ABSTRACT

Plastics play crucial rules in almost every aspect of life. Unique properties of plastics like chemical and light resistant, strong, moldable, and low cost make plastic materials useful in many aspects of our global society. However, largely relying on feedstock resources like fossil fuels, plastics production is not sustainable. Thus, plastic recycling could be an efficient alternative to save feedstock resources as well as to reduce production cost.

Recently, a series of polymer materials synthesized via topochemical polymerization are considered as strong candidates for next generation recyclable plastics. It is well-known that topochemical polymerization has high efficiency and environment-friendly features, such as solvent-free and catalyst-free reaction conditions, high reaction yield without side reactions, and atom economy. Yet, there exist few studies on depolymerizing and recycling those polymers. A unique topochemically polymerizable polyindenedione derivative [2,2'-Bi-1H-indene]-1,1'-dione-3,3'-diyl dialkylcarboxylate (polyBIT) with rapid and quantitative depolymerization was discovered via breakage of elongated carbon-carbon (C-C) bonds with bond length of 1.57∼1.63 Å. The elongated C-C bonds have been proven theoretically and experimentally to have significantly lower bond dissociation energies than normal C-C bonds, and it is the major driving force to depolymerize polyBIT polymer single crystals.

Different from most traditional polymers that can be dissolved or melt processed, topochemical polymer single crystals are not soluble in most common solvents due to their highly crystalline and ordered nature. This unique feature inhibited topochemical polymer crystals from practical applications. To convert needle-like polyBIT crystals into useful forms, I developed an ultrasonication method to break large polymer crystals into small fibers that can be uniformly suspended in organic solvents. Followed by vacuum filtration and heat press, polyBIT crystals can be processed into robust and freestanding polymer thin films. The processed thin films presented reasonable mechanical properties with Young's modulus of over 600MPa and are stable under harsh conditions.

Topochemical polymerization reactions require specific monomer packings before applying external stimuli, and a small change in monomer structure may completely alter the reactivity. Therefore, functionalizing monomer structures for topochemical reactions is quite challenging. In

the polyBIT system, we attempted to functionalize BIT monomer with several linear and branched side chains. After preparing monomer crystals, only needle-like 1D monomers can be photopolymerized, while plate-like 2D monomer crystals became photostable. Introducing heteroatoms (such as oxygen, sulfur, bromine, chlorine) can induce different non-bonding interactions and interactions, which combined can push monomers away from one another to make them unreactive. Introducing branched side chains will also change the distances between two BIT monomers and leads to unreactive crystals when the branched side chain is too bulky (such as when tertbutyl group is on the end of side chain). Functionalizing side chains for polyBIT crystals can further tune the mechanical properties of the crystals: swapping end methyl group with a simple bromine atom can induce multiple intermolecular and interchain interaction including weak hydrogen bonding and C−H···Br interactions. These interactions bind all the polymer chains together to provide a strong 1D polymer fiber with elastic modulus over 10.6 GPa. These results suggest that the crystalline polymers synthesized from simple photochemistry and without expensive catalysts are promising for practical applications with complete materials circularity and wide range of structural and mechanical turnabilities.