JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

What Really Drives Chemical Reactions on Contact Charged Surfaces?

Bilge Baytekin,‡ H. Tarik Baytekin,‡ and Bartosz A. Grzybowski*

Department of Chemistry and Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, United States

Supporting Information

ABSTRACT: Although it is known that contact-electrified polymers can drive chemical reactions, the origin of this phenomenon remains poorly understood. To date, it has been accepted that this effect is due to excess electrons developed on negatively charged surfaces and to the subsequent transfer of these electrons to the reactants in solution. The present study demonstrates that this view is incorrect and, in reality, the reactions are driven by mechanoradicals created during polymer–polymer contact.

Contact electrification (CE)[1] is a phenomenon in which transfer of charge occurs when two surfaces are brought into contact (with or without friction) and then separated. Although its mechanism and the nature of charge carriers (i.e., ions[2b] or electrons[6,7]) remain incompletely understood,[2] CE has long been applied in several useful technologies, including photocopying,[3] laser printing,[4] and electrostatic separations.[5] Recently, a series of interesting studies[6,7] suggested that polymers contact charged to negative polarity[6] can act as solid-state reagents and drive chemical reactions (e.g., reduction of metal salts and metal complexes, hydrogen production, or chemiluminescence) in aqueous solutions. It was proposed that these reactions are of a redox type[6] and are related to the transfer of the so-called "cryptoelectrons"[7]—that is, electrons residing in high-energy states on or near the polymer surface. In these studies, "impurities or additives in the polymer, reactive end groups of the polymers, cosmic rays, unique states of polymer chains or surface states induced by the mechanical breakage of the bonds"[7] were proposed as the possible sources of these electrons. Later work by Lubomirsky and co-workers[8] put the involvement of cryptoelectrons in driving solution reactions in doubt. Specifically, these authors repeated some of the PMMA/Teflon contact-charging experiments and, using XPS, have demonstrated that the negatively charged Teflon does not reduce Pd(II) or Cu(II) salts but only promotes adsorption of the metal cations. [It should be noted, however, that the effects of oxygen plasma (used to clean the polymers) on these results have spurred some debate.][23] Additional concern about the reactions involving transfer of free electrons comes from our own recent work,[9] where we showed that during CE, the contacting materials do not charge uniformly but, instead, both contacting surfaces develop "mosaics" of positive and negative charges (see Figure 2)—thus both surfaces, and not only the one with the net negative charge, should be able to supply "cryptoelectrons".

Notwithstanding these negative findings, the idea of driving chemical reactions by surfaces activated during contact electrification remains enticing. In the present work we show this idea is, indeed, realistic and can be implemented with various types of contact-electrified polymers. However, the reactions driven by the polymeric surfaces are not electron (or free electron) reduction but are due to mechanoradicals[10] whose creation accompanies surface electrification and material transfer during materials' contact/separation.

Our experiments (Figure 1a) were similar to those described in the previous CE literature[6,7]—specifically, we used the contact-electrified surfaces to reduce metal salts and to bleach redox-active dyes. We tested various types of polymers (e.g., polydimethylsiloxane, PDMS; poly(methyl methacrylate), PMMA; Tygon; polytetrafluoroethylene, Teflon; polyvinylchloride, PVC; polystyrene, PS; polycarbonate, PC; polyoxymethylene, POM) that were contact charged either by pressing against one another and then separating, or by mechanically rubbing against one another. Irrespective of the manner of charging, all combinations of materials gave qualitatively similar results as narrated below.

For each pair of contact charged polymers, one piece developed a net positive (+) charge, and the other a net negative (−) charge of the same magnitude. These net charges, Q, were measured by a Faraday cup connected to a high-precision electrometer (Keithley, 6517), and their magnitudes ranged from ~0.2 to 3.0 nC/cm^2 depending on the specific polymer (e.g., Q values of ~0.5 nC/cm^2 for PDMS/PDMS charging, ~1.0 nC/cm^2 for PDMS/PTFE, and ~2.0 nC/cm^2 for PVC/PTFE),[11] which matches the values previously measured by us[1d,9,11] and others.[1b,12] Once charged, the pieces were immersed in an aqueous solution of a desired reagent(s) and caused reactions illustrated in Figure 1b (bleaching of an organic dye) and Figure 1c–e (reduction of $HAuCl_4$ salt to gold nanoparticles).

Previously, it was proposed[6] that these reactions are driven by the negatively charged polymers (contact charged Teflon in ref 6a, and contact charged nylon and polyethylene in ref 6b) which possess excess electrons. It was also stated in these references that surfaces depleted of electrons should not drive these reactions. We observed, however, that pieces with either net (−) or (+) charge were able to affect the same reactions.

Received: January 28, 2012
Published: April 11, 2012

dx.doi.org/10.1021/ja300925h | J. Am. Chem. Soc. 2012, 134, 7223−7226

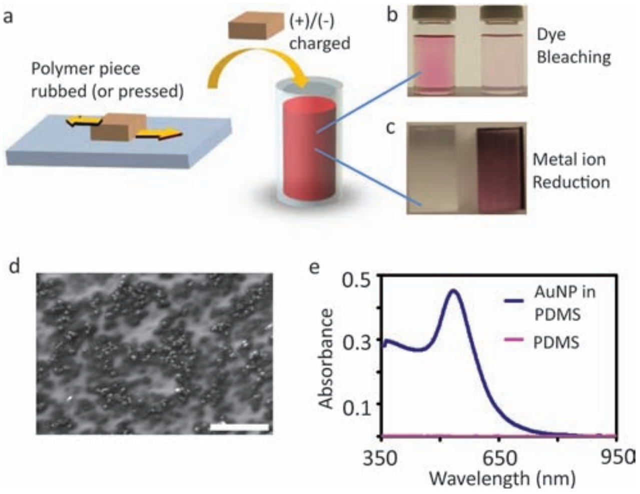

Figure 1. (a) Schematic of the experimental arrangement. Polymer pieces are charged by rubbing or pressing against one another and are then immersed into aqueous reagent solution. Both the negatively charged (−) and the positively charged (+) pieces can drive chemical reactions in solution. (b) Bleaching of Neutral Red dye (2.5 μM in water) by PVC pieces (four pieces, 16 cm^2 total surface area) positively charged by pressing against PTFE and placed into the solution. (c) How PDMS charged positively by rubbing against Teflon transforms $HAuCl_4(aq)$ (1 mg/mL) into Au nanoparticles. (d) SEM image zooming on the Au NPs deposited on the surface of (+) contact charged PDMS (scale bar = 1 μm). (e) UV−vis spectrum featuring an SPR peak centered at 520 nm and characteristic of Au nanoparticles.

This is illustrated in Figure 2a, which plots the kinetics of bleaching of a Neutral Red, NR, dye by PDMS charged either positively ($Q \approx 1$ nC/cm^2) by rubbing against Teflon or charged negatively ($Q \approx -2$ nC/cm^2) by rubbing against PC.

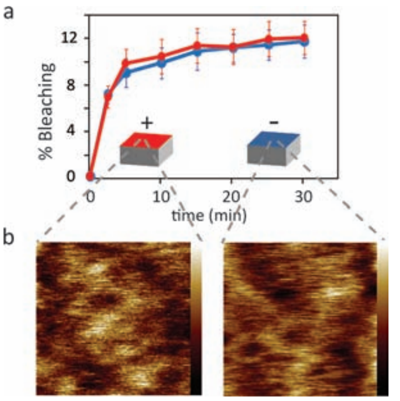

Figure 2. (a) Kinetics of % bleaching of Neutral Red (NR) aqueous solutions (2.5 mL, 2.5 μM, pH 5.0 acetate buffer) by PDMS charged negatively (net charge $Q \approx -2$ nC/cm^2) by rubbing against PC (red line) and charged positively ($Q \approx 1$ nC/cm^2) by rubbing against Teflon (blue line). Surface area of PDMS was the same in both cases (16 cm^2). Reaction progress was monitored by the intensity of an internal charge-transfer band (due to donor dimethylamino group and acceptor phenazine[14] with maxima at $\lambda = 535$ nm). Error bars are based on five independent experiments for each curve. Time is measured from the immersion of the polymer into solution. (b) KFM potential maps of positively (left) and negatively (right) charged PDMS pieces showing both surfaces are "mosaics" of positively and negatively charged nanoscopic domains. Color scales span potentials from −1 V (dark) to 1 V (light). Scanned area is 5.5 μm × 5.5 μm for both images.

Remarkably, both the (+) and the (−) PDMS pieces cause bleaching with virtually identical rates. The ability of the positively charged PDMS—and other positively charged polymers we studied—to drive reactions in solution is also observed in the reduction of metal salts to nanoparticles (see Figure 1c−e).

At first sight, these results seem to rule out the involvement of electrons—after all, the positively charged polymers should not be able to act as source of electrons. This conclusion, however, is premature as it is based on a conventional view of contact electrification in which the contacting surfaces charge either uniformly negatively or uniformly positively. We have recently shown[9] that, in reality, each of the charged surfaces features a "mosaic" of (+) and (−) regions of nanoscopic dimensions (Figure 2b), and the overall charge of the macroscopic piece of material corresponds to the sum of charges over these domains. Since the individual nanodomains are highly charged (on the order of μC/cm^2),[9] the (−) regions on each of the contact charged pieces of polymer could, in principle, provide enough electrons to drive redox reaction in the surrounding solution. Therefore, the macroscopically measured (e.g., by Faraday cup) polarity of an electrified material cannot alone prove or disprove whether electrons mediate the reactions affected by the contact charged polymer.

To resolve this issue we performed a series of experiments in which we studied the reduction of pH dependent dye indicators (Neutral Red, NR, and Methylene Blue, MB) by charged polymers. We chose these dyes because (i) they are known to be bleached to the so-called "leuco" forms[13] and (ii) the progress of the bleaching reaction can be easily quantified by UV−vis spectroscopy.

If the observed dye bleaching were due to electron-mediated reduction, the extent of this reduction should increase with decreasing pH (this follows from the relation between the pH of the solution and standard electrode potentials of the dyes, see ref 13). In sharp contrast, for both dyes, the extent of bleaching increases with increasing pH (Figure 3a,b)—this behavior is observed for all types of polymers tested, for both (+) and (−) charged polymer pieces. Second, we performed experiments in which mixtures of NR and MB were bleached by charged polymers. If bleaching were due to a redox process, one should expect the dyes to be reduced in the order of their standard electrode potentials (for MB, 0.108 V at pH 5; for NR, −0.198 V at pH 5). Instead, we observed (Figure 3c and SI, Figure S1) that both dyes were bleached concurrently, as evidenced by the concomitant decrease in the characteristic UV−vis bands at 535 nm (for NR) and 664 nm (for MB).[14] Also, analysis of the reaction for NR by ESI-MS (Figure S3) showed that the dye was broken down to smaller fragments and the reduced forms of the dye—expected if the reaction were an electron transfer process—were not present.[15]

Next, we examined whether the observed reactions depend on the presence of charge on the polymers or on the physical contact between them. To this end, we performed experiments in which polymer pieces were charged "non-mechanically", by an ionic gun.[16] As illustrated by the black curve in Figure 3d (also see Figure S2 for other polymers), such charged polymers were not able to drive any of the reactions tested. On the other hand, polymers that were mechanically compressed but not charged (as verified by Faraday cup measurements) effected all of the reactions discussed above (Figure 3d blue curve).

Together, the experiments summarized in Figures 2 and 3 indicate that it is not the charges developed by CE but only the

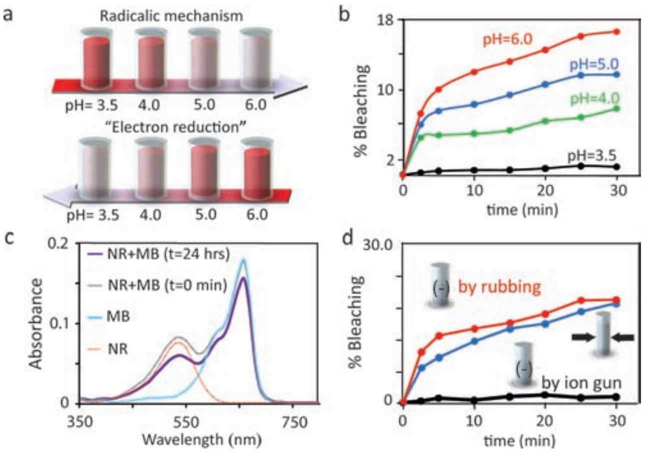

Figure 3. (a) Schematic illustration of the trends expected assuming either radicalic or redox bleaching of the NR dye. If electron reduction mechanism were operative, the dye color would fade more with decreasing pH. However, the experimental trend follows the radicalic mechanism, in which bleaching increases with increasing pH. This trend is quantified in (b), which plots the kinetics of % bleaching of NR by positively charged PDMS, buffered (acetate buffers) at pH 6.0 (red), 5.0 (blue), 4.0 (green), and 3.5 (black). Reaction progress was monitored by the intensity of an internal charge-transfer band (due to donor dimethylamino group and acceptor phenazine with maxima at λ = 535 nm). (c) Bleaching of a mixture of 1.25 μM Neutral Red and 1.25 μM Methylene Blue (in pH 5.0 acetate buffer) by negatively charged Teflon pieces (trend is similar if either positively or negatively charged polymer pieces of various types are used; see SI, Figure S1). (d) % Bleaching of 2.5 mL of 2.5 μM (pH 5.0, acetate buffer) aqueous solution of NR poured into hollow TYGON tubes (see SI section 1.3 for details): (red) the inner surface of the tube was charged negatively by rubbing against a PS rod; (blue) the tube was compressed from the outside (compression ~25%), but its inner surface was not contacted by any material and was uncharged; and (black) the inner surface of the tube was charged by an ionic gun (here, $Q \approx -2$ nC/cm^2; positive Q's gave similar results) but not rubbed/touched by any material. As seen, only mechanical deformation—but not charge by itself—is required to drive bleaching. For similar results with other flexible polymers see SI, Figure S2.

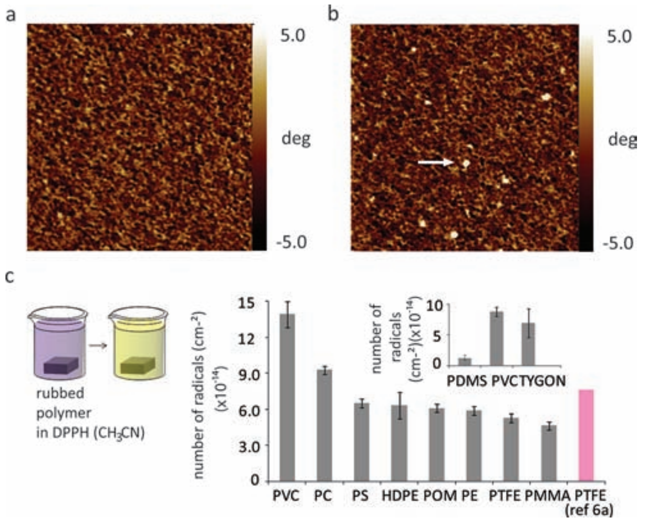

Figure 4. MFM image of (a) uncharged and (b) positively charged PDMS surface touched against another PDMS. Mechanoradicals generated on the surface in (b) correspond to the lighter areas in the MFM map (one of which is marked with a white arrow). Images taken after charge decayed to zero. Scanned area is 5.0 μm × 5.0 μm for both images. Color scales span the range from −5.0 to 5.0°. (c) Bleaching of DPPH radical scavenger solutions confirms the creation of mechanoradicals on contact electrified pieces. Gray bars in the histogram on the right correspond to the surface densities of mechanoradicals created on 1 cm × 1 cm × 0.5 cm polymer pieces charged up to ~1−2 nC. Standard deviations based on triplicate experiments are 5−15% of the bar heights; inhomogeneities in rubbing such as normal force applied, surface roughness are the main sources of the error. The inset has the corresponding results for hollow polymer tubes used in dye-bleaching experiments Error bars are standard deviations based on the analysis of at least three different samples for each polymer. Pink bar on the right corresponds to cryptoelectron estimate from refs 6a.

mechanical deformation of the polymers—invariably accompanying charging during polymer touching/rubbing—that enables the reactions in the surrounding solution. This conclusion points to the involvement not of electrons but of mechanoradicals that are known to be created in mechanically stressed polymers.[17] In fact, we detected such radicals at the surfaces of polymers that were contact charged mechanically (e.g., by touching or rubbing) by magnetic force microscopy (MFM). Figure 4 shows typical MFM images of uncharged and positively charged PDMS surfaces. The lighter spots in the MFM image of the charged surface correspond to the created mechanoradicals (as in previous MFM imaging of radical-containing polymers[18]); these features are absent in the MFM maps of uncharged materials.

Finally, we performed two sets of experiments to directly confirm that (1) radicals are transferred from the contact electrified pieces into solution and (2) the numbers of these radicals are commensurate with the previously reported numbers of purported cryptoelectrons driving solution reactions. To show this, 1 cm × 1 cm × 0.5 cm pieces of PTFE, PMMA, PVC, POM, PC, PS, PE, and HDPE were contact charged to ~ (+) or (−) 1−2 nC and were then immersed into 2.5 mL of 10 μM degassed acetonitrile solutions of radicals scavenger DPPH[19a−f] (2,2-diphenyl-1-picrylhydrazyl). The mechanoradicals from the polymers reacted with the surrounding DPPH solution and bleached it. Monitoring the decrease in solution's absorbance at λ_{max} = 517 nm then allowed for the quantification[19a−f] of the numbers of mechanoradicals created per the unit area of the polymer surface. The results of these studies and summarized in Figure 4c. For comparison, the rightmost bar in this histogram gives the number of purported cryptoelectrons that the authors of ref 6a deduced would be necessary to account for the changes they observed in their experiments. While their estimate as to the sheer number was on the cue, we now know that it was not cryptoelectrons but, instead, the mechanoradicals that were operative in causing the solution reactions. We also observe that the values given in Figure 4c agree with the concentration changes observed in the dye bleaching studies (cf. earlier in the text and SI, section 3) and with the previous ESR studies of mechanically treated polymers.[19g,h]

With the above observations in mind, the chemical reactions we observe can be fully rationalized as being caused by radicals. For example, it has been shown previously that Au NPs can be synthesized via a reaction initiated by radical species[20] and that MB and NR dyes can also be bleached by radicals.[21]

In summary, although charges developed by CE cannot be readily converted into chemical energy, the mechanical deformations accompanying contact charging[22] of polymers give rise to mechanoradicals capable of driving chemical reactions. Looking forward, we suggest this concept could provide a novel route to surface functionalization whereby one would chemically activate the polymer's surface simply by rubbing—we will describe such effects in a series of upcoming papers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further experimental details, charging curves, and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

grzybor@northwestern.edu

Author Contributions

‡B.B. and H.T.B. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Nonequilibrium Energy Research Center, which is an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award DESC0000989. We thank Prof. Allen J. Bard for valuable discussions.

■ REFERENCES

(1) (a) Lowell, J.; Rose-Innes, A. C. *Adv. Phys.* **1980**, *29*, 947. (b) Horn, R. G.; Smith, D. T. *Science* **1992**, *256*, 362. (c) Horn, R. G.; Smith, D. T.; Grabbe, A. *Nature* **1993**, *366*, 442. (d) Apodaca, M. M.; Wesson, P. J.; Bishop, K. J. M.; Ratner, M. A.; Grzybowski, B. A. *Angew. Chem., Int. Ed.* **2010**, *49*, 946. (e) Grzybowski, B. A.; Wiles, J. A.; Winkleman, Y.; Brummer, Y.; Whitesides, G. M. *Nat. Mater.* **2003**, *2*, 241.

(2) (a) Thomas, S. W., III; Vella, S. J.; Kaufman, G. K.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 6654. (b) McCarty, L. S.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2188. (c) Grzybowski, B. A.; Fialkowski, M.; Wiles, J. A. *J. Phys. Chem. B* **2005**, *109*, 20511. (d) Rezende, C. A.; Gouveia, R. F.; da Silva, M. A.; Galembeck, F. *J. Phys. Cond. Matter.* **2009**, *21*, 263002. (e) Shein, L. B. *Science* **2007**, *316*, 1572.

(3) Schein, L. B. *Electrophotography and Development Physics*; Laplacian: Morgan Hill, CA, 1996.

(4) Pai, D. M.; Springett, B. E. *Rev. Mod. Phys.* **1993**, *65*, 163.

(5) (a) Kwetkus, B. A. *Part. Sci. Technol.* **1998**, *16*, 55. (b) Forward, K. M.; Lacks, D. J.; Sankaran, R. M. *Phys. Rev. Lett.* **2009**, *102*, 028001.

(6) (a) Liu, C.-Y.; Bard, A. J. *Nat. Mater.* **2008**, *7*, 505. (b) Liu, C.-Y.; Bard, A. J. *Chem. Phys. Lett.* **2010**, *485*, 231.

(7) Liu, C.-Y.; Bard, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 6397.

(8) Piperno, S.; Cohen, H.; Bendikov, T.; Lahav, M.; Lubomirsky, I. *Angew. Chem., Int. Ed.* **2011**, *50*, 5654.

(9) Baytekin, H. T.; Patashinski, A. Z.; Branicki, M.; Baytekin, B.; Soh, S.; Grzybowski, B. A. *Science* **2011**, *333*, 308.

(10) (a) Lacks, D. J.; Sankaran, R. M. *J. Phys. D: Appl. Phys.* **2011**, *44*, 453001. (b) Sakaguchi, M.; Shimad, S.; Kashiwabara, H. *Macromolecules* **1990**, *23*, 5038. (c) Wang, D.; Klaassen, A. A. K.; Janssen, G. E.; de Boer, E. *Polymer* **1995**, *36*, 4193.

(11) Baytekin, H. T.; Baytekin, B.; Soh, S.; Grzybowski, B. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 6766.

(12) (a) Nemetha, E.; Albrecht, V.; Schubert, G.; Simon, F. *J. Electrostat.* **2003**, *58*, 3. (b) Cole, J. J.; Barry, C. R.; Wang, X.; Jacobs, H. O. *ACS Nano* **2010**, *4*, 7492.

(13) Bishop, E. *Indicators*, 1st ed.; Pergamon Press: 1972. pH dependence of the electrode standard potential is given by the equation

$$E = E^0 + (RT/2F)\ln(([\mathrm{H}^+]^4 + K_{\mathrm{r1}}[\mathrm{H}^+]^3 + K_{\mathrm{r1}}K_{\mathrm{r2}}[\mathrm{H}^+]^2)/([\mathrm{H}^+] + K_{01}))$$

where E is the electrode potential at a given pH, E^0 is the standard electrode potential, and K_{01}, K_{r1}, and K_{r2} are the ionization constants at 30 °C (for NR, $K_{01} = 1 \times 10^{-6}$ M, $K_{\mathrm{r1}} = 5.0 \times 10^{-6}$ M, and $K_{\mathrm{r2}} = 5.5 \times 10^{-7}$ M, and $E^0 = 0.240$ V; for MB, $K_{01} \approx 0$, $K_{\mathrm{r1}} = 3.0 \times 10^{-5}$ M, and $K_{\mathrm{r2}} = 1.4 \times 10^{-6}$ M, and $E^0 = 0.532$ V).

(14) Singh, M. K.; Pal, H.; Bhasikuttan, A. C.; Sapre, A. V. *Photochem. Photobiol.* **1998**, *68*, 32.

(15) Also, assuming the dyes were reduced to their "leuco" forms by the "cryptoelectrons" from the charged polymers, it should be possible to reoxidize them. However, bubbling air through the solutions (O_2 is known to oxidize the leuco form) was not able to regenerate the original forms of the dyes.

(16) The nature of ions generated by the corona discharge depends on whether the ion gun's (here, Zerostat, Aldrich) trigger is pulled or released. The emitted positive ions are $(H_2O)_nH^+$ with $(H_2O)_2H^+$ as the most abundant species, and the negative ions are CO_3^-, NO_3^-, NO_2, O_3^-, and O_2^-. For both polarities, the ions generated adsorb onto polymer's surface. For details, see: (a) Waltman, M. J.; Dwivedi, P.; Hill, H. H., Jr.; Blanchard, W. C.; Ewinga, R. G. *Talanta* **2008**, *77*, 249. (b) Rezende, C. A.; Gouveia, R. F.; da Silva, M. A.; Galembeck, F. *J. Phys.: Condens. Matter* **2009**, *21*, 263002. (c) Jacobs, H. O.; Whitesides, G. M. *Science* **2001**, *291*, 1763.

(17) (a) Beyer, M. K.; Clausen-Schaumann, H. *Chem. Rev.* **2005**, *105*, 2911. (b) Potter, W. D.; Scott, G. *Eur. Polym. J.* **1971**, *7*, 489. (c) Porter, R. S.; Casale, A. *Polym. Eng. Sci.* **1985**, *25*, 129. (d) Sohma, J. *Colloid Polym. Sci.* **1992**, *270*, 1060.

(18) (a) Nishide, H.; Ozawa, T.; Miyasaka, M.; Tsuchida, E. *J. Am. Chem. Soc.* **2001**, *123*, 5942. (b) Miyasaka, M.; Saito, Y.; Nishide, H. *Adv. Funct. Mater.* **2003**, *13*, 113.

(19) (a) Ayrey, G.; Moore, C. G.; Watson, W. F. *J. Polym. Sci.* **1956**, *19*, 1. (b) Baranwal, K. *J. Appl. Polym. Sci.* **1968**, *12*, 1459. (c) Chandra, S.; Roy-Chowdury, P.; Biswas, A. B. *J. Appl. Polym. Sci.* **1964**, *8*, 2653. (d) Chandra, S.; Roy-Chowdury, P.; Biswas, A. B. *J. Appl. Polym. Sci.* **1966**, *10*, 1089. (e) Meyer-Plath, A. *Vak. Forsch. Praxis* **2005**, *17*, 40 (DOI: 10.1002/vipr.200590029). (f) Damm, C.; Peukert, W. *Langmuir* **2009**, *25*, 2264. (g) Devries, K. L.; Royland, D. K.; Williams, M. L. *J. Polym. Sci. Part A-1* **1970**, 237. (h) Backman, D. K.; Devries, K. L. *J. Polym. Sci. Part A-1* **1969**, 2125.

(20) McGilvray, K. L.; Decan, M. R.; Wang, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **2006**, *128*, 15980.

(21) (a) Alnuaimi, M. M.; Rauf, M. A.; Ashraf, S. S. *Dyes Pigments* **2007**, *72*, 367. (b) Guha, S. N.; Moorthy, P. N.; Mittal, J. P. *J. Chem. Soc., Perkin Trans.* **1993**, *2*, 409. (c) Dutta, K.; Mukhopadhyaya, S.; Bhattacharjee, S.; Chaudhuri, B. *J. Hazard. Mater.* **2001**, *B84*, 57.

(22) (a) Sow, M.; Widenor, R.; Kumar, A.; Lee, S. W.; Lacks, D. J.; Sankaran, R. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 2695. (b) Baytekin, H. T.; Baytekin, B.; Incorvati, J. T.; Grzybowski, B. A. *Angew. Chem., Int. Ed.* **2012**, DOI: 10.1002/anie.201200057. (c) Williams, M. *AIP Adv.* **2012**, *2*, 010701. (d) Matsusaka, S.; Maruyama, H.; Matsuyama, T.; Ghadiri, M. *Chem. Eng. Sci.* **2010**, *65*, 5781. (e) Castle, G. S. P *J. Electrostat.* **1997**, *40*−*41*, 13. (f) Lowell, J. *J. Phys. D: J. Appl. Phys.* **1977**, *10*, L233. (g) Salaneck, W. R.; Paton, A. *J. Appl. Phys.* **1976**, *47*, 144.

(23) Williams, M. W. *AIP Advances* **2012**, *2*, 010701.