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Chemical Redox Reactions Induced by Cryptoelectrons on a PMMA Surface

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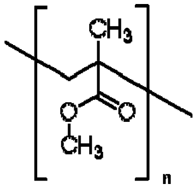
Abstract: We show that pristine PMMA can spontaneously transfer electrons to species in a liquid, thereby inducing a variety of electron transfer reactions. The electrons that are transferred we call cryptoelectrons; these have a surface density of the order of 5×10^{13} cm^{-2} and are at a considerably more negative reduction potential than the PMMA bonding electrons. For example, metal ions including Ag^+, Cu^{2+}, and Pd^{2+} were reduced and plated on a PMMA surface and $Fe(CN)_6^{3-}$ was reduced to $Fe(CN)_6^{4-}$. Moreover, protons were reduced when PMMA powder was dropped into a slightly acidic solution, resulting in a pH increase and hydrogen generation. Chemiluminescence was produced in a solution containing $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$ with the addition of PMMA powder. These results clearly demonstrate that there are available electrons in PMMA that can participate in redox reactions at a rather negative potential. We also show that contacting PMMA with Teflon depletes this electronic surface charge. However, the PMMA used for a redox reaction or contacted with Teflon that was depleted of the electronic surface charge could be recharged by contacting with a suitable reductant.

Introduction

We recently reported[1] that polytetrafluoroethylene (PTFE or Teflon), charged by contact electrification (or tribocharging) with poly(methyl methacrylate) (PMMA or Lucite) when immersed in appropriate solutions, could carry out electron transfer reactions with solution species in an analogous way to that found with metallic electrodes in electrochemistry. Following rubbing, PMMA became positively, and PTFE negatively, charged. The mechanism of contact electrification, a familiar phenomenon for thousands of years,[2,3] is still poorly understood for dielectrics like polymers, and whether this involves electron or ion transfer is an ongoing debate.[4−14] It has been difficult to distinguish between these two models with existing theory,[11] and it is possible that an “exclusive ion- or electron-transfer mechanism cannot explain contact electrification”.[13] Our earlier study provided evidence that electrons were involved in the contact electrification of polymers (and presumably other dielectrics) and that such charged PTFE could be used to carry out “single electrode” electrochemical reductions.[1] It is still not clear, however, whether the electrons transferred initially resided on PMMA and were then transferred to PTFE during rubbing as suggested by the electron transfer model or whether they were liberated in the rubbing process, e.g., by bond cleavage. The charge could not come from the HOMO molecular levels of the PMMA chains or be transferred to the LUMO molecular levels of PTFE. However, there may be other electronic states in the solid PMMA, for example, surface states, where electrons can reside with energies that are very different from these MOs. If these electronic states exist in the materials themselves and such electrons were indeed transferred from PMMA to PTFE, one should be able to find these by dipping as-received (noncontacted) PMMA into a solution containing reducible species and observing direct electron transfer reactions. We propose to call these *cryptoelectrons*, which are somewhat analogous to what is termed “excess electrons” on ionic oxide dielectrics.[15]



We report that the PMMA surface is indeed capable of inducing a variety of chemical reactions, for example, chemical analysis of the liquid composition before and after contact with PMMA provides evidence for the electron transfer hypothesis. Thus, metals such as silver, copper, and palladium were deposited on PMMA surface after brief contact with solutions

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containing their ions, Ag^+, Cu^{2+}, and Pd^{2+}. Additionally, the pH increased and hydrogen was produced when PMMA powder was dropped into a slightly acidic solution. When PMMA contacted a $Fe(CN)_6^{3-}$ solution, some of it became reduced to $Fe(CN)_6^{4-}$. Finally chemiluminescence was generated by PMMA in a mixture of $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$ solution. Details of the experiments are given below.

Experimental Section

PMMA samples consisted of 1.83 m long tubing (Regal-Plastics, Austin, Texas) and powder (M_w = 120 000, Aldrich). The inner surface of PMMA tubing was used for metal deposition and $Fe(CN)_6^{3-}$ reduction yielding reproducible results for over 15 different measurements. PMMA samples did not contain any additives, and their total amount of trace metal impurities was reported to be below 0.1 ppm. All other chemicals used were reagent grade. Milli-Q deionized water was used to prepare all solutions. The pH change was measured with a pH meter (Orion Research, model 701A). For hydrogen generation, D_2O (D, 99 atom %, Aldrich) and DCl (35 wt % in D_2O, Aldrich) were used to avoid any H_2 background. D_2 was determined with a high-resolution magnetic sector mass spectrometer (Autospec, Waters) with electron ionization at 70 eV. Deposited Cu on PMMA surface was inspected with an optical microscope (Olympus). In the $Fe(CN)_6^{3-}$ reduction to $Fe(CN)_6^{4-}$ experiment, a drop of $Fe(CN)_6^{3-}$ solution, which occupies about 5 mm of the PMMA tubing inner surface, was moved slowly from one end of the tube to the other and then back so that the solution touched the entire inner surface of the tubing. Cyclic voltammetry was carried out with a 23 μm diameter Pt ultramicroelectrode and a Model 100a electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN).

Chemiluminescence was detected with a photomultiplier tube (PMT, Hamamatsu R4220P) in a black box located inside a double-door dark room to minimize effects of stray background radiation. $Ru(bpy)_3^{2+}$ and $Na_2S_2O_8$ solutions were mixed in the dark room before each measurement to avoid any possibility of photochemical reactions. The emission spectrum was obtained with narrow band-pass filters (Optical Industries, Inc.) with each data point being an average of three to seven separate measurements. The recharging experiment was carried out in a nitrogen atmosphere glovebox (Terra Universal) with 0.3% w/w sodium amalgam that was diluted from a 5% Na amalgam (Aldrich) with Hg.

Results

Metal Plating. The PMMA surface spontaneously induced surface electron transfer reactions that were easily visualized through the metal deposition. When a fresh piece of PMMA tubing (9.53 mm o.d. and 6.35 mm i.d.) was dipped to a depth of 0.5−1 cm for about 1 s into a solution containing 1 mM Ag_2SO_4 followed by washing with deionized water, isolated spots of plated Ag about 10 μm in size were clearly seen under an optical microscope. In the same way copper and palladium could be plated on the PMMA surface from solutions of saturated $PdCl_2$ and 1 mM $CuSO_4$, respectively. The Cu spots were the easiest find because of the sharp color contrast with the PMMA. Smaller metal particles also plated on the PMMA surface. The presence of deposited metal could be amplified significantly through an electroless deposition process, in which metal is deposited in the presence of a reducing agent by catalysis by a metal center. For example, metallic Pd is known to be a good catalyst for electroless Cu deposition in the presence of formaldehyde ($H_2C{=}O$).[16] After Pd was deposited as described above, the PMMA tube was thoroughly washed and then placed into a electroless Cu plating bath containing $CuSO_4$, $KNaC_4H_4O_6$, NaOH, and $H_2C{=}O$.[16] A large amount of Cu deposited on the PMMA surface over several hours as shown in Figure 1 with the evolution of bubbles from the bath. As expected, more Cu was plated with longer times and the blue color of the plating bath disappeared overnight, indicating that most of the Cu^{2+} in the bath was consumed. Note that the enlarged image of Cu film (Figure 1) was taken at the interface between Cu and the tube inner surface rather than a Cu surface exposed to air, and the features, such as deep colored lines and spots, appearing on the image represent surface structure of the PMMA tube, since similar features were seen on a PMMA tube without Cu under an optical microscope. A control experiment in which a fresh PMMA tube without the Pd step contacted the electroless deposition bath for the same period of time under the same conditions showed no visible sign of Cu deposition. Similar electroless deposition amplification methods can probably be used with other metals, like Ag, and are very useful in detecting low levels of charge on the surfaces.

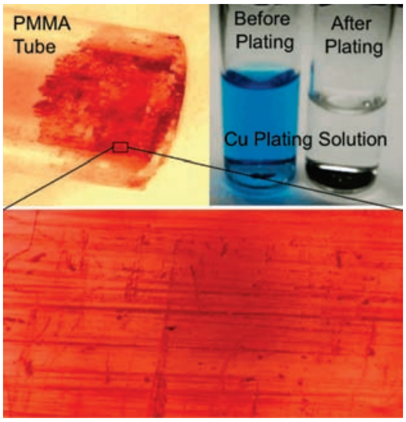

Figure 1. Copper plated on untreated PMMA surface. (Upper left) An optical image of copper film deposited on a PMMA tube inner surface. No Cu was seen on the outer surface that had been previously contacted with PTFE. (Bottom) Enlarged image of the copper film (0.8 mm × 0.6 mm) where features such as lines reflect the surface structure of the tube instead of scratches. (Upper right) Images of two glass test tubes containing copper plating solution before and after the plating. The blue color of the solution disappeared following the deposition.

These results show that *cryptoelectrons*[17] on the PMMA surface could cause the reduction of cations in the solution, leading to metal deposition with electron transfer occurring from PMMA to the liquid phase. This is analogous to a PMMA-rubbed PTFE surface that subsequently acquired electrons capable of reducing some chemical species.[1] Therefore, electron transfer from PMMA to PTFE can reasonably be identified as the charging process. To see whether a PMMA surface depleted of electrons by contact with PTFE could still cause metal deposition, a fresh PMMA tube was rubbed with PTFE tape, then dipped into a $PdCl_2$ solution briefly as before, followed by washing and immersion into an electroless Cu plating bath for different time periods. No Cu was observed on the PTFE-rubbed PMMA tube and the blue color in the solution did not fade even when the PMMA was left in the bath for over six months. In another test, a portion of the PMMA tube's outer

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(17) We define cryptoelectrons as the electrons existing in a material, whatever their source (e.g. surface states, impurities, bulk defects), with energies significantly different from those expected from molecular states (or bands) in the material.

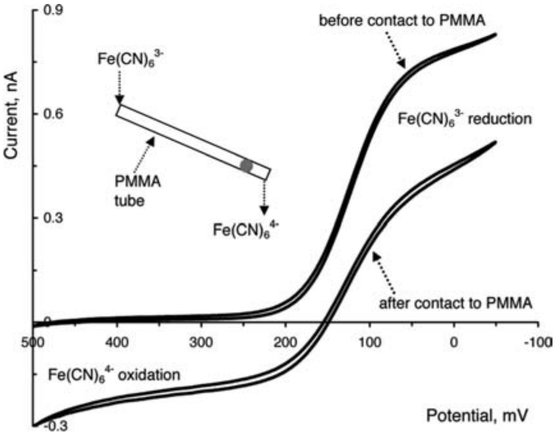

Figure 2. As-received PMMA reduced $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$. Cyclic voltammograms (10 mV/s) with a 23 μm diameter glass-encased Pt ultramicroelectrode in an aqueous solution of 0.2 mM $Fe(CN)_6^{3-}$ and 0.1 M KCl before and after the solution passed through PMMA tubes as illustrated in the inset. A similar result was obtained by dropping PMMA powder into the same solution.

surface was tightly wrapped with PTFE tape and then rolled over on a bench to induce contact electrification. In this case the outer surface became depleted and on immersion into the $PdCl_2$ solution followed by the electroless deposition bath Cu was deposited only on the inner surface that had not contacted the PTFE (Figure 1). These results clearly demonstrate that electron transfer from PMMA to PTFE causes depletion of the cryptoelectrons and reinforces the model that contact electrification between two dissimilar insulating polymers involves electronic charge transfer.[6−9]

$Fe(CN)_6^{3-}$ Reduction. To obtain a more quantitative measure of the cryptoelectron surface density on PMMA, experiments were carried out to measure the extent of reduction of an oxidized redox species in solution followed by electrochemical analysis. The change in the concentrations of the oxidized and reduced species from the initial solution to the one after contact with PMMA can be used to gauge the number of faradaic electrons transferred. When 0.2 mL of an aqueous solution containing 0.2 mM $Fe(CN)_6^{3-}$ and 0.1 M KCl was slowly passed through a 1.83 m long PMMA tube (6.35 mm i.d.), some of $Fe(CN)_6^{3-}$ was reduced to $Fe(CN)_6^{4-}$. The solution composition was determined by voltammetry. Typical cyclic voltammograms before and after the solution contacted the PMMA surface in Figure 2, show the appearance of a wave for $Fe(CN)_6^{4-}$ oxidation that did not appear in the original solution that showed only reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$. The concentration of $Fe(CN)_6^{4-}$ doubled and tripled after the same drop passed through one and two additional fresh PMMA tubes, respectively, accompanied by a proportional drop in $Fe(CN)_6^{3-}$ concentration. Following each passage, the solution volume became slightly smaller after the small volume contacted the large area (365 cm^2) of PMMA in the tubes, indicating that some liquid adhered to the tube walls. From the total amount of $Fe(CN)_6^{3-}$ consumed in the electron transfer reaction divided by the overall surface area of the PMMA tube contacted, an average electron density of 4.5×10^{13} cm^{-2} was obtained. This is essentially the same as the total electrostatic charge density on an atomically flat mica surface contacted with silica determined with a different technique.[18]

Note that when the same solution was passed through glass, Tygon (silicone), or low-density polyethylene tubes with similar or much larger surface areas compared to PMMA, no production of $Fe(CN)_6^{4-}$ was detected. To check if the reductive behavior was an inherent surface property of PMMA or the result of contamination in a particular product, other PMMA tubes of different sizes stored for various times or randomly picked from a large variety all behaved in the same way. Similarly, PMMA powder showed the same property as PMMA tubes. For example, when PMMA powder was dropped into the same solution, $Fe(CN)_6^{3-}$ was reduced to $Fe(CN)_6^{4-}$, which was clearly detected in voltammograms similar to those in Figure 2. PMMA powders newly purchased or stored in the laboratory for years showed essentially the same extent of the reduction reaction. Thus it is unlikely that contamination cause the observed reaction. Note that total metallic impurities in PMMA are below 0.1 ppm and should not make any appreciable contribution to the reaction. As expected, the yellowish color of the initial solution diminished after contact with a PMMA tube or powder and the optical absorption peak at 420 nm also decreased as a result of reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$. The calculated electron density on PMMA powder was about 8×10^{13} mg^{-1} or roughly 4×10^{13} cm^{-2} assuming an average particle diameter of 25 μm, although the particle size of the PMMA powder shows a wide size distribution up to the millimeter scale.

Hydrogen Production. Gas formation was another faradaic reaction induced by PMMA. First, when 0.25 g of PMMA powder was dropped into 2 mL of 10^{-4} M HCl, its pH increased from 4.0 to 4.3, indicating that protons were reduced. Ten separate experiments using different amounts of PMMA powder (50−515 mg) and solution (2−4 mL) whose initial pH varied from 2.5 to 4.2 yielded an average electron density in the order of 10^{14} mg^{-1} from the pH change; this is slightly higher than that obtained from $Fe(CN)_6^{3-}$ reduction. However, in the latter case some small amount of proton reduction might also have occurred and consumed some electrons. More importantly, gaseous hydrogen was generated as a result of proton reduction. In this case, D_2O was used to avoid the hydrogen background in the mass spectrometric measurement. After 150 mL of PMMA powder was dropped into 100 mL of D_2O solution containing 3 mL of DCl (35%), the glass reactor vessel was sealed with a rubber stopper and shaken vigorously so that all of the powder contacted the solution. A clear D_2 peak above the background was observed. A reference sample was prepared in the same way without the PMMA. A small He signal at *m*/*z* 4.0026 was detected from the background and a strong new signal of D_2 at *m*/*z* 4.0282 was seen after the introduction of our sample. Note that the intensity of D_2 signal was over 10 times stronger than that of He. Both intensity and location made the D_2 and He signals well distinguishable in the mass spectrum.

Chemiluminescence Generation. The generation of solution-phase chemiluminescence (CL) is more complicated, compared to the reduction reactions described above, but has the advantage of being very sensitive and easy to detect. We reported recently that electrons on PTFE produced by rubbing with PMMA were able to reduce $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$, leading to an emission of CL, which we called electrostatic CL (or ESCL).[1] If the electrons on the PTFE came from PMMA during contact as suggested by the experiments above, then electrons on PMMA by itself should also be capable of carrying out the same CL reaction based on energetic considerations. A complication is that PMMA dissolves in acetonitrile (MeCN), thus the mixture of MeCN/water (1:1, v/v) used in the ESCL experiment with

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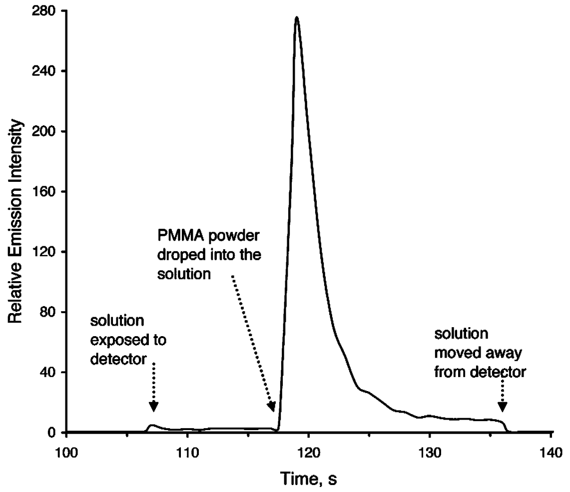

Figure 3. PMMA generated CL. Relative emission intensity as a function of time when 0.15 g of PMMA powder was introduced into 2 mL of water containing 1 mM $Ru(bpy)_3^{2+}$ and 18 mM $Na_2S_2O_8$.

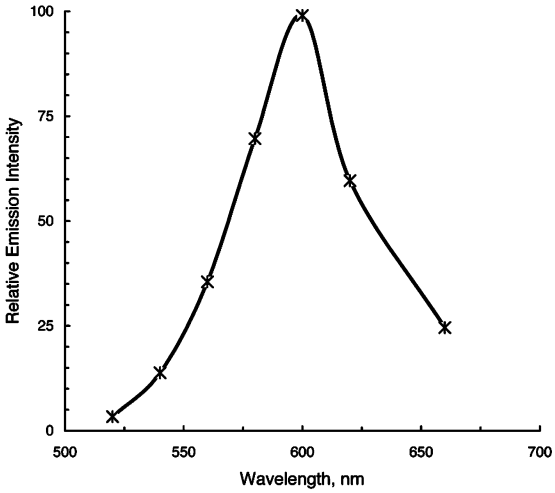

Figure 4. PMMA induced CL. Emission spectrum obtained by the introduction of 0.15 g of PMMA powder into 2 mL of water containing 1 mM $Ru(bpy)_3^{2+}$ and 18 mM $Na_2S_2O_8$.

charged PTFE could not be used. Therefore, all the CL measurements were performed in 2 mL of water containing 1 mM $Ru(bpy)_3Cl_2 \cdot 6H_2O$ and 18 mM $Na_2S_2O_8$. Generally, the emission is significantly weaker without MeCN, since reduction of the oxidized intermediates becomes more important.[19]

As shown in Figure 3, the background level was negligible when the PMT was exposed to the solution and the environment in a darkroom. However, a strong emission was seen when 150 mg of PMMA powder was introduced into the solution in an analogous way to exposure to the strong reductant, Mg powder, in a similar system.[19] As expected, the emission decreased over time as the number of available electrons diminished. The reaction mechanism should be the same as that reported earlier, e.g., on charged Teflon.[1] In this case, $Ru(bpy)_3^{2+}$ was the luminophor and $S_2O_8^{2-}$ was the coreactant, both species were reduced by electrons on the PMMA surface triggering a series of chemical reactions leading to the generation of $Ru(bpy)_3^{2+*}$ responsible for the observed emission. This mechanism was further confirmed with an emission spectrum as shown in Figure 4, which matched the spectra for $Ru(bpy)_3^{2+}$, both photoluminescence and CL.[20] Moreover, when the solution contained only one species, either $S_2O_8^{2-}$ or $Ru(bpy)_3^{2+}$, the total emission detected was at the few nanoamp level, barely above the background. This result clearly demonstrated that PMMA was able to reduce the two species just as with charged PTFE, which basically acted as a relay receiving electrons from PMMA and delivering them to the reactants to produce CL. Without contact to PMMA, PTFE could not initiate a CL reaction as described earlier.[1]

Recharging of Depleted PMMA. We described above the depletion of cryptoelectrons from PMMA, e.g., by contact of the PMMA with solution species or PTFE. An important question is whether the PMMA could then be recharged by contact with a suitable electron donor. It is known that in vacuum contact electrification, PMMA surfaces could be reversibly charged, discharged, and recharged between positive and negative in cycles by consecutive contacts with metals with different work functions,[21] and a wide distribution of electronic states on a PMMA surface were proposed.[22] Note that fully discharged PMMA could not carry out reduction reactions. For example, after a $Fe(CN)_6^{3-}$ solution passed through a fresh PMMA tube and $Fe(CN)_6^{3-}$ was reduced to $Fe(CN)_6^{4-}$ as described earlier, when the same solution passed through that tube again, the total change in $Fe(CN)_6^{4-}$ detected was below 5% of that produced in the first run. This small amount of $Fe(CN)_6^{4-}$ obtained in the second run was probably mainly leftover residual from the first run. The PMMA tube was then kept in the laboratory environment for two months. A repeat of the experiment at that time showed no $Fe(CN)_6^{4-}$ detected. After another 6 months, still no $Fe(CN)_6^{4-}$ was detected. Thus, the PMMA tube, once depleted, did not recharge on standing, e.g., from adventitious reductants in the air or from cosmic rays.

However, it should be possible to recharge the PMMA, just as in the vacuum contact electrification experiments, with a suitable reductant. In this case the depleted PMMA tube inner surface was thoroughly washed with deionized water and dried with an argon flow. Then, 0.8 mL of 0.3% w/w sodium amalgam was passed through the tube. Following this, the tube was contacted with the $Fe(CN)_6^{3-}$ solution as described earlier. The amount of $Fe(CN)_6^{4-}$produced was about 10 times higher than that with a fresh tube. This indicates that the PMMA tube was recharged and able to carry out reduction reactions again. In a separate experiment, a Na amalgam recharged PMMA tube was dipped into a saturated Pd^{2+} solution briefly, then washed and immersed into an electroless Cu plating bath as described above. Cu quickly deposited on the internal recharged surface of the tube and, in less than 20 s, could clearly be seen with the naked eye, indicating that the electron density on the recharged surface was significantly higher than that of a fresh tube consistent with the results of $Fe(CN)_6^{3-}$ reduction. As expected, Cu deposition was not seen on the outside of the tube, nor on its end that was depleted previously and never touched the amalgam for recharging.

We chose to recharge the tube with a metal amalgam because we felt it would involve a gentle contact with less physical damage to the surface structure than contact with a solid metal. However, this metal contact could also leave a trace of metal on the PMMA surface that could also produce a chemical reaction with solution species. Although we cannot exclude the possibility that small

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amounts of amalgam may be left on the surface, e.g., in small cracks and defects, we found in the plating experiment that the deposition of metal covered the whole recharged surface immersed into the plating bath and not just a few spots where possible residues of the amalgam might be located. We are currently investigating other soft approaches to surface recharging.

Discussion

All the data reported here are consistent with PMMA spontaneously transferring electrons rather than ions upon contact to other polymers or solutions that are capable of inducing a variety of electron transfer reactions. However, these studies raise the question of the nature of the charge on the polymers, e.g., the physical location of such charge and their energy level on a typical potential scale. More specifically, where do the electrons come from in the PMMA? In terms of the sites for the cryptoelectrons, general possibilities include (1) *impurities* or dopants; however, these are small (<0.1 ppm) for PMMAs used in this work and the powders, for example, should not be contaminated substantially; (2) *additives*; however, these were not intentionally introduced in the manufacture for all of the PMMA samples used here; (3) *cosmic rays*, which in principle could excite electrons to produce trapping sites; however, the total number of those energetic particles are too low to make a meaningful contribution; (4) *end groups* on the polymer chains that originate in the polymerization of monomers; however for polymers with the molecular weights studied here, such end groups would represent only about 0.1% or less; (5) *unique sites* created by special configurations of the chains or intrinsic molecular ion states formed in a charge transfer reaction;[9] however, in experiments to be reported elsewhere similar electron transfer capability was also found with a different polymer, polyamide (Nylon), suggesting that this effect is not unique to PMMA. Note that the PMMA surface and that of other polymers could be charged and discharged reversibly by contact with different metals in a vacuum;[22] and (6) s*urface states* induced by mechanical breakage of bonds. Such states should be able, depending on their nature, to accept or donate electrons to other substances upon contact. Surface damage could occur during formation of the polymer, handling, or by rubbing or contact with other surfaces.

In terms of the energy of the cryptoelectronic level in PMMA, we can examine the potentials of the various redox reactions that have been carried out (Figure 5). The most negative reaction involved the reduction of $Ru(bpy)_3^{2+}$ in the ESCL reaction, which, on the basis of measurements in acetonitrile, would have a potential of about −1 V vs NHE in water. Thus, the occupied electronic energy level on the PMMA surface is above (more negative than) this value and any chemical species with a redox potential less negative than this value could be reduced. In contact electrification experiments, PMMA is usually placed at or near the top in several triboelectric series becoming positively charged upon contact with other dielectrics and most metals, in which the amount of transferred charge increased with increasing metal work function.[23−25] On the basis of the electron transfer mechanism for contact electrification as proposed above, PMMA has the highest tendency to donate electrons to contacted materials compared to other polymers. Thus, contacting PMMA with Zn or other metals with a larger work function cause the PMMA to become positively charged. However, contacting PMMA with Mg with a small work function produced negatively charged PMMA, which is generally consistent with the energy level suggested by the solution phase experiments (Figure 5). This analysis agrees with the results that the PMMA surface could be reversibly charged, and discharged between positive and negative in repeated cycles with consecutive contacts with metals of different work functions.[22]

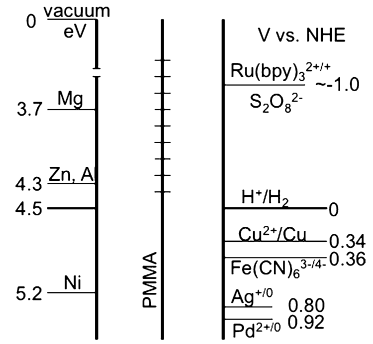

Figure 5. Proposed energy states on PMMA surface in relation to several standard redox potentials on the right and metal electron work functions on the left.

In addition to obtaining an estimate of the energy levels, analysis of reaction products of dielectrics offers an accurate way to determine the charge density on a surface. This is a difficult problem in studies of contact electrification since the true contact area between two solids cannot be precisely measured with conventional techniques. Moreover, the usual measurement of charge with an electrometer results only in the determination of the total charge (electronic and ionic), while the chemical approach determines only the electronic component. Systematic investigation of polymers and other dielectrics is currently underway to examine the generality of this behavior. Such studies will help in the development of "single electrode electrochemistry"[26] where a charged dielectric can play the role of a charged metal.

Although the available charge in PMMA from the cryptoelectrons is small, of the order of 10^{-10} mol equiv cm^{-2}, it is sufficient to cause surface modification of the material. The chemical effects would be even more important if they involved species that were catalytic. PMMA is widely used, for example in medical implants where inertness in the biological environment is important,[27,28] and it is perhaps appropriate to investigate the possibility that reactions by cryptoelectrons can be significant in its properties.

As mentioned in the Introduction, ion transfer is a competing mechanism to electron transfer in explaining contact electrification and the historical evolution of the ion transfer mechanism has been reviewed in detail.[14] If ion transfer is the mode of contact electrification, the existence of the electron transfer reactions found would then require a mechanism for transducing excess ionic charge into electronic charge, e.g., by processes caused by high surface fields. It is less clear how inherent ionic charge on PMMA could explain the properties described here.

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