obtained.[5-6] Having the flexibility, soft materials are able to sense the change in shape resulting from the exertion of external forces, behaving much more sensitively than those hard wares do, which makes soft materials ideal ingredients for developing robotic manipulation as well as soft sensors. [7-8]Additionally, some soft smart materials applied have extraordinary sensibility, making them appealing for the manufacture of flexible sensors, which are employed for detecting external stimuli and converting them into signals in ample realms including healthcare monitoring, and environmental monitoring.[9] Additionally, with high shape adaptability and fabrication scalability, flexible sensors are made to withstand mechanical deformation and perform great sensing functions simultaneously. Smart packaging with embedded sensors is invented for quality monitoring, and can also be used for medical measurements of the human body such as continuous glucose level measurement[10].

As a typical smart soft material, ionogel can effectively convert mechanical energy (even small deformation) into electrical energy, thereby completing the sensing of external stimuli.[11-13] Structurally, ionogels usually consist of a polymer network and a mobile ionic liquid. According to the different construction methods of the polymer network, the polymer network can be divided into two types: covalently cross-linked network and physically cross-linked network. The molecular chains of the former are connected by covalent bonds, so the network cannot be dissolved or melted. Also, the covalent cross-linked ionogel makes it difficult to undergo long-range deformation, resulting in an ultimate strain usually less than 200%. For the physically cross-linked network, there is usually a strong physical intermolecular interaction, resulting in the cross-linked network being

generated through the aggregation and assembly of molecular chains, thus such ionogel is also named supramolecular ionogel. The reversible network in supramolecular ionogel can be dissolved or melted and often has a large deformability. However, the modulus and strength of the ionogel are dependent on the content of the ionic liquid[14-16]. Therefore, there are still great challenges in designing high-performance ionogels.

Besides, the synthesis methods of physically cross-linked ionogels are often very complicated, not only need to select the appropriate soft segment and hard segment structure but also tend to free radical polymerization and/or stepwise condensation polymerization in the synthesis methodology.[17-19] Moreover, the cumbersome synthesis equipment and complicated post-precessing are required. So, finding a simple and green synthesis method is crucial for the preparation of high-performance ionogels. As a simple atomic economic reaction, click chemistry has gained the interest of researchers in recent years.[20-21] Click chemistry is a simple reaction to generate substances by connecting small modular units.[22-23] It has the advantages of fast reaction rate, high yield, and green due to its non-pollution characteristics, it has been widely used in the fields of chemical proteomics, pharmacology, bionics, and molecular machinery[24-28].

Therefore, a modular polymer was constructed in this work, which is based on the principle of click chemistry. The polymer can assemble itself into ionogels with physical crosslinking properties. The supramolecular ionogel embodies the structural characteristics of the phase separation of soft phase and hard phase. At the same time, in order to avoid damage to the strength and leakage caused by the liquid ionic additives, we chose to integrate the ionic monomer into the polymer backbone. Finally, a supramolecular ionogel with the mechanical properties adjustable is achieved. The Young's modulus, strength, and elongation at break reach up to 25.17 MPa, 9.67 MPa, and 1063%, respectively. Moreover, the stress-sensing ability is also been demonstrated.

2. Experiment

2.1 Materials:

Hexamethylene diisocyanate, methacrylamide, 2,2'-[1,2-ethanediylbis(oxy)]bis(ethanethiol) (EDB) as well as diallyldimethylammonium bistrifluoromethanesulfonimide (DB) were bought from Aladdin (China). Dimethylformamide was bought from J&K scientific. All reagents were commercially available and used as supplied without further purification.

2.2 Synthesis

First, methacrylamide and hexamethylene diisocyanate were dissolved in DMF solvent respectively, and then the two were mixed at a molar ratio of 2:1, and kept stirring for 1 hour. After the solvent evaporated, a white powder was obtained, namely the hard segment unit. Second, the hard segment unit, EDB and DB were dissolved in DMF respectively, and irradiated with ultraviolet light (wavelength 360nm) for 1 hour. Finnally, the product was dried in the oven at 60°C for 24 hours.

2.3 Characterisation

^{1}H Nuclear Magnetic Resonance (^{1}H-NMR) spectra were measured by AVANCE III 400MHz spectrometer using $CDCl_3$ as a solvent at room temperature. Thermogravimetric Analyzer (TGA) experiments were carried out with a TA instruments' TGA209F1, the heating rate is 20 °C/min, the heating range is 50 to 700 °C. The thermal beharior was investigated by differential scanning calorimetry (DSC) was carried out with NETZSCH DSC214, a cyclic heating/cooling run programme was taken with a heating/cooling rate of 10 °C/min, and the temperature is -100 to 160 °C. Mechanical properties conducted at room temperature by using an MTS (2 kN) tensile machine. Three specimens of each composition were tested, the data reported were the average values. The resistance change were collected by electrometer (Keithley 6514).

3. Results and Discussion

3.1 Molecular Design

For the supramolecular ionogel, the strength and modulus are always supported by the strong binding force among hard segments, while the deformability is obtained from the flexibility of soft segment, so the supramolecular ionogel often have the phase separation characteristics between hard phase and soft phase. However, the crosslinking points of supramolecular ionogels are often hydrogen bonds, metal coordination bonds, π-π interactions, etc. When ionic liquids are introduced, these crosslinking points will also interact with ionic liquids, thereby weakening the strength and modulus. Therefore, here we should integrate the ionic monomer on the polymer backbone instead of introducing ionic liquid for the purpose of avoiding the damage to the strength and the leakage caused by the liquid ionic additives.

In this work, methyl acrylamide and hexamethylene diisocyanate were first chosen to construct a carbamate group that can form multiple hydrogen bonds, and it was named as hard segment. The reaction process was shown in Scheme 1. The formed hydrogen bond aggregates are shown in Scheme 2. The carbon-carbon double bonds were still retained at both ends of the hard segment unit, which can participate in the next click chemical reaction.
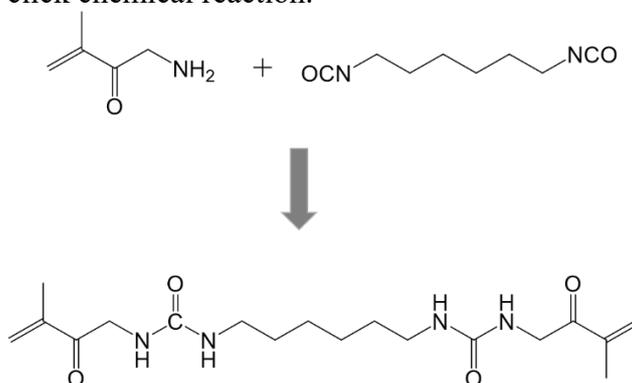
Scheme 1. Synthesis route of hard segment.
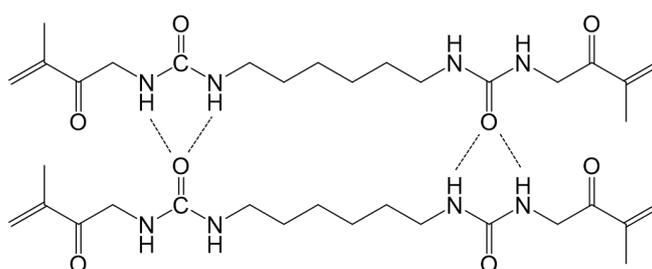
Scheme 2. The hydrogen bond aggregates among hard segments.

Secondly, EDB (Scheme 3) was chosen as the soft segment, which can undergo a thiophene addition reaction with a carbon-carbon double bond on the hard segment. Furthermore, ionic chemical diallyldimethylammonium bistrifluoromethanesulfonimide (DB) is also selected as the soft segment, but it can be reacted with EDB. Thus, it is only necessary to adjust the molar ratio of the hard segment and DB to realize the construction of the phase-separated microstructure and achieve the regulation of the mechanical properties of the supramolecular ionogel.
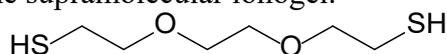
Scheme 3. The chemical structure of EDB.

The NMR spectrum of DB is shown in **Figure1**. The bands with chemical shifts of 6.13 and 5.76 belong to the hydrogen atoms on the vinyl group. After the click chemical reaction, the signal belonging to the vinyl group disappears, as shown in **Figure 2**, proving that click chemistry had occurred. **Scheme 4** is a diagram of the ionogel of the micro morphology, the polymeric chains,

hydrogen bond aggregates, positive and negative ion pairs are represented by green lines, green rectangles and crcles, respectively.
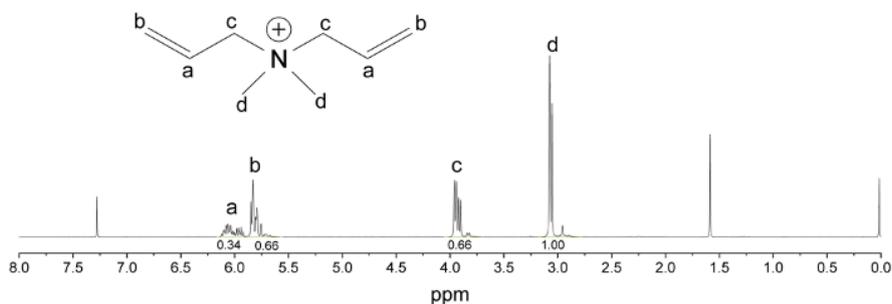
Figure 1. The NMR spretrumof DB.
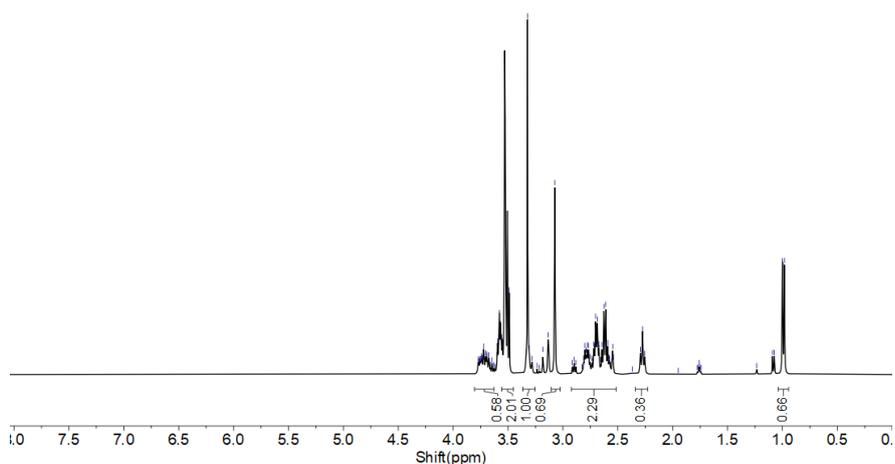
Figure 2. The NMR spretrum of the synthesized ionogel via click chemistry.
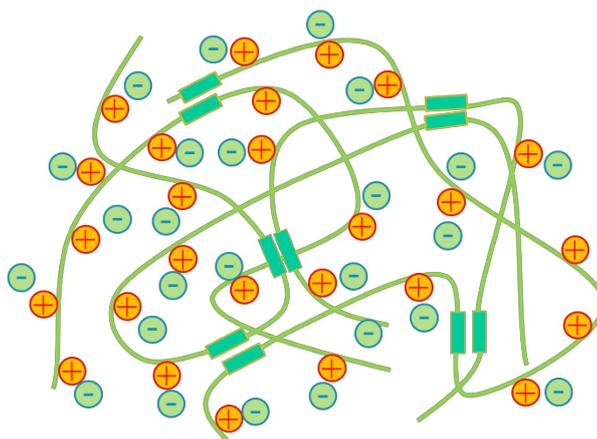
Scheme 4. The schematical illustration of the aggregate structure of phase separated ionogel.

3.2 Structural Analysis

Here, a series of supramolecular ionogels are obtained by changing the hard segment content. With the increase of the hard segment content, the glass transition temperature (T_g) of the supramolecular ionogel gradually increased. As shown in **Figure 3**, in the case of the content of hard segment is 5 mol%, 10mol% and 20mol%, its glass transition temperature is -1°C, 3°C and 25°C, respectively. Due to the poor regularity of the molecular chains of the supramolecular ionogel and the existence of strong intermolecular interactions, it is difficult to crystallize, so that no crystallization behavior was observed in the DSC curve.
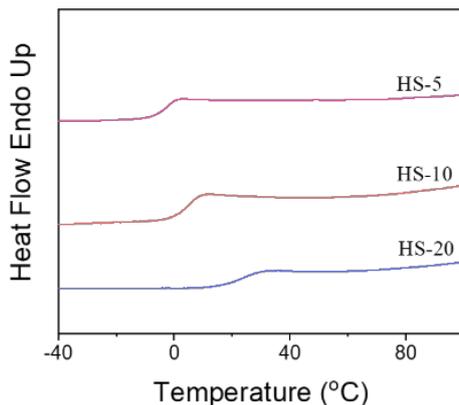
Figure 3. DSC heating curves of such synthesized ionogels.

A thermogravimetric analyzer is carried out here to characterize the thermal stability of the supramolecular ionogel. As shown in Figure 4, regardless of the hard segment content, the three samples all have good thermal stability. Here, the thermal decomposition temperatures (T_d) is defined as the temperature of residual mass is 95% [29], thus the T_d of the three samples are all around 310 °C, indicating that the supramolecular ionogel has excellent thermal stability.
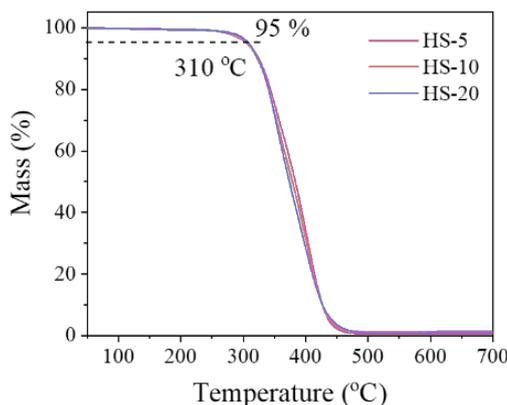
Figure 4. TGA curves of synthesized ionogels.

3.3 Mechanical performance

The typical engineering stress-strain curves of the ionogels are shown in Figure 5. Obviously, the mechanical properties are strongly depandant on the content of hard segment. For example, the Young's modulus of the ionogel increases from 4.37 MPa, 25.17 MPa to 129.94 MPa, the strength increases from 4.34 MPa, 9.67 MPa to 18.39 MPa, and the elongation at break decreases from 1129%, 1063% to 797%, for HS-5, HS-10 and HS-20, respectively.
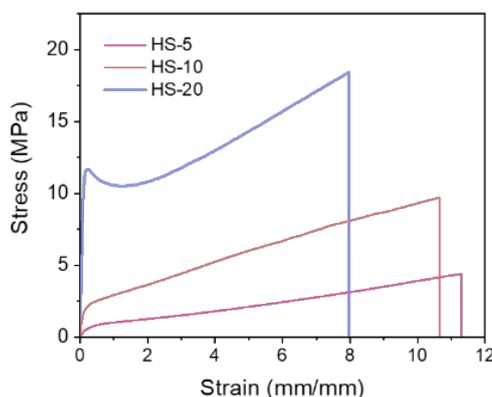
Figure 5. The engineering stress-strain curves of such synthesized ionogels.

In order to further verify the strain recovery ability of the supramolecular ionogel, **Figure 6** shows the cyclic strain of HS-10. When the strain reaches 200%, it begins to rebound. When the stress is released to zero, the residual strain is less than 30%, meaning the strain residual rate is less than 15%. After unloading the sample from the fixture, it quickly returns to its original shape. In order to demonstrate its strain recovery ability more clearly, after the unloaded sample resting for 30 min and then tested its cyclic stress-strain curve under the same conditions, the two runs show similar stress-strain behavior, which further indicated that the supramolecular ionogel has good resilience. We believe that this good strain resilience is related to the hard phase which formed by the aggregation of hydrogen bonds.[30]
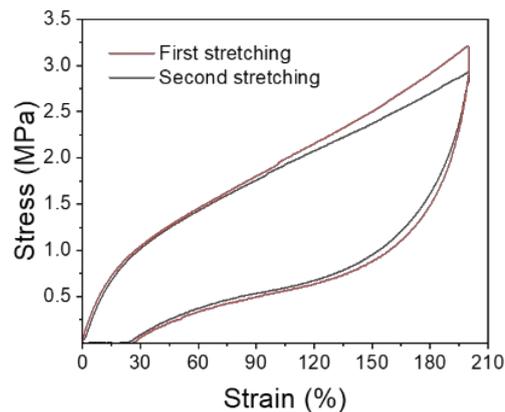
Figure 6. The cyclic stretching of HS-10 specimen.

In addition, **Figure 7** demonstrates the compressive mechanical behavior of the supramolecular ionogel. The supramolecular ionogel is rich in hydrogen bond aggregates, which makes it have excellent compression resistance and strain resilience. When the compression strain reaches 90%, the strength reaches 140MPa, but it is still not broken. When the stress is unloaded, the strain can be fully recovered, and the stress-strain hysteresis loop is small, exhibiting excellent strain resilience, which is comparable to that exhibited by cyclic stretching.
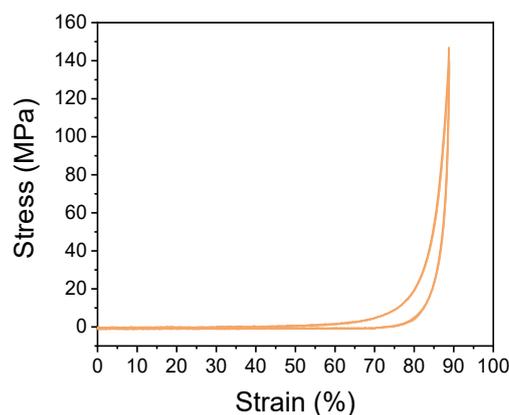
Figure 7. The compression force-strain relationship of HS-10 specimen.

3.4 Sensor performance

After a comprehensive comparison, HS-10 has a more appropriate T_g and mild modulus and strength, which can be selected as the research object to analyze and characterize its strain-induced electrical behavior. **Figure 8** shows the resistance change rate of HS-10 under different strains of cyclic stretching. When the strain reaches from 100% to 300%, the resistivity change reaches 115%, 290% and 500%, respectively, indicating that the supramolecular ionogel has excellent electrical response characteristics and can be used as a strain sensor.
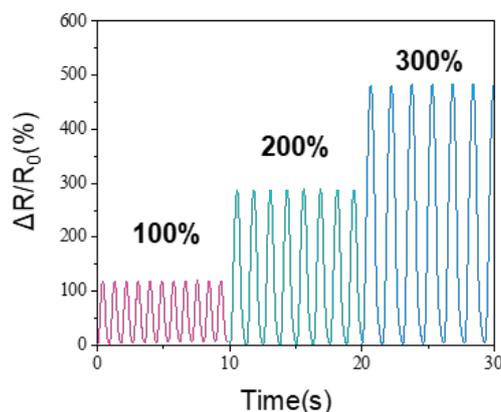
Figure 8. The resistance variation of HS-10 specimen under cyclic stretching

In order to verify the stability of its strain-resistance change, we conducted a cyclic tensile test up to 500 times. As shown in **Figure 9**, HS-10 showed excellent stability. When the number of cyclic strains reached 500, it still exhibited the same resistance change rate as the initial state, suggesting the excellent stability of its strain-resistance change.
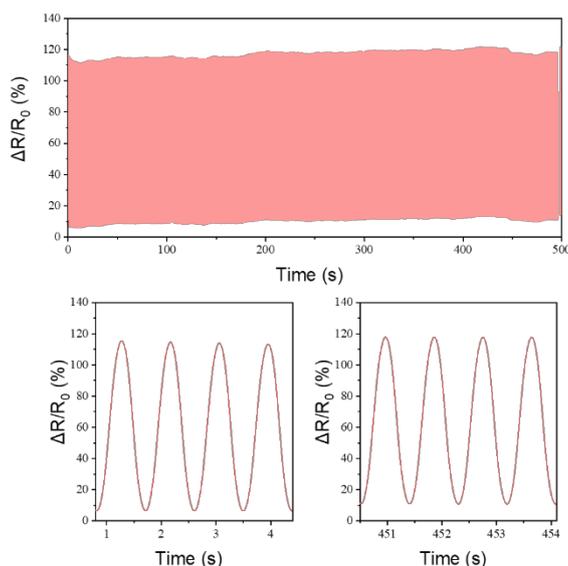
Figure 9. The resistance variation of HS-10 specimen under cyclic compression at the strain range of 0%~50%.

4. Conclusion

In summary, a supramolecular ionogel based on the principle of click chemistry is constructed in this work. The supramolecular ionogel shows a hydrogen-bonds aggregates microstructure. the mechanical properties are strongly depandant on the content of hard segment. The Young's modulus of the ionogel increases from 4.37 MPa, 25.17 MPa to 129.94 MPa, the strength increases from 4.34 MPa, 9.67 MPa to 18.39 MPa, and the elongation at break decreases from 1129%, 1063% to 797%, for HS-5, HS-10 and HS-20, respectively. Meanwhile, the supramolecular ionogel shows good stress-sensing ability and stability, it has broad application prospects in flexible sensing, soft robots, and other fields.

Acknowledgments

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