VIP Mechanochemistry Very Important Paper

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Mechanically Driven Activation of Polyaniline into Its Conductive Form**

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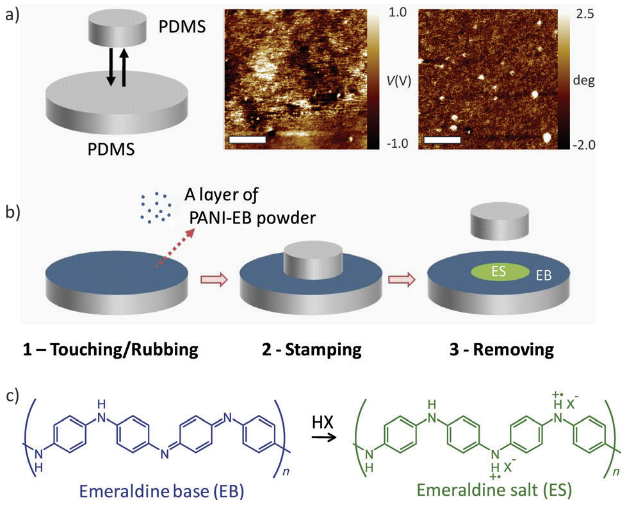
Abstract: *Mechanical treatment of polymers produces surface cations and anions which, as demonstrated here for the first time, can drive chemical reactions. In particular, it is shown that such a mechanical treatment transforms nonconductive polyaniline into its conductive form. These results provide a mechanical means of patterning conductive polymers and also coating small polymer objects with conductive polyaniline films preventing accumulation of static electricity.*

Recent research on polymer mechanochemistry[1]—which aims to break or modify chemical bonds in polymers by mechanical stimuli—has demonstrated a range of mechanically driven reactions using both synthetic[2] and biological polymers[3] and sometimes displaying new reaction pathways.[4] In one exciting example, mechanochemical treatment of polymers incorporating *trans* and *cis* isomers of a 1,2-disubstituted benzocyclobutene unit enabled electrocyclic ring opening, which, according to the Woodward–Hoffmann orbital symmetry rules,[5,6] should not be possible. In another work, 1,3-dipolar cycloreversions (reverse “click” chemistry), which are not possible under moderate thermal treatment, were made possible by mechanical input. These and several other reactions were enabled by incorporating into the polymers the so-called mechanophores,[6,7] which are functional groups designed to undergo a desired transformation.[8] Moreover, we[9] and others[10] have recently shown that it is also possible to drive mechanochemical reactions without the presence of mechanophores, using common polymers. In these systems, mechanical deformation of a polymer causes homolytic bond scission creating radicals, which then react with the surrounding solvent to yield hydrogen peroxide in quantities sufficient to synthesize nanoparticles, bleach dyes, or even turn on fluorescence visible to a naked eye.



Scheme 1. Mechanochemical transformation of the PANI emeraldine base into emeraldine salt. a) Left: scheme of the contact-charging experiment in which a PDMS piece is repeatedly pressed against another PDMS block. Middle: imaging by Kelvin force microscopy (KFM) reveals the presence of charge “mosaics” comprising both positively and negatively charged nanoscopic domains.[11a] Right: magnetic force microscopy (MFM) imaging of the same surface shows the presence of mechanoradicals (white dots) on the charged surfaces.[11d,e] Scale bars are 2 μm. b) A thin layer of PANI-EB on PDMS is activated into PANI-ES by mechanical activation. The structures of these two forms are shown in (c).

Homolytic cleavage is, of course, not the only pathway by which polymer bonds can break upon mechanical treatment. The bonds can also break heterolytically, forming surface-bound cations and anions, which form (+/−) “mosaics” (Scheme 1) of surface charges of both polarities.[11a] In a recent series of publications, we[11] and others[12] have shown how these processes relate to the accumulation of static electricity which is a technologically useful process (e.g., in xerography) but also a source of shocks, explosions, and damage to electronic equipment. However, despite early reports[13]—which, were later refuted[11d,14]—it has so far proven impossible to use these mechanochemically created surface charges in chemical applications, largely because the charges are rapidly annihilated in aqueous solutions.[15] Here we show, for the first time, that in non-aqueous but protic environments, these mechanoions can drive chemical reactions at material interfaces. In particular, we demonstrate that they can transform the non-conductive form of polyaniline (PANI) into its conductive salt. With spatially localized activation, our mechanical treatment allows for imprinting conductive patterns into otherwise non-conductive, thin PANI films. We also show how the mechanical treatment/agitation of small polymeric particles can coat them in a conductive PANI thereby preventing their electrostatic charging—this result can be practically important for limiting unwanted charging of powders as well as mechanically

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actuated polymer-based microcomponents (e.g., gears of micromachines[16]).

PANI can exist in various forms (see Figure S1 in the Supporting Information) including non-conductive emeraldine base (EB) and its protonated form, the conductive emeraldine salt (ES; Scheme 1 c). The conductivity of the latter depends on the degree of doping and can approach conductivity of metals.[17] The ability to switch between EB and ES forms and the polymer's high stability have enabled the use of polyaniline in electrode coatings, sensors, and batteries. In these applications, EB is converted to ES by adding salts (protonated, HX; see Scheme 1 c). In our approach, the salt is replaced by mechanically generated ions at a polymer surface.

In our experiments we used macroscopic pieces of poly(dimethylsiloxane, PDMS) elastomer. Typically, a PDMS substrate was covered with EB wetted with a small amount of ethanol, methanol, or 2-fluorophenol. AFM measurements evidenced that the film thus formed was several micrometers thick. As shown in Figure 1 a, the color of this film was dark blue and remained such for days. When, however, a PDMS block/"stamp" contact charged and mechanically activated by touching/rubbing was placed on the film and allowed to rest there for several minutes (for 2-fluorophenol) or several tens of minutes to hours (for ethanol or methanol), the area below the stamp gradually changed color from blue to green, suggesting a change from EB to ES. This change was indeed confirmed by several spectroscopic techniques summarized in Figure 1 b–d: UV/Vis, Attenuated Total Reflectance Fourier-Transform Infrared (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS). Most importantly, after solvent drying, the green, stamped regions had surface conductivity of 2.84×10^{-9} S, which is ca. eight orders of magnitude higher than the 5.42×10^{-17} S conductivity of the blue, non-stamped regions (for further experimental details, see the Supporting Information and also Ref. [18]).

By using PDMS stamps with features embossed in bas-relief, the procedure could be extended to films with conductive ES micropatterns. For example, Figure 2 a,b show light and FTIR microscopy (total reflectance) images of an array of 100 μm thin lines printed in this way. In Figure 2 c,d, the conductive nature of the patterned regions is evidenced by Kelvin force microscopy, whereby ES regions have average surface potentials ca. −1.06 V vs. 1.08 V for non-conductive regions. We note that the ES and EB regions did not differ in terms of AFM height profiles (Figure 2 e).

We make three further observations regarding the ES-to-EB transition: First, it did not occur solely due to the contact with PDMS. In regions where PANI was resting on PDMS but was not pressed by the contact-charged PDMS stamp, there was no EB-to-ES transition, even after long times. In other words, mechanical compression by contact-electrified stamps is a sine qua non for the phenomenon to be observed. Second, the conversion to ES occurred when methanol or ethanol were used as solvents but not with water, acetonitrile, or aprotic organic solvents (Figure S3). In other words, the phenomenon requires the use of polar protic solvents. Third, transformation of EB to ES PANI was observed using polymers other than PDMS. This is illustrated in Figure 3 which summarizes a series of experiments in which millimeter-sized polymer beads of various polymers (see also Figure S4 for a complete list) were shaken in glass vials or polymer containers. Without PANI-EB present, the beads charged readily (either positively or negatively depending on the material[11c] and with typical charge magnitudes of 100–200 pC per bead), repelled one another, and also stuck to the walls of the vial/container. When, however, few milligrams of PANI-EB in a drop of ethanol were added, the beads charged much less (typically, ca. 10 pC per bead) and clumped at the bottom of the vial. This effect was observed over many shaking cycles, even when ethanol was completely evaporated—that is, the beads became permanently antistatic. (No permanent reduction in bead charging was observed when only methanol, without EB, was used and evaporated.) Importantly, this drastic change in the beads' charging properties reflected a molecular process in which PANI-EB transformed into the conductive PANI-ES on the beads'

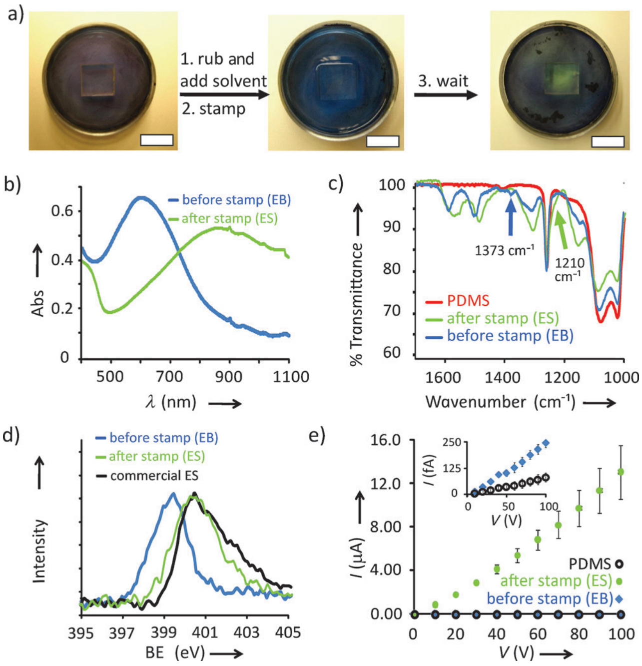

Figure 1. Mechanically driven formation of conductive emeraldine salt (ES) of PANI. a) Upon contact with contact-charged PDMS, the color of EB film gradually changes to green (ES; scale bar = 1 cm, see also Figure S3). The EB-to-ES transformation is evidenced by various spectroscopic analyses before and after stamping: b) UV/Vis absorption peak of EB at 590 nm disappears and that of ES at 850 nm appears; c) characteristic ATR-FTIR band of ES at 1210 cm^{-1} due to C−N$^{+\cdot}$ stretching (indicated by the green arrow) appears after stamping, and that of EB (C−N aromatic stretching) at 1373 cm^{-1}, blue arrow) decreases in intensity (see Figure S2 for enlarged view); d) High resolution XPS of the N 1s region before and after stamping shows the appearance of a peak centered at 400.5 eV (=NH^{+}), which is present only in ES. The peak at 399.4 eV (=N- and =NH), which is present only in EB disappears. The black curve gives a spectrum of a commercial ES (from Aldrich, cat. # 428329). e) *I–V* curves of the stamped and unstamped regions show a marked difference in conductivity—by eight orders of magnitude (see the Supporting Information for details). The inset magnifies the conductivity of PDMS and EB—note the *y* scale: fA vs. μA in the main plot.

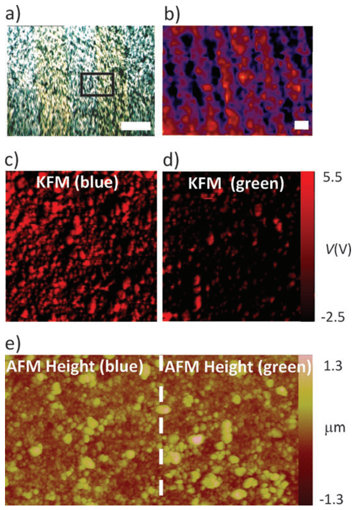

Figure 2. Mechanostamping of conductive ES patterns into thin films of non-conductive EB. a) An optical and b) total reflectance FTIR (over the whole wavelength range 3500–600 cm^{-1}) images of an array of 100 µm wide lines. Scale bars = 100 µm. c,d) KFM potential maps of the non-conductive (blue) and conductive stripes (green) taken over the black-box region in (a); size 36 µm × 72 µm. e) AFM height image over the same region.

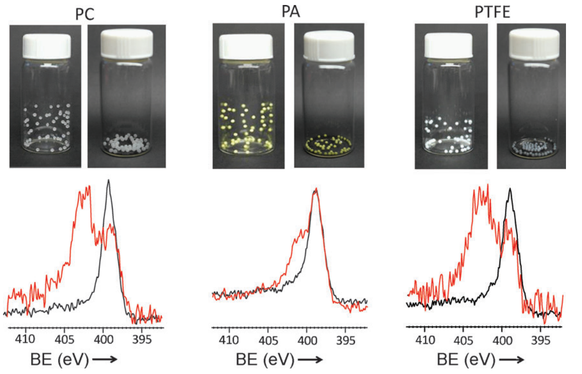

Figure 3. Mechanically activated formation of ES on various polymeric beads shaken in glass vials. From left to right, polycarbonate (PC), polyacetate (PA), and polytetrafluoroethylene (PTFE) beads (for more examples, see Figure S4). The left images in each pair show vials in which only beads and no EB/ethanol were placed and vigorously shaken for 10 min. The right images in each pair are for the beads also shaken for 10 min but with EB/ethanol added. The bottom row compares the HIRES XPS spectra before and after shaking. Note the emergence of the N 1s peak (400.5–403.0 eV (=NH^{+}), red lines) after shaking. This peak is characteristic of the ES form but is absent in the spectra of EB (399.4 eV (=N- and =NH), black lines) before shaking.

surfaces. This was confirmed by the XPS spectra of the beads taken after shaking whereby the emergence of the N 1s peak (400.5–403.0 eV (=NH$^{+\cdot}$)) is indicative of ES formation. We emphasize that this peak was not observed when EB/ethanol was introduced but the beads were not shaken, indicating that, as in the studies of PDMS described earlier, input of mechanical energy is essential for the EB-to-ES transformation. Taken together, these observations mean that it is the mechanically induced heterolytic cleavage of bonds at the bead surfaces that "activates" them—irrespective of specific polymer the beads are made of—toward the formation of (conductive) ES "surface coatings" which facilitate charge dissipation and prevent the build-up of static electricity on the beads.

Based on the above characteristics, a mechanism that can rationalize the mechanically driven EB-to-ES transformation can be proposed as in Figure 4a (here, discussed for our model system of PDMS but likely similar in other polymers since all of them exhibit heterolytic bond cleavage upon mechanical deformation[11a]). When PDMS is mechanically activated, the heterolytic cleavage of the chains gives chains terminated in -$(CH_3)_2SiO^-$ and -$(CH_3)_2Si^+$ species. This is in line with the high-resolution XPS analysis of PDMS before and after activation (Figure 4c) whereby the O 1s peak for unbroken chains (i.e., -$Si(CH_3)_2O$-) shifts to a lower energy, by 0.2 eV, upon bond rupture and formation of -$(CH_3)_2SiO^-$ anions. The $\equiv Si^+$ cations add ethanol or methanol (introduced together with the EB salt) to form -$(CH_3)_2Si$-ORH^+, where R is ethyl or methyl (formation of solvent complexes of silylium ion, $\equiv Si^+$ is known[19]). This complex can now donate its acidic proton to EB forming $NH^{+\cdot}$ groups and resulting in aromatization (Figure 4a) and increased conductivity of the ES

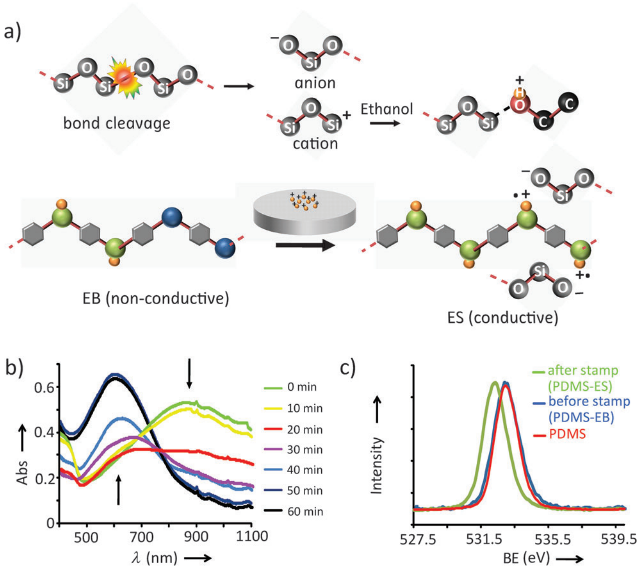

Figure 4. Proposed mechanism of the EB-to-ES transformation driven by mechanical activation of a polymer (here, PDMS). a) Upon activation, PDMS chains near the surface break heterolytically forming -$(CH_3)_2SiO^-$ and -$(CH_3)_2Si^+$ species. Cations are complexed with ethanol (or methanol) to form -$(CH_3)_2Si$-ORH^+ which facilitates the proton donation from this complex to EB chains. After protonation, charge neutrality of the formed ES is ensured by the surrounding SiO^- ends of the broken chains. Methyl groups on PDMS are omitted for clarity. b) Time-lapse UV/Vis spectra of a PDMS-ES piece immersed in water demonstrate that the process can be reversed (i.e., UV/Vis absorption peak of EB at 590 nm reappears and that of ES at 850 nm disappears). Water converts the "mechanoions" to neutral species. c) High-resolution XPS spectra of the O 1s region before and after PDMS activation; the 0.2 eV shift to lower energies is indicative of the formation of SiO^- anions.

form. Note that 1) the positively charged species -(CH$_3$)$_2$Si-ORH$^+$ are charge-balanced by the proximal -(CH$_3$)$_2$SiO$^-$ anions, thus ensuring overall electroneutrality, and 2) contrary to the historical belief that bond rupture in contact electrification of polymers is a very infrequent event[20] (charging one in about 10000 groups present on the surface), recent work demonstrated that at least 1 of 100 surface groups undergoes heterolytic bond cleavage resulting in local charge densities in μC cm^{-2} (corresponding to ca. 10^{12} charged groups per cm^2; see Ref. [11a] for further discussion). This relatively high concentration explains why the changes in the conductivity of PANI we observe are substantial.

Regarding the role of the solvent (see also Figure S3), we observe that neither methanol nor ethanol itself can donate a proton directly to EB—indeed, suspensions of EB in these protic polar solvents remain stable for weeks with no change to ES. This means that an intermediate step of forming -(CH$_3$)$_2$Si-ORH$^+$ through mechanically induced bond breaking is essential for the subsequent proton transfer to PANI. Importantly, the presence of ethanol on the mechanically activated PDMS surface was verified experimentally by XPS: we have studied a PDMS/2,2,2-trifluoroethanol (CF$_3$CH$_2$OH) system which gave a small F1s peak around 690 eV (see Figure S6 and Figure S5 for pH measurements corroborating the proposed role of ethanol as a proton source). We also note that organic solvents more acidic than ethanol, such as 2-fluorophenol (pK_a = 8.73; Figure S7) were effective in assisting mechanochemical transformation of EB to ES, further supporting the proposed protonation of EB by the solvent-mechanoion complex.

As is often the case, water acts differently than alcohols, as it converts -(CH$_3$)$_2$Si$^+$ and -(CH$_3$)$_2$SiO$^-$ into -(CH$_3$)$_2$SiOH by hydrolysis[21] thus annihilating the surface charges.[15] In fact, when water is added to the prepared conductive PDMS-ES pieces, it protonates the -(CH$_3$)$_2$SiO$^-$ ions and reacts with -(CH$_3$)$_2$Si$^+$ to form -(CH$_3$)$_2$SiOH (Figure 4b).

Looking forward, we feel the present work has both fundamental and practical ramifications. In the former context, our results are the first chemical demonstration of mechanically generated anions and cations driving a chemical reaction. Although formation of mechanoanions[22a–d] and mechanocations[10] on mechanically fractured polymers was chemically proven at 77 K and under vacuum, there is no other method to simultaneously detect these species under ambient conditions. KFM maps such as those in Scheme 1 and in our previous works[11] evidence charge domains but do not per se show the chemical nature of the charged species and their relation to bond-breaking. Also, doping of polyaniline, which can only be done by salts (ions), proves unequivocally that the charged species on mechanically treated polymers are not electrons, or protons, or the putative "cryptospecies"[13b]—instead, they are ions.

Naturally, the current approach could be extended to other polymers—this possibility is given credence by the preliminary experiments we describe in Figure S8 whereby EDOT was converted and mechanically activated into ion-doped PEDOT polymer (used as a conductive polymer in photographic films, touch-screens, capacitors, and anti-static materials).

Perhaps the most impactful application of the present work will be the activation of EB into ES on small, mechanically agitated polymeric objects (Figure 3). Our simple shake-and-coat protocol to reduce charging should be of interest to precision manufacturing industry where small polymeric pieces accumulating static electricity readily clump together and are often hard to position and/or manipulate (e.g., in watch industry which nowadays often relies on polymeric parts).

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