Investigation of H_2SO_4-doped, ring-deuterated poly(*p*-phenylene vinylene) using solid state ^2H quadrupole echo n.m.r. spectroscopy

Jeffrey H. Simpson, David M. Rice and Frank E. Karasz*
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA
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Ring-deuterated poly(*p*-phenylene vinylene) has been doped with concentrated sulphuric acid and examined with ^2H quadrupole echo nuclear magnetic resonance spectroscopy. Doping is observed to change the relative population of fast *versus* slow flipping *p*-phenylene rings. This relationship has been investigated over a range of temperatures. Modelling this system as a two-site chemical exchange shows that the change in the relative populations of fast *versus* slow 'flippers' corresponds to an increase in the activation energy for the 180° ring flip. The width of the distribution of flip rates is also observed to increase upon doping. At elevated temperatures the samples studied undergo a significant loss of mass which corresponds to a loss of dopant. The chemistry of this process is examined.

(Keywords: poly(*p*-phenylene vinylene); spectroscopy; doping)

INTRODUCTION

Recently, much attention has been focused on polymers containing fully conjugated backbones[1–3]. These materials can be made electrically conductive when treated with appropriate chemical reagents or when electrochemically doped[4–7] and have also been found to possess non-linear optical properties[8] in their untreated forms. Poly(*p*-phenylene vinylene) (PPV) can be synthesized via a water-soluble precursor polymer route[9,10] rendering it easily processible. The PPV precursor polymer can routinely be drawn to 10 times its original length upon heating under tension[5,11] because the elimination of volatile by-products from the sample serves to plasticize the polymer chains. After complete thermal conversion, a sample of PPV is air stable indefinitely.

In its pristine state, PPV is an insulator, while upon the addition or removal of electrons from the chains a sample of PPV becomes conductive. Ordinarily, the increase in the electrical conductivity of PPV is brought about by oxidation with AsF_5, SbF_5 or H_2SO_4 (refs 4–6, respectively). Electrochemical oxidation can also be accomplished with the ClO_4^- ion[7]. Using these techniques, conductivities on the order of 1000 S cm^{-1} can be obtained.

PPV must be oxidized to obtain good conduction, an indicator of the imperfections inherent in its structure. Band theory predicts that a large, single crystal of PPV would have very low resistance to conduction along the crystallographic *c* axis. There would exist a virtual continuum of electronic states due to the extended conjugation of the polymer. Shortening the conjugation length of the PPV chain will increase the band gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital, requiring the addition or removal of electrons to render the material conductive.

Any defect that disrupts the ability of the p_z orbitals of the backbone to overlap should degrade the conductivity of the sample. Out-of-plane ring motion has been observed in pristine PPV, including a 180° flipping motion of the *p*-phenylene rings about the backbone single bonds[12,13]. Ring flips have been studied with solid state ^2H quadrupole echo nuclear magnetic resonance (n.m.r.) spectroscopy.

Removal of electrons from the conjugated structure of PPV should mix the single and double bond character of the backbone bonds. This can be seen by comparison of the resonance structures for a section of a neutral PPV chain and with one electron removed (*Figure 1a*). The presence of a formal positive charge introduces many resonance structures with double bonds in place of the backbone single bonds. Additional double bond character should increase the activation energy of the ring flip motion of PPV and result in fewer rapidly moving rings.

In this paper we show this effect through characterization of the ring flip behaviour of H_2SO_4-doped, ring-deuterated PPV (PPV-d_4) by means of solid state ^2H quadrupole echo n.m.r. spectroscopy. Additional information about the chemistry of the doping process and the importance of thermal history will also be presented.

EXPERIMENTAL

Samples of PPV-d_4 (*Figure 1a*) were prepared from perdeutero-α,α'-dichloro-*p*-xylene. This synthesis has been described in detail elsewhere[14]. After reaction with tetrahydrothiophene to form the sulphonium salt, strong base was added to form the precursor polymer. During the

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* To whom correspondence should be addressed

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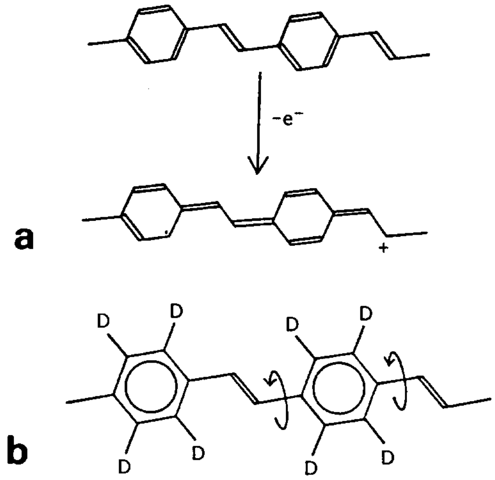

Figure 1 (a) An illustration of how doping can increase the double bond character of the backbone single bonds. (b) A section of PPV chain with its ring protons replaced with deuterons. Arrows indicate the bonds about which the ring rotates

polymerization the deuterons not located on the ring exchanged with protons from the aqueous solvent solution leaving deuterons only on the ring sites. Two to three per cent solutions of the precursor polymer solution were degassed and poured onto a poly(methyl methacrylate) sheet. Dry nitrogen gas was passed over the solutions for ~24 h to form clear, yellowish films with typical thicknesses of 30–40 μm. Films of the precursor polymer were annealed at 300°C for 4 h under vacuum to attain complete conversion to PPV. Sulphuric acid doping was accomplished by immersing a sample of PPV in 98% H_2SO_4 for 4 h. After removing the films from the acid, they were washed with dry acetonitrile to remove excess acid and placed in an evacuated chamber overnight to remove any residual volatiles.

Mass uptake of the samples was determined by obtaining the mass of the film in a tared, sealed container before and after doping. After doping, the sample was kept in an inert (argon) atmosphere to prevent reaction with atmospheric oxygen or water vapour.

Conductivity measurements were carried out using the standard four contact geometry[4] and a Keithley autoranging multimeter. The doped films were affixed to the contact using low resistance graphite cement (E.F. Fullam no. 14820).

^2H quadrupole echo n.m.r. spectra[15] were acquired at 46 MHz on a Bruker MSL-300 n.m.r. spectrometer. Samples were sealed under vacuum in 5 mm n.m.r. tubes (Wilmad 506-PP) cut to a length of 3 cm. The 90° pulses were 2.3 μs long with intervals of 20 μs to allow for transient decay. Acquisition of the free induction decay (f.i.d.) was begun ~3.2 μs prior to the echo maximum; the accumulated average of all the scans was later left-shifted to the echo maximum before Fourier transformation. The pulse sequence employed an eight-member phase cycle to minimize instrumental artifacts. A spectral width of 2.5 MHz was used. For a typical acquisition, 1024 scans of 2048 points were averaged together. Prior to Fourier transformation, the f.i.d.s were zero padded to a total size of 4096 points and exponentially multiplied with a Lorentzian line broadening of 4 kHz. Minimum recycle times were determined using progressive saturation methods[16] and were <60 s at 298 K and <2 s at 498 K.

^{13}C cross polarization/magic angle spinning (CP/MAS) spectra[17] were acquired at 75 MHz on a Bruker MSL-300 n.m.r. spectrometer. Samples were either ground to a powder with a SPEX freezer mill or were cut into small pieces to facilitate even rotor packing. Spinning rates of 4 kHz were typically used. ^1H 90° pulse widths were 3.5 μs and contact times were 1 ms. The f.i.d. was acquired with a spectral width of 20 kHz with quadrature detection, and 10^4 scans were averaged to obtain a good signal-to-noise ratio. The f.i.d. was 2048 points long and was zero padded to a total size of 4096 points. The recycle time between scans was 3 s.

The ring flip motion of the *p*-phenylene group of PPV-d_4 was modelled as a two-site exchange. The inclinations of the two sites with respect to the crystallographic *c* axis were taken as 67.7 and 52.3° in accordance with earlier work[18]. Simulation of the ^2H quadrupole echo n.m.r. spectra was carried out with a home-written FORTRAN program capable of modelling two-site exchange using the methods of Wittebort *et al.*[19]. The simulated spectra appearing in the figures were modelled as a weighted sum of individual spectra of varying flip rates. The width of the distribution of flip rates for the observed spectra was determined by comparing the change in normalized quadrupole echo height with the calculated echo height for various sums of simulated spectra[20]. In all cases the distribution of the logarithm of flip rates was modelled as Gaussian[21].

Elemental analysis of doped PPV-d_4 samples was carried out at the University of Massachusetts Elemental Analysis Laboratory.

RESULTS

Figure 2a shows a solid state ^2H quadrupole echo n.m.r. spectrum of a film of H_2SO_4-doped PPV-d_4 obtained at ambient temperature and *Figure 2b* shows a spectrum of a film of pristine PPV-d_4. It has been shown that the spectrum of pristine PPV results from two components[13]. The outer 'Pake' doublet[22] splitting results from static phenylene rings, compared to the ^2H quadrupole coupling constant ($\leqslant 10^6$ s^{-1}). The central splitting results from the peaks of a ring flip spectrum which results from phenylene rings which undergo fast 180° jumps ($\geqslant 10^6$ s^{-1}) about the 1,4-axis of the ring. For the doped PPV-d_4 sample, the ring flip component of the spectrum is attenuated. This attenuation has been attributed to a slowing of the flip rates resulting from an increase in the activation energy for the jump process. This increase might be caused by intermolecular effects such as steric hindrance from nearby dopant counterions or by an electronic effect such as the increase in the double bond character of the phenylene-vinylene single bonds resulting from the delocalization of the positive charge of the oxidized PPV. The barrier to rotation about the single bonds of *trans*-stilbene is estimated[23] to be 20–40 kJ mol^{-1}. The barrier for *cis–trans* isomerization[24] of a vinylene group approaches 250 kJ mol^{-1}. An increase in the double bond character of the phenylene-vinylene single bonds is expected to increase the activation energy for the *p*-phenylene ring flip. For pristine PPV-d_4, the mean ring flip activation energy has been determined[13] to be 63 kJ mol^{-1} through measurement of the temperature dependence of the ring flip rate. This procedure can

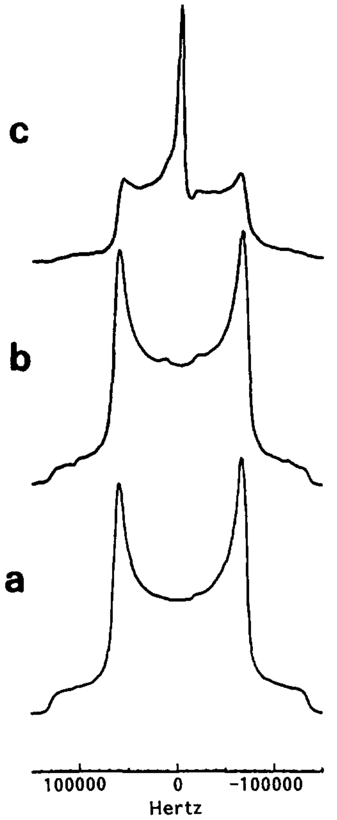

Figure 2 (a) ^2H quadrupole echo n.m.r. spectrum obtained from a sample of H_2SO_4-doped PPV-d_4 at 298 K. (b) Spectrum obtained from a sample of pristine PPV-d_4 at 298 K. (c) Spectrum obtained from a sample of H_2SO_4-doped PPV-d_4 heated to a temperature of 398 K

also be applied to H_2SO_4-doped PPV-d_4 to observe an increase associated with doping.

Figure 2c shows the spectrum obtained from a sample of H_2SO_4-doped PPV-d_4 which has been sealed in a glass tube and heated to a temperature of 398 K. A narrow resonance is observed at the centre of the spectrum. This centre resonance is due to a mobile deuterium-containing species in the sample tube. Subsequent cooling of the sample to ambient temperature does not remove the centre resonance. This component is irreversibly removed from the sample by heating to 498 K under vacuum and further heating up to this temperature yields no more of the mobile component. Only a small portion of the deuterium is removed from the sample, that which remains is still covalently bound to the *p*-phenylene ring. The absence of scrambling of deuterium between phenylene and vinylene groups was confirmed by solid state ^{13}C CP/MAS n.m.r. (using dipolar dephasing[25]) and also with ^2H quadrupole echo n.m.r. (deuterium present on the vinylene group has a different quadrupolar splitting than on the phenylene ring[26]). *Figure 3a* shows the ^2H spectrum obtained from a sample of evacuated, heat-treated, H_2SO_4-doped PPV-d_4 at 298 K. The spectrum is similar to that obtained from H_2SO_4-doped PPV-d_4 before heating (*Figure 2a*).

Figures 3a–e show five ^2H quadrupole echo n.m.r. spectra acquired at temperatures ranging from 298 to 498 K in 50° increments. *Figures 3f–j* show the corresponding best fit simulations of these spectra based upon a distribution of ring flip rates as described in the Experimental section and reference 13. As in previous work[13], the quadrupole coupling constant and the asymmetry parameter are taken to be 133 kHz and 0.03, respectively. The two adjustable parameters of the present fitting procedure are the width of the rate distribution (which is the same for all of the simulations) and the median rate for each simulation. These spectra show that, as with pristine PPV-d_4, the population of rapidly flipping rings can be increased with increasing temperature. Unlike pristine PPV-d_4 at 498 K, not all phenylene rings of doped PPV-d_4 undergo fast jumps. At any given temperature the number of fast moving rings is fewer than that observed for pristine PPV-d_4.

Doping also increases the width of the distribution of jump rates. When a ring flip occurs at an intermediate rate (approximately equal to the quadrupole coupling constant), its n.m.r. signal will be attenuated due to relaxation during the quadrupole echo ('echo distortions')[16,21,27]. If the distribution of jump rates for a given ensemble of spins is narrow, then the spectral intensity generated by these spins will show a marked drop over the temperature range where the observed lineshape passes from the slow exchange lineshape to the fast exchange lineshape. The magnitude of this drop provides for measurement of the width of the jump rate distribution. For pristine PPV-d_4, the intensity drops by 40% at intermediate temperature, and this drop is consistent with a ring flip rate distribution of $\Delta \log(k) = \pm 2$. For doped PPV-d_4 there is no observable intensity drop and this behaviour is consistent with a ring flip rate distribution of $\Delta \log(k) = \pm 4$ or greater. A log-Gaussian distribution of rate has been chosen for simulations (see

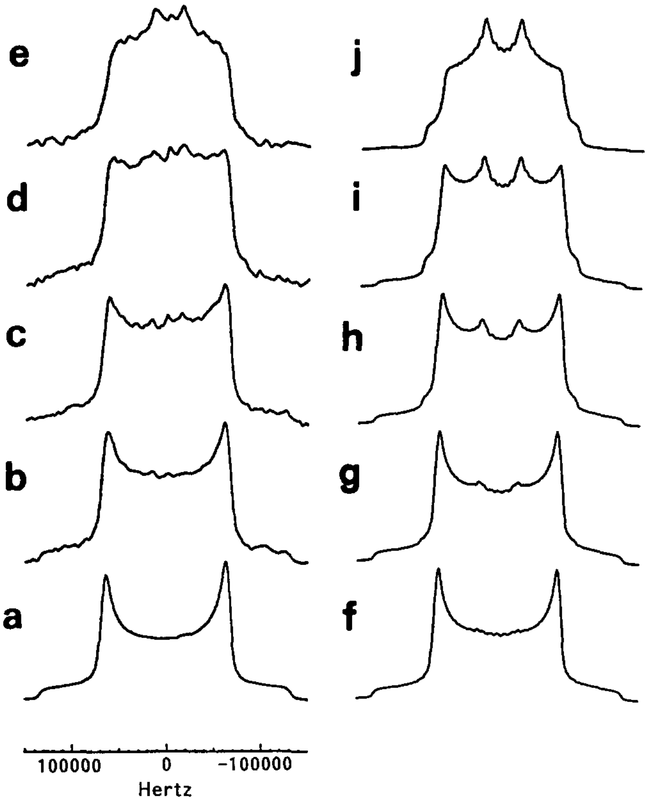

Figure 3 (a–e) ^2H quadrupole echo n.m.r. spectra obtained from a sample of H_2SO_4-doped PPV-d_4 at: (a) 298; (b) 348; (c) 398; (d) 448; (e) 498 K. (f–j) The corresponding best-fit simulations. The logarithm of the median jump rates are: (f) 1.2; (g) 2.8; (h) 4.2; (i) 5.4; (j) 7.6. All rate distributions are modelled as Gaussian with a width of $\pm 10^4$ Hz

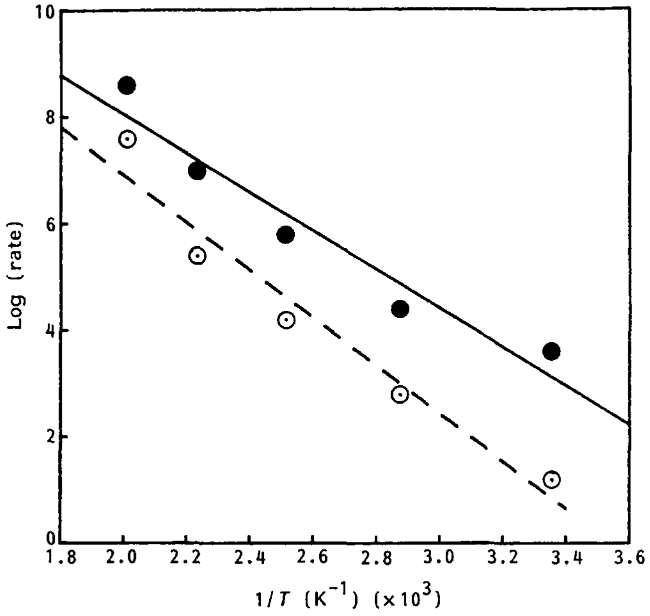

Figure 4 Plot of the logarithm of the mean rates of the best-fit simulations *versus* inverse temperature for undoped (●) and doped (⊙) PPV-d_4. The solid line is that calculated for the undoped median jump rates and the broken line is that for the doped median jump rates

Experimental section)*. This broadening of the ring flip rate distribution indicates that doping introduces greater heterogeneity of the phenylene ring environment into PPV-d_4. A ring flip distribution width of seven orders of magnitude or greater is often observed for amorphous polymers, while a distribution width for pristine PPV-d_4 is similar to behaviour observed in crystals of low molecular weight compounds in which there is homogeneity of ring environments[28–30]. Masse *et al.*[31,32] have shown that H_2SO_4-doped PPV has a nearly complete crystalline structure. It seems most likely that the observed broadening is due to a greater range of crystalline environments in which the *p*-phenylene groups reside. To clarify the last point, we note that Masse[33] observed that the doping process begins at crystallite grain boundaries and other regions where the dopant molecules can more easily diffuse into the pristine PPV lattice and proceeds towards the centre of the PPV crystallites. Because the new crystalline phase originates at a previously disordered site in the sample, it is expected that the degree of perfection of the new crystalline phase is lower than the old. This crystal transition is also evident when excess dopant is rapidly removed by washing with acetonitrile. An H_2SO_4-doped PPV film experiences local stresses that cause it to flex as excess dopant is removed. This view of how the doping process proceeds also has important implications regarding the reversibility of doping of PPV, particularly in light of the electrochemical applications that have been considered for these materials.

Figure 4 shows a plot of the logarithm of the calculated centre rates for the ring flip process for pristine and H_2SO_4-doped PPV-d_4 *versus* inverse temperature according to the familiar Arrhenius expression: $\log(k) = \log(k_0) - 2.303\Delta E_a/RT$. The slope of the fitted line for the doped PPV-d_4 film is greater than that of the pristine film and the calculated activation energies are 88 and 63 kJ mol^{-1}, respectively. The distribution width can also be attributed to a distribution of activation energies and $\Delta\log(k) = -\Delta E_a/RT$. Through this equation the observed ring flip rate distribution [$\Delta\log(k) = \pm 4$] can result from $\Delta E_a = \pm 23$ kJ mol^{-1}. Doping increases the median activation energy by broadening the distribution of activation energies upward.

When a sample of PPV is doped with H_2SO_4, its mass increases by $\sim 60 \pm 5\%$. This mass uptake corresponds to two H_2SO_4 molecules per three repeat (C_8H_6) units. Earlier studies have shown there is a wide range of mass uptakes for this doping procedure[31,32] indicating that the chemical reactions here are not well defined. Some possible reasons for this are: there may be complex equilibria involved with the chemical reactions occurring in the sample, for example in the crystalline regions as opposed to the crystallite grain boundaries or in the bulk compared to at the sample surface; doping reaction products may experience difficulty in diffusing out of the sample, so sample thickness may play a role in the mass uptake; minor temperature variations may affect the kinetics of various competing doping reactions. Macroscopic heterogeneity of doping is not considered here because X-ray diffraction has shown that H_2SO_4 doping of PPV proceeds to completion in the sample used in the present studies[31,32], yielding a completely new diffraction pattern with no residual of the pristine diffraction pattern. When a film of PPV is doped, its electrical conductivity increases dramatically[6]. For a sample of PPV drawn to 10 times its original length, the conductance of the sample in the draw direction will increase from $< 10^{-10}$ to $> 10^3$ S cm^{-1} after doping[31,32].

The heat treatment associated with the elevated temperatures of ring flip rate measurements causes a loss of dopant. For the set of experiments performed, the weight loss varied by no more than $\pm 5\%$ of the total weight. After heat treatment a doped film typically loses two-thirds of its dopant. Elemental analysis has shown that the volatile component contains sulphur and oxygen in addition to protons (and deuterons). The pH of this volatile component has also been tested and is found to be low (< 1.0). One can readily conclude from these data that partially deuterated H_2SO_4 is liberated from a doped sample upon heating.

A heat-treated, doped sample also loses its electrical conductivity. This could simply be a consequence of losing H_2SO_4 or it could be due to some other chemical reaction such as sulphonation that renders the PPV chains unable to conduct electricity effectively. ^{13}C CP/MAS n.m.r. has shown no new resonances that would be attributable to this or similar chemical reactions. A sample of heat-treated, H_2SO_4-doped PPV will regain its conductivity if it is redoped with H_2SO_4 indicating that irreversible sample degradation has not taken place. Based on these data, we conclude that the measured ring flip activation energy for fully doped PPV-d_4 is at least 88 kJ mol^{-1} and quite possibly greater because dopant is removed from the sample during measurement. The additional breadth of the ring flip rate distribution could also be due to a heterogeneous loss of dopant.

Before doping, a sample of PPV is yellow–orange in colour. After doping, the sample takes on a much darker colour (it will appear to be virtually black) with either a slight yellowish or a bluish hue. If a sample of H_2SO_4-doped PPV is exposed to the atmosphere at

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* It should be noted however that data obtained from either pristine or doped PPV-d_4 are not sufficiently precise to determine the exact shape of the distribution

ambient temperatures for a period of several weeks or immersed in water for a shorter period, it will undope to the point where it is no longer conductive and it regains its former appearance. Initially, an H_2SO_4-doped film that is exposed to the atmosphere loses its shiny surface. This is due to the migration of H_2SO_4 to the sample surface where it picks up atmospheric moisture because of its hygroscopic nature. Over a period of time, the acid is eventually lost and the film completely undopes. The resulting film, though similar in colour, is more brittle than before doping. The more brittle nature might be attributed to chain scission associated with local stresses brought on by the crystal–crystal phase transition that occurs upon doping[31,32] or by incomplete reversibility of the crystal transition. This has important implications regarding the mechanical stability of PPV films that might be used in electrochemical applications[7]. It is noted that a heat-treated, H_2SO_4-doped film will retain its optical characteristics indefinitely upon exposure to the atmosphere at ambient temperature. Heat treatment does fix some dopant in the film, but does not prevent restoration of conductivity. This system is currently under further study to determine the nature of the various chemical reactions that take place during doping and subsequent sample heating.

CONCLUSIONS

Sulphuric acid doped PPV-d_4 has been characterized with ^{2}H quadrupole echo n.m.r. spectroscopy. It has been shown that ^{2}H n.m.r. can provide new information about the chemistry of PPV doping, and through ring flip rates indirectly provide data about the electronic structure of the phenylene vinylene bond. Doping increases the *p*-phenylene ring flip activation energy from 63 kJ mol^{-1} in the pristine state to at least 88 kJ mol^{-1}. This increase can be attributed to an increase in the double bond character of the phenylene vinylene bonds. The width of the distribution of ring flip rates also increases from $\Delta\log(k) = \pm 2$ Hz in the pristine state to $\Delta\log(k) = \pm 4$ Hz in the doped state, indicating that a greater degree of sample heterogeneity exists. This heterogeneity is attributed to a lower degree of crystalline perfection in the new crystalline (doped) phase and also to the indeterminate placement of the dopant counterions in the unit cell of the doped material.

Sulphuric acid doped samples are found to lose some of their dopant upon heating and also undergo a chemical reaction that fixes dopant into their structure. Nevertheless, heating does not permanently destroy sample conductivity. Subsequent redoping will restore electrical conductivity. Upon exposure to ambient conditions, an unheated, doped sample will eventually lose all its dopant and regain its former (undoped) appearance but with a significant loss of its mechanical properties.

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