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Reversible Photochemical Tuning of Net Charge Separation from Contact Electrification

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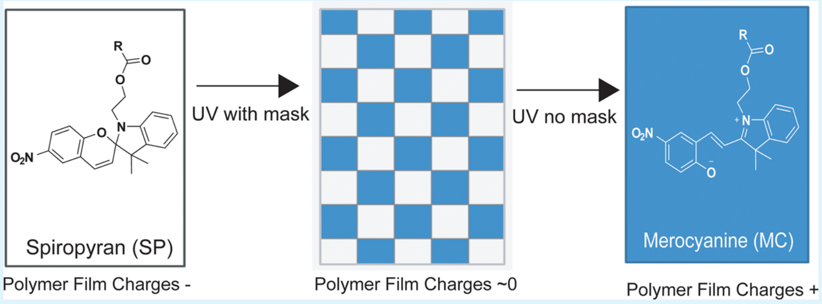
Supporting Information



ABSTRACT: This paper describes the photochemical tuning of net charge that develops from contact electrification. The net charge separation and/or rate of charging of photochromic spiropyran (SP)-containing polymer films can be controlled by irradiation with UV light. The isomerization of the SP form to the more hydrophilic merocyanine (MC) by irradiation with UV light always leads to films that charge more positively than before irradiation. The incorporation of a halogenated comonomer into ring-opening metathesis polymerization (ROMP) yields films that charged negatively before irradiation so that a change in sign of the net charge separation of the film could be observed upon irradiation. An important advantage to our photochromic system is that light can be used to tune the charging behavior of the material, with spatial or temporal control of irradiation, leading to films that resist charging. Furthermore, the observed trends can be reversed by the exposure of the SP-containing polymer films to heat or visible light.

KEYWORDS: *contact charging, polymer films, ROMP, spiropyran, photochromism, triboelectric charging*

■ INTRODUCTION

This paper describes polymers that show tunable charging by contact electrification using reactions of photochromic pendant groups on polymer films. Contact electrification is the separation of charge that occurs when contacting materials separate.[1−4] This process, which can readily generate electrical potentials in the range of tens of kilovolts, is critical in a number of applications that rely on electric fields to control the movements of small particles such as (i) electrophotography and laser printing,[5] (ii) electrostatic spray and powder coating,[6] (iii) sorting of recyclable plastics and other materials,[7,8] and (iv) other demonstrations of templated and nontemplated self assembly.[9−17] In addition, the development of high potentials on materials can be problematic because of both unwanted adhesion of particles to surfaces such as solar panels and space suits[18−20] and electrical discharges that can ignite explosions of fuels or dust or damage sensitive electronic equipment such as computer chips and Cochlear implants.[21,22]

A number of approaches exist that address the still-unsolved problems of controlling the sign and distribution of net charge accumulated on insulators. Known methods to control the sign of net charge accumulated through contact electrification include (i) using the empirical "triboelectric series" to predict the sign of charges on contacting materials,[9,23] (ii) introducing additives to toner formulations known as charge-control agents (CCAs),[24−26] (iii) varying the substituents on pendant aromatic rings,[27,28] (iv) sulfonation of polystyrene,[29] and (v) covalent binding of cationic or anionic functional groups to a surface.[13,14,30−33] A more recent study reported stress-induced, reversible switching of the sign resulting from tribocharging of latex.[34] Methods to control the distribution or pattern of net charge on a surface have included: (i) irradiation of photoconductors (this method is used in copying and printing applications),[5] (ii) the use of patterned electrodes,[12,15,16] and (iii) patterning of formally charged self-assembled monolayers or polyelectrolyte multilayers using soft lithography.[13,31,32,35]

A current challenge is the design of new materials that have tailored charging properties. Highlighting this challenge is the fact that chemically identical materials develop charge upon contact and separation[36−38] and that, regardless of the sign of net charge accumulated, a mosaic of both positive and negative charge is observable on the nanoscale for contact electrified materials.[39] Uncertainty about the exact mechanism(s) of contact electrification at the molecular level,[2,30,40−44] the role of

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water,[45,46] and other mechanical variables exacerbates the difficulty inherent to rational chemical design. The transfer of material between contacting surfaces has been shown to be both ubiquitous and important to contact electrification.[34,39,47,48] Varying the electronegativity of polymers through linear free energy relationships and designing surfaces that have net formal charges are several of the approaches rooted in physical organic chemistry that have been reported.[27,28,13,14,30−33]

Our group has previously reported polymers that bear photochromic nitrospiropyran pendants that can undergo reversible change in the rate of charging by contact electrification upon irradiation with light. Additionally, one such polymer comprising nitrospiropyrans and fluorinated groups as side chains switched the sign of net charge separation upon UV irradiation.[49] Poly(tetrafluoroethylene) (PTFE) is at the negative end of the triboelectric series,[43] meaning that it develops a net negative charge upon undergoing contact electrification with most other materials. Regardless of the operational mechanism in the process of contact electrification of these materials, explanations for the typical net negative charging grounded in electron transfer,[42,44,50] ion transfer,[30,43] and the mechanochemical cleavage of covalent bonds[51] have been proposed for halogenated polymers; we expected that incorporating fluorinated monomers into our photochromic materials would cause these materials to be lower on a triboelectric series and be more likely to develop a net negative charge.

The overall objectives of this work were to (i) develop relationships that correlate the structures of new photochromic polymeric materials to their observed stimuli-responsive charging behavior and, in doing so, expand the range of materials that were responsive in their net charging rate and sign and (ii) use spatial and temporal control of light to "tune" the net charge separation of the spiropyran-containing polymers. These results are important for the development of next-generation materials that resist the development of "static" charge.

■ EXPERIMENTAL SECTION

All chemicals were purchased and used as received except for methacryloyl chloride which was freshly distilled before each use. All synthetic steps were completed with standard inert atmosphere techniques with magnetic stirring unless noted. Silica gel (230−400 mesh) was used as the stationary phase for flash chromatography. Dry solvents were obtained using an Innovative Technologies PureSolv 400 solvent purifier. The following compounds were synthesized according to literature procedures: NB-Cl[52] and BuNB.[53]

NMR spectra were acquired on a Bruker DPX-300 spectrometer or Bruker Avance III 500 spectrometer. Chemical shifts were reported relative to residual protonated solvent (7.27 ppm for $CHCl_3$). Molecular weight distribution measurements of the polymers were conducted with a Shimadzu Gel Permeation Chromatography (GPC) System equipped with a TOSOH TSKgel GMHh-M mixed-bed column and guard column using THF as the mobile phase at 0.75 mL/min calibrated with low polydispersity poly(styrene) standards (TOSOH, PSt Quick Kit). Electronic absorbance spectra were acquired with a Varian Cary-100 instrument in double beam mode using plain glass slides for background subtraction spectra. Irradiation of samples was performed with a 200 W Hg/Xe lamp (Newport-Oriel) equipped with an automatic shutter. Irradiation was performed with a UG-11 bandpass filter or a 515 nm long-pass filter and in combination with a 1.0 OD neutral density filter when noted.

F5NB Synthesis. F5NB was synthesized using a procedure adapted from the literature.[54] 5-Norbornene-2-carboxylic acid (500 mg, 3.65 mmol) (mixture of *endo* and *exo* isomers) and pentafluorophenol (740 mg, 4.02 mmol) were dissolved in 5 mL of anhydrous dichloromethane and cooled to 0 °C. *N*,*N*′-Dicyclohexylcarbodiimide (829 mg, 4.02 mmol) was added to the reaction mixture followed by the dropwise addition of a solution of dimethylaminopyridine (49 mg, 0.40 mmol) in 1 mL of dry tetrahydrofuran. After stirring at 0 °C for 1 h, the reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was then washed with sodium bicarbonate solution, water, and brine. The organic layers were dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The crude product was purified via flash chromatography (hexanes) to yield F5NB as a mixture of the *endo* and *exo* stereoisomers. Yield: 493 mg (43%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.30−6.06 (m, 2H), 3.44−2.61 (m, 3H), 2.08−2.03 (m, 1H), 1.57−1.55 (m, 2H), 1.55−1.39 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.3, 170.6, 142.3−142.1, 140.3−140.1, 138.9−138.5, 138.5, 136.8, 135.3, 131.8, 49.7, 47.0, 46.4, 46.3, 42.9, 42.7, 42.6, 41.8, 30.7, 29.3.

SPN Synthesis. (*R*/*S*)-2-(3′,3′-Dimethyl-6-nitro-3-*H*-spiro-[chromene-2,2′indol]-1′-yl)ethanol (synthesized as previously reported[49]) (300 mg, 0.853 mmol) and pyridine (80.9 mg, 82.3 μL 0.852 mmol) were dissolved in 30 mL of dry tetrahydrofuran. NB-Cl (133 mg, 0.852 mmol) in 10 mL of tetrahydrofuran was added dropwise over the course of 5 min, and the reaction mixture was then stirred overnight at room temperature. The precipitate that formed was filtered off, and the reaction mixture was concentrated *in vacuo*. The crude product was purified via flash chromatography (hexanes/ethyl acetate (6:1 v/v)) to yield SPN as a mixture of the *endo* and *exo* isomers. Yield: 111 mg (27 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03−8.01 (m, 2H), 7.22−7.20 (m, 1H), 7.11−7.09 (m, 1H), 6.94−6.91 (m, 2H), 6.77−6.70 (m, 2H), 6.15−5.90 (m, 3H), 4.21−4.14 (m, 2H), 3.47−3.40 (m, 2H), 3.25−2.89 (m, 3H), 1.92−1.83 (m, 1H), 1.44−1.36 (m, 2H), 1.29 (s, 3H), 1.27−1.25 (m,1H), 1.18−1.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.6, 159.5, 159.4, 146.8, 146.7, 141.1, 137.9, 137.8, 135.7, 132.3, 132.2, 128.3, 128.3, 127.9, 126.0, 122.8, 121.9, 121.9, 121.8, 119.9, 119.9, 118.5, 115.6, 106.8, 106.6, 106.5, 62.4, 62.3, 52.9, 49.7, 49.7, 46.6, 46.4, 45.7, 43.3, 42.5, 42.4, 42.4, 41.6, 30.5, 29.3, 29.3, 25.9, 19.9.

General Ring-Opening Metathesis Polymerization Procedure. SPN and comonomer were dissolved in dichloromethane (50 mg/mL). Grubb's 3rd generation catalyst was added, and the reaction mixture was stirred for approximately 30 min or until complete monomer consumption as indicated by TLC. The polymerization was terminated by the addition of 5 equiv of ethyl vinyl ether, and the solvent was removed *in vacuo*. The polymer was then dissolved in chloroform, precipitated into hexanes twice, collected by vacuum filtration, and dried in a vacuum oven at 70 °C to yield pure polymer.

Polymer NMR Data. *PSPN (100%).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09−7.85 (2H), 7.23−7.11 (1H), 7.11−6.99 (1H), 6.99−6.78 (2H), 6.76−6.55 (2H), 5.95−5.70 (1H), 5.48−4.94 (2H), 4.32−3.93 (2H), 3.56−3.22 (2H), 3.18−2.51 (3H), 2.50−2.10 (1H), 2.06−1.66 (2H), 1.40−0.85 (7H).

PSPN-F5NB (48%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05−7.91 (2H), 7.25−7.01 (2H), 6.97−6.79 (2H), 6.78−6.55 (2H), 5.93−5.75 (1H), 5.69−5.00 (4H), 4.31−3.93 (2H), 3.53−1.57 (14H), 1.30−0.97 (8H).

Contact Charging Experiments. Polymer films for contact charging were made using 10 mg/mL solutions in toluene, filtered through a 0.4 μm PTFE syringe filter, and then spun cast onto a clean glass FisherBrand microscope slide (75 × 50 × 1 mm) using a Laurell Technologies spin coater (WS-400-NPP-Lite) and dried in a vacuum oven at 70 °C (−30 in Hg) for at least 1 h. The program for the spin coater was as follows: spin at 300 rpm for 5 s (acl 330 rpm/s) and spin at 2500 rpm for 20 s (acl 1650 rpm/s). Spheres used were ferromagnetic stainless steel spheres (type 440C McMaster-Carr, 3.2 mm diameter), parylene coated steel spheres (VP725, V&P Scientific, 2.47 mm diameter), or poly(methyl methacrylate) (PMMA; McMaster-Carr, 3.2 mm diameter). Steel spheres were washed with water, acetone, hexanes, and dichloromethane and dried in a vacuum oven at 70 °C for at least 1 h before each use. Topographical data was acquired using an Asylum Research MFP-3D Atomic Force Microscope (Santa Barbara, CA) on a film with lines scored by a razor blade. Scanning was performed in contact mode with a silicone cantilever, nominal spring constant $k = 26$ N/m. Scans were performed over 40 × 40 μm regions at a scan rate of 1 Hz.

Contact charging experiments were performed in a grounded Faraday box to minimize the effects of external electric fields. Contact charging measurements were performed at 20−25% relative humidity (RH) and at room temperature. Experiments took place in a controlled environment chamber (Electro-Tech Systems, Inc., Model 5503) to control relative humidity or under ambient conditions at times when the ambient humidity was less than 25%.

An instrument described in the literature was used for the real time detection of contact charging.[55] A glass slide, coated with a thin film of polymer, was placed on a magnetic stir plate (Ikamod RCT) that allows a ferromagnetic steel sphere to roll on the surface of the slide. An aluminum foil electrode (10 mm width) was taped to the bottom of the slide to sense the charge developing on the surface of the film, which was detected by an electrometer (Keithley 6514) attached to the electrode through a triaxial cable. The electrometer recorded the charge on the electrode as a function of time and was recorded by a LabView program. When the sphere was far from the electrode, the electrometer reported only the charge on the polymer film close to the electrode. When the sphere was on top of the electrode, the resultant peak in charge corresponded to the charge on the sphere and the polymer. For real time irradiation and charge detection, light from a 200 W Newport-Oriel lamp was directed on the film with a mirror.

For those samples with which we measured the steady-state magnitude of charge on the sphere, a polymer film was placed in a cardboard box (77 × 54 mm) and the sphere of interest was placed on the film and discharged with a Zerostat anti-static gun. A Corning stir plate was used to roll the magnetic sphere for 1 min. The sphere was then removed from the box with plastic tweezers and dropped into a Faraday cup attached to an electrometer, which measured the charge on the sphere and recorded this value in a custom LabView program. Insulating spheres that were not magnetic were rolled in a uniform fashion on the polymer film manually for 1 min. Multiple insulting spheres were charged at one time.

■ RESULTS AND DISCUSSION

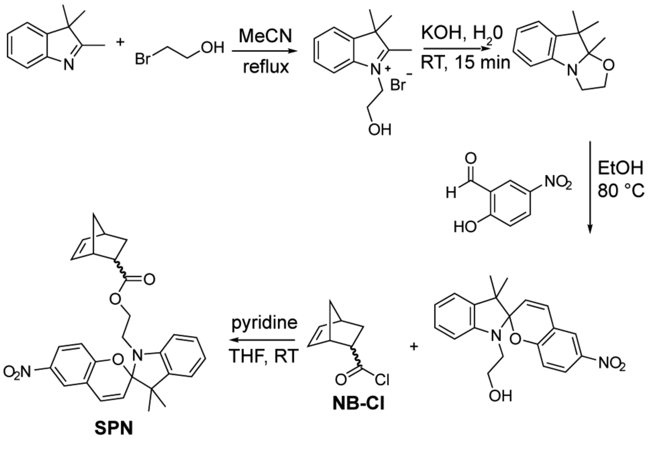
Spiropyrans (SPs) are a class of photochromic materials that reversibly form a zwitterionic merocyanine (MC) upon irradiation with UV light.[56] Irradiation with longer wavelengths of light reverts the hydrophilic merocyanine back to the hydrophobic spiropyran. An important characteristic of photochromic materials in the pursuit of applications, particularly for the minimization of net charge accumulation on contacting materials, is the sign of the net charge of contact charging before and after irradiation. In *all* experiments with SP-substituted polymers reported previously and herein, the charge developing on rolling steel spheres was more negative (or less positive) upon photoisomerization from SP to MC; i.e., the polymer film has a greater tendency to charge positively in the MC form. Therefore, the key to developing polymers that reliably undergo a change in the sign of net charge is to design guidelines for photochromic polymers that develop a net negative charge by contact electrification before photoisomerization.

To study the contact electrification of our polymers, we used two different methods. The first, an instrument described in the literature,[55] uses a steel sphere that rolls on the polymer film in a circular path propelled by a rotating bar magnet. The continuously changing contact between the steel sphere and the polymer film yields charge of equal magnitude and opposite sign to develop on the contacting surfaces. A capacitively-coupled electrode measures the charge on the sphere when the sphere rolls over it and measures the charge on the polymer film when the sphere is far from the electrode. For photochromic polymer films, light from a 200 W Hg/Xe lamp is incident on the films allowing for real-time dynamic control over and monitoring of light-induced changes in contact electrification. Our second method uses a steel sphere rolled in a random manner on a polymer film using a stir plate for 1 min; we then measured the net charge on the sphere with a Faraday cup coupled to an electrometer. Electrically insulating spheres were shaken manually on the polymer film for 1 min before measurement of net charge using the Faraday cup.

All the responsive polymers reported in our previous work used the same photochromic methacrylic monomer SPMA, and the same polymerization reaction, thermally-initiated free radical chain polymerization with azobis(isobutyronitrile) (AIBN) as the initiator, of SPMA together with different vinyl comonomers. To expand the diversity of responsive materials, we synthesized polymers that contain SP moieties as side chains by a nonradical mechanism, ring-opening metathesis polymerization (ROMP), and investigated the contact charging properties of their thin films to determine if our design hypothesis would be applicable to different types of polymer backbones. In addition to a variety of advantageous features,[57] ROMP can be a useful synthetic alternative to radical polymerization for polymers that contain pendant nitroaromatic rings[53] and has been used to grow photoresponsive polymer brushes.[52]

To enable ROMP of nitrospiropyran-containing monomers, we prepared norbornene-based monomer SPN using a strategy similar to that of Locklin and coworkers as a mixture of *endo* and *exo* isomers that reflects the stereoisomeric mixture of the commercially available norbornene carboxylic acid (Scheme 1).[52] Standard esterification procedures also yielded norbornene-containing esters of pentafluorophenol (F5NB) or *n*-butanol (BuNB) as comonomers for ROMP with SPN (Scheme 2). Exposure of these monomers to Grubbs's 3rd-generation catalyst in dichloromethane at room temperature yielded the targeted polymers in high yields (Scheme 2). Table 1 shows that these ROMP polymers had number-average molecular weights (M_n) in line with expected values based on monomer-to-initiator ratios and polydispersity indices (PDI) less than 1.4, as determined by gel-permeation chromatography referenced with polystyrene standards; these observations indicate that these polymerizations were well-controlled. In

Scheme 1. Synthesis of SP-Containing Norbornene-Based ROMP Monomer SPN



Scheme 2. ROMP Polymerization with Grubb's 3rd Generation Catalyst of SPN with Comonomers to Synthesize PSPN-F5NB and PSPN-BuNB

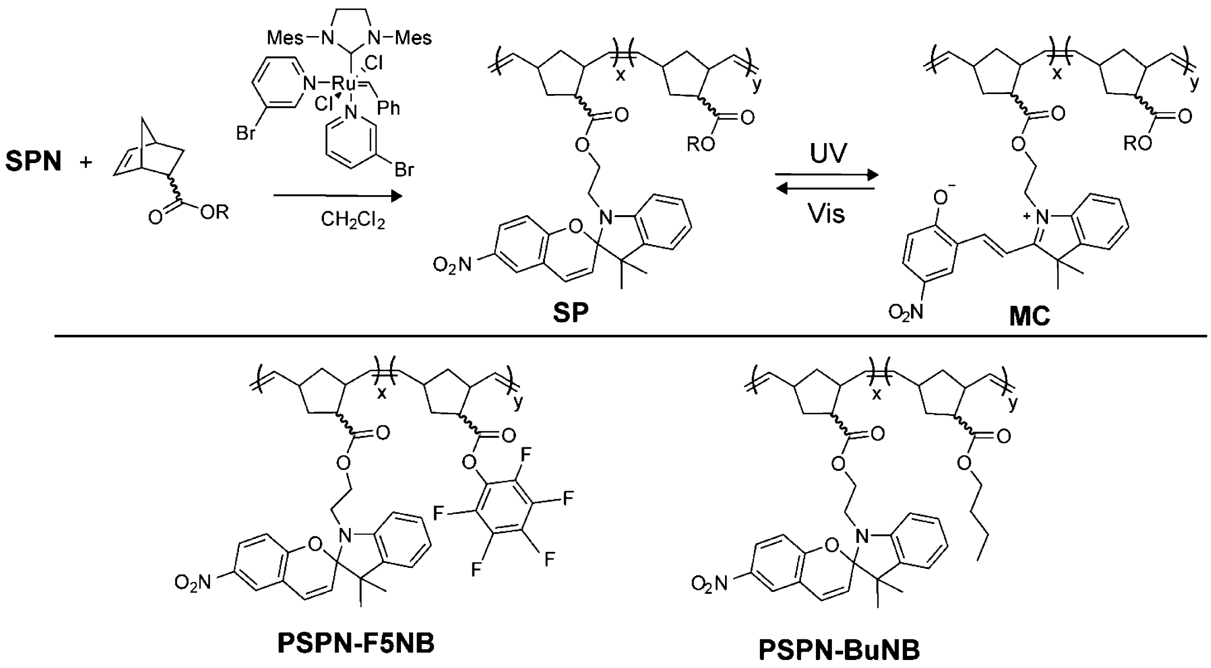


Table 1. Number-Average Molecular Weight M_n, Polydispersity Indices (PDIs), and Molar Ratios for ROMP SP-Containing Polymers

polymer (*X*/*Y*)	*X*/*Y* (theo)	*X*/*Y* (expt)[a]	$M_n/10^3$ (theo)	$M_n/10^3$ (expt)[b]	PDI[b]
SPN (100%)	n/a	n/a	8	11	1.1
SPN (48%)-F5NB	1.0:1.0	1.0:1.1	13	19	1.3
SPN (21%)-F5NB	1.0:3.0	1.0:3.7	34	55	1.1
SPN (11%)-F5NB	1.0:8.3	1.0:8.4	52	79	1.3
SPN (3%)-F5NB	1.0:20	1.0:33	107	176	1.4
SPN (48%)-BuNB	1.0:1.0	1.0:1.1	8	14	1.2

[a] Determined by ^1H NMR integrations. [b] Determined by gel-permeation chromatography in tetrahydrofuran relative to narrow PDI polystyrene standards.

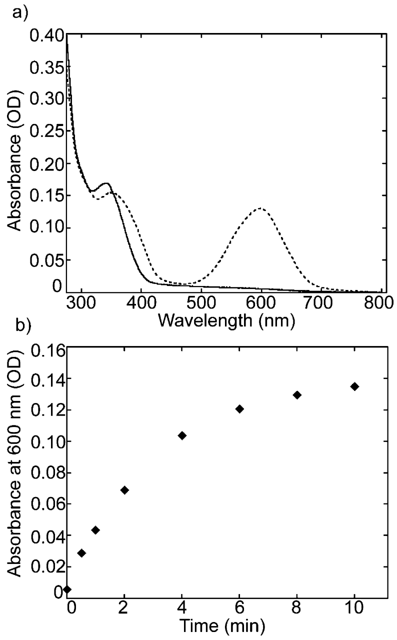


Figure 1. (a) Absorbance spectra of a thin film of PSPN before and after UV irradiation. (b) Optical density at 600 nm as a function of time for film of PSPN.

addition, the molar ratio of monomer units in random copolymers as determined by NMR spectroscopy reflected the initial molar ratio of monomers. All the ROMP polymers described here formed optically clear films upon spin-casting from chloroform.

Figure 1a shows the UV irradiation of a film of PSPN, the homopolymer of monomer SPN derived by ROMP. Irradiation using a 200 W Hg/Xe lamp with a UV bandpass filter (0.8 mW/cm^2) results in the growth of a new absorbance band at 600 nm, consistent with the MC photoisomer.[56] Under these irradiation conditions, the photochrome reaches a photostationary state after about 8 min of continuous irradiation of the film (Figure 1b).

We measured the contact charging behavior of films of PSPN with our two different experimental methods. Using the real-time measurement method, a steel sphere rolling on a polymer film of PSPN shows a dramatic change in charging behavior upon irradiation with UV light concurrent with the photoisomerization (Figure 2a). This method allowed us to measure the rates of charge accumulation on the rolling sphere after fully discharging both the sphere and the polymer film with a “Zerostat” anti-static device. Before irradiation, the steel sphere developed either a small positive or negative net charge through contact electrification with PSPN: the sign of net charge separation before irradiation varied between experiments. In the experiment shown in Figure 2a, the sphere developed a negative charge at a rate of −2.7 pC/s before irradiation. However, the sphere *always* developed a negative charge from contact electrification on the MC-containing photoisomerized polymer film. After UV irradiation for 5 seconds and after 40 seconds of charging, the sphere developed a negative charge at a rate of −28.5 pC/s in Figure 2a. We also examined the

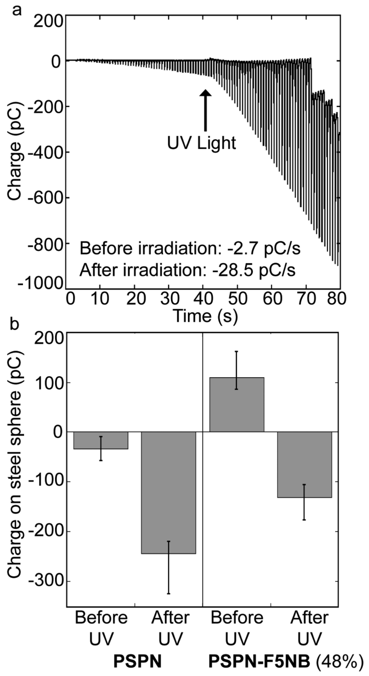


Figure 2. (a) Contact electrification of a steel sphere rolling on a thin film of PSPN. The steel sphere develops negative charge an order of magnitude faster after irradiation. (b) Mean net charge of steel spheres after contact electrification by rolling a thin polymer film of either PSPN or PSPN-F5NB (48%). Heights of the bars are the mean net charge on at least 5 spheres, while error bars represent one standard deviation.

contact charging of PSPN with our second method of data collection that allows us to obtain the charging behavior of multiple spheres. The net average charge that developed on steel spheres rolling on a film of PSPN for 1 min before irradiation was −34 ± 24 pC and after irradiation was −245 ± 81 pC. Therefore, in this experiment, the rate of charge transfer and magnitude of charge that develops via contact electrification in the steady state changed upon photoisomerization, with the sphere developing more negative charge upon MC formation than before MC formation; qualitatively, this result is in agreement with our previously reported result using SP-substituted acrylic polymers[49] and demonstrates the broad applicability of the SP-MC isomerization for photoresponsive contact electrification.

The incorporation of comonomers into the spiropyran-containing ROMP polymers allows us to tune the charging properties of the material. To determine if our design principle of incorporating halogenated comonomers into SP-containing polymers would cause a change in the sign of charging of the film upon irradiation, we tested the charging behavior of a film of a random copolymer comprising nearly equal molar ratios of the SP-substituted and pentafluorophenyl-substituted norbornenes (PSPN-F5NB (48%)) with a thickness of 800 ± 40 nm determined by AFM (See Supporting Information). Consistent with our expectation, and in contrast with PSPN, inclusion of the heavily fluorinated comonomer causes the spheres to charge positively (110 ± 52 pC) before irradiation through contact electrification with the polymer film, but upon irradiation and SP to MC conversion, the spheres charge negatively (−131 ± 46 pC) (Figure 2b). The importance of the halogenated comonomer on the sign of net charge separation before and after irradiation for these ROMP polymers is illustrated by the charging of films of PSPN-BuNB. Spheres rolling on a film of PSPN-BuNB, which has an alkyl chain instead of a fluorinated arene, charged negatively before irradiation, while upon irradiation the rate of charging on the spheres increased but did not switch sign. An example of contact electrification of a sphere rolling on a film of PSPN-BuNB is shown in the Supporting Information.

In addition to qualitative control over the sign of charge separations using comonomer structure, we determined the degree of spiropyran substitution on the polymer backbones that was required to reliably observe photochemical switching of charge. The fluorinated ROMP polymer with 21% of its monomer units functionalized with spiropyran [PSPN-F5NB (21%)] showed a detectable change in charging only occasionally, and fluorinated ROMP polymers with a smaller percentage of spiropyran-containing monomer units never showed any detectible change in the rate of charging upon irradiation (Supporting Information). Additionally, steel spheres rolling on a film of PSPN-F5NB (48%) reliably switched their net sign of charge even after eight SP-MC photochromic cycles (Supporting Information); heating the film to 70 °C or irradiating it with visible light ($\lambda > 515$ nm) for at least 1 h drove the reverse photochromic reaction to completion in each cycle.

All the photochromic polymers reported in this paper and our previous work have a greater propensity to charge positively after photoisomerization with UV light than they do before. There are a number of reasons, which could be operational alone or in some combination, that could be causing this consistent observation: (i) increasing the hydrophilicity upon photoisomerization affects the distribution of aqueous ions adsorbed to the contacting surfaces,[30] (ii) the photoisomers have different tendencies to either transfer material or participate in mechanochemistry; the effect of photoinduced strain[58] on the change on contact charging in these films may be significant,[34] and (iii) redox reactions involving surface states have consistently different driving forces between the photoisomers. Regardless of the mechanism that is operational at the molecular level, we expect that this changing of net charge is likely due to a subtle yet consistent difference in the balance of positive and negative charges on the nanoscale resulting from contact charging of each pair of photoisomers.[39]

The photochromic nature of SP is advantageous due to the ability for spatiotemporal control over delivery of photons and, therefore, control over contact charging. This is especially useful in the photochemical control of contact electrification because materials often have high variability in the rate and magnitude of charging between different samples and under different conditions. By controlling the percentage of photoisomerization spatially or temporally, we are able to “titrate” the charge that develops on contacting materials.

Selectively irradiating areas of a film with a photomask enabled control over the contact electrification of SP films. Figure 3 shows that before irradiation spheres rolled on a film of PSPN-F5NB (48%) charged positively. Using a mask that exposed 50% of the film to UV light, only those areas of the film of PSPN-F5NB (48%) behind the transparent portions of the mask underwent photoisomerization. The charge that developed on the spheres was less positive when the film was irradiated, consistent with the spheres developing a more negative charge in the irradiated areas and a positive charge in the nonirradiated areas. By controlling the spatial delivery of light, we were able to within experimental error achieve a net

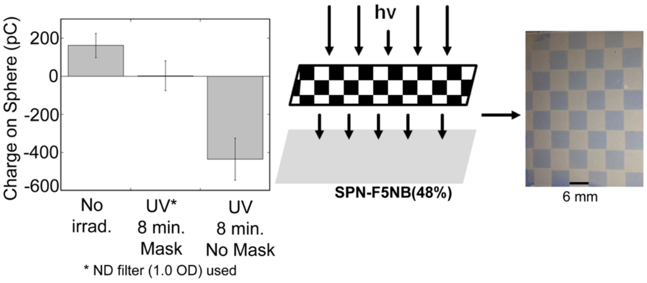


Figure 3. Spatial control of contact charging of steel spheres on a film of PSPN-F5NB (48%) before UV irradiation and after UV irradiation with and without a mask. The heights of the bars are the mean net charges on at least 4 spheres after charging for 1 min; error bars represent one standard deviation.

charge separation of zero. Upon removal of the mask and irradiation of the entire film, the spheres charged negatively.

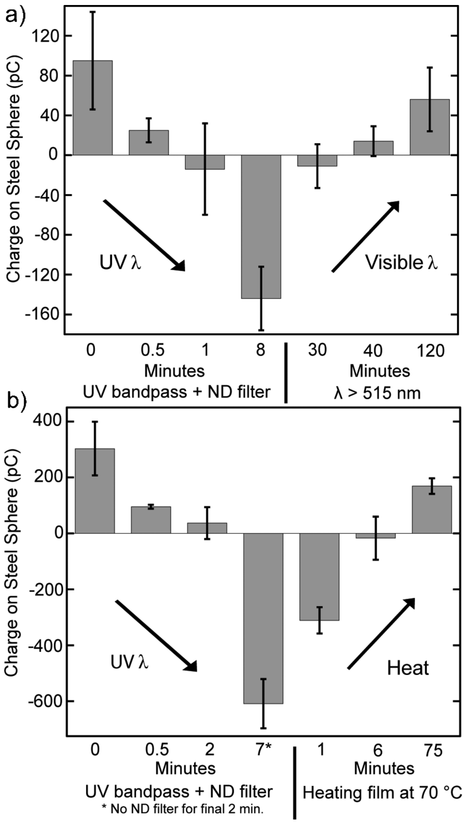


Figure 4. Temporal control of the contact electrification of steel spheres rolling film of PSPN-F5NB (48 %) exposed to UV light and (a) visible light (average values represent a minimum of 4 spheres) and (b) heat (70°C) (average values represent a minimum of 3 spheres). Error bars represent one standard deviation.

The magnitude and sign of charge developed through contact charging can also be controlled by the duration of irradiation. Initially, in Figure 4a,b, steel spheres charged positively through contact charging with a film of PSPN-5FNB (48%). Increasing the duration of irradiation time caused the spheres to charge increasingly more negative, as the conversion from SP isomer to MC isomer increased with increasing duration of irradiation. By controlling the length of time the film is exposed to UV light, we could tune the charge on the film to values close to 0 pC. In both cases, after longer irradiation times and contact charging with the polymer film, the spheres consistently charged negatively. One of the unique features of controlling the contact charging of a photochromic polymer film is that the charge on the sphere can be tuned in the opposite direction by exposing the film to visible light or heat. Irradiation with light of $\lambda > 515$ nm or heating reverts the MC form of the polymer back to the SP form. Data in Figure 4a illustrate how exposure of the film to $\lambda > 515$ nm can titrate the charge that develops on the spheres through contact charging in the opposite direction. Irradiation with visible light caused the magnitude of charge on the sphere to decrease. After 120 min of exposure to visible light, the average charge on the spheres was positive and similar to the initial charge on the spheres before irradiation.

Figure 4b shows a similar process using heat to convert the MC form of the polymer back to the SP form. Heating the slide for 1 and 6 min at 70 °C led to increasingly positive charges on the spheres after contact charging and the ability to tune the charge to approximately 0 pC. After 75 min, the charge that developed on the steel spheres was similar to the charge that developed on the spheres before irradiation. Another important aspect of these data shows that, under identical conditions, samples prepared in seemingly identical manners show significantly different charging behavior including differences in both the rate of charge and the net charge that develops. Our approach still allows minimization of net charge separation, even in cases of significant differences in initial charge separation due to sample variability, which underscores the importance of being able to dynamically control the contact charging characteristics of a material using light.

We conducted similar charge tuning experiments using spheres that have electrically insulating surfaces, parylene coated steel spheres and poly(methyl methacrylate) (PMMA) spheres, to determine if the change in charging behavior of PSPN-based films was unique to steel spheres. Although we were unable to observe a switch in direction of net charge separation using these materials with photochromic polymer films, the trends in charging were consistent with all previous experiments. Parylene-coated steel spheres rolled on a film of PSPN-F5NB (48%) charged negatively before irradiation (Figure 5). After UV irradiation of the polymer film for 8 min, the spheres developed more net negative charge upon contact charging, conforming to the trend that has been observed in all of our SP-containing polymers. PMMA spheres in contact with a film of PSPN-F5NB (48%) initially charged positively. After irradiation of the film with UV light for 8 min,

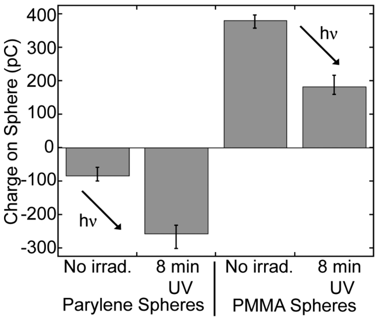


Figure 5. Average net charge on parylene coated steel spheres and PMMA spheres (minimum of 6 spheres) due to rolling on a film of PSPN-F5NB (48%) for 1 min, before and after irradiation with UV light. Error bars represent one standard deviation of the data.

the PMMA spheres charged less positively, also consistent with our observed trend.

■ CONCLUSION

This work reports light-enabled minimization of net charge separation from contact electrification using photochromic polymers. The spiropyran-merocyanine photoisomerization gives highly reliable and reversible photoinduced changing of charging behavior from contact electrification, regardless of the chemical structures of the comonomers and the polymer backbone to which it is bound. The incorporation of comonomers with halogenated groups into the photochromic polymers is a generally useful strategy for adjusting the initial rate of charging, as well as achieving a reliable photoinduced change in sign of charging with steel. Varying the temporal or spatial irradiation of films of SPN enabled control over the rate and magnitude of charge that develops on a film, ameliorating problems that arise from inherent variability of contact charging. The ability to control contact charging has importance in areas such as the prevention of fires and explosions,[22] limiting damage to electronics,[59,60] and pharmaceutical processing.[61] The most consistent outcome of this study is that in all cases studied in our laboratory the UV-induced photoisomerization reaction results in the polymer being more likely to develop a net positive charge. The structural factors that cause this trend remain uncertain, although recently published evidence points to the importance of mechanical factors such as strain,[34] which irradiation of photochromic films can induce,[62] as well as cohesive energy and Young's modulus, in understanding the role of material transfer in contact electrification.[63]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional contact charging data for SPN-containing polymers with various percentages of halogentated comonomers and alkyl comonomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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