Stable photo-reversible surface energy switching with azobenzene polyelectrolyte multilayers†

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Self-assembled multilayers of azobenzene polyelectrolytes produced a reversible change in surface energy that is stable over time, in a host material that is biocompatible for eventual applications of directed cell growth.

Polymers containing azobenzene chromophores exhibit a photoinduced and reversible trans-cis isomerization between two distinct geometric shapes. (Fig. 1.) This isomerization is fast and clean, and the resulting differences in physical and optical properties between the two isomer states can be significant. Azo-containing materials have thus received much interest for a variety of potential applications as photo-reversible systems for optical switching, reversible information storage, and other photo-active and photo-mechanical devices. Most recent interest in azo materials has been drawn to more biological applications however, where the azo group can be incorporated into peptide or DNA structures, micelles, vesicles, or surfaces that interface compatibly with biological systems to provide reversible sensing or signaling. In contrast to more commonly employed reversible properties which can be temporarily interconverted with light such as shape, size, dipole, and colour, we focus here on indefinitely stable changes achievable to the geometric orientation of the sidegroups, which can still be photo-switched reversibly, providing a robust mechanism for changing the surface energy of a thin film of azobenzene polyelectrolyte, reversibly yet indefinitely, self-assembled as a multilayer. As a host material for the photochemistry, polyelectrolyte multilayers have emerged as an ideal platform for tailoring a biological interface, as their water and ion content can be tuned with simple preparation parameters such as pH, as can their modulus and surface chemistry, to mimic biological systems effectively. Importantly, the novel azo materials described in this work for these biological applications are all completely water soluble, in contrast to the previous work on more specialized hydrophobic monolayers, that responded only dynamically between stable trans and transient cis states, such that relaxation of the surface energy change always accompanies the inevitable thermal relaxation of the cis form back to the trans. Our goal here is to provide a more general strategy for surface energy switching for biological applications in a completely aqueous environment, where the azo groups are incorporated into a readily-prepared polyelectrolyte, and subsequently a soft multilayer with high water content which is biocompatible, as demonstrated by successful cell adhesion, growth, and function. Our aim was to develop a more static surface energy change mechanism, whereby a permanent re-orientation of the stable trans form would be responsible for surface switching, as opposed to a transient production of cis isomer.

This Communication describes the preparation and characterization of a series of water-soluble copolymers with various mole fractions of azobenzene chromophores based on Disperse Red 1 (DR1) dye monomers, and acrylic acid (AA) repeat units by free-radical copolymerization: p(DR1A-co-AA). As part of a larger project to eventually reversibly control neural cell growth with light using these bio-azo surfaces, we were also concerned with demonstrating non-toxicity to various cell types, so that these platforms could function as directed cell growth surfaces, in systems where increases in surface energy have been implicated as guiding and steering mechanisms (such as outgrowth of neurites in neural cells). Stable surface energy switching was observed for all films, and displayed a curious dependence on irradiation parameters such as the direction and polarization of the light, and an increase in the level of order achieved as compared to traditional hydrophobic thin solid films.

Disperse Red 1 acrylate (DR1A) monomer was prepared by reacting 3.3 g (0.011 mol) of DR1 with 0.995 g (0.011 mol) of acryloyl chloride and 1.5 ml of triethylamine in THF for one hour at 0 °C, followed by stirring at room temperature for another 6 h, as per

Fig. 1 The photo-conversion of azobenzene between the trans and cis geometric forms.
To prepare soft, hydrophilic films with high water content suitable for eventual bio-compatible directed cell growth studies, the electrostatic sequential layer-by-layer self-assembly technique was employed to fabricate the azo-functionalized multilayer films on silica substrates. Typically, 0.1 mmol L⁻¹ aqueous solutions of poly(diallyldimethylammonium chloride) (PDADMAC) and of the synthesized p(DR1A-co-AA) copolymers were used as the polycation and the polyanion, respectively. Films studied ranged in thickness from approx. 10 nm up to 500 nm, controlled both with the number of layers deposited, and by depositing near the pKₐ of a AA groups, which leads to layers of longer loop length, decreased modulus, and greater capacity to absorb water, all factors advantageous to successful cell adhesion and behaviour. The surfaces were tested with a variety of cell types, including neural cells, an eventual advantage to successful cell adhesion and behaviour. The surfaces were tested with a variety of cell types, including neural cells, an eventual advantage to successful cell adhesion and behaviour. The surfaces were tested with a variety of cell types, including neural cells, an eventual advantage to successful cell adhesion and behaviour. The surfaces were tested with a variety of cell types, including neural cells, an eventual advantage to successful cell adhesion and behaviour. The surfaces were tested with a variety of cell types, including neural cells, an eventual advantage to successful cell adhesion and behaviour.

Due to this strong polarization dependence of the surface energy switching, and the permanence, it is suspected that the mechanism for this effect is due to the reorientation of the dipoles of the trans azo chromophores perpendicular to the direction of polarization. The half life of the cis isomer in these systems is less than 5 s, so cannot contribute much to any effect in the dark after this time. This photo-reversible molecular orientation is a well studied phenomenon in these films, where it was originally investigated as a mechanism for reversible optical information storage. There are a great number of optical and dipole properties that are changed when azo chromophores are irradiated, but it is proposed here that this reversible surface energy switching observed is simply due to a geometric molecular reorientation which exposes different functional groups to the surface before and after linearly polarized light is introduced, and being ‘erased’ with circularly polarized light, as is introduced, and being ‘erased’ with circularly polarized light,

Fig. 2 A schematic depiction of the photo-reversible surface effect and corresponding photo measurements of contact angles.
which randomizes the directors. Specifically, it is suggested that as a result of isomerization cycling from trans to cis, many of the more polar NO2 groups of the DR1 bend downward away from the surface, exposing the less polar aromatic character of the phenyl rings to the surface. This would result in increased hydrophobicity on the surface, and higher contact angles of the water droplets. To lend support to this hypothesis, the molecular orientation of the films was determined in situ, as transmission of light through crossed polarizers on either side of the sample, to measure the photo-induced birefringence of the sample under the same conditions as that which photo-switch the surface wettability. These birefringence measurements are presented in Fig. 4, performed as described previously for optical storage studies.

Further support for orientation-induced hydrophobicity upon irradiation can be drawn from the observation of contact angle switching on the same p(DR1A-co-AA) coated films using olive oil. Contrary to water, olive oil itself is hydrophobic, and its droplets initially wet the surface upon irradiation with a high contact angle, and showed a decline in contact angle on irradiation. These observations in tandem suggest that the poly-azo-modified multilayer films turned more hydrophobic following the trans to cis isomerization, and subsequent reorientation.

In Fig. 4, irradiation conditions employed are that which yield a maximum of surface switching, with the laser beam incident at 15° from normal, polarized at +150° from the TM orientation. Upon 70 mW cm⁻² irradiation of the 488 nm pump beam at \( t = 20 \) s (region 1), the trans azobenzene chromophores quickly re-orient from randomly arranged to lie perpendicular to the polarization direction of the pump beam, thus inducing birefringence. When the light is removed at \( t = 200 \) s (region 2), there is a slight relaxation of the orientation, but this is stable over many hours, since all azo groups are in the stable trans form until the introduction of circularly polarized light at \( t = 250 \) s, which quickly re-distributes the chromophores (region 3), and restores disorder. This curve can be repeated many times.

A full study of these birefringence plots, now underway, in combination with the irradiation and polarization effect curves shown in Fig. 3, should provide more insight for optimizing this photo-reversible effect, and offer a more complete picture of the exact orientation of the azo chromophores in the assembled films. Since the bio films investigated in the current work possess a very high moisture content, one advantageous effect is that the high inherent water content appears to lubricate the films, providing more free volume for each azo group’s motion, and increasing the level of photo-orientation achievable. Indeed, the birefringence values observed of >0.2 near maximum are greater than the values of 0.1 typically observed for hydrophobic thin azo solid films, and closer to that observable in high-motion liquid crystal azo films of typically 0.3. Furthermore, one important difference between the molecular orientation studies described here, vs. materials used in previous studies, is that these self-assembled materials are highly hydroscopic, exhibiting water contents from 20% by volume to more than 75% by volume in some films, in equilibrium with just humid air. We have also demonstrated that this orientation can be photo-induced completely under water, and is again stable after relaxation, also the subject of a full future study in parallel.

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Fig. 4 Molecular orientation as a function of time measured through birefringence. Region 1: orienting beam linearly polarized; region 2: relaxation with light off; 3: surface energy reversing (restoring) beam circularly polarized.
References


