

Research Progress of Photomechanical Motion

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Abstract

The development of actuators based on materials that reversibly change shape and/or size in response to external stimuli has attracted interest for some time. A particularly intriguing possibility is offered by light-responsive materials, which allow remote operation without the need for direct contact to the actuator. The photo-response of these materials is based on the photoisomerization of constituent molecules, which gives rise to molecular motions and thereby deforms the bulk material.

Keywords

Photomechanical Motion; Polymer; Molecular Crystals.

1. Introduction to photomechanical motion

Converting other forms of energy into kinetic energy is a basic energy conversion process in nature [1]. Stimulus-responsive materials can change in shape or size under external stimuli, thereby converting energy into mechanical motion. This discovery makes stimulus-responsive materials have the prospect of being used in brakes. External stimuli mainly include light, heat, electricity, pH and so on. In all external stimuli, light is a clean and ideal tool to control the brake. Photons can penetrate into various media and transmit information while transmitting energy, and can be implemented remotely, real-time, and accurately. It is precisely because of these advantages that various light-responsive materials and systems have been extensively studied in the field of photomechanical motion.

The generation of photo-induced macroscopic mechanical motion is actually the result of changes in molecular structure caused by photochemical reactions at the molecular level, which are then extended to the performance of macroscopic materials [9]. Among the numerous macroscopic materials, materials capable of reversible photochemical reactions can produce repeated photomechanical motions, thus having greater application prospects. The reversible photochemical reaction is that when exposed to a specific wavelength of radiation, compound A can undergo a specific reaction to obtain product B, and under the action of another wavelength of light radiation or heat, product B can undergo a reverse reaction to regenerate compound A (Fig. 1).

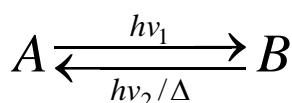


Fig. 1 Photochemistry of compound

In most cases, the structural changes caused by the photochemical reaction of a single molecule are not enough to be directly observed. For example, the molecules are dissolved in a solution or the molecules are arranged out of order, as shown in Fig. 2a. Therefore, to produce a macroscopically

visible photomechanical motion system requires the following two characteristics: 1) There are photoisomerized functional groups in the molecule; 2) These functional groups can be arranged in an orderly manner in the solid, and all the molecules will move towards the same one. Directional movement, as shown in Fig. 2b [2]. The widely studied photo-induced mechanical motion systems include polymers, molecular crystals, etc.

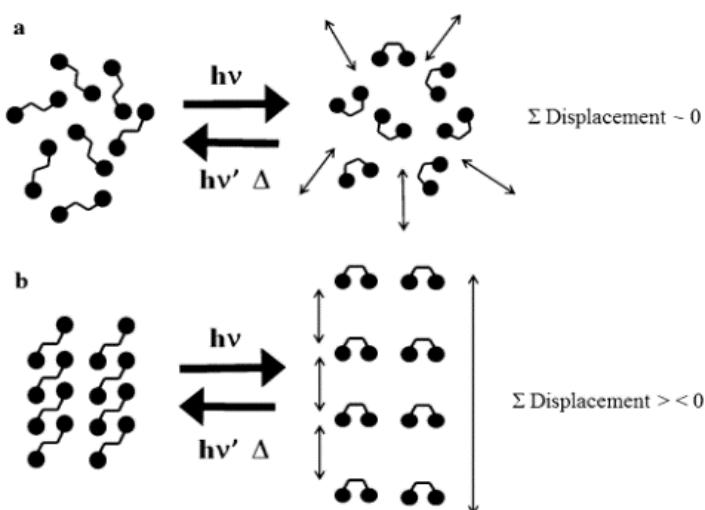


Fig. 2 (a) A disordered system of photoreactive molecules; (b) a ordered array of photoreactive system

2. Research status of photomechanical motion

2.1 Photomechanical motion of Polymer

The most direct method to prepare solid photomechanical materials is to prepare photoactive molecules as polymers. Obviously, a drawback of this method may be that the arrangement of photoactive functional groups in the polymer may be random, which may eventually lead to the situation in Fig. (2a), that is, no photo-induced mechanical motion is observed. However, in recent research there are indeed some polymers that can produce photo-induced bending.

Athanasiou et al. studied a light-responsive polymer with a low glass transition temperature (PEMMA doped with a spirochet derivative) [3]. The polymer can cause MC (Merocyanine) to undergo photoisomerization during the alternating ultraviolet and visible light irradiation process, and it was found that the polymerized MC isomers caused the change of the polymer volume and achieved transient bending. However, this method of doping photochromic molecules cannot greatly improve the reactivity of the polymer. Therefore, in order to make the raw materials simple and achieve the greatest degree of photo-induced bending, researchers are gradually using molecules that can form polymers on their own and have photo-responsive units.

Guab et al. studied a single-molecule-level polymer that contains photoisomerized azophenyl groups linked by covalent bonds [4]. By measuring the topological changes caused by photoisomerization of single molecular polymer chains, the net molecular displacement, stress and free energy changes caused by photoisomerization can be obtained. Although the single polymer chain from this study is not directly related to the macroscopic material, the study does prove that this single molecule can generate photo-induced mechanical stress. Later, Rack et al. studied a ruthenium metal organic polymer, which undergoes cis-trans isomerization under the action of light radiation, and finally produces a reversible photo-induced bending phenomenon (Fig. 3) [5]. The above results all show that the serious study of the cis-trans isomerization of azobenzene is of great significance to the study of amorphous polymer photomechanical materials.

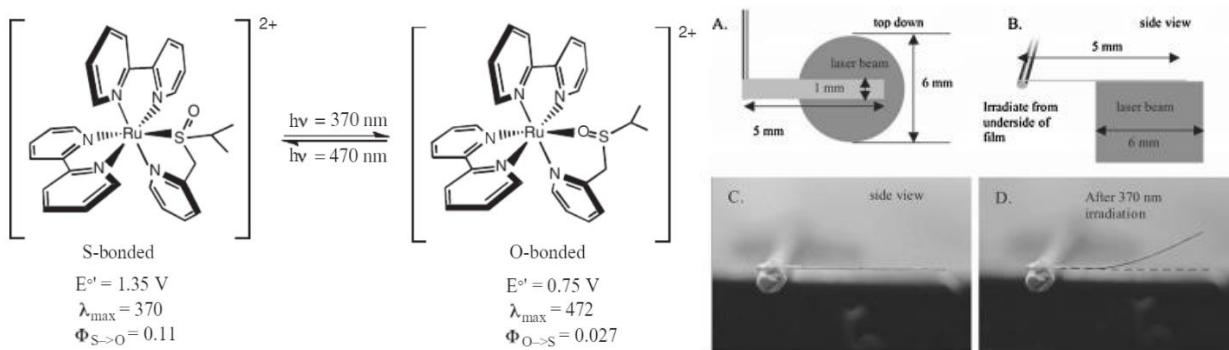


Fig. 3 The photomechanical bending motion of a polymer film composed of a ruthenium organometallic complex

Although amorphous polymers have shown great potential as photomechanical materials, most of the current researches tend to focus on more ordered systems in polymers [2]. In ordered materials, the arrangement of photosensitive molecules can ensure that the displacement of light-induced motion is in the same direction, and in a highly ordered system, most of the space can be used to generate greater deformation. In order to obtain an ordered system, the liquid crystal intermediate is generally combined with photochromic molecules, and finally a series of ordered polymer solids composed of liquid crystal elastomers are formed.

Finkemann et al. [6] used polymer liquid crystal elastomers doped with azobenzene derivatives to prepare a highly ordered photoactive system for the first time. This study proved that 40% of the ordered structure occurred after light exposure. Deformation, compared with previous research, this deformation has an order of magnitude breakthrough. After this research, many other researchers used similar methods to obtain a variety of reversible opto-mechanical motion systems. In 2003, the study by Ikeda et al. [7] proved that the polarization direction of light can control the bending direction of the azobenzene liquid crystal elastomer. When the film is irradiated with 366 nm ultraviolet light with a polarization angle of 0 °, the film bends toward the light. The bending direction is parallel to the direction of polarized light; after subsequent irradiation with light with a wavelength greater than 540 nm, the film returns to the original flat state. As the polarization angle changes, the bending direction of the film also changes, and it is always parallel to the polarization angle.

All of the above phenomena can explain that when optomechanical materials are exposed to light, the internal molecules of these materials will shrink or expand asymmetrically, forming a model similar to a double reed brake, but the polymer state material cannot pass X-rays. Diffraction results in the position of atoms and changes in chemical bonds. Therefore, in order to more accurately study how changes in the molecular level cause shape changes, more attention is now being paid to higher-order systems, such as single crystals.

2.2 Photomechanical motion of molecular crystals

Photomechanical polymers are usually synthesized by covalently bonding photoactive groups, while photomechanical crystals are obtained through the non-covalent self-assembly crystallization process of photoactive molecules. While the orderliness has been significantly improved, the replacement of soft polymer materials with hard crystalline materials also brings many challenges. The reason is that the volume change during the photoreaction process will cause phase separation and contact in the reaction crystals. The strain generated by the domain often breaks or fragments the original crystal. The usual solution is to reduce the intensity of the light source, use a long-wavelength light source to illuminate or use two-photon excitation, but there are very few examples of the conversion of reactants into products while maintaining the original crystal form in the actual research process. The second problem is that the dense and orderly ordering in the solid may inhibit geometric changes, and there is no guarantee that the photoactive molecules are still photoactive in the solid state. P-diphenylethylene molecules and azobenzene molecules are prone to photoisomerization in the

solution state, but in the solid state due to the steric hindrance of the surrounding molecules, it is difficult for these two molecules to undergo photoreaction, so the photochemical reaction process. The arrangement of middle crystal molecules has become a wide range of research objects.

In 1992, Lange et al. published for the first time a semiquinone rhodium complex molecular crystal that can produce reversible bends. By irradiating a fine needle-like crystal with near-infrared 1600 nm light, the crystal can produce a reversible bend of nearly 45° . This reversible bending needs to be performed in the presence of oxygen. If the crystal is exposed to the air all day, this bending performance will be lost [8]. In the following 10 years, the photomechanical molecular crystals did not attract enough attention. Until 2007, Irie's research group proved that diarylethylene derivative crystals can undergo reversible deformation under different wavelengths of light [9]. The molecule can undergo opening and closing ring changes under UV/visible light irradiation, and the macroscopic performance is the color change and macroscopic deformation of the crystal before and after light irradiation. The amplitude of the deformation is very small (<1%), if it is in a vacuum environment, the amplitude of the photo-induced deformation will be greater.

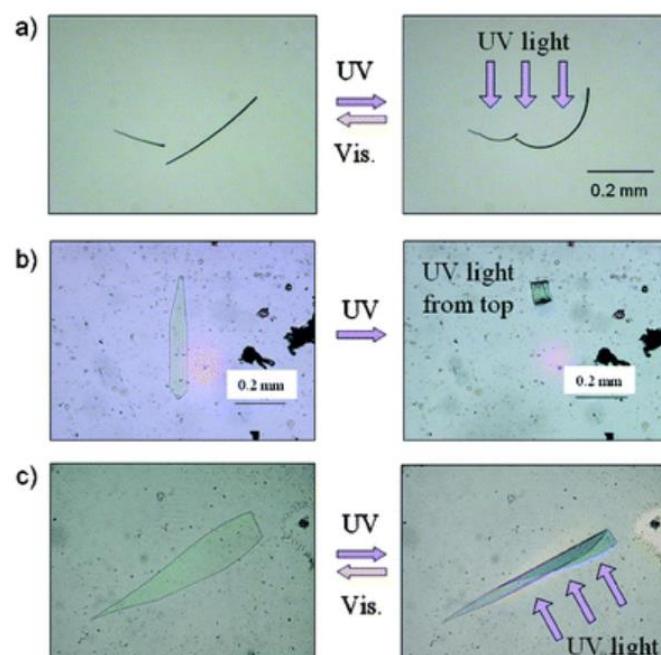


Fig 4 The photomechanical bending, curling motions of different forms of crystals under UV light

Irie and other researchers have done a lot of photomechanical application studies on the ring-opening and closing reactions of diarylethylene [10]. One of the interesting applications is that the reversible reaction of microfibers on the crystal surface can affect its wetting properties. Feringa et al. used the sublimation method to prepare chiral diarylethylene crystals with a thickness of less than 1 μm . Under 365 nm ultraviolet light irradiation, it can be twisted instead of bending. This twisted state is under light irradiation with wavelengths greater than 500 nm. It can be restored to the original flat state [11]. As shown in Fig. 4, The photomechanical bending, curling motions of different forms of crystals under ultraviolet light. Diarylethylene crystals have also been found to be capable of motions such as light bursts (photo-induced jumping). Under light irradiation, diarylethylene can react quickly and produce a reversible reaction with greater stress. The above advantages make this material still subject to extensive research in the future.

Other materials that can produce intramolecular photoreactions are also used as photomechanical materials. Under ultraviolet light irradiation, furan fulgide crystallites can bend and curl up. Similar to diarylethylene, this reaction can open and close the ring under alternating ultraviolet and visible light irradiation. Koshima et al. found that the photo-cis-trans isomerization reaction that cannot be

carried out in azobenzene crystals can be reversibly bent in amino azobenzene derivative crystals. Salicylidene aniline has also been proven to undergo cis-trans isomerization. Research by Koshima et al. showed that the photoreversible reaction in the solid can cause the crystal to undergo reversible bending motion [12].

3. Conclusion

Based on the analysis of existing literature, the principle of photo-induced mechanical motion at the molecular level is basically recognized by the majority of researchers. The photo-mechanical motion has been deeply studied in polymer and molecular crystals, mainly studying the photo-mechanical motion amplitudes of polymer or crystals with different thicknesses. But for the arrangement of the internal molecules of the object and the interaction between the molecules during the movement, there is still too little research on force.

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