

## Structure, properties and applications of polymers based on dynamic covalent chemistry

Traditionally, a chemical design of a certain material should fulfill the requirements of certain thermal, mechanical or electronic properties, which needs stable and passive structures to afford these functionalities. Efforts have been made to ensure the chemical bonds to remain intact when exposed to external stimuli in the environment (e.g. heat, light, stress, chemical, etc.) to achieve a prolonged life span of the material. Unlike traditional chemistry, which treat dynamicity as a drawback, dynamic chemistry takes dynamicity and reversibility as advantages and useful tools in construction of new dynamic systems or modification of existing systems. The rapid development of dynamic chemistry requires exploration of existing or new reversible reactions. A relatively high stability (large  $K$ ) and a reasonably fast response ( $k_1$  and  $k_{-1}$  should not be too small) are both required for a good reversible bond in dynamic systems.



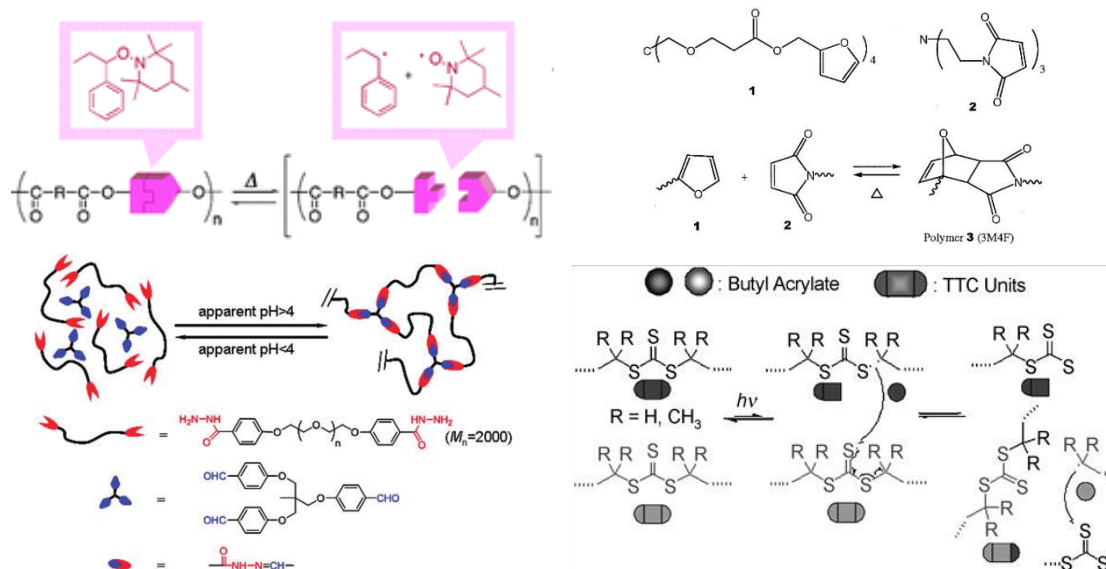
**Fig 1.** Dynamic covalent bonds: Types and kinetic parameters<sup>1</sup>

Dynamic covalent polymers may be defined as polymeric entities whose monomeric components are linked through reversible covalent connections and have therefore the capacity to modify their constitution by exchanging and reshuffling of their components<sup>2</sup>. Recent progress on dynamic covalent polymers include moieties based on various reversible reactions, such as: radical reactions, reversible cycloaddition, imine chemistry, olefin metathesis and transesterification. These have greatly improved the diversity of molecular designs while giving the resulting polymers fascinating properties, like self-healing<sup>3</sup>, stimuli-responsiveness<sup>1</sup>, shape-memory<sup>4</sup>, malleability for thermosets<sup>5</sup>, etc. Several examples of dynamic covalent polymers will be discussed.

**Alkoxyamines:** Alkoxyamines can reversibly cleave on C-O bond to form two radicals upon heating. Takahara et al designed a linear polyester with alkoxyamine in the main chain<sup>6</sup> (**Fig 2**, upper left), and proved that two polymer samples with different  $M_n$  and PDI could be merged into a single peak in GPC trace upon heating, indicating that radical exchange reactions happened. In another work, they presented two random PMMA copolymers with unsymmetrical alkoxyamine groups as side-chain crosslinking points<sup>7</sup>. Heating the mixture of these two polymers would result in crosslinking between the chains via radical exchange reaction. By removing the small alkoxyamine molecules formed during radical exchange, the equilibrium will be shifted towards a higher degree of crosslinking, leading to gelation of the system. The reverse process could also be achieved by simply adding excess amount of small alkoxyamine molecules to the gel while heating, which would give a soluble polymer blend.

**Reversible cycloaddition:** Wudl et al developed two self-healing crosslinked polymer systems, one was based on a trifunctional maleimide and a tetrafunctional furan<sup>8</sup> (**Fig 2**, upper right), while the other was based on dicyclopentadiene macrocyclic monomer<sup>9</sup>. Both materials could be healed repeatedly via equilibrium between retro-DA and DA reaction upon heating, with a high ratio of mechanical properties recovered each time.

**Imine species:** By polycondensation of dihydrazides with dialdehydes, Lehn et al prepared two non-fluorescent polymer films with hydrazine C=N bonds<sup>10</sup>, which were cut into different shapes, overlapped and then heated. With a catalytic amount of acid, the two non-fluorescent polymers exchanged their components to produce a fluorescent polymer in the overlapped regions. Chen et al produced a gel by mixing a trifunctional aldehyde with a bifunctional acylhydrazine capped polyethylene oxide in DMF with catalytic amount of acid<sup>11</sup> (**Fig 2**, lower left). The resulting product showed reversible gelation imposed by pH control. Excess amount of acid (pH < 4) resulted in dissolution of the gel, and addition of trimethylamine (pH > 4) would recover the gel from the sol. Besides, two gel samples could be held together to fuse into one single piece, and could be repeatedly cut and healed.



**Fig 2.** Some examples of applying dynamic chemistry in polymeric materials.

**Sulfur radicals:** Upon light irradiation, disulfide bond can produce sulfenyl radicals that can exchange and recombine. Takahara et al designed a polyester with disulfide bonds in the main chain<sup>12</sup>. The photoresponsiveness was proved by mixing two polyester samples with different  $M_n$  and PDI, which showed two distinct peaks in GPC trace. After irradiated by UV light for 1 h, GPC trace showed only a single peak, indicating that light-induced disulfide metathesis took place and rearranged the molecular weight distribution. Similar to disulfide bond, TTC species could also reversibly cleave on C-S bond with UV stimulation. Takahara et al showed that a photoresponsive polymer with trithiocarbonate (TTC) functionalities could undergo repeated self-healing via reshuffling of TTC species<sup>13</sup> (**Fig 2**, lower right). The material was built by RAFT copolymerization of n-butyl acrylate and a bifunctional TTC crosslinker, which could perform self-healing both in bulk and in solution upon UV irradiation.

To sum up, researches on applying dynamic chemistry to polymers aims to design “smart” dynamic materials that show great adaptability to the environment. The incorporation of dynamic features into polymer chemistry has opened a new field of study, yielding many dynamic polymer designs with novel functionalities, which are hard to achieve by fixed covalent polymers. Self-healing, shape memory, reversible depolymerization, stimuli (heat, light, pH, etc) responsiveness and many other functionalities have already been realized in dynamic covalent polymers, while retaining the characteristics of traditional polymers. Possible improvements may include milder conditions for dynamicity, reducing the usage of catalysts, fast and multiple responsiveness, etc. A few catalyst-free, low-temperature dynamic covalent chemistries have already been applied in the synthesis of dynamic polymers. Hopefully, many of these designs will be developed into practical use and benefit people in real life.

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