Photochromism

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Controlling Contact Electrification with Photochromic Polymers**

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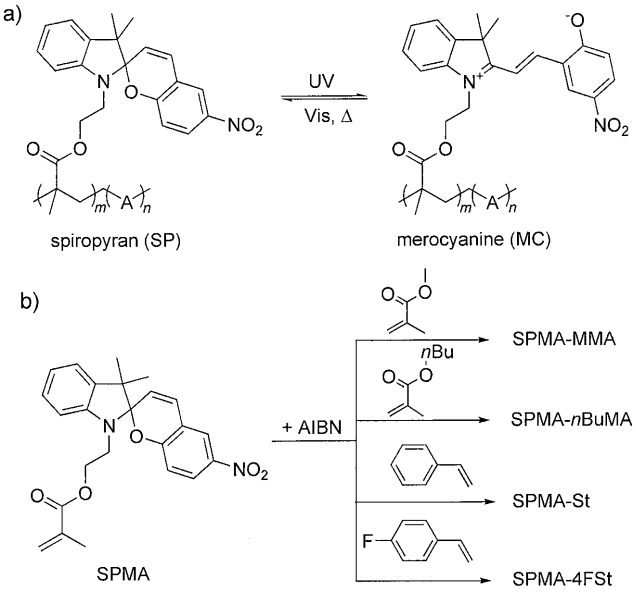
Contact electrification, the separation of charge when contacting materials separate,[1] is important in a number of applications including electrophotography[2] and the beneficiation of coal.[3] Contact electrification also causes adhesion of particles that inhibit the performance of equipment,[4] or discharges that ignite flammable vapors.[5] Controlling contact electrification, however, remains an unsolved problem. Chemical approaches to controlling contact electrification include aggressive treatments like plasma or mineral acids to chemically modify the surface in a largely undefined manner,[6] additives such as charge-control agents,[7] or covalently modifying surfaces with groups that bear "mobile" ions that are not covalently bound (ionic electrets).[8] Whether the mechanism of insulator contact electrification involves the transfer of ions,[8b,9] electrons,[10] or a combination thereof[7,11] is a matter of debate; a correlation appears to exist, however, between the hydrophobicity of materials that are not ionic electrets and their charging.[9]

Photochromic molecules[12] transition reversibly between chemical structures upon absorption of light, often with substantially different degrees of hydrophobicity.[13] Their applications (among many) include color-changing eyewear,[14] fluorescence imaging,[15] and molecular logic.[16] Herein we describe spiropyran-based photochromic polymers that reversibly change contact electrification behavior upon irradiation.

We used a previously described instrument to measure the dynamics of contact electrification.[8c,17] Briefly, a magnetic stir plate causes a ferromagnetic steel sphere to roll in a circular path on an electrically insulating film. Our experiments interrogate the effect of the chemical structure of the insulating film on contact electrification of the rolling sphere. With each revolution of the sphere, it passes over an electrode (connected to an electrometer) that measures charge on the sphere. When the sphere is far from the electrode, it measures only the charge on the dielectric close to the electrode. Because the sphere passes over the electrode repeatedly, we can determine the rate of contact electrification. We performed studies in a Faraday cage to mitigate artifacts from external electric fields, at 20–25% relative humidity (RH) and 20–22°C.

We prepared the nitrospiropyran-containing methacrylic monomer **SPMA**[18] in four steps using modified literature procedures.[19] Photochromic spiropyrans reversibly form zwitterionic merocyanines (MC) upon UV irradiation (Scheme 1a).[20] As summarized in Scheme 1b, we prepared



Scheme 1. a) Photochromic reaction of spiropyran-containing copolymers that reversibly yields hydrophilic merocyanines upon UV irradiation. The label "A" in the main chain represents a non-reactive comonomer in the random copolymers. b) Synthesis and names of the four spiropyran-containing random copolymers.

copolymers (**SPMA-A**) of **SPMA** and either styrene-based or methacrylate-based comonomers **A** by AIBN-initiated radical polymerization in toluene at 65°C. The copolymers contained 20–40 mol% of **SPMA**. Spin-casting these polymers from 1% solutions (w/v) in toluene onto glass slides at 2500 rpm gave optically clear films that were 35–80 nm thick.

As expected, spiropyran-containing films turned blue ($\lambda_{max} = 591$–596 nm, see Supporting Information) upon irradiation with UV light for two minutes (200 W Hg/Xe lamp equipped with a UV bandpass filter) due to formation of MC moieties. In addition, the films became more hydrophilic as demonstrated by decreased advancing and receding water contact angles upon MC formation (see Supporting Information). This result is important because the surface of the film rather than the bulk is responsible for contact electrification. In contrast, homopolymers without SP groups, such as

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poly(styrene) and poly(methyl methacrylate), showed no change in absorbance spectra or contact angles after UV irradiation.

Before irradiation of the films, steel spheres rolling on the **SPMA**-containing copolymer films charged with the same rates, within the error of the experiments, as when they rolled on films of homopolymers of the corresponding inert monomer. For example, as summarized in Table 1, steel spheres charged positively with an initial rate of $11 \pm 4\ pC\,s^{-1}$ when rolling on poly(4-fluorostyrene) (P4FSt), compared to $8 \pm 4\ pC\,s^{-1}$ **SPMA-4FSt**, but negatively ($-9 \pm 4\ pC\,s^{-1}$) when rolling on poly(*n*-butyl methacrylate) (PBuMA) and **SPMA-*n*BuMA** ($-8 \pm 2\ pC\,s^{-1}$) before UV irradiation. Therefore, the presence of the spiropyran did not have a statistically significant impact on the rate of contact electrification.

Table 1: Initial rates of charging of rolling steel spheres on polymer films. Tabulated values are the means of at least eight measurements; standard deviations are in parentheses.

Copolymer	Rate of charging [$pC\,s^{-1}$]		
	Before UV irradiation	After UV irradiation	Unreactive homopolymer
SPMA-*n*BuMA	−8 (2)	−60 (30)	−9 (4)
SPMA-MMA	−4 (2)	−57 (20)	−11 (4)
SPMA-St	−2 (2)	−106 (46)	0.7 (0.7)
SPMA-4FSt	8 (4)	−20 (6)	11 (4)

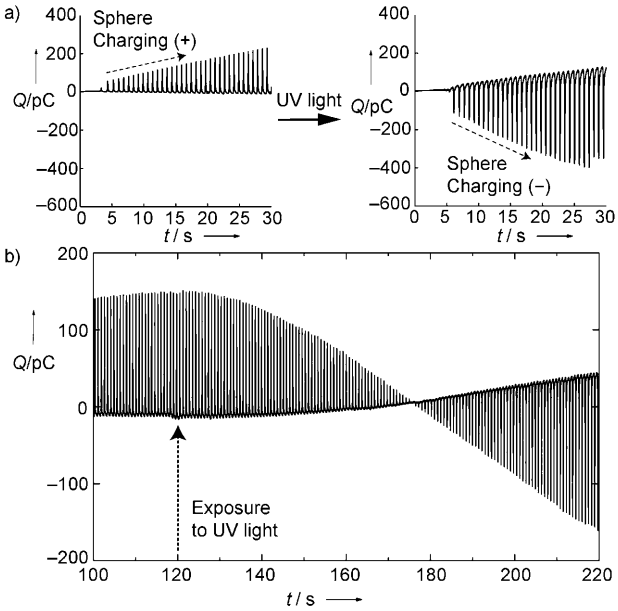

Figure 1. Contact electrification of a steel sphere rolling on a film of **SPMA-4FSt**: a) The steel sphere charges positively before and negatively after irradiation of the film with UV light for 2 min. b) Real-time measurement of the change in charge on the steel sphere caused by irradiation of a film of **SPMA-4FSt**. UV irradiation began at $t = 120$ s.

Upon irradiation of the photochromic films for two minutes, steel spheres rolling on these films developed negative charge significantly faster than they did before irradiation (Table 1). Figure 1a shows charging of a steel sphere rolling on a film of **SPMA-4FSt**: it charges positively ($+8\ pC\,s^{-1}$) before UV irradiation of the film, and negatively ($-20\ pC\,s^{-1}$) after. Steel spheres rolling on the other photochromic polymers we examined show the same trend: their rate of negative charging increased by circa one order of magnitude upon UV irradiation of the photochromic films for two minutes. In addition, the initial rate of charging correlates roughly with the absorbance of the MC (see Supporting Information). The sharp discontinuities in charge accumulation observed are consistent with electrostatic discharge events between the rolling sphere and dielectric surface.[8c] Exposing corresponding homopolymers that did not include the photochrome **SPMA** to identical conditions of UV irradiation yielded no change in the rate or sign of charging.

Table 1 summarizes that in all cases, steel spheres had a much stronger tendency to charge negatively after UV irradiation than before. This observation is consistent with our expectations: based on the apparent dependence of the sign of charging on hydrophobicity[9] we anticipated that a material contacting the hydrophilic MC would have a stronger tendency to develop negative charge than one contacting the non-ionic SP. We observed the same behavior when the experiment was conducted in an atmosphere of N_2 or when the SP group was irradiated selectively at 365 nm. Therefore, neither oxidative decomposition of the photochrome nor photochemical reaction of the polymer backbone caused the consistent change in charging observed upon UV irradiation.

The fast nature of SP-to-MC conversion enables real-time monitoring of the change in charging behavior. As shown in Figure 1b, a sphere rolling on a film of **SPMA-4FSt** switched from having positive charge to negative charge less than one minute after beginning continuous UV irradiation. Our approach of monitoring the change in characteristic charging between photoisomers mitigates the common problem of variability between samples that commonly plagues studies of contact electrification.[21]

The switching of charging behavior of these films is reversible: consistent with the photochromic nature of spiropyrans, the UV/Vis spectra and contact angles of UV-irradiated films (duration of UV irradiation: 20 s) reversed to the initial SP state after thermal (1 h at 60 °C) or photochemical treatment (irradiation at $\lambda > 515$ nm for 1 h). Concurrently, the rate of charging became characteristic of the unirradiated film. Following this reversal from MC to SP, additional UV irradiation recovered approximately 80% of the MC absorbance at 595 nm, decreased the advancing and receding contact angles, and again caused the sphere to charge negatively without a statistically significant decrease in the rate of charging from the first cycle. Figure 2 shows an example of this photochemically reversible charging behavior with **SPMA-MMA**. Although these films show fatigue of photochromism after a few cycles by monitoring the UV/Vis spectra, we have demonstrated up to three cycles of this reversible photochemical control of contact electrification (reversed either thermally or photochemically; see Support-

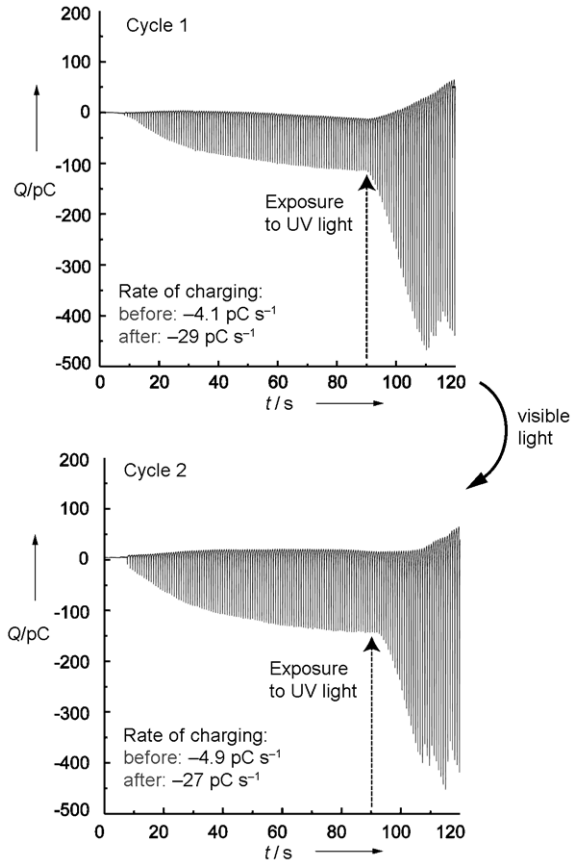

Figure 2. Reversibility of modulation of contact electrification of a steel sphere rolling on a polymer film of **SPMA-MMA**. After cycle 1, the film was irradiated with visible light (515 nm high-pass filter) for 1 h.

ing Information). This reversibility provides strong evidence for attributing the switching of charging behavior to the SP–MC conversion.

In all examples studied, the rolling sphere had a greater propensity to charge negatively upon formation of the hydrophilic merocyanine, while the photochromic polymer films had a greater propensity to charge positively; this observation is consistent with the previously mentioned correlation between hydrophobicity and sign of contact electrification.[9] These results, however, are not strong evidence for or against any of the potential mechanisms of contact electrification. Nevertheless, we do note that the narrowed HOMO–LUMO gap of MC upon irradiation of SP results from a decrease in LUMO energy, that is, MC is easier to reduce than SP,[22] which suggests that electron transfer involving frontier molecular orbitals (FMOs) of individual photochromic molecules is not causing contact electrification in these examples. Others have highlighted that electron transfer between FMOs of insulators would be highly endergonic;[9] our results do not address mid-gap surface states that are reported to participate in the electron-transfer model of contact electrification.[10a]

In conclusion, we have developed a new strategy for controlling contact electrification with light using well-defined organic chemistry: the photochromic reactivity of a nitrospiropyran. This approach has three important characteristics: 1) it uses the intrinsic properties of electrically insulating materials, on which static charge is notoriously difficult to control, 2) it is reversible, and 3) it measures the change in charging between two states without moving the sample, which we expect to yield increasingly accurate structure–property relationship studies. In addition, our ability to tune the light-induced switching of charging with the choice of non-reactive comonomer is an additional, readily implemented design parameter for using organic chemistry to control contact electrification. Ongoing work in our laboratory is focusing on elucidating the effect of polymer composition, improving fatigue resistance, and demonstrating applications of this capability to switch the sign and magnitude of contact electrification with light, such as electrostatic self-assembly or actuation.

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