Artificial Muscles: Photomechanic Actuators

Melinda Sindoro Literature Seminar January 24, 2013

Muscles are sophisticated devices that sustain numerous life functions. They combine both sensors and actuators functions into a compact system which directly transforms chemical energy into heat and mechanical deformation. One special attribute of muscles is the selective activation of muscle fibers which make them capable of anisotropically contracting or expanding at a controlled rate. If you can scan the words on these lines one by one, it is due to the fine precision of the extraocular muscles that control your eye movement. This efficient operation provides a biomimetic inspiration for creating artificial actuators without the need of external combustion engines or energy storage methods. For applications such as micro- or macro-scale joints and motors, single step energy conversion is an attractive system since the actuator will be comparatively more fuel efficient and compact.¹

In the development of device miniaturization, the type of energy to fuel an actuation system becomes an important consideration. Chemical cues, pH or redox reaction, are the closest mimic to natural muscle triggers. This chemical to mechanical energy conversion can be performed by various polymeric gels² and molecular machines (catenanes, rotaxanes)³,⁴. However, the chemical fuel is converted to chemical waste in every working cycle. Moreover, the need to sustain an electrolytic environment introduces limitations in the design and compatibility with many applications. Electric charge is another fuel source that is common for many electroactive polymers (EAP).⁵ Nonetheless, the large driving voltage (~100 MV/m) required to induce the strain translates to excessive heat generations, large dipole hysteresis, and reduced life cycles.⁶ Additionally, electric sources must be wired to the actuator which then prevents scalability to micrometer machines.

![E/Z - Isomerization](image)

Figure 1] Photochromic molecules. Switching between two independently addressable states on the molecular level affects the macroscopic properties. Based on their accessible states, they are classified in two groups: isomerization (azobenzenes and stilbens) and ring formations (diarylethenes, spyropyranes, and fulgimides) based.

Light is a versatile trigger for wireless actuators. The photon to mechanical energy conversion is instantaneous (picosecond timescale) without diffusion limited transport which is inherent in chemical trigger.⁷ In contrast to magnetic triggers, light sources have simpler set-ups and can be localized to a domain. The photon-fueled molecules, called photochromes, should possess reversible geometric or electronic states.⁸ Currently, the most well studied photochrome for mechanical actuation is azobenzene because of its large structural change (3.5 Å) during isomerization. Despite geometric change at molecular level, actuation cannot be efficiently translated beyond molecular length scales without orientational order. Hence, alignment order is introduced by incorporation of azobenzene into the backbone of liquid crystal network (azo-LCN).⁹

LCNs consist of polymers and have self-organizing nature. They form highly ordered structure such as nematic phases and random ordered structures such as isotropic phases depending on the temperature.¹⁰ In trans configuration, the azo-LCN polymers adopt a rod like shape that favors ordering into a nematic phase. Under UV illumination, cis isomers adopt bent shape and destabilize this ordering. The conversion from nematic to isotropic phase generates volume changes that correspond to lateral macroscopic deformation. Alternately, the cis to trans isomerization under visible light can recover the initial ordering of the nematic phase. These azo-LCNs have
significantly better response (20% strain)\(^9\) compared to the conventional incorporation of azobenzene crosslinker (0.25% strain).\(^{11}\) Aside from lateral expansion or contraction, unidirectional bending is commonly observed for azo-LCN films thicker than 10 µm. 99% of the light is absorbed at the surface due to the high extinction coefficient of azobenzene moieties (10\(^8\) L/mol.cm).\(^{12}\) As a result, large volume changes are only induced on the illuminated surface, causing anisotropic bending behavior perpendicular to the pre-aligned direction.

From simply bending and lateral contraction or expansion motion, various proof-of-concept photomobile materials have been reported for inchworm locomotion,\(^{13}\) flexible robotic arm,\(^{14}\) high-frequency photo oscillators,\(^{15}\) photo origami shape reconstruction,\(^{16}\) and plastic motors.\(^{13}\) Fundamentally, all of the aforementioned devices share the challenge in maximizing work output. The work efficiency for macroscopic response can be quantified through the bending angle which is a product of geometry (thickness, width, curvature) and strain (elongation compared to the initial length). This means that the ideal azo-LCD system should require minimum light intensity to achieve either maximum bending angle or the fastest bending response.

Ikeda \textit{et. al.} showed that bending time is significantly affected by light intensity only in region below 6 mW/cm\(^2\) due to a dependency on isomerization rate.\(^{17}\) On the other hand, \textit{trans} to \textit{cis} conversion rapidly reaches the thermodynamic equilibrium state at high intensities and the polymer segment relaxation becomes the rate determining step. Independent of the illumination intensity, the ratio of the area to film thickness is the main variable in achieving faster bending responses. As the sample thickness increases, the bulk volume increases while the photoresponsive volume remains constant on the surface, causing longer polymer relaxation times and a slower bending response. This also implies a geometrical limitation for the bending behavior on which low area-to-thickness ratio gives smaller work output.

Since the driving force for deformation is suggested to arise from the azo-LCN orientation, the concentration of cross-linker should constrain the molecular order parameter. Indeed, the maximum bending angle (Figure3D, bending angle >90\(^\circ\)) was observed for a densely cross-linked film where the alignment layers have a higher dichroic ratio.\(^{18}\) The problem here is that bending time was no longer directly proportional to the area-to-thickness ratio since the glass transition temperature (\(T_g\)) had changed. At high cross-linking densities, \(T_g\) is higher and the polymer mobility decreases. Therefore, highly cross-linked domains will bend slower but attain greater angles.

Polymer network crosslinking is not the only variable that affects the photomechanical response. There is a strong relationship between crystallinity that affects local molecular free volume and the efficacy of photoisomerization. To clarify the role of crystallinity, two types of polymers were used to polymerize the azobenzene: the structurally rigid pyromelitic dianhydride (azo-PI-PMDA) and the flexible propane dianhydride (azo-PI-6FDA).\(^{19}\) Under illumination, amorphous azo-PI-6FDA displayed a bending response while the semi-crystalline azo-PI-PMDA did not.
The photomechanical output was further examined using 6FDA/PMDA copolymer which crystallinity decreased with increasing PMDA fractions. The overall dependence showed that the bending angle increases as crystallinity decreases.

Figure 3 | A) Structures of monoacrylate (A6B2) and diacrylate cross-linker (DA6AB) used in the study. Still photograph of azo-LCN films with B) 5mol %, C) 10mol %, and D) 50mol % cross-linker exhibiting anisotropic reversible bending behavior.

In conclusion, the mechanism for single step photon to mechanical energy conversion has been studied in detail through the use of photochromes. For natural muscle, deformation is precisely controlled at the molecular level. Similarly, the construction of efficient artificial actuator requires two factors: 1) large geometrical changes at the molecular level and 2) disruption of a well-ordered alignment as local strains are amplified toward macroscopic response.

(1) Madden, J. D. Science 2007, 318, 1094.
(4) Bruns, C. J.; Stoddart, J. F. Nat Nanotechnol 2013, 8, 9.