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Martin Tress et al.
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same degree retains static electricity and paper sheds for more than a day (Fig. 3C).

Arguably, the most impactful application of the charge-radical regulation is illustrated in Fig. 3D. There, PS doped with DPPH is used to protect electronic components from failure due to electrostatic discharge, which is a ubiquitous problem in the microelectronics industry, damaging semiconductor-based devices (either upon direct contact or arcing) and resulting in losses currently measured in billions of dollars per year (3). The circuit shown comprises n-channel junction field-effect transistors (JFETs) (2N 4861A, Soliton Devices) connected serially to light-emitting diodes (LEDs). When exposed to consecutive positive/negative cycles of electrostatic/dielectric stresses, the LEDs connected to undamaged transistors go cyclically “on” and “off.” If, however, the accumulation of static electricity on the gate damages the transistor, its associated LED should always be “on” (23). In our circuit, we used four types of transistors: #1 was an intact JFET; #2 was a JFET with the metal shield removed but with the gate covered with a ~200- to 500-μm-thick layer of PS doped with 1.8% w/w DPPH; #3 had the shield removed, but the gate was covered with pure PS; and #4 had the shield removed with no polymer on the gate. As shown in Fig. 3D, the ion gun causes the damage of all transistors but #2, for which DPPH helps scavenge the radicals produced by corona discharge, thus destabilizing the accumulated charges and preventing the build-up of static electricity to damaging levels (see fig. S11 and, for additional experiments, fig. S12). Because similar effects are observed with other types of polymers and scavengers we studied—notably, the edible and biocompatible vitamin E—our results can herald a general, technically straightforward and environmentally “green” way of protecting electronics of various types from the untoward effects of static electricity.

### References and Notes

16. L. B. Loeb, Electrical Coronas (Univ. of California, Berkeley, 1965).
17. Materials and methods are available as supplementary materials on Science Online.

### Glassy Dynamics in Condensed Isolated Polymer Chains

**Martin Tress,1 Emmanuel U. Mapesa,1 Wilhelm Kossack,1 Wycliffe K. Kipnusu,1 Manfred Reiche,4 Friedrich Kremer1**

In the course of miniaturization down to the nanometer scale, much remains unknown concerning how and to what extent the properties of materials are changed. To learn more about the dynamics of condensed isolated polymer chains, we used broadband dielectric spectroscopy and a capacitor with nanostructured electrodes separated by 35 nanometers. We measured the dynamic glass transition of poly(2-vinylpyridine) and found it to be bulk-like; only segments closer than 0.5 nanometer to the substrate were weakly slowed. Our approach paves the way for numerous experiments on the dynamics of isolated molecules.

Many applications in modern technology (e.g., photoreists, sensors for drug delivery, batteries, etc.) rely on materials that are subject to confinement and/or finite size effects. How and to what extent the properties of a material—especially a polymer—are changed...
under such conditions is a topic of intense debate (1–8). The ultimate objective is isolated molecules and their properties in comparison to the bulk. Various techniques are available to deposit (9, 10) and to manipulate (11) single low-molecular weight polymeric molecules on a surface and to characterize (12–16) their structure and conformation. In contrast, little is known about the dynamics in such systems as measured in a broad spectral range and at widely varying temperatures. Investigations have been limited to nanometer thin films of low molecular weight (17) and polymeric (1–7, 18) layers. Here, we report an approach (8) that enables the study of both conformation and dynamics of isolated polymer coils by combining atomic force microscopy (AFM) and broadband dielectric spectroscopy (BDS).

Using nanostructured electrode arrangements (19) (Fig. 1, A to C), we assembled a capacitor with a separation of 35 nm and isolated polymer coils deposited on one of the electrodes (Fig. 1D and supplementary materials). As a model system, we used poly(2-vinylpyridine) (P2VP), which is known to establish attractive interactions with the native silica on the silicon electrodes. Consideration of the bulk density and the number-averaged molecular weight enables us to estimate the average volume of a single chain, V_chain (supplementary materials). A comparison with the coils shown in Fig. 1E (close-up and profile) reveals volumes close to 7.8 V_chain (left profile, V ~ 1.8 V_chain; right profile, V ~ 0.4 V_chain). In view of the molecular weight distribution, this diversity of volumes is expected for single chains. The average coil volume corresponds to 0.9 V_chain, hence on average, there is only one (isolated) P2VP polymer chain per nanodroplet. In the semi-isolated case, we detected volumes equal to 7.8 V_chain and 5.1 V_chain for two different molecular weights (Table 1).

In BDS measurements, the dynamic glass transition is associated with the so-called α-relaxation (20). Our measurements show that this relaxation process is still present in samples containing only isolated condensed polymer chains (Fig. 2). Because they, and similarly semi-isolated agglomerates consisting of ~5 to 10 chains, have a large surface-volume ratio, one would expect notable interactions with the supporting substrate, as is the case for thin polymer layers, for which the literature predicts and reports enhancement or reduction (1–3) of the glassy dynamics (depending on the type of polymer-substrate interaction). Such changes would result in a shift of the α-relaxation with respect to the bulk. Although similar scenarios have been reported (1–3), the results are contradictory. Several studies found no alteration of the glassy dynamics in thin polymer layers in the linear response regime (4–7). In our measurements, the maximum position of the α-relaxation in semi-isolated and isolated condensed polymer chains shows (i) a Vogel-Fulcher-Tammann (VFT) temperature dependence (see supplementary materials), which is the characteristic signature of the dynamic glass transition, and (ii) no deviations from the bulk within the experimental uncertainty (Fig. 3). A close look at the α-relaxation peak reveals a broadening in the case of polymer coils relative to the bulk; this is most pronounced in the case of isolated chains (Fig. 2). The dielectric loss spectra normalized with respect to the peak maximum show that this broadening happens almost exclusively on the low-frequency side (Fig. 3, inset). The observed broadening of the α-relaxation peak accounts for 12% of the total

Fig. 1. Sample arrangement required to study condensed (semi-)isolated polymer coils by means of BDS and their topography. (A) Two highly doped, conductive silicon electrodes (measures for bottom and top electrode: 4 × 10 mm² and 1 × 1 mm², respectively) are assembled to build the sample capacitor. (B) The top electrode has an array of strongly insulating silica nanostructures as spacers on its lower side, which cover about 1% of the surface area. (C) Spacers of a height of 35 nm, as shown in this AFM image, were used to conduct measurements of condensed isolated P2VP chains. (D) AFM scans of the same sample studied by BDS were taken to analyze the volume of the polymer coils. (E) Averaged profiles of two coils from D (shown in the close-ups) demonstrate the variation in height, radius, and volume among the coils. The error bars correspond to the standard deviation of the four height profiles as indicated by the colored lines (which are the basis of the averaged profiles); this illustrates a high degree of symmetry within each coil. The percent values give the volume proportion of the layer of chain segments in direct contact with the solid substrate.

Table 1. Specification of the polymers used and mean coil volume analysis of the condensed polymer coils of the samples that have successfully been measured by BDS. The molecular weight and number-average molecular weight (M_n and M_w, respectively) as well as the polydispersity index (PDI) were determined by gel permeation chromatography.

<table>
<thead>
<tr>
<th>Polymer property</th>
<th>Polymer 1 values</th>
<th>Polymer 2 values</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_w (kg/mol)</td>
<td>1020</td>
<td>2250</td>
</tr>
<tr>
<td>M_n (kg/mol)</td>
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<td>1510</td>
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<tr>
<td>PDI</td>
<td>1.33</td>
<td>1.49</td>
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<tr>
<td>T_g (K) by DSC</td>
<td>371 (+1)</td>
<td>375 (+1)</td>
</tr>
<tr>
<td>V_chain (nm³)</td>
<td>1142</td>
<td>2251</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Chain distribution</th>
<th>Semi-isolated</th>
<th>Semi-isolated</th>
<th>Isolated</th>
</tr>
</thead>
<tbody>
<tr>
<td>V_coil (nm³) ± SE</td>
<td>8864 (±2500)</td>
<td>11,564 (±3500)</td>
<td>2033 (±500)</td>
</tr>
<tr>
<td>V_coil / V_chain ± SE</td>
<td>7.8 (±2.2)</td>
<td>5.1 (±1.6)</td>
<td>0.9 (±0.2)</td>
</tr>
<tr>
<td>Coil density (μm⁻²)</td>
<td>37.5</td>
<td>10.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Area analyzed (μm²)</td>
<td>8</td>
<td>8</td>
<td>13.75</td>
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<tr>
<td>Number of analyzed coils</td>
<td>300</td>
<td>80</td>
<td>55</td>
</tr>
</tbody>
</table>

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To connect this insight concerning the dynamics to the interfacial topology of the (semi-)isolated polymer coils, the height distribution of the volume is deduced from AFM images. Because two or three monomer segments constitute the structural unit underlying glassy dynamics (21), this volume is subdivided into layers, each with a thickness of ~0.4 nm, approximating the width of a P2VP chain (16). The most reasonable conjecture is that the segments closest to the solid substrate (Fig. 1E) account for the slower relaxation modes in the case of attractive interactions, as present in the investigated system. The volume fraction of the first layer of segments in direct contact with the solid substrate accounts for 25 to 30% and 15 to 20% of the total coil volume in the cases of isolated and semi-isolated chains, respectively. These proportions are considerably larger than the fraction of slower relaxation modes (~12%), indicating that not all segments that are in direct vicinity of the solid interface contribute to the detected slower dynamics.

Examination of the interactions at the P2VP-silica interface using infrared (IR) spectroscopy revealed that ~50% of the terminal hydroxyl (OH) groups of the silica surface interact with the pyridine ring of the P2VP segments (fig. S3 and supplementary materials). Because the size of a segment is similar to the distance between the OH groups (22), we conclude that only about half of the segments in the first layer at the interface are subject to hydrogen bonding. Hence, the amount of broadening found in the BDS data is in accord with the volume fraction of the first segment layer in the polymer coils. However, it remains unknown whether the interacting proportion of segments exhibits the detected slower dynamics, or whether they are completely immobilized and the slower relaxations have to be assigned to those segments neighboring the pinned ones. The latter scenario is suggested by other studies on the adsorption of polymer chains at solid interfaces (23).

A cooperative process such as the dynamic glass transition (24) can take place even in condensed isolated polymer chains because the length scale on which this fluctuation takes place—which typically corresponds to two or three polymer segments (21)—is much smaller than the extension of the coil as a whole (Fig. 3, lower left).
Lewis Acidity of Organofluorophosphonium Salts: Hydrodefluorination by a Saturated Acceptor

Christopher B. Caputo, Lindsay J. Hounjet, Roman Dobrovetsky, Douglas W. Stephan*

Phosphorus(III) Lewis bases are widely exploited as ligands in transition metal coordination and organometallic chemistry; however, the electrophilic nature of phosphorus centers has garnered lesser attention. P(III) phosphonium cations have been explored by Gudat, Burbard, and Ragona, among others (1, 2). In recent computational work, phosphonium cations have been predicted to exhibit fluorophilicities comparable to those of known neutral Lewis acids, but experimentally weaker than those of electrophilic cations such as [Me3Si]+ (Me, methyl) (3). Although P(V) Lewis acids have been explored less (4), it is noteworthy that the P(V) centers in ylide reagents account for the classic Wittig reactions with ketones (5). Similarly, phosphonium cations have been used to facilitate additions to polar unsaturates (6) and Diels-Alder reactions (7). In related efforts, Hudnall et al. have also recently exploited the acceptor capabilities of phosphonium cations, in tandem with boranes, to develop a series of fluoride ion sensors (8).

Here, we report the Lewis acidity and catalytic application of electronically saturated phosphorus-centered electrophilic acceptors. Organofluorophosphonium salts of the formula [(C6F5)3-P-PhPF][B(C6F5)4] (x = 0 or 1; Ph, phenyl) are shown to form adducts with neutral Lewis bases and to react rapidly with fluoroalkanes to produce difluorophosphoranes. In the presence of hydrosilanes, the cation [(C6F5)3-PF]4+ is shown to catalyze the hydrodefluorination of fluoroalkanes, affording alkane and fluorosilane. The mechanism demonstrates the impressive fluoride ion affinity of this highly electron-deficient phosphonium center.

References and Notes

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