Recent Approaches Toward Mechanochromic Polymeric Materials

Junfeng Chen Literature Seminar November 10th

Mechanochromism is the phenomenon that the color of chemicals in solid state is changed by mechanical grinding, crushing or stretching. Mechanochromic polymeric materials has attracted considerable interest in recently years due to their potential applications in detecting critical stress or recoding the mechanical history of polymer through direct optical measures.

There are two most practical ways to build polymers with mechanochromic properties that give optical response to visible light.[1] The first approach is the direct dispersion of organic dyes into the pristine polymer matrix, which is usually colorless, and the absorption of organic dyes inside the polymer matrix can change as the supramolecular aggregation structure is disrupted by a mechanical stimuli.[2] The second method, which is developed only recently, takes advantage of polymeric mechanochemistry. In detail, covalent bonds can break and form by applying mechanical force along polymer chains, leading to structural and color changes of specific moieties. This abstract will mostly focus on the recently progress in building mechanochromic polymeric materials by mechanochemistry reactions.

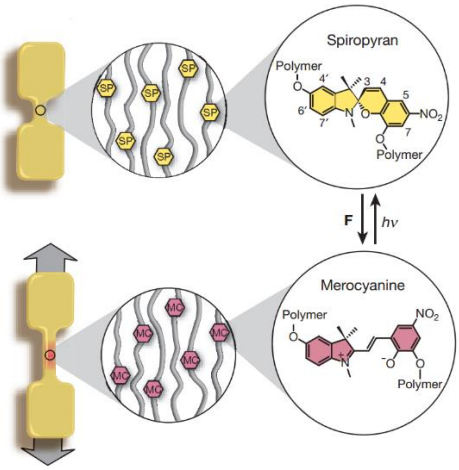

Figure1: Mechanochromic polymers with spiropyran

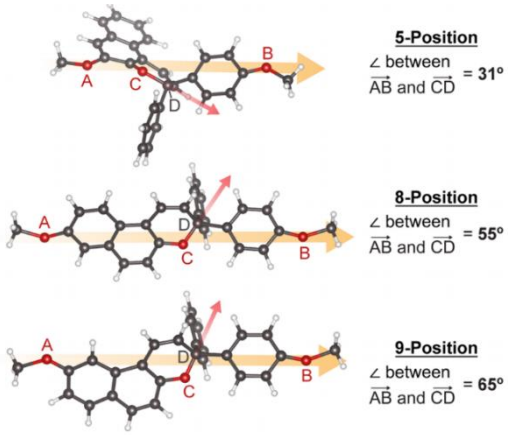

Figure2: Mechanical force from different direction

Moore and Sottos[3] groups pioneered in the design of mechanochromic polymers utilizing chemical reaction induced by mechanical force. Specifically, the mechanochromic property was achieved by covalently linking two sites from spyropiran dyes into polymer chains, and the reversible transformation between spyropiran and merocyanine structure resulted in enormous change in visible light absorption. Naphthopyran group was also utilized as a new mechanophore to develop mechanochromic polymers by the Moore group.[4] And in this work, regioisomer-specific mechanochromic polymers were achieved by synthesizing three different types of naphthopyran derivatives with different substitution sites at 5-, 8- and 9-positions. Mechanical

forces from different directions could be applied on these derivatives after linking to polymer chains, and the difference of their behavior upon receiving mechanical stimuli as well as DFT calculation indicated the relationship between mechanochemical reactivity and mechanical force directions.

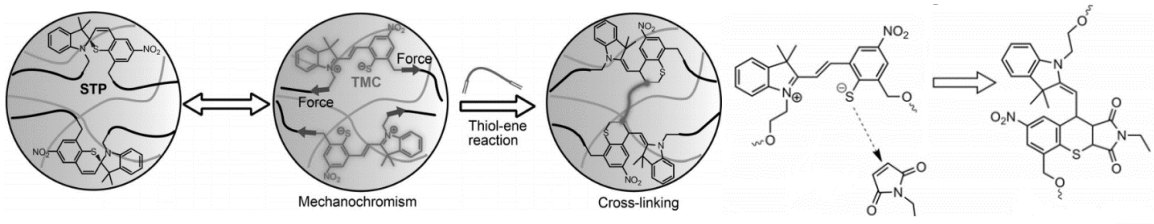

Figure3: Dual mechanochemistry of spirothiopyran

In 2016, Weng and co-workers[5] reported the mechanochromic polymeric materials with spirothiopyran (STP) moieties which provided unique dual mechanochemical responses. STP was incorporated into the polymer backbones and converted into green-colored thiomeocyanine (TMC) by applying mechanical force in both solution and solid state. Then the free thiol groups provided by TMC moieties could undergo thiol-ene reaction with 1,6-bismaleimidohexane and crosslink the polymer. This work combined mechanochromism and load-induced chemical reaction, and the dual mechanochromic polymer may have potential applications in damage-sensing and load-triggered self-strengthening.

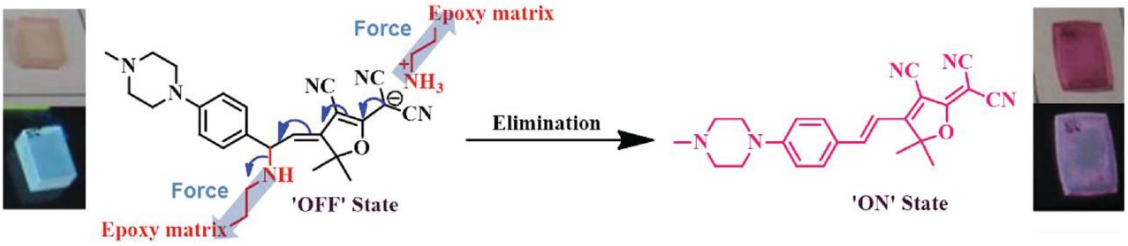

Figure4: Schematic diagram of sensitive built-in strain sensor

Recently, Jen and Flinn[6] groups designed a new built-in strain sensor in epoxy composites with the ability of detecting mechanical strain of very low level. The mechanochromic polymeric materials were achieved by covalently linking mechanophores which could regenerate dipolar structure with strong intramolecular charge transfer upon applying mechanical force. The advantage of this design was that the visible light absorption and emission could change dramatically with much lower activating energy, which opens the possibility of detecting barely visible impact damage. Meanwhile, the 'ON' state is less photosensitive and is more compatible with epoxy polymers.

In summary, recent progress in mechanochemical reaction of organic dyes has shown its potential in designing new mechanochromic polymeric materials. More mechanophores need to be designed to achieve mechanochromic property by applying different levels of mechanical forces in the future, and the detection of mechanical stress in polymeric materials though mechanochromic chemistry is likely to play an important role in developing future smart materials.

Reference:

1. Ciardelli, F.; Ruggeri, G.; Pucci, A. Dye-containing polymers: methods for preparation of mechanochromic materials. *Chemical Society reviews* **2013,** *42* (3), 857-70.
2. Crenshaw, B. R.; Burnworth, M.; Khariwala, D.; Hiltner, A.; Mather, P. T.; Simha, R.; Weder, C. Deformation-Induced Color Changes in Mechanochromic Polyethylene Blends. *Macromolecules* **2007,** *40* (7), 2400-2408.
3. Davis, D. A.; Hamilton, A.; Yang, J.; Cremar, L. D.; Van Gough, D.; Potisek, S. L.; Ong, M. T.; Braun, P. V.; Martinez, T. J.; White, S. R.; Moore, J. S.; Sottos, N. R. Force-induced activation of covalent bonds in mechanoresponsive polymeric materials. *Nature* **2009,** *459* (7243), 68-72.
4. Robb, M. J.; Kim, T. A.; Halmes, A. J.; White, S. R.; Sottos, N. R.; Moore, J. S. Regioisomer-Specific Mechanochromism of Naphthopyran in Polymeric Materials. *Journal of the American Chemical Society* **2016,** *138* (38), 12328-31.
5. Zhang, H.; Gao, F.; Cao, X.; Li, Y.; Xu, Y.; Weng, W.; Boulatov, R. Mechanochromism and Mechanical-Force-Triggered Cross-Linking from a Single Reactive Moiety Incorporated into Polymer Chains. *Angewandte Chemie* **2016,** *55* (9), 3040-4.
6. Li, Z.; Toivola, R.; Ding, F.; Yang, J.; Lai, P. N.; Howie, T.; Georgeson, G.; Jang, S. H.; Li, X.; Flinn, B. D.; Jen, A. K. Highly Sensitive Built-In Strain Sensors for Polymer Composites: Fluorescence Turn-On Response through Mechanochemical Activation. *Advanced materials* **2016,** *28* (31), 6592-7.