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

Nasir M. Ahmad,[c] Xiaoyu Lu[ab] and Christopher J. Barrett*[ab]

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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.[1] 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.[2] 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.[3] 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,[4] 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 reorientation 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 (0.0 11mol) 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

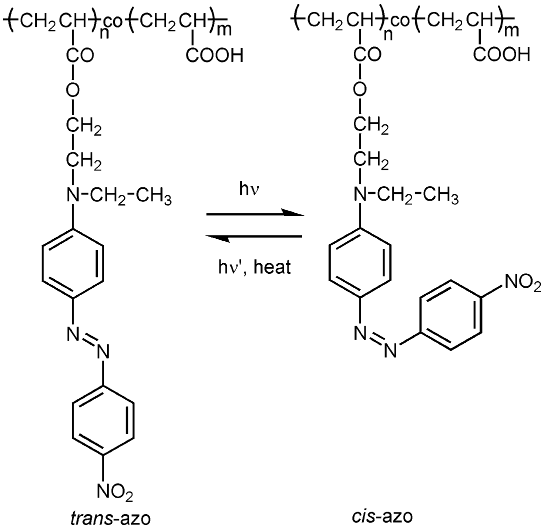

Fig. 1 The photo-conversion of azobenzene between the *trans* and *cis* geometric forms.

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[a] *Department of Chemistry, McGill University, Montreal, Canada. E-mail: Christopher.Barrett@mcgill.ca*
[b] *Centre for Collaborative NeuroEngineering, Montreal Neurological Institute, Montreal, Canada*
[c] *School of Chemical and Materials Engineering, National University of Science and Technology (NUST), Islamabad, Pakistan*

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previous literature.[5] Further preparation and characterization details are provided as ESI.† With this polymer however, water solubility of the eventual material was achieved through co-polymerization of DR1A with varying concentrations of acrylic acid (in place of methyl methacrylate) in THF at 60 °C to prepare a copolymer series p(DR1A-co-AA) with varying azo content from 1% to 40%. Concentrations of the monomers were kept at approximately 0.5 M, and AIBN initiator was used with a concentration of 7.5% (w/w) relative to the monomer. Polymerization was carried out in custom-made rota-flo glass ampules, with three times freeze-thaw cycling to ensure an oxygen-free ambient environment. These copolymers were characterized by NMR spectroscopy, DSC, GPC, and UV-Visible spectroscopy (available in the ESI†).

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.[3] 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 pK_a 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 goal of this project, and demonstrated as compatible, leading to eventual neurite outgrowth. Full cell behaviour studies are the subject of a parallel report in preparation. To measure surface energy changes inducible with light, wettability experiments were performed through the standard sessile drop technique, to determine the static contact angle of water (Milli-Q purified) and oil (olive), before and after irradiation with light. An argon ion laser line at 488 nm or 514 nm and up to 250 mW cm^{-2} was used as the light source, varying the incident angle and orientation of linear polarization, as well as irradiation intensity and duration, concurrent with *in situ* measurements of contact angles. On irradiation for 30 s, 50 microlitre drops of water are observed to bead up, as measured by an increase in contact angle at the liquid/air/surface interface, photographed in the plane of the film. These results are depicted schematically in Fig. 2, accompanied by photographs of the drop shape before and after irradiation. In order to confirm that the drop shape change was not occurring over time due to secondary effects, we also observed the same contact angle shifts between successive separate drops, before and after irradiation, allowing them to rest for 20 s each before photographing. When the first drop was blown off and the surface dried, the film was then irradiated in the same manner as described, and then the laser turned off. A second drop was then placed on the same irradiated spot, allowed to settle for the same 20 s duration, and then photographed. This data is shown in Fig. 3, as the increase in contact angle after irradiation. This contact angle change on irradiation is a general finding for all azo films prepared, varying the azo content and the multilayer thickness, and for all irradiation conditions tested of intensity, duration, polarization angle, and impinging beam direction to surface normal, for water drops. Oil drops exhibited the opposite effect of a contact angle lowering, which will be discussed presently. A full study is under way to determine the effect of all of these material and irradiation parameters independently for optimization, but in general the effect saturates at around 70 mW cm^{-2}, and 30 s duration, with longer or higher power irradiations not enhancing the observed contact angle shift. Most importantly, this increased contact angle is stable over time after the light is removed, for many hours (until the drops evaporate), but subsequent irradiation with circularly polarized light returns the drops reversibly to their original lower contact angle.

Perhaps the most curious aspect of this surface energy switching is the strong dependence on the two geometric factors that influence the water contact angle shift before and after laser irradiation: (a) the direction of the incoming laser beam (incident angle to normal), and (b) the relative orientation direction of its linear polarization axis, presented in Fig. 3. The surface switching dependence on polarization displays two minima at 90° (s-polarized; TE to the surface) and at 0° (also equal to 180°, p-polarized; TM to the surface), and two symmetric maxima at approximately +30° and +150° (also equal to −30°). The surface switching dependence on incident angle displays two independent maxima at approx. 15° and 45°, and at least three separate minima at 0° (normal to the surface) 30°, and greater than 50°, where the geometry of the experiment prevented more shallow irradiation angles from being probed. These maxima and minima are general features that have been observed with all materials prepared, in films of all thicknesses, and in each instance through dozens of separate trials. A full study to map out this switching dependence in this large 2-d parameter space is underway.

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,[5,6] 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,

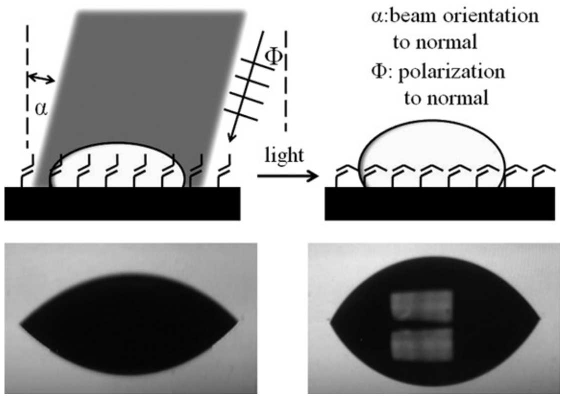

Fig. 2 A schematic depiction of the photo-reversible surface effect and corresponding photo measurements of contact angles.

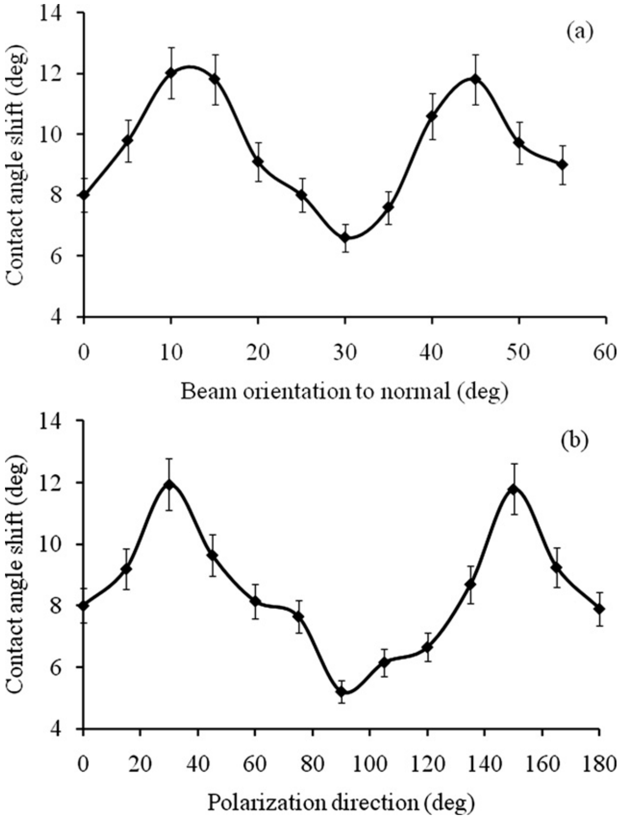

Fig. 3 Dependence of the two irradiation parameters influencing the water contact angle shift: (a) incoming beam direction (polarization direction was fixed to 0°) and (b) polarization axis (incoming beam direction was fixed to normal). Irradiation was 70 mW cm^{-2} at 488 nm for 30 s. The film thickness was 100 nm, and the initial contact angle was 62°.

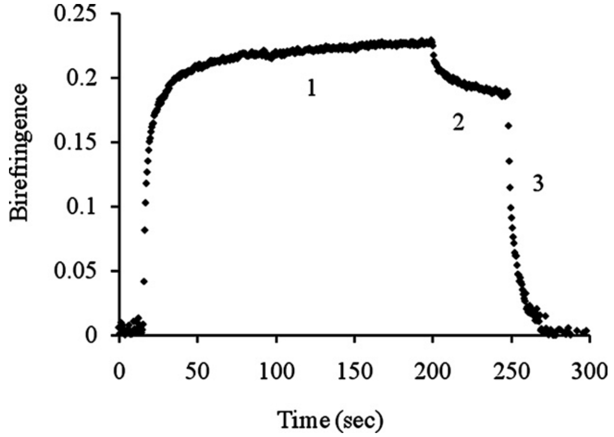

Fig. 4 Molecular orientation as a function of time measured through birefringence. Region 1: orienting beam linearly polarized; region 2: relaxation with light off; 3: surface energy reversing (restoring) beam circularly polarized.

which randomizes the directors. Specifically, it is suggested that as a result of isomerization cycling from *trans* to *cis*, many of the more polar NO_2 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 birefriengence measurements are presented in Fig. 4, performed as described previously for optical storage studies.[5] 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,[7] 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.[7] 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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