

Nature-inspired self-healing for organic electronics

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The shift from portable to wearable gadgets is unavoidable as electronic devices become more ingrained in our daily lives. The significance of this change is highlighted in the importance of creating devices that can be worn on the skin for uses such as medical diagnostics and monitoring how to deliver better healthcare in the future. This is why skin-inspired electronic materials are required. Over the six weeks, my research was focused on the creation of a self-healing electronically conducting polymer as due to their inherent flexibility and ionic conductivity, organic conjugated polymers are the ideal material for this role. Conjugated polymers are a class of organic semiconductors that have gained interest due to the crucial role that they play in the development of organic electronics. They are made of repeating units with the polymer backbone consisting of conjugated double bonds. This creates a delocalized pi-electron system allowing enhanced electronic properties. They also exhibit self-healing traits due to the presence of various chemical and physical properties such as dynamic bonds, reversible cross-links and hydrogen bonding. There are vast revolutionary applications of stretchable electronic devices (which are made due to the existence of conjugated polymers) such as soft robotics, e-skin sensors, wearable electronics and energy-storage devices. To achieve the self-healing aspect, which is vital as such material must have the ability to heal and restore their mechanical and electronic properties upon deformation, supramolecular interaction such as hydrogen bonding can be utilised. Previously synthesised devices have failed due to physical deformations, scratching and wear and tear upon application. However, the main drawbacks of this field in research stem from the failure to find a balance between mechanical, electrical and chemical properties. Often materials that are good conductors, which is a vital characteristic as electronic devices need efficient charge transport, have a well-established extended pi-conjugation backbone. This results in quite a rigid structure limiting flexibility and stretchability which is a failure when the goal is to achieve ideal self-healing upon deformation. Some possible solutions include structural optimization and chemical modification, but in my research, I focused on ionoelastomers based on polyionic liquids (PILs). PILs combine properties of both elastomers and ionic liquids which means that they have unique advantages such as enhanced flexibility and mechanical properties as well as ion conductivity and charge transport. They therefore can contribute to overcoming some of the existing issues.

Method

The following is the scientific procedure I followed in the synthesis of the ionic liquid:

1. N-methylimidazole (4.84 cm³, 60.75 mmol) was added to a round bottomed flask, and to that 6-bromo-1-hexanol (7.23 cm, 55.23 mmol) was added dropwise under inert atmosphere and room temperature. The reaction was left to heat to 70°C overnight. The reaction was then allowed to cool to room temperature. The solution observed was an orange very viscous liquid. It was then washed with both diethyl ether and water and separated using a separating flask. The residue solvent was removed using a rotary evaporator, initially removing the diethyl ether and then reducing pressure and increasing temperature to 45°C to remove the water. Solution was left under vacuum overnight. The work up was repeated as well as the drying under vacuum as some starting material remained in the solution (shown in the NMR)
2. LiTFSI (62.36 mmol, 17.9021 g) was measured and dissolved in 47.24 mL of water. This solution was added to a solution of 1-(6-hydroxyhexyl)-3-methylimidazolium bromide (14.9194 g, 56.6911 mmol), which was previously dissolved in 81.809 mL of water. The reaction mixture was left to stir for 1 hour at room temperature. Then the aqueous layer was extracted 3 times using DCM and the organic layer was dried over MgSO₄. The solution was then filtered using gravitational filtration and placed on the rotavapor until all the DCM was evaporated. NMR sample taken showed DCM solvent peak; most likely due to viscosity of the ionic liquid the DCM was trapped. The solution was placed under high vacuum for several hours as a result.
3. 2.65 mL acryloyl chloride was placed in a round bottomed flask and was cooled in an ice bath under inert gas to 0-1°C. Then 9.9 g of the product from the previous step was added dropwise using a syringe with gentle stirring. The solution was left to stir for 1.5 hours in the water bath. Then it was left to stir for 2 hours at room temperature and finally it was left overnight at 40°C.

I successfully synthesised the monomer at this stage, and I confirmed this by running an NMR and a mass spectrometry which proved that the product had the correct composition. However, the synthesis stage that followed (which involved the polymerisation of the monomer) proved to be extremely difficult and I did not manage to synthesise the polymer.

The following is the polymerisation process and the different attempts and materials I used to try to get the right product:

1. Approximately 2 mg (0.5 mol % with respect to the total monomer) of photo initiator 184 was weighed and placed in a vial which was placed under nitrogen. 0.5 g of [EIC₆A][TFSI] (around 0.3 mL the density of this monomer is not known) and 0.13 mL of HFBA was weighed out respectively using micro syringes and added into the vial. The solution was then degassed for 20 minutes, by removing the exit needle and using the Nitrogen needle to bubble nitrogen through. During the last 10 minutes of degassing the solution was sonicated. The solution was then cured under UV light for 3 hours, no observable changes were noted. Then the contents were dissolved in 1 mL of acetone and precipitated in 20 mL of deionised water. No solid formed however white globs formed at the bottom of the beaker. Solution was left in the fridge over the weekend. The solution turned a cloudy colour. This reaction was not successful.
2. Then I tried another method as I thought that the problem stemmed from the existence of water in the monomer since it is very moisture sensitive. Therefore the monomer synthesised previously was dried using freeze pump thaw, which was repeated 4 times. A microwave vial was placed in the oven and then cooled under nitrogen. Approximately 2 mg of photoinitiator 184 was measured and added to the microwave vial which was then weighed to determine how much of the monomer CD-003-01 would be added. 0.2 g of the monomer which was dried using freeze pump thaw were collected and added to the vial. 62.5 microliter of HFBA was measured using a micro syringe and added to the vial. The solution was degassed via bubbling nitrogen

gas through it for 20 minutes and then it was sonicated for 10 minutes. This reaction also was not successful.

3. Again I tried another method with no luck where a microwave vial was placed in the oven and then cooled down under $N_{2(g)}$. 0.5g and 0.16mL of the monomer synthesised in CD-003-01 and of HFBA, respectively, were weighed using a syringe and added into the vial. After degassing for 20 minutes via the bubbling of $N_2(g)$ through, the solution was sonicated for 10 minutes. 3.2 μ L of 2,5-Dimethyl-2,5-di-(tert-butylperoxy)hexane was measured using a micro syringe and added to the vial. The solution was once again sonicated. It was then left to heat to 160 °C, under $N_{2(g)}$, overnight. The solution turned into a brown very viscous and sticky substance. It was dissolved in a small amount of acetone and precipitated in isopropanol (no solid formed), and dried on the rotavapor to remove the solvent.
4. This was my last attempt at the polymerisation which unfortunately was not successful. 0.7g of the monomer previously synthesised was weighed and added to a vial using a syringe. 0.25mL of HFBA was also added along with 10mg of AIBN. These were then flushed under nitrogen. 10mL of DMSO was added and $N_{2(g)}$ was bubbled through the solution for 45 minutes. The solution was removed from being under $N_{2(g)}$ and the super seal was replaced with a cap. The reaction was left to stir and heat at 65°C overnight. The solution was dissolved into acetone and precipitated into isopropanol, however it completely dissolved. The isopropanol was evaporated, and the solution was reprecipitated into water. Although it looked successful a layer of sticky goo was stuck at the very bottom. Everything was redissolved in acetone and put on the rotavapor.

Conclusions and Reflections

Upon reflection a possible reason as to why the polymerisation was not successful, is that the UV lamp used was not strong enough. I hypothesise that using a more powerful lamp would make future attempts work more likely to prosper. Although the failed attempts were discouraging and frustrating in the moment, it showed me a realistic view on research and how it requires so many failed reactions and resilience for one reaction to succeed. This also offered me the chance to problem-solve and try new strategies to improve the outcomes of every method. From changing equipment to changing material, I experimented with all types of things in order to solve the problem at hand. Throughout the six weeks, I was asked to keep a detailed record of everything that I was doing (by keeping an accurately written lab book) even the failed experiments which helped me see the value in accurate writing as it guided my future experiments. Not only was I able to develop myself academically through gaining new knowledge in the field of chemistry, by learning how to run an NMR or a mass spectrometry, I was also able to grow on an individual level. I was given the opportunity to present some of my findings in a group setting which helped me a lot in terms of public speaking, confidence and learning how to get my point across eloquently and clearly. Overall, it was a very humbling experience and it served as a constant reminder that science is often challenging and unpredictable. I also learned that even the smallest contributions and discoveries made offer big steps for future work, even the failed reactions will act as guideline for the people that will continue in this research project.

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