Comparing the Principles of Reversible Covalent Chemistry and Supramolecular Chemistry Points to New Directions in the Development of Polymers

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Abstract. Polymers are some of the most widely used materials for human use and have greatly facilitated people's lives. However, with the use of polymer materials, traditional thermoplastic and thermoset materials are unable to meet the more diverse needs, and traditional processing methods are not able to significantly improve the performance of polymer materials. Some researchers have found that by applying the principles of reversible covalent and supramolecular chemistry in dynamic chemistry in the development of polymers, the properties and functions of polymers can be changed from the bottom up. Therefore, this paper analyses the similarities and differences between the principles of reversible covalent chemistry and supramolecular chemistry by collecting applications of reversible covalent chemistry and supramolecular chemistry in the field of polymer synthesis and comparing the two to provide assistance for future developments in the field of polymers.

Keywords: Reversible covalent chemistry, Supramolecular chemistry, Polymers, Dynamic bonds.

1. Introduction

The advent of polymers has greatly improved human life and brought more convenience to people. Polymers are aggregates with complex structures formed by various physico-chemical interactions. Their properties are closely related to the morphological structure formed during the moulding process and its post-processing. Traditionally, polymers are usually divided into thermoplastic and thermosetting polymers depending on structure. In thermoplastic polymers, each linear molecule is connected to each other by intermolecular interactions. Their polymer systems generally have poor mechanical properties and are thermally fusible. While, the molecules in thermoset polymers are interconnected by covalent bonds, forming a three-dimensional structure with strong mechanical properties and thermal non-fusibility. The poor performance of thermoplastic materials and the inability to recycle thermoset materials, the shortcomings of both prevent their use in more complex scenarios.

In order to solve such problems, researchers have introduced the new concept of dynamic chemistry. Dynamic chemistry includes two branches, dynamic covalent chemistry and supramolecular chemistry. Dynamic covalent chemistry is the dynamic exchange and reorganisation of molecules by introducing a series of covalent bonds with reversible properties into a polymer, enabling it to undergo thermodynamic equilibrium reactions between molecules under specific conditions [1-3]. Supramolecular chemistry, on the other hand, is the directed joining of individual molecules through strong, weak interactions such as hydrogen bonding to form stable supramolecular systems [4, 5]. Although both are dynamic chemical systems and possess properties such as reversibility and repairability, dynamic covalent chemistry and supramolecular chemistry also have different application scenarios due to their different core mechanisms.

In this paper, the differences between dynamic covalent chemistry and supramolecular chemistry will be analyzed by listing their applications in their respective fields, and some ideas will also be proposed for the future development of polymers.

2. Reversible covalent chemistry

In recent years, reversible covalent chemistry has become a popular research direction in the field of chemistry and materials. Many researchers have applied reversible covalent chemistry to the field of polymers, resulting in many high-performance functional macromolecules which are recyclable, self-healing and stimulating responsiveness. The core of reversible covalent chemistry is reversible covalent bonding, which combines the reversibility of non-covalent bonds in supramolecular chemistry with the stability of irreversible covalent bonds in conventional chemistry. It maintains stability when there are not stimuli and shows reversibility under specific conditions, while at the same time it has higher bonding energy compared to non-covalent bonds, enhancing the mechanical properties of the polymer [6]. Based on the principles of reversible covalent chemistry, adaptive polymers have also been designed by some researchers, where the polymer structure can be adjusted in response to environmental changes, depending on the conditions of their application.

However, for industrial applications, not all reversible covalent bonds are of interest. Thermodynamic and kinetic should be considered: 1. Thermodynamically, the equilibrium of the reversible reaction should favour the direction of bonding to facilitate the formation of the polymer and prevent its self-depolymerisation. 2. Kinetically, the reversible reaction should be chosen at a higher rate to facilitate the manufacture of the material in a reasonable time, which can also be regulated by adding a catalyst or increasing the temperature [6]. Following a study by Ying et al [7] of urea bonds, it was found that urea bonds with both a large equilibrium constant ($7.9 \times 10^5\ s^{-1}$) and small dissociation constant ($1.2 \times 10^{-5}\ s^{-1}$) could be highly dynamic while maintaining stability. In a study of borate and silyl ether bonds, Guan and others [8, 9] found that dynamic polymers with faster exchange rates possessed better reversibility and faster stress relaxation behaviour.

Based on the existing applications of reversible covalent bonds, researchers have divided reversible covalent reactions into two categories, general reversible covalent chemistry (e.g. reversible addition, reversible condensation, etc.) and dynamic reversible covalent reactions (e.g. reversible exchange, reversible homolytic/recombination of C-ON bonds, etc.) [6]. The main difference between the two is the magnitude of the effect of environmental changes on the equilibrium constants. In the former, the positive and negative reactions usually have different triggering conditions, such as pH, temperature, redox agent and so on. For instance, environmental changes can have a greater impact on the equilibrium constant and therefore the dissociation reaction tends to depolymerise the whole cross-linked network. Luo et al [10] have designed thermally unstable epoxy adhesives by using a Diels-Alder (D-A) addition reaction between furan and maleimide, which exhibited similar properties to conventional epoxy adhesives at ambient temperature and complete degradation with dynamic D-A bond breaking above 160°C. In the latter case, on the contrary, the positive and negative reactions of dynamically reversible covalent bonds proceed simultaneously under the same conditions, i.e. environmental factors have less influence on the equilibrium constants. For example, the hydrolysis and polymerisation of ester groups, because their positive and negative reactions are affected by temperature to a comparable degree, changing the temperature does not have a large effect on the equilibrium constant [6].

The two types of reversible covalent reactions described above can be used for different purposes. For general reversible covalent reactions, it can be utilized to design stimulus-responsive materials or structurally variable polymers. Dynamic reversible covalent reactions can be used to design self-healing polymers, such as self-healing hydrogels. Depending on the needs, the knowledge of reversible covalent chemistry can be applied to design multifunctional polymers with excellent performance.

2.1. Reversible covalent chemistry in new 3d printing materials

Rapid Prototyping (RP) is a technology developed in the 1980s and 1990s that integrates CAD (Management Software Computer Aided Design, MS-CAD), CNC (Computerized Numerical Control) technology, new material technology and laser technology into a prototype manufacturing technology for parts, also known as 3D printing technology. It is based on digital model files and uses bondable materials such as powdered metal or plastic to construct objects by printing layer by layer, and it has great potential for development in the aerospace industry, automotive and other fields.

However, the materials used in 3d printing have been a constraint to the development of this technology. As the materials for 3d printing need to be thermoplastic in nature, the polymeric materials typically used are linear thermoplastics such as polycarbonate, polyether ether ketone etc. The mechanical properties of thermoplastic materials are generally lower than those of bulk polymer plastics. In addition, as 3d printing is based on the principle of layered manufacturing, stacked layer by layer, it often fails to link in the z-direction, leading to the creation of voids and consequently a reduction in strength [11].

To solve this problem, Xia et al [11] and others used reversible covalent chemistry to design materials for Selective Laser Sintering (sls) 3d printing (Figure 1a), poly (bromobisphenol-urea ester) (PBP-PU-2). Isophosphoryl ketone diisocyanate (IPDI) and hexamethylene diisocyanate trimer (tri-HDI) were chosen as isocyanates to react with TBBPA to obtain cross-linked poly (bromobisphenol-urea ester (PBP-PU-2). PBP-PU-2 has a reversible brominated bisphenol carbamate bond which breaks upon laser irradiation. Due to the breaking of dynamic bonds, the polymer network depolymerises and the overall viscosity drops, changing to a free-flowing molten polymer. On cooling to below 80℃, the brominated bisphenol carbamate bonds regenerate, restoring the cross-linked polymer structure. z-axis direction becomes stronger due to covalent bonding, and the voids between the fillers are greatly reduced due to the regeneration of the bulk polymer. Both of these aspects greatly enhance the mechanical properties of the finished product in all directions. As shown in Figure 1c, compared to T90A (a commercial high-performance TPU powder without dynamic bonding), PBP-PU-2 has a more even tensile strength in all directions and a great advantage in the z-axis direction.

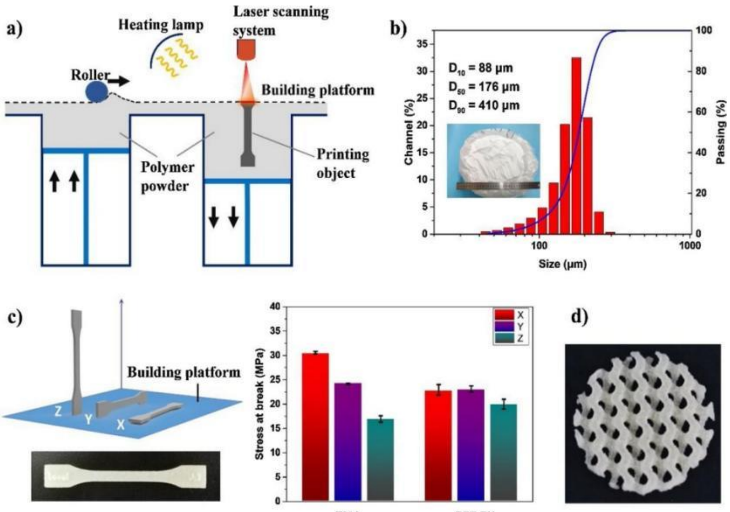

Figure 1. (a) SLS printing process diagram. (b) Photograph and particle size of PBP-PU-2 powder. (c) Schematic diagram and results of tensile strength tests on T90A and PBP-PU-2 in different directions. (d) Product printed with PBP-PU-2 material. [11]

2.2. Reversible covalent chemistry in degradable polymer materials

Traditional thermoset materials are used in a variety of applications because of their low density, strength, heat and impact resistance. However, because of their three-dimensional mesh structure, they are insoluble and non-fusible and cannot be degraded for recycling. Traditional thermoset plastics that cannot be degraded and recycled cause serious pollution to nature. In response, researchers have introduced reversible covalent chemistry into the cross-linked network of thermosets in order to develop bulk degradable materials that retain their original excellent mechanical properties. The D-A addition reaction is a common reversible reaction in which electron-rich and electron-deficient dienes can form cyclohexene adducts by [4+2] cycloaddition at around 70℃ and undergo reverse decomposition at high temperatures. Because of the simplicity of the reaction, it was used in the development of epoxy resins by Chen [12, 13] and others at the beginning of the 21st century to obtain new epoxy resins that are degradable and have self-healing capabilities. In addition, the crystallinity, hardness and softness of this degradable polymer can also be well adjusted by varying the reaction temperature and time through the D-A addition reaction of furan and maleimide.

In addition to thermally degradable bulk polymers, pH-sensitive degradable polymers have also been produced by Wang et al. [14] The epoxy resin MB containing mono-epoxy and aldehyde groups was obtained by the epoxidation of vanillin, and the MB was cured with 4, 4'-methyl-alkenebicyclohexylamine (PACM) to give a Schiff base structure ($R_2C=NR'$). Schiff base structure is a special reversible covalent bonding structure that allows the decomposition to be regulated by adjusting the pH of the solution. The carbon fibre composites made from this resin have excellent degradation properties, with complete degradation of a 10cm x 10cm x 0.045mm composite within 15h at room temperature in a 0.1mol/L HCl solution, with no damage to the surface of the recovered carbon fibre material and 95% of the original mechanical properties.

2.3. Reversible covalent chemistry in Self-healing polymers

The self-healing properties are also an advantage gained by the introduction of reversible covalent bonds. Conventional thermoset polymer materials are highly stable, but this poses the problem that the material are often unable to be repaired after it has been mechanically damaged, resulting in material waste and environmental pollution. Reversible covalent chemistry solves this problem, as thermoset materials made using normal reversible covalent chemistry can be repaired by depolymerisation and repolymerisation; researchers also apply dynamic reversible covalent chemistry to make the polymer self-healing.

Fei et al [15] found that the urea bonds formed by amines and isocyanates are reversible and that the resulting urea-bonded polymers can be depolymerised and reconnected by the combined action of zinc ions and heat, and that they can achieve up to 90% of their original performance after polymerisation.

In 2010, Yoshie [16] continued their studies on the recoverability and soft and hard conversion rates of network polymers synthesized from reversibly reactive far-helical prepolymers and found that the network structures constructed by the D-A reaction between furan-based far-helical poly (ethylene adipate) ($PEAF_2$) and trimaleimide (M_3) were similarly repairable (Figure 2). By investigating the repair mechanism, they suggest that the possible repair mechanism in $PEAF_2M_3$ is the polymerisation of the polymer chains following the breakage of the D-A bond and the simultaneous exchange of furan (maleimide) groups between the D-A adducts, eventually joining the two parts.

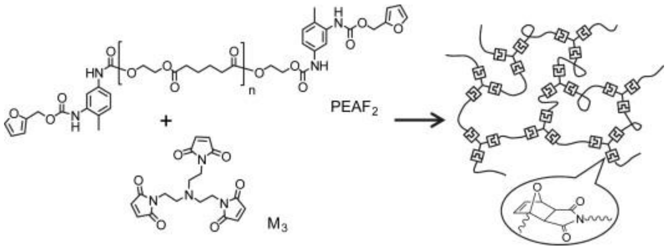

Figure 2. Reticulated polymer formed by D-A addition of PEAF2 and M3. [16]

3. Supramolecular chemistry

For a long time, the focus of research in the discipline of chemistry has been on the formation and properties of various types of covalent bonds. Scientists believe that molecules are the smallest units that maintain the properties of matter, and that intermolecular forces, which mainly constrain the spatial structure of multiple molecules, have an impact on the properties of matter. With the gradual development of crown ether chemistry, it was slowly realised that intermolecular forces act in concert to supramolecular chemistry is slowly coming into focus as the importance of intermolecular synergy in the formation of substances and their physicochemical properties is being realised.

In 1967, C. J. Pederson published the first paper on the synthesis of crown ethers and the selective complexation of alkali metals, which led to a discussion of the selectivity of molecules and molecular aggregates in terms of their morphology for chemical reactions. Later, D. J. Cram, based on his work on the chemistry of complexation of macrocyclic ligands with metals or organic molecules, introduced the subject-object chemistry with the ligand (acceptor) as the object and the complex (substrate) as the main body, officially opening up the new field of supramolecular chemistry. In contrast to covalent chemistry, which is based on covalent bonding and the study of molecules, supramolecular chemistry is based on the study of multiple molecules assembling with each other through weak interactions. Supramolecular chemistry is the study of complex, ordered and functionally specific aggregates of molecules formed as a result of multiple weak interactions, also known as supramolecules. In simple terms, supramolecular chemistry is the study of functional systems that are formed by non-covalent bonding. [4]

At the heart of supramolecular chemistry lies the interconnection of molecules through weak interactions. Supramolecules usually consist of interconnections between a host molecule and one or more guest molecules. The guest molecule is an electron-deficient molecule and acts as an electron acceptor (A), e.g. acid, cation, electrophile, etc. In supramolecular chemistry, molecules are connected to each other by weak interactions similar to coordination chemistry and are part of the same donor chemistry, but instead of classical coordination bonds, supramolecular hosts and objects are connected by weak molecular interactions with bond energies of about 5% to 10% of those of covalent bonds. [17]

Supramolecular systems are spontaneous aggregations of a number of different compound molecules or particles such as ions, which are fundamentally different from individual molecules in which the atoms are connected by covalent bonds. Supramolecules are formed without high energy input, without breaking existing molecular and covalent bonds, and without strong chemical bonds between molecules. This results in the need for a high degree of mutual fitness between individual molecules, in terms of spatial structure, charge, energy, etc. [18] This also gives supramolecular systems a property of high recognition properties. Only molecules that satisfy a number of conditions can form highly ordered supramolecular systems; if the host and object are defective or mismatched, supramolecular aggregates will not form. A well-designed artificial supramolecular system can also have functions such as molecular recognition, energy conversion, selective catalysis and material transport. The molecular recognition function is the basis for other supramolecular functions.

One of the most important applications of supramolecular chemistry is the design of polymer assemblies from supramolecular chemistry systems in which a large number of molecules spontaneously aggregate. Due to the molecular recognition function of supramolecular systems, the polymer assemblies formed using them are rich in structure and stability. At the same time, the composition of the supramolecular system can be regulated to provide special functions such as self-healing, electrical conductivity, and specific condition responsiveness.

3.1. Supramolecular chemistry in responsive adhesives

Adhesives have always been a common chemical product used in everyday life to join two separate objects together. Traditionally, adhesives were formed by reacting the chemicals in the adhesive with oxygen in the air to form a bulk polymer that joined the two surfaces, which was usually irreversible and damaged the surface of the original substance. With the increasing use of adhesives, scientists are pursuing reversible adhesives that are recyclable and do not destroy the original surface interface. [19] This facilitates the recycling of industrial products such as mobile phones and automobiles. The on-demand debonding properties of supramolecular systems have made them a major area of research. Numerous studies have been carried out to produce various types of adhesives that can degrade quickly under specific conditions. Another reason for choosing supramolecular systems for adhesive research is their mild debonding conditions. As is typical with thermally capacitive adhesives, debonding can occur under heated conditions, however it may precede the adhesive when faced with some substrates that are more affected by heat. The same type of hot-melt supramolecular compound, on the other hand, is more likely to debond at lower temperatures due to its lower bond energy. Supramolecular chemistry therefore holds great promise for applications in responsive adhesives.

A thermally responsive supramolecular adhesive was designed by Long et al [20]. They synthesised a series of uracil (UPy)-functionalised polyacrylates, where two uracil moieties can be attached to each other by hydrogen bonding attraction and are susceptible to disruption under heating conditions, and which were experimentally measured to be self-decomposable at 80℃ [21, 22]. The reaction temperature is lower than that of a typical thermally degraded molecular polymer and is less likely to damage the surface structure of the material. Bosman et al. [23] also synthesised siloxane polymers containing the same uracil segment on the basis of a siloxane polymer backbone. It exhibits thermal reversibility at 120℃ and has quite excellent mechanical properties.

In addition to thermally responsive adhesives, Balkenende et al. [24] have also designed a molecule containing three ureido-4-pyrimidinone (UPy) groups, UPy functionalized 1, 1, 1-tris (hydroxymethyl) propane ((UPyU)$_3$TMP), by exploiting the properties of uracil (UPy). The three uracil groups in (UPyU)$_3$TMP can be hydrogen bonded when cooled. It can be interlinked on cooling to form a bulk polymer with the same mechanical properties as conventional adhesives. When exposed to UV light, the energy of the UV light forces the molecules to vibrate more, breaking the hydrogen bonds and causing the adhesive to debond (Figure 3). Due to the need for light de-bonding, these adhesives can only be used in transparent materials such as glass.

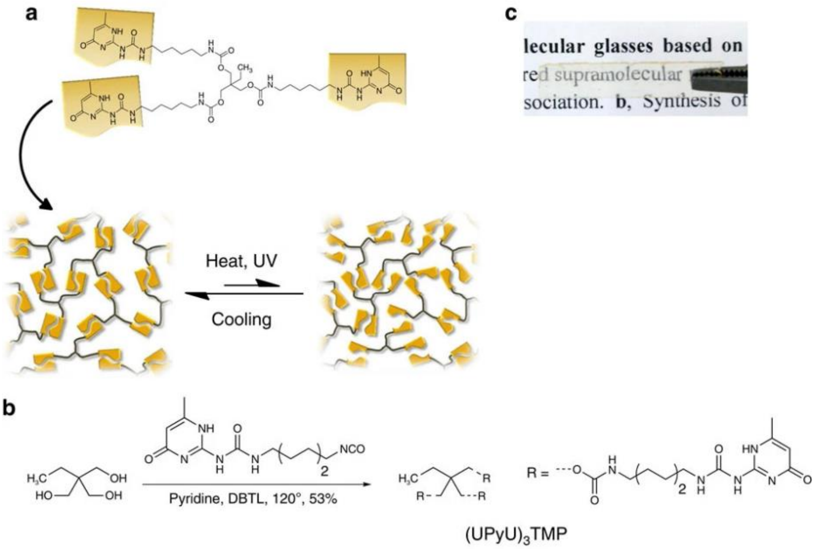

Figure 3. (a) Formation of (UPyU)3TMP supramolecular networks and its principles of thermal and light-induced decomposition. (b) The synthesis of the (UPyU)3TMP. (c) Picture of a self-supported (UPyU)3TMP film prepared by compression molding at 145 ℃. [24]

3.2. Supramolecular chemistry in self-healing materials

Self-healing materials are also a major area of research in supramolecular materials. As a special functional material, self-healing materials can repair themselves when subjected to mechanical damage. Self-healing is generally divided into extrinsic healing and intrinsic healing. Extrinsic healing generally involves the addition of microcapsules or microvessels to the exterior of the material, which automatically rupture when the material is mechanically damaged and release the healing agent, either chemically or physically, to the damaged area. However, this method has some limits due to the fact that microcapsules or microvessels are a one-off repair [25]. Therefore, researchers have re developed intrinsic repair methods using dynamic chemistry. Supramolecules, one of the major branches of dynamic chemistry, have been used to develop a wide range of self-healing materials.

Hydrogen bonding has attracted the attention of researchers due to its high bond energy compared to other weak interaction forces and its excellent dynamic reversibility. Yoshie et al. [26] used the hydrogen bonding interaction mechanism of uracil to design a polyurethane based triblock copolymer containing a UPy group which could depolymerise and repolymerise at 50°C to repair the damage.

The introduction of metal ions into supramolecular systems to produce self-healing materials has also been a focus of research. The introduction of metal ions, which chemically link multiple molecules via reversible metal ligand coordination, promotes the self-healing effect of molecules and enhances the mechanical properties of supramolecular systems. Weder et al. [27] have formed self-healing polymeric materials by linking molecules containing pyridine groups via reversible metal coordination bonds with zinc ions as guests (Figure 4).

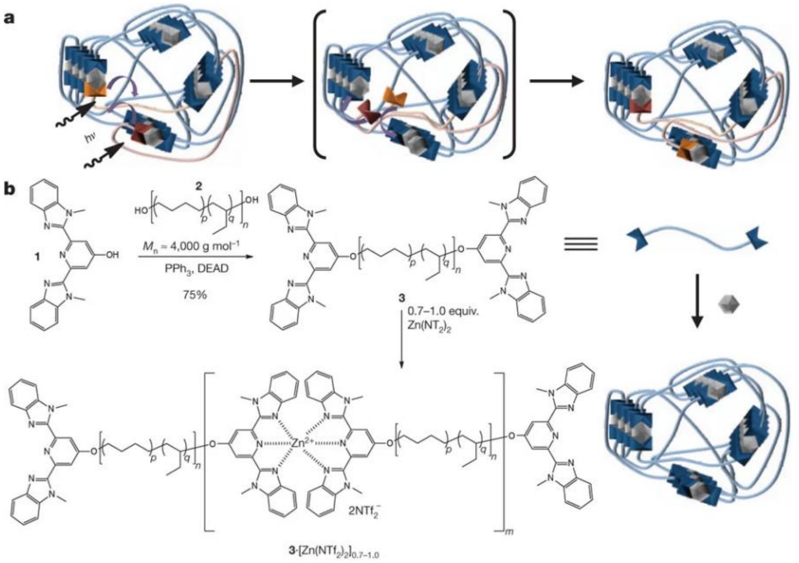

Figure 4. (a) Optical healing principles for metal supramolecular and phase separation networks. (b) Synthesis of macromonomer 3 and polymerization by addition of Zn(NTf2)2. DEAD, diethyl azodicarboxylate. [27]

4. Comparation of Dynamic covalent chemistry and Supramolecular Chemistry

Supramolecular chemistry and dynamic covalent chemistry are two parts of dynamic chemistry, both of which are dynamically reversible. Dynamic reversibility gives them a variety of excellent properties beyond those of conventional polymers, such as specific condition responsiveness, self-healing, degradability, etc. The differences between the two stem mainly from the different bonding mechanisms, with dynamic covalent chemistry linking multiple molecules through the formation of reversible covalent bonds between molecules to form polymers [6], and supramolecular chemistry linking molecules through weak interactions [2, 4]. This core difference brings different properties and applications to the two types of systems. In terms of bonding energy, as dynamic covalent chemistry materials are connected by covalent bonds while supramolecular systems are connected by non-covalent bonds, there is a huge difference in bonding energy between the two, with non-covalent bonds typically having 5-10% of the bonding energy of covalent bonds [17]. As a result, the mechanical properties of dynamic covalent chemical materials are generally superior to those of supramolecular chemical materials for similar structures, and are often used in the design of materials that require stronger mechanical properties. Furthermore, because of the difference in bonding energy between the two, supramolecular chemical mechanisms are often applied when making readily degradable materials, such as designing binders that degrade at lower temperatures [20]. In addition, a high degree of mutual fitness is required between individual molecules of supramolecular chemistry, in terms of space structure, charge, energy, etc. This also confers a property on supramolecular systems, namely a high degree of recognition properties. The highly recognisable nature of supramolecular systems facilitates the dissociation and reconfiguration of inter- and intramolecular hydrogen bonding interactions, resulting in a more homogeneous polymer network structure and thus better energy dissipation. At the same time, the high recognition property also gives the supramolecular system the ability to self-assemble, which can be used to direct the formation of supramolecular systems and to design self-healing materials that do not require other conditions [17]. Although the core mechanisms of dynamic covalent chemistry and supramolecular chemistry are different and have different applications, they are not completely opposed to each other and can be used simultaneously at different stages of the same molecular design. Using the highly recognisable properties of supramolecular chemistry, researches can use it to guide electron-rich and reversibly covalently bonded groups to form stronger and better performing polymeric materials. For example, in the fabrication of polymer fibres, Liu and Luo et al. [28] have designed to use the self-assembly properties of supramolecular chemistry to direct the attraction of electron-rich double bonds to each other, and then to trigger D-A addition reactions of the double bonds by light, resulting in fibres with enhanced mechanical properties.

5. Conclusion

In summary, this review highlights the application of dynamic covalent chemistry and supramolecular chemistry to make conditionally responsive, recyclable and repairable polymers. A comparative analysis of the advantages of dynamic covalent chemistry and supramolecular chemistry in the polymer field is presented by citing relevant studies. Dynamic covalent chemistry and supramolecular chemistry will become increasingly important in the field of polymer synthesis as the focus on environmental protection increases. However, although researchers have been able to synthesise highly advantageous polymeric materials through dynamic chemistry, the high cost and extremely low yields still limit their application in a wider range of applications. In the future, the need to improve yields and reduce costs while maintaining material quality will be one of the key areas of development.

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