



Electrostatic electrochemistry: Nylon and polyethylene systems

Chong-yang Liu, Allen J. Bard*

Center for Electrochemistry, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712, United States

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ABSTRACT

Electrostatic charges generated on polymer surfaces by contact electrification e.g. polyethylene (PE) contacted with polyamide (Nylon), are capable of carrying out redox reactions. For example, metal ions such as Pd^{2+} , Ag^+ , and Cu^{2+} were reduced, leading to a metal film deposition on the polymer, $\text{Fe}(\text{CN})_6^{3-}$ was reduced to $\text{Fe}(\text{CN})_6^{4-}$, and chemiluminescence was produced. These results reinforce the electron transfer mechanism of contact electrification and the concept of ‘single electrode electrochemistry’ using PE or Nylon (or PTFE) as the source of charge. From the extent of the redox reactions, one estimates charge densities of up to about $10^{14}/\text{cm}^2$.

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1. Introduction

We have previously described experiments in which the polymers PTFE (Teflon), following contact electrification with PMMA (polymethylmethacrylate or Lucite), could be employed to carry out a variety of reduction reactions [1]. These reactions were the same as those carried out at a metal electrode in an electrochemical cell, so the charged polymer could be considered as capable of ‘single electrode electrochemistry,’ powered by bringing two materials into contact and then separating them with or without rubbing. Such ‘single electrodes’ could be useful, for example, in carrying out redox reactions in very small volumes.

Contact electrification is a well-known phenomenon [2,3]. Despite its long history and wide existence, the origin of the potential difference that forms remains poorly understood for dielectrics (insulators) such as polymers [4–6]. Potential differences arise from excess charge, but whether this charge is electronic vs. ionic for nonionic polymers like PE and Nylon has not been elucidated [5–7]. For example, studies with metal/polymer contacts show that charge generation on some polymers increased with an increasing metal work function, suggesting an electron transfer mechanism similar to those that form contacts (Schottky junctions) at metal/semiconductor interfaces [8–10]. This tendency was not seen, however, on other polymers [10]. Kornfeld, on the other hand, assumed that insulators are not electrically neutral due to structure imperfections and compensated by ions from air and proposed that ion transfer occurs when two ion-covered insulators touch each other [11]. However, ‘the overall electrical effect of a positive ion

being transferred from a surface cannot be distinguished from an electron transferred to that surface to neutralize the ion’ [6].

The effects of conditions and materials (metal/metal, metal/polymer and polymer/polymer and so on) on contact electrification were comprehensively reviewed [6]. When polymer blends containing a molecular salt or ionomer were used, ion transfer was detected by XPS measurement [12,13] and a detailed model was developed which relates the sign and magnitude of the charge with ion concentration, mobility, stability and other physical characteristics. Its general expression, interestingly, was similar to that derived from electron transfer model and thus did not allow one to distinguish between them since both models shared the same premise [12–15], consistent with a dual mechanism model for metal/polymer contact [16]. In this case, an important issue becomes how much contribution to the overall charge separation comes from ion or electron transfer. Note that in addition to charge transfer, bulk material transfer is also known to occur in contact electrification [6] and could be responsible for at least some of the ions transferred especially for those polymer blends with about 10 wt% intentionally incorporated ions whose concentration on the surface can be 3–10 times higher than that in the bulk for molecular salts [17]. In other studies with nonionic polymers, an exclusive ion-transfer model was also proposed [4,7], although it has also been said that an ‘exclusive ion- or electron-transfer mechanisms cannot explain contact electrification’ [18]. We have recently dealt more extensively with these questions [19].

One issue is that electrostatic measurements alone have not been able to resolve the problem and the surface concentrations of the charging species are relatively small ($\sim 10^{12}$ – 10^{14} cm^{-2}) so carrying out chemical reactions with these is difficult. We recently suggested a chemical approach based on very sensitive techniques that could identify redox events and showed that these occurred for PTFE generated by rubbing with PMMA, and proposed that the electron was the generated charge carrier, and that it was

* Corresponding author. Address: University of Texas at Austin, Chemistry and Biochemistry, 1 University Sta. A5300, Austin, TX 78712-0165, United States. Fax: +1 512 471 0088.

E-mail address: ajbard@mail.utexas.edu (A.J. Bard).

transferred from PMMA [1,20]. To demonstrate that this model is not unique to the particular couple of PMMA/PTFE, but also occurs with other polymers, we carried out similar experiments with Nylon and polyethylene (PE), which are listed as close to PMMA and PTFE, respectively, in some triboelectric series [21–23], suggesting that couples of PMMA/PE, Nylon/PE, and Nylon/PTFE should show similar behavior in contact electrification. We report here such studies.

2. Experimental

Four different polymers were used here. PTFE and PMMA were the same as used in our earlier work [1]. Both UV stabilized and non-UV stabilized PE rod, plate and tubing of different shape and size as well as structure including ultra high molecular weight and low density were employed (purchased from US Plastics Corp., OH). The PEs with additives, however, behaved essentially the same as the more pure samples. For example glass vial PE plugs were also used in $\text{Fe}(\text{CN})_6^{3-}$ reduction experiments and showed very similar results. Nylon 6 rods and plates as well as Nylon 11 tubing were used. Polymers were purchased from both US Plastics Corp. and local stores. Polymers were contacted and rubbed by hand in the manner reported earlier [1]. Following the contact electrification, the polymers were separated and one of the charged materials was dipped into a solution to carry out the desired chemical reaction. Contact without intentional rubbing generated charge of the same nature on each polymer, but with lower charge density. Thus, all the experiments in this work were carried out with rubbed polymers. All other chemicals were reagent grade. MilliQ deionized water was used to prepare the solutions. An electrometer (Model 6517, Keithley Instruments) was used to measure the charge on the polymer surface and current as well as voltage in other experiments. For $\text{Fe}(\text{CN})_6^{3-}$ reduction experiments, PE disks or glass vial PE plugs were first charged through contact electrification with PMMA or Nylon plates and then touched the solution containing 0.2 mM $\text{Fe}(\text{CN})_6^{3-}$ and KCl one after another. Chemical composition of the solution before and after the treatment with charged polymer were analyzed with an electrochemical method in which cyclic voltammetry in the $\text{Fe}(\text{CN})_6^{3-/4-}$ experiments was carried out with a 23 μm Pt ultramicroelectrode controlled by an electrochemical analyzer (Model 100A, Bioanalytical Systems, West Lafayette, IN). For metal deposition, charged polymers were dipped briefly into a solution containing metal ions. For catalytic Cu plating, Pd was plated first on charged polymer that was then washed and immersed into a copper plating bath consisting of 3.6 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; 204 g/L $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$; 3.8 g/L NaOH and 10 mL HCHO (37%). All the luminescence experiments were performed in a black box located inside a double-door dark room with a photomultiplier tube (PMT, Hamamatsu R4220P). The solutions were mixed inside the dark room to avoid possible photochemical reactions. Measurement techniques followed earlier studies [1,20].

3. Results and discussion

Since electrons cannot be distinguished from negatively charged ions by an electronic probe, as in our previous paper [1] the identity of the charge carrier on a polymer surface was determined by a chemical method in which the charged polymers were brought into a solution containing some reducible species. A chemical reaction could occur upon contact if the charge carriers were electrons, analogous to a faradaic process on a cathodic electrode in conventional electrochemistry. On the other hand, no reduction reaction should occur when negative ions like OH^- , Cl^{2-} or SO_4^{2-} contact the same solution. Analysis of the chemical composition in the solution before and after the immersion of a charged poly-

mer provides strong evidence to the identity of the charge carrier. The specific methods and results are discussed below.

3.1. $\text{Fe}(\text{CN})_6^{3-}$ reduction

In this case, $\text{Fe}(\text{CN})_6^{3-}$ was used as an indicator. As with Teflon, the PE surface became negatively charged by rubbing with PMMA or Nylon and those negative charges were able to reduce $\text{Fe}(\text{CN})_6^{3-}$ to $\text{Fe}(\text{CN})_6^{4-}$. For example, after 0.13 mL of an aqueous solution consisting of 0.2 mM $\text{Fe}(\text{CN})_6^{3-}$ and 0.2 M KCl contacted 10 PE disks (19 mm in diameter) sequentially that had been charged through rubbing on PMMA plates ($18 \times 18 \text{ cm}^2$), about 15% of the $\text{Fe}(\text{CN})_6^{3-}$ molecules in the solution were reduced to $\text{Fe}(\text{CN})_6^{4-}$ as determined by an electrochemical analysis with a 23 μm glass-encased Pt ultramicroelectrode [1]. Fig. 1 shows the cyclic voltammograms of the solution before and after contact with the charged PE disks and the drop in the steady state cathodic current plateau corresponding to $\text{Fe}(\text{CN})_6^{3-}$ reduction and the new anodic plateau corresponding to $\text{Fe}(\text{CN})_6^{4-}$ oxidation that appeared following the treatment with charged PE disks. The decrease in $\text{Fe}(\text{CN})_6^{3-}$ and increase in $\text{Fe}(\text{CN})_6^{4-}$ concentration was essentially the same. The generation of $\text{Fe}(\text{CN})_6^{4-}$ species in a $\text{Fe}(\text{CN})_6^{3-}$ solution clearly indicates the occurrence of a reduction reaction on the PE surface upon contact to the solution as previously found with PTFE. The same results were obtained with glass vial PE caps that were charged in the same way. This chemical measurement also provides an accurate way of determining the electron density induced by contact electrification on a polymer surface – a longstanding challenge in electrostatic studies, since a physical probe is unable to precisely sense all the charges on a rough surface that is often the case for a polymer and to distinguish electronic charge from ionic charge when both may be present on the surface. Here, the total amount of reaction product, i.e., the $\text{Fe}(\text{CN})_6^{4-}$ species, divided by the apparent surface area of all the PE disks involved in the treatment, gave an average electron density of $7.9 \times 10^{13} / \text{cm}^2$ (geometric area) on the charged PE, assuming 100% $\text{Fe}(\text{CN})_6^{3-}$ reaction efficiency. This density is over 10 times smaller than that found for charged PTFE [1]. This is consistent with PE usually being listed above PTFE (less tendency to become negatively charged) in the triboelectric series. Another factor could be surface roughness, since PE is smoother than PTFE and therefore has a relatively smaller real surface area.

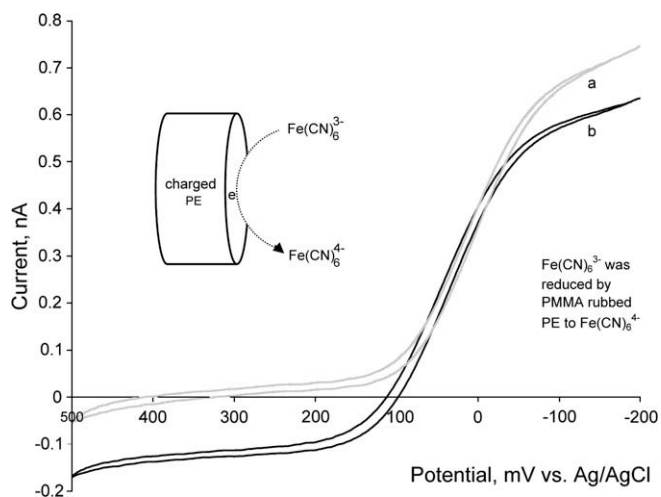


Fig. 1. Cyclic voltammograms (10 mV/s) at a 23 μm glass-encased Pt ultramicroelectrode in water containing 0.2 mM $\text{Fe}(\text{CN})_6^{3-}$ and 0.2 M KCl before (a) and (b) contact with PMMA rubbed PE disks.

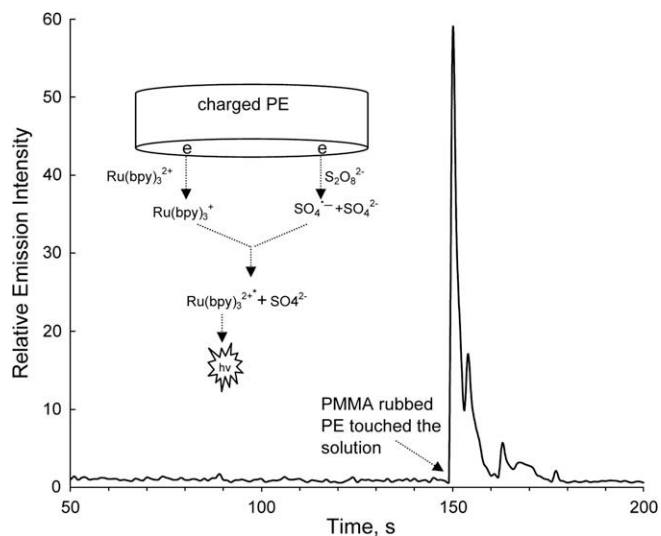


Fig. 2. Relative intensity of chemiluminescence as a function of time when a PMMA rubbed PE rod dipped into a MeCN/H₂O (1:1, v/v) mixture containing 2.5 mM S₂O₈²⁻ and 0.25 mM Ru(bpy)₃²⁺. Insert shows the reaction mechanism.

3.2. Chemiluminescence (CL) generation

CL can be generated through a ‘reductive oxidation’ process in a solution containing a coreactant and a luminophore molecule, where both of them are reduced at an electrode [24]. The reduced coreactant decomposes to form a highly oxidizing species that can react with the reduced form of the luminophore. The subsequent annihilation reaction leads to CL, as found earlier with PTFE, that we termed electrostatic chemiluminescence (ESCL) [1]. We tested the same concept here for PE rubbed with either PMMA or Nylon. If the negative charges on PE are indeed electrons, then these electrons can generate CL in the well studied system consisting of tris(2,2′-bipyridine)ruthenium (II) perchlorate [Ru(bpy)₃(ClO₄)₂] and the coreactant sodium persulfate, Na₂S₂O₈ in an aqueous/acetonitrile (MeCN) medium [25]. Indeed, a strong CL was detected with charged PE. In these experiments, a PE rod was first rubbed with PMMA and then immersed into an MeCN/water (1:1, v/v) mixture containing the typical ECL reagents, i.e., 0.25 mM Ru(bpy)₃(ClO₄)₂ and 2.5 mM Na₂S₂O₈, producing clear ESCL as shown in Fig. 2. Here, available electrons on the PE reduced Ru(bpy)₃²⁺ and S₂O₈²⁻ to generate the emitting excited state. The CL signal decayed over time as the electrons diminished. Note that some air bubbles were trapped on the PE surface upon the first immersion into the solution and blocked some of the charged area. As those bubbles moved and were displaced by solution, more electrons became available and generated the irregular emission spikes shown in Fig. 2. As expected, with either of the two reagents absent, the emission was barely seen above the background level upon charged PE introduction. This result is consistent with our earlier work with PMMA-contacted PTFE. Note that same result was also obtained with Nylon rubbed PTFE and PE. That contact electrification occurs with all the couples of PE/Nylon, PE/PMMA, PTFE/PMMA and PTFE/Nylon, demonstrates the generality of this ESCL process.

3.3. Metal deposition

The electron transfer reaction induced by electrostatic charges on a polymer surface could also be visualized through metal plating. When PMMA- or Nylon-rubbed PE materials of different size, shape, branching and density (low density, high density, ultra high

molecular weight) were immersed for a few seconds into a solution containing 1 mM Ag₂SO₄, saturated PdCl₂ or 1 mM CuSO₄, followed by a thorough wash with deionized water, metals of Ag, Pd and Cu, respectively, were found to be plated on the PE surface. Under an optical microscope, about 10 μm size metal deposits were clearly seen at isolated spots. Just like PMMA, Nylon rubbed-PTFE also showed metal deposition. Note that Cu deposition could be significantly amplified and accelerated when Pd was deposited, because it is a good catalyst for electroless Cu deposition [1,26]. This amplification makes it easy to recognize the occurrence of a redox reaction for a relatively small number of electrons. For example, following the plating of Pd by immersion of a charged PE rod in saturated PdCl₂, it was washed and then placed into a Cu plating bath containing CuSO₄, KNaC₄H₄O₆, NaOH, and HCHO [26]. Since Pd serves as a catalyst for the electroless deposition of Cu, large amounts of Cu were deposited that were clearly visible as shown on the top right of Fig. 3. During this process numerous bubbles were formed and almost all of the Cu²⁺ available in the bath was consumed in several hours as the blue color of the plating bath completely disappeared. Although at least 5 mm of the PE rod was immersed into the plating solutions, Cu was deposited only at the end surface that was the only area initially charged through rubbing with PMMA. These results, again, clearly demonstrate that electrons are produced on the PE surface through rubbing with other polymers including PMMA and Nylon, and those electrons were able to carry out redox reactions.

When metal ions were reduced and deposited on a rubbed polymer surface whose negative charges were neutralized, the solution became negatively charged due to the presence of uncompensated anions. This solution charge could be directly measured with an electrometer. To two identical cells made of aluminum foil and well insulated from ground the same solution of 1 mM CuSO₄ was added. The voltage between those two cells as measured between the Al was initially zero, as expected. After a PTFE or PE

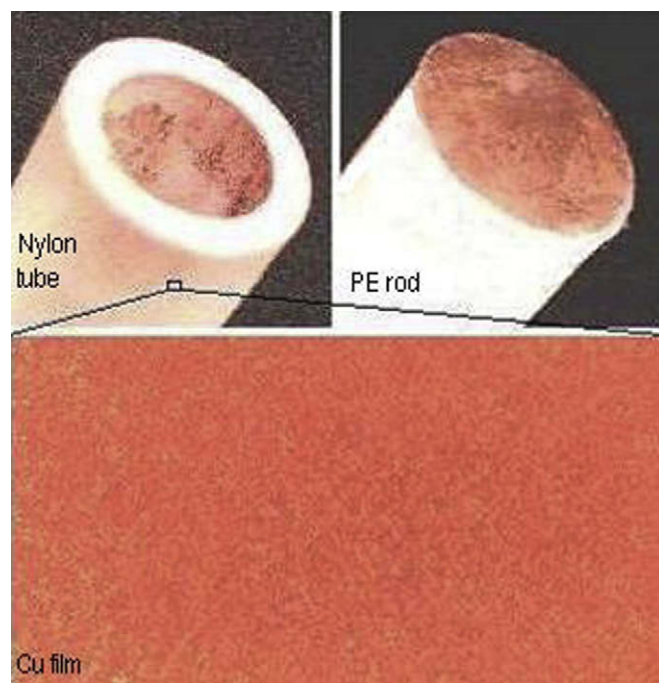


Fig. 3. Top right: an optical image showing Cu deposited on the end of a PMMA rubbed PE rod and no Cu plated on other surface that was not rubbed. Top left: an optical image showing Cu deposited on untreated inner surface of a Nylon tube. No Cu was seen on PE rubbed outer surface and the end. Bottom: enlarged optical image (0.8 × 0.43 mm²) of the Cu film on Nylon inner surface.

rod rubbed on a PMMA plate was dipped briefly into one cell contacting the solution but never touching the Al foil, a stable voltage over 100 V was shown on the electrometer clearly indicating that the cell became negatively charged following the contact of charged polymer.

3.4. Origin of the charges transferred

All of the above reduction chemical reactions are consistent with the model that electrons are the charge carriers on the PE surface, as previously shown with PMMA-rubbed PTFE. In that case we demonstrated that PMMA itself has electrons (that we called *cryptoelectrons*) with an energy and density that could produce the observed effects upon transfer to PTFE [20]. Note that PMMA, depleted by contact with PTFE or with solutions containing oxidants, would not show these reactions. If the electron transfer model also holds with the Nylon/PE system, then electrons were transferred from the Nylon to the PE, i.e. Nylon is an electron donor. In this case, as with PMMA, one should be able to see similar redox reactions with fresh (uncontacted) Nylon. This was tested by briefly dipping a Nylon tube that had not been contacted with PE into a solution containing reducible chemical species such as Ag^{2+} , Pd^{2+} and Cu^{2+} . Indeed, metal deposition on the Nylon surface occurred as seen by isolated metal deposits under an optical microscope.

An experiment in which only part of a Nylon rod was contacted by PE and then exposed to a plating solution was also carried out. The outer surface and the end of a Nylon tube were first rubbed on a PE plate and then immersed into the 1 mM Pd^{2+} solution, followed by washing and immersion in the Cu electroless deposition bath. No metal was deposited on the rubbed area; electrons from this area had been depleted by transfer to the PE during rubbing. However, deposition still occurred on the tube's inner wall that had never contacted PE or other surfaces, as shown on the top left of Fig. 3, in which Pd was deposited first followed by a catalytic electroless Cu deposition as described above. Note that Nylon tubing is not very transparent and this leads to the fuzzy appearance of the Cu film when observed through the Nylon wall. However, small Cu particles could be clearly seen when looking directly at the Cu film on the inner Nylon surface (Fig. 3). This result clearly indicated that Nylon acted as an electron donor that is capable of transferring electrons to a solid such as PE or a solution containing chemical species upon contact, and those electrons whether they resided on Nylon or transferred to PE had the same capability to reduce metal ions leading to the metal deposition on either Nylon or PE, respectively as shown in the top two images in Fig. 3. These findings, and especially the reduction reaction on uncharged Nylon (as previously seen with PMMA) strongly support an electron transfer model for contact electrification.

Nylon, like PMMA is also listed near the top of the triboelectric series [23], meaning that it is among the best electron donors, either to other materials or to solutions containing reducible species upon contact. Indeed, untreated Nylon that had never contacted other objects was able to carry additional chemical

reactions in addition to metal deposition. For example, $\text{Fe}(\text{CN})_6^{3-}$ molecules were reduced to $\text{Fe}(\text{CN})_6^{4-}$ when a $\text{Fe}(\text{CN})_6^{3-}$ solution passed through a fresh Nylon tube as determined by an electrochemical analyzer as described earlier [20]. The average density of the electrostatic charge on Nylon was $1.3 \times 10^{12}/\text{cm}^2$, about twice the density determined by a metal contact on Nylon in vacuum [9] in which the contact area could not be measured accurately.

4. Conclusions

A variety of redox reactions including metal deposition, $\text{Fe}(\text{CN})_6^{3-}$ reduction and chemiluminescence follow the same pattern as previously found for PTFE/PMMA and are consistent with an electron transfer mechanism for contact electrification between two dissimilar polymers: PE/Nylon, PE/PMMA, PTFE/Nylon. That electrons transferred through rubbing can carry out conventional electron transfer reactions extends the concept of polymer electrostatic electrochemistry using a single polymer electrode without a power supply to both polyethylene and Nylon.

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