Synthesis of Strong and Tough Supramolecular Elastomer based on Step Polymerization

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Abstract. The development of high-performance functional polymers is of great importance in modern industry. In particular, the requirements for strength, toughness and other basic properties are more stringent. However, the methods for increasing strength and toughness are often the opposite. Therefore, from a molecular engineering perspective, a series of supramolecular polymers were synthesized in this work based on a stepwise polymerization, which involves mainly chemical reactions between hydroxyl, amino groups and isocyanate groups respectively. Since strong multiple hydrogen bonds are formed between the resultant urethane and urea groups, thereby an energy dissipation mechanism is conferred to the material. Meanwhile, the molecular structure was optimized to attenuate the adverse effect of chain entanglement on the toughness, resulting in three-arm polymers that exhibit excellent mechanical strength of 5280 kPa and toughness of 28850 kJ/m3. In addition, the aggregation of tertiary nitrogen atoms endows considerable fluorescence. More importantly, the existence of extensive internal hydrogen bonds can make it an adhesive with excellent bonded strength of 8.9 MPa when bonded with stainless steel, which can be used as a structural adhesive. This work is an important milestone in giving both high performance and functionality to the material through molecular structure design from the molecular synthesizing perspective.

Keywords: Supramolecular Polymer; Hydrogen Bond; Strength; Toughness; Step Polymerization.

1. Introduction

Functional polymers are polymers with specific functional groups or structures that exhibit specific functions or respond specifically to changes in environmental conditions. The development of high-performance functional polymers has a wide range of applications in artificial intelligence, industrial manufacturing, optical displays, and even adhesives [1-5]. Therefore, the research and development of high-performance functional polymers has an irreplaceable role in expanding the application and scope of polymers, and is one of the most active areas of polymer research and one of the most important directions of polymer development. Mechanical property, as a fundamental performance, is the basis and prerequisite for all materials to work. Among the many mechanical property indicators, the mechanical strength and toughness are usually tended to be opposite, so it is often difficult to improve the strength and toughness simultaneously. [6-7] This is due to the fact that as crystallization increases, the yield stress, strength, modulus, and hardness of the polymer increase, while elongation at break and impact toughness do the opposite, making the polymer hard and brittle. For instance, the greater intermolecular interactions will lead to the higher strength of the polymer [8-9]. However, the increased intermolecular interactions can restrict the polymer chain movement to a certain extent, making the polymer less tough [10].

The strength of the material is the ability of a material to retain its structure when being compressed or extended under external forces. While the toughness of the material is defined as the ability of a material to absorb energy before fracturing. So as the tough material will be more likely to be deformed (both elastic deformation and plastic deformation) in ordered to suit, spread, distribute and dilute the outer forces equally to a maximum in the structure. In comparison, the high-strength materials need to withstand the stress without breaking, which in usual case, it means the molecular structure of the material has a low mobility. Thus, these materials are likely to absorb less energy and breakdown mechanically after falling into the plastic deformation region. Yet, it does not mean that such material with excellent performance in both strength and toughness is impossible to be synthesized.

Consuming the external force by overcoming intermolecular interaction is an inspiring idea due to its reversible dynamics [11-13]. Moreover, the synthesis of organic molecules can be directed to select the type of functional groups, adjust the spatial site resistance and spatial arrangement structure of compounds, and thus change the interactions between molecular chains. This allows the compound to be strengthened while improving its toughness. Recently, various enhanced mechanical abilities and/or adaptability made the supramolecular polymer an ideal option in future applications majoring in materials studies while possibly also facilitating the pharmaceutical designs[14-16]. The forms of interactions between supramolecular polymer chains are numerous, such as hydrogen bonds, dipole-dipole, π-π interactions, ionic bonds and metal-ligand interactions, etc[7], [17-20]. Among such different types of interactions, hydrogen bonding is well known account for its resultant excellent properties including the high strength, high toughness, auto-repairing, thermos-sensing, etc. [21-22] Among them, quadruple hydrogen bonding is a stronger intermolecular force [23]. The resultant polymers can be simply classified as main chain type and side chain type according to the position of the quadruple hydrogen bonds units. When the quadruple hydrogen bonding unit is in the backbone, resulting a higher glass transition temperature and thus shows higher strength, but further increase in the content of the quadruple hydrogen bonds unit will lead to brittleness [23-25]. When the quadruple hydrogen bonding is on the side chain, it will relatively balance strength and toughness, but the synthesis process of this strategy is extremely complicated, resulting in increased cost [26-27]. In addition, molecular chain entanglement is one of the main structural factors affecting strength and toughness. The higher the entanglement degree, the higher the strength, but excessive chain entanglement is not conducive to molecular chain movement, i.e., it is not conducive to energy dissipation during deformation.

Therefore, in this work, our strategy is neither to increase chain entanglement nor to introduce quadruple hydrogen bonding units into the main chain or side chains, but to synthesize molecular constructs with multi-armed structures and introduce quadruple hydrogen bonds at the end of the chain bond units. The coordination effect of hydrogen bonding facilitates the formation and stabilization of ductile long chains, and this weak compound is the key to ensuring both molecular elasticity and ductility. Here, the supramolecular elastomers were synthesized through stepwise polymerization. Stepwise polymerization occupies an important position in polymer chemistry and polymer synthesis industry due to it is a very important synthesis method for polymer materials [28]. Here, we select diisocyanates to undergo stepwise polymerization with hydroxyl and amino groups to construct three-arm polymers. The results show that such supramolecular polymers have an improved mechanical strength of 5280 kPa while maintaining the high toughness of 28850 kJ/m^3. Furthermore, the restricted movement of the tertiary nitrogen at the center of the molecule endows the polymer with considerable fluorescence properties. The design strategy provides important guidance for the design of functionally thermoplastic polymers.

2. Experimental Section

2.1 Materials

2-amino-4-hydroxy-6-methylpyrimidine, tris(2-aminoethyl)amine, dimethylformamide (DMF), Dibutyltin dilaurate (DBTDL), polycaprolactone diol (PCL) (Mn=1000g/mol), and isophorone diisocyanate (IPDI) were purchased from Aladdin (Shanghai, China).

2.2 Synthesizing Steps

In a typical route, the first step is to solve polycaprolactone diol and isophorone diisocyanate in the DMF solution by the settled molar ratios into the reaction apparatus. Here, the molar ratios of polycaprolactone diol and isophorone diisocyanate were settled to be 3:4, 6:7 and 9:10 respectively, so the final sample obtained was also named Cx, with x referring to the molar ratio of polycaprolactone diol. In this step, the chemical reaction occurred between isocyanate and hydroxyl group is catalyzed by DBTDL at 80 °C for 2 hours to make sure the chemicals react efficiently and

completely. Similarly, 2-amino-4-hydroxy-6-methylpyrimidine must first be solved in the DMF solution. The ratio of the newly-added reactant and the existing product should be kept at 1:1, so that only one end of the polymer is sealed by the pyrimidine. The mixture solution prepared should still be kept at temperature of 80°C but only 0.5 hours of heating is enough since the isocyanate group has a higher reactivity with amines than primary alcohols. Lastly, tris(2-aminoethyl)amine was added to connect three polymer strips and finally result a three-arm supramolecular polymer. Thus ratio of tris(2-aminoethyl)amine to the synthesized product dropped to 1:3. The condition required for the reaction to be fully conducted is the same as the first process. The final product of the elastomer is being collected and cooled down in a mold to give it a regular shape.

2.3 Characterization

Thermogravimetric analyzer (TGA) experiments were carried out with a TA instruments, the heating rate is 20 °C/min. The Fourier transform infrared spectroscopy (FTIR) (Nicolet 6700) was carried out here for charactering the chemical structure, operating in transmission mode from sample films cast onto KBr disks. Differential scanning calorimetry (DSC) was carried out with a TA instruments Q200, a cyclic heating/cooling run was taken, the heating/cooling rate is10 °C/min. The mechanical properties conducted at room temperature by using an MTS tensile machine. Dynamic mechanical analysis (DMA) was carried out with a TA instruments Q800 with a heating run was taken, the heating rate is 3 °C/min. The Photoluminescence emission spectra were recorded on a fluorometer under, the excitation wavelength is 360 nm.

3. Results and Discussion

3.1 Molecular Design and Reaction Mechanism

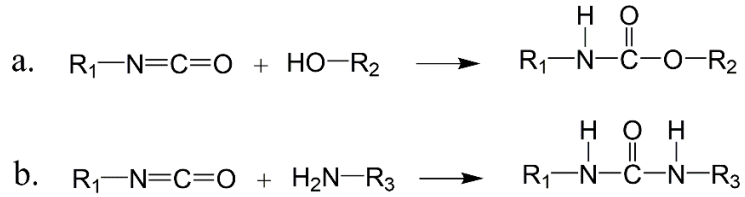


Figure 1. The reaction mechanism of hydroxyl group (a), amine group (b) and isocyanate group, respectively

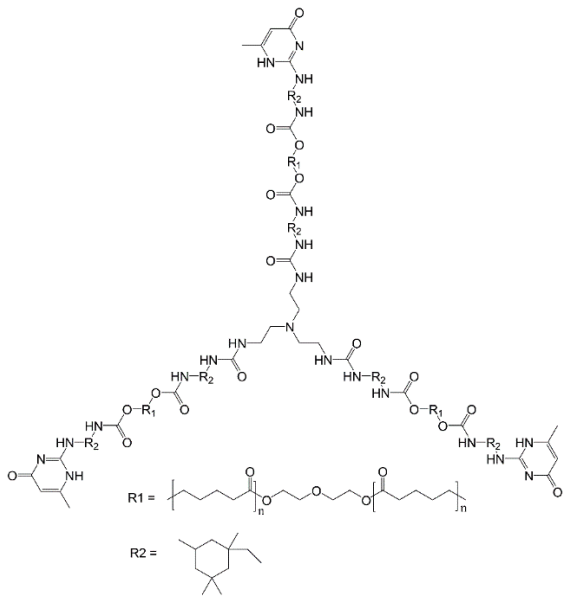


Figure 2. The chemical structure of such supramolecular polymers

The strategy carried out in this work to simultaneously improve strength and toughness is introducing a large number of hydrogen bonds and constructing supramolecular structures with multiple arms. Here the polycaprolactone was used as soft segment to favor the deformation. The reaction mechanism of isocyanate and hydroxyl group is shown in **Figure 1a**, and the resulting product is the urethane group. Then the 2-amino-4-hydroxy-6-methylpyrimidine was added and reacted with the excess isocyanate group, the mechanism is shown in **Figure 1b**, which results the urea group. Both the urethane group and the urea group as the junctions of the polymer providing the hydrogen bonds. The tris(2-aminoethyl) amine, as mentioned, is used to be the central molecule. The three amine groups on each of its arms can form a urea linkage that binds the molecule together. The final molecular structure is expressed as **Figure 2**. It should be clearly emphasized here that a large number of hydrogen bonds would be formed intermolecular with supramolecular polymer, and these hydrogen bonding units include quadruple, duplex, and single hydrogen bonds, as shown in **Figure 3**.

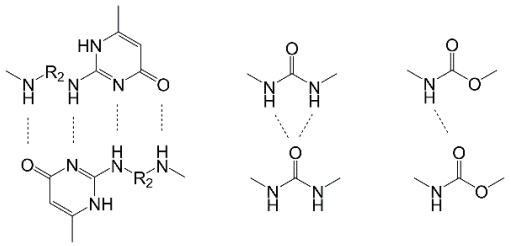


Figure 3. The quadruple (left), duplex (middle), and single hydrogen bonds (right), respectively.

3.2 Structural Analysis

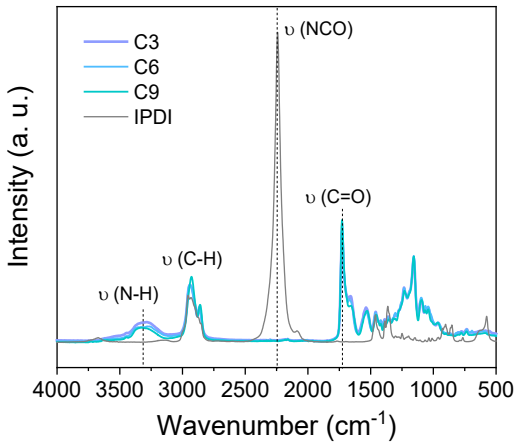


Figure 4. The FTIR spectra of such supramolecular polymer and IPDI chemical respectively

The chemical structures of such supramolecular polymers were confirmed by the FTIR spectroscopy, as shown in **Figure 4**. Clearly, the disappearance of 2250 cm^{-1} assigned to ν(-N=C=O) group indicates the IPDI compound has been fully involved in the reaction and the band at 1650 cm^{-1} attributed to the ν(C=O) group indicates the formation of a significant internal hydrogen bond. Correspondingly, the band at 3310 cm^{-1} attributed to the ν(N-H) group also demonstrates the formation of a large number of hydrogen bonds internally.

The TGA graph showed us how the polymer has been decomposed into gaseous molecules under high temperature. The rate of the decomposition is indicated by the loss of mass compared to the original percentage of 100%. The elastomer will be thermally broken down physically and chemically into small vaporized (monomer) molecules. As they diffused into the open air, the weight within the container measured by the apparatus will decrease. Three supramolecular polymers showed similar trends in their thermal decomposition, as shown in **Figure 5**. Its weight remains constant up to 325 °C before degradation starts, indicating the excellent thermal stability of the supramolecular polymer.

Despite the large number of hydrogen bonds inside, the lack of mass loss around 100 °C indicates that the supramolecular polymer does not absorb water when placed in the ambient environment, and exhibits good hydrophobic properties.

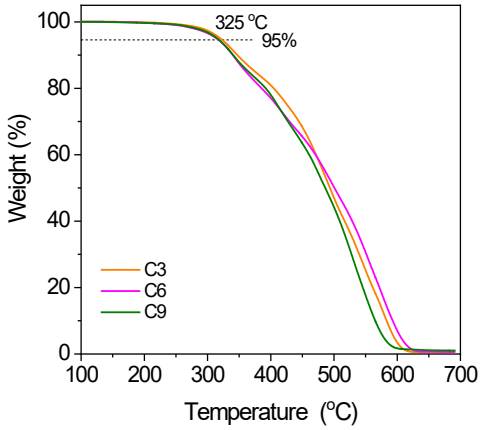


Figure 5. The TGA curves of such supramolecular polymers.

Figure 6 shows the DSC heating profiles of such supramolecular polymers. It is shown in the diagram that the range of T_g shifts to a higher value as the content of PCL segment decreasing. Thereby, the C9 shows the lowest T_g of -52°C, while the C3 exhibits the highest T_g of -49 °C. This trend is easy to understand because the higher the PCL content means the lower terminal quadruple hydrogen bonding unit, and the lower the internal hydrogen bonding content, which reduces the restriction on the soft segment motion of the supramolecular polymer and therefore exhibits a lower glass transition temperature.

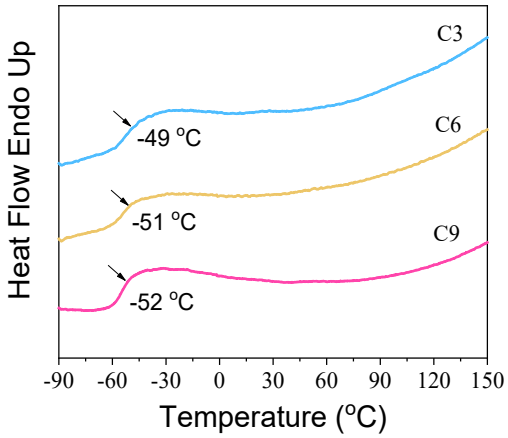


Figure 6. The DSC heating profiles of such supramolecular polymers.

3.3 Material Properties

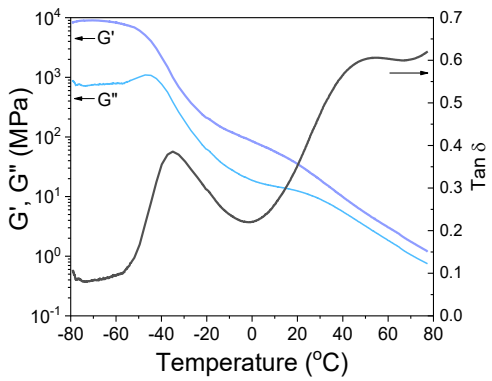


Figure 7. The dynamic mechanical properties of C6.

The DMA graph can also be used to determine the T_g of the material. However, the elastic and viscous response is more of the focus as the change in the modulus of the materials is being measured. **Figure 7** shows the dynamic mechanical properties of C6 for example. The two lines starting from the top left G' and G'' are the storage modulus and loss modulus, respectively. The grey line corresponding to the right axis is tanδ, which represents the damping factor of the material. This is the measured phase lag between the applied stimulus and the response, and it is calculated by the energy loss (G'') over the energy stored (G'): tanδ=G''/G'.

Obviously, as the temperature increases, the storage modulus decreases, while the loss modulus increases slightly around -45 °C, indicating that the PCL segment begins to enter the glass transition region. This result is consistent with the DSC results, and a peak appears in Tan δ, which means that the supramolecular polymer has entered an elastic state at around 0 °C. The storage modulus still has tens of megapascals even at room temperature, indicates the supramolecular polymer has excellent elasticity at room temperature. With further heating, both the storage modulus and loss modulus decreased, while the value of tan δ increased sharply, indicating that the internal viscosity increased, which was mainly attributed to the association-dissociation dynamic of intermolecular and intramolecular hydrogen bonds. During this process, the material will be further softened, and the material loses its mechanical strength gradually with temperature.

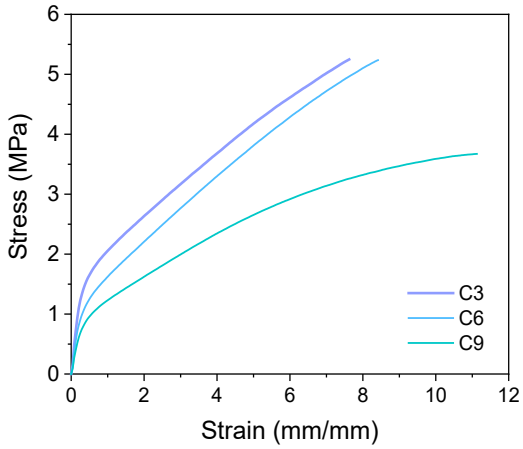


Figure 8. The stress-strain curves of such supramolecular polymers

Here, we have systematically tested the stretch behavior of such supramolecular polymers at ambient temperature, and the results are shown in **Figure 8**. It is clear that the higher content of PCL favors the deformation, which can be attributed to the looser hydrogen bonding stacking within it. As the PCL content gradually decreases, the density of hydrogen bonds inside the supramolecular polymer increases, so it exhibits higher modulus and strength. The mechanical indicates of such supramolecular polymer, as shown in **Table 1**. C3 has the highest strength of 5.28 MPa, the highest Young's modulus of 5.96 MPa and comparable toughness of 26.51 MJ/m^3, while the C9 has lower strength of 3.68 MPa and lower Young's modulus of 3.28 MPa, but increased toughness of 28.85 MJ/m^3. Therefore, the mechanical properties of such supramolecular polymers can be well tuned by changing the PCL content.

Table 1. The mechanical properties of such supramolecular polymers

Specimens	Young's Modulus (MPa)	Strength (MPa)	Toughness (MJ/m^3)
C3	5.96	5.28	26.51
C6	4.66	5.25	27.74
C9	3.28	3.68	28.85

The results of the DMA show that C6 is in an elastic state at room temperature and therefore will have considerable recovery from deformation, for which a cyclic stretching experiment was performed to characterize its stress-strain behavior under cyclic stretching, the results of which are shown in **Figure 9**. After the first cyclic stretching of C6, the strain was not instantaneously recovered, but a more pronounced residual strain was generated, indicating that the large amount of hydrogen bonds present inside the supramolecular polymer generates a significant energy consumption, further demonstrating its improvement in material toughness. When the supramolecular polymer was self-rested for 60 min without any intervention, a second cycle of stretching was performed. In the second cycle, the stress-strain curve was almost identical to that of the first, indicating that the hydrogen bonding network within the material that destroyed during the first stretching was reconstructed, allowing the modulus and mechanical strength to be restored to their original levels, demonstrating a good elastic recovery.

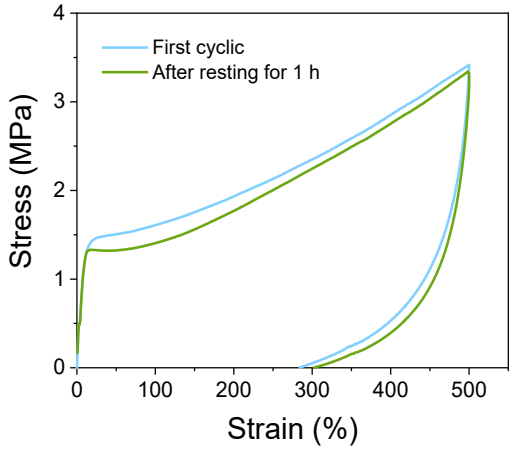


Figure 9. The stress-strain curves of C6 under cyclic stretching testing

3.4 Fluorescent Adhesive

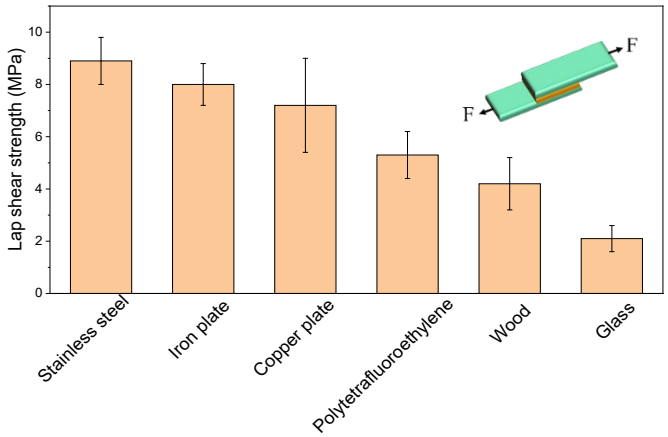


Figure 10. The lap-shear strength of C6 bonded with different substrates. Inset shows the adhesive mode under loading

It can be seen that the hydrogen bonding network formed by a large number of hydrogen bonding units in the system not only helps to improve the modulus and strength of the material, but also helps to enhance the toughness of the material, while achieving strengthening and toughening. Another main feature of hydrogen bonding is the ease of generating strong forces with other polar groups, which motivates us to think that the supramolecular polymer can be used as an adhesive [29]. Here, the stainless steel, iron, aluminum, Teflon, wood and glass were selected as bonding objects and tested them in the lap-shear bonding mode. The lap-shear model and bond strength are shown in **Figure 10**. Here the C6 was chosen to bond with stainless steel, iron, aluminum, Teflon, wood and

glass at 150 ºC, the bonding strength can reach up to 8.9 MPa, 8 MPa, 7.2 MPa, 5.3 MPa, 4.2 MPa and 2.1 MPa, respectively. Assuming that the area of bonded stainless steel is 1 cm^2, i.e. 100 mm^2, the maximum weight can reach 890 N, which is enough to bear the weight of adult (the weight of adults is calculated by 75 kg), showing a strong interface bonding capacity.

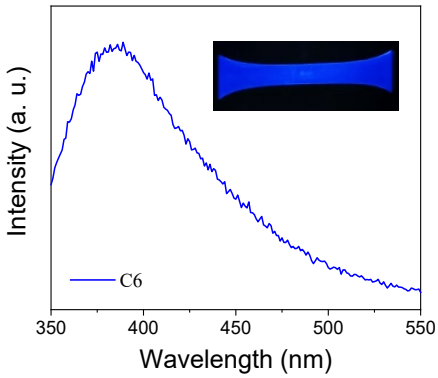


Figure 11. The fluorescence spectra of C6 when irradiated with 360 nm UV light

Furthermore, it is well known that when an aggregated tertiary amine is activated to an excited state by photons, it cannot return to the ground state by conventional methods due to the restricted motion of the tertiary amine (three chemical bonds and lone pairs cannot move). The electrons of the tertiary amine in the excited state return to the ground state by radiation, resulting in aggregation-induced emission (AIE) [30], so AIE is a phenomenon in which a compound exhibits large light emission when the molecules aggregate into a solid state or aggregate in a concentrated solution. **Figure 11** shows the fluorescence spectrum of such supramolecular polymer (C6) when irradiated with 360 nm UV light. Apparently, the fluorescence wavelength was around 400 nm, which belonged to the blue light range. Since the emission mechanism of fluorescence is generated by the atomic aggregation inherent in the material, it does not change with deformation. The inset of **Figure 11** exhibits the clear blue fluorescence when C6 is stretched to 5 times its original length, which shows its good deformation adaptability. Therefore, combined with the high bonding ability, this type of supramolecular polymer can be used as an adhesive that can detect the interfacial bonding state by fluorescence in real time.

4. Conclusion

In this work, in order to solve the contradiction between the strength and toughness of polymer, a three-arm structure of supramolecular polymer based on stepwise polymerization was synthesized. The molecular arms of such supramolecular polymer contain a large number of urea and urethane groups, which can form a large number of intramolecular and intermolecular hydrogen bonds. The association-dissociation dynamics of hydrogen bonds upon deformation consumes a great of energy, thus the tough and strong supramolecular polymers are achieved. On the other hand, the presence of a large number of hydrogen bonds also gives the polymer a good interfacial adhesion ability, so that the bond strength with stainless steel can reach 8.9 MPa. Meanwhile, the tertiary nitrogen atoms at center point of the molecular structure give them considerable fluorescence properties, which have potential uses in the field of in situ detection of interfacial damage in the future.

Statement of Liability

The participating team declares that the papers submitted are research work and research results obtained under the guidance of the instructor. To the best of the team's knowledge, the paper does not contain research results that have been published or written by other people, except for the content

listed in the text and the acknowledgment. If there is any inaccuracy, I am willing to bear all related responsibilities.

Acknowledgments

I am very grateful that I can participate in the project and join this competition. Thus, I would like to give thanks to the people who are supporting me though the days and nights of working.

I am very thankful to my chemistry teacher Mrs. Wang Meng from our school. She provides with advanced chemistry knowledge and experience beyond the curriculum that enhances my understanding the mechanism of synthesizing the polymer. In addition, I would also like to give credits to our school: Shenzhen College of International Education (SCIE). The school's lab has tried their best to provide suitable chemicals and apparatus to make the experiment possible. The department also created free lab to use after school time which is very helpful.

Last but not least, I would like to give thanks to my parents as they have always supported me in the field of Chemistry. Besides, without their financial support, I am not able to achieve so many results so far in my study. I sincerely hope that anyone who has helped me will be praised.

References

[1] Li, H.; Tang, Z.; Liu, Z.; Zhi, C. Evaluating Flexibility and Wearability of Flexible Energy Storage Devices. Joule 2019, 3, 613-619.

[2] Lai, Y.; Kuang, X.; Zhu, P.; Huang, M.; Dong, X.; Wang, D. Colorless, Transparent, Robust, and Fast Scratch-Self-Healing Elastomers via a Phase-Locked Dynamic Bonds Design. Advanced Materials 2018, 30, 1802556.

[3] Kang, J.; Son, D.; Wang, G.-J. N.; Liu, Y.; Lopez, J.; Kim, Y.; Oh, J. Y.; Katsumata, T.; Mun, J.; Lee, Y.; Jin, L.; Tok, J. B.-H.; Bao, Z. Tough and Water-Insensitive Self-Healing Elastomer for Robust Electronic Skin. Advanced Materials 2018, 30, 1706846.

[4] Koo, J. H.; Kim, D. C.; Shim, H. J.; Kim, T.-H.; Kim, D.-H. Flexible and Stretchable Smart Display: Materials, Fabrication, Device Design, and System Integration. Advanced Functional Materials 2018, 28, 1801834.

[5] Tan, M. W. M.; Thangavel, G.; Lee, P. S. Rugged Soft Robots using Tough, Stretchable, and Self-Healable Adhesive Elastomers. Advanced Functional Materials 2021, 31, 2103097.

[6] Ritchie, R. O. The conflicts between strength and toughness. Nature Materials 2011, 10, 817-822.

[7] Li, Z.; Zhu, Y.-L.; Niu, W.; Yang, X.; Jiang, Z.; Lu, Z.-Y.; Liu, X.; Sun, J. Healable and Recyclable Elastomers with Record-High Mechanical Robustness, Unprecedented Crack Tolerance, and Superhigh Elastic Restorability. Advanced Materials 2021, 33, 2101498.

[8] Wu, J.; Cai, L.-H.; Weitz, D. A. Tough Self-Healing Elastomers by Molecular Enforced Integration of Covalent and Reversible Networks. Advanced Materials 2017, 29, 1702616.

[9] Wang, S.; Liu, Z.; Zhang, L.; Guo, Y.; Song, J.; Lou, J.; Guan, Q.; He, C.; You, Z. Strong, detachable, and self-healing dynamic crosslinked hot melt polyurethane adhesive. Materials Chemistry Frontiers 2019, 3, 1833-1839.

[10] Liu, M.; Liu, P.; Lu, G.; Xu, Z.; Yao, X. Multiphase-Assembly of Siloxane Oligomers with Improved Mechanical Strength and Water-Enhanced Healing. Angewandte Chemie International Edition 2018, 57, 11242-11246.

[11] Sun, P.; Li, Y.; Qin, B.; Xu, J.-F.; Zhang, X. Super Strong and Multi-Reusable Supramolecular Epoxy Hot Melt Adhesives. ACS Materials Letters 2021, 3, 1003-1009.

[12] Wu, M.; Liu, Y.; Du, P.; Wang, X.; Yang, B. Polyurethane hot melt adhesive based on Diels-Alder reaction. International Journal of Adhesion and Adhesives 2020, 100, 102597.

[13] Foster, E. J.; Berda, E. B.; Meijer, E. W. Metastable Supramolecular Polymer Nanoparticles via Intramolecular Collapse of Single Polymer Chains. Journal of the American Chemical Society 2009, 131, 6964-6966.

[14] Razgoniaev, A. O.; Mikhailov, K. I.; Obrezkov, F. A.; Butaeva, E. V.; Ostrowski, A. D. Supramolecular elastomers: Switchable mechanical properties and tuning photohealing with changes in supramolecular interactions. Journal of Polymer Science Part A: Polymer Chemistry 2018, 56, 1003-1011.

[15] Aida, T.; Meijer, E. W.; Stupp, S. I. Functional Supramolecular Polymers. Science 2012, 335, 813-817.

[16] Goor, O. J. G. M.; Dankers, P. Y. W. 5.12 - Advances in the Development of Supramolecular Polymeric Biomaterials. In Comprehensive Supramolecular Chemistry II; Atwood, J. L., Ed.; Elsevier: Oxford, 2017, 255-282.

[17] Cui, J.; Del Campo, A. 4 - Photo-responsive polymers: properties, synthesis and applications. In Smart Polymers and their Applications; Aguilar, M. R.; San Román, J., Eds.; Woodhead Publishing: 2014, 93-133.

[18] Yao, Y.; Xu, Z.; Liu, B.; Xiao, M.; Yang, J.; Liu, W. Multiple H-Bonding Chain Extender-Based Ultrastiff Thermoplastic Polyurethanes with Autonomous Self-Healability, Solvent-Free Adhesiveness, and AIE Fluorescence. Advanced Functional Materials 2021, 31, 2006944.

[19] Cao, J.; Lu, C.; Zhuang, J.; Liu, M.; Zhang, X.; Yu, Y.; Tao, Q. Multiple Hydrogen Bonding Enables the Self-Healing of Sensors for Human–Machine Interactions. Angewandte Chemie International Edition 2017, 56, 8795-8800.

[20] Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. Supramolecular Polymers. Chemical reviews 2001, 101, 4071-4098.

[21] Deng, W.; You, Y.; Zhang, A. 7 - Supramolecular network-based self-healing polymer materials. In Recent Advances in Smart Self-healing Polymers and Composites; Li, G.; Meng, H., Eds.; Woodhead Publishing: 2015, 181-210.

[22] Song, Y.; Liu, Y.; Qi, T.; Li, G. L. Towards Dynamic but Supertough Healable Polymers through Biomimetic Hierarchical Hydrogen-Bonding Interactions. Angewandte Chemie International Edition 2018, 57, 13838-13842.

[23] Kushner, A. M.; Vossler, J. D.; Williams, G. A.; Guan, Z. A Biomimetic Modular Polymer with Tough and Adaptive Properties. Journal of the American Chemical Society 2009, 131, 8766-8768.

[24] Yan, X.; Liu, Z.; Zhang, Q.; Lopez, J.; Wang, H.; Wu, H.-C.; Niu, S.; Yan, H.; Wang, S.; Lei, T.; Li, J.; Qi, D.; Huang, P.; Huang, J.; Zhang, Y.; Wang, Y.; Li, G.; Tok, J. B. H.; Chen, X.; Bao, Z. Quadruple H-Bonding Cross-Linked Supramolecular Polymeric Materials as Substrates for Stretchable, Antitearing, and Self-Healable Thin Film Electrodes. Journal of the American Chemical Society 2018, 140, 5280-5289.

[25] Fan, C.-J.; Huang, Z.-C.; Li, B.; Xiao, W.-X.; Zheng, E.; Yang, K.-K.; Wang, Y.-Z. A robust self-healing polyurethane elastomer: From H-bonds and stacking interactions to well-defined microphase morphology. Science China Materials 2019, 62, 1188-1198.

[26] Yang, M.; Lu, X.; Wang, Z.; Fei, G.; Xia, H. A novel self-catalytic cooperative multiple dynamic moiety: towards rigid and tough but more healable polymer networks. Journal of Materials Chemistry A 2021, 9, 16759-16768.

[27] Chang, X.; Geng, Y.; Cao, H.; Zhou, J.; Tian, Y.; Shan, G.; Bao, Y.; Wu, Z. L.; Pan, P. Dual-Crosslink Physical Hydrogels with High Toughness Based on Synergistic Hydrogen Bonding and Hydrophobic Interactions. Macromolecular Rapid Communications 2018, 39, 1700806.

[28] Klesczewski, B. Polymerization Chemistry of Polyurethanes. In Encyclopedia of Materials: Science and Technology; Buschow, K. H. J.; Cahn, R. W.; Flemings, M. C.; Ilschner, B.; Kramer, E. J.; Mahajan, S.; Veyssière, P., Eds.; Elsevier: Oxford, 2001, 7632-7634.

[29] Frisch, K. C. Chapter 16 - Chemistry and technology of polyurethane adhesives11This chapter is dedicated to my father, Dr. Kurt C. Frisch (1918-2000), urethane pioneer, founder and director of the Polymer Institute-University of Detroit Mercy. In pace requiescat. In Adhesion Science and Engineering; Dillard, D. A.; Pocius, A. V.; Chaudhury, M., Eds.; Elsevier Science B.V.: Amsterdam, 2002, 759-812.

[30] Jiang, G.; Sun, X.; Wang, Y.; Ding, M. Synthesis and fluorescence properties of hyperbranched poly(amidoamine)s with high density tertiary nitrogen. Polymer Chemistry 2010, 1, 1644-1649.