Mechanisms of Chemical Undoping of Conducting Polymers by Ammonia

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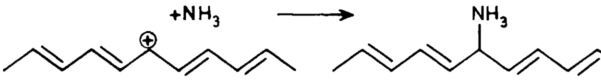
The chemical compensation of p-type conducting polymers by ammonia gas can occur by several mechanisms, which lead to products of very different quality.

The commonest and most highly-conductive of the organic conducting polymers have a conjugated carbon backbone and, as usually obtained, they are p-type semiconductors with mobile positive charges on the polymer chains. Various applications or physical experiments require these polymers to be 'undoped', *i.e.*, that the positive charges be compensated, and treatment with ammonia has often been used as a convenient chemical means of achieving this. We have studied the interaction of ammonia with several conducting polymers, and have found that it occurs *via* at least three mechanisms, which lead to different degrees of efficiency and freedom from degradation for different polymers.

High-quality polyacetylene (PA) films 1 to 20 μm thick, were formed by heating a precursor polymer *in vacuo* for 12 h at 80 °C,[1] and doped homogeneously by treatment with AsF_5 gas[2] to make them strongly p-type (equation 1).

$$(CH)_x + 3xyAsF_5 \rightarrow [CH(AsF_6)_{2y}]_x + xyAsF_3 \qquad (1)$$

The volatile AsF_3 by-product was removed by prolonged pumping under high vacuum, and the product (with $2y = 0.05$) had a conductivity of 50 S cm^{-1} as measured by a 4-probe method. Compensation by 50 torr of dry ammonia gas rapidly reduced the conductivity to $<10^{-2}$ S cm^{-1}. The resulting weight uptake was almost irreversible by pumping at 100 °C, and corresponded to one NH_3 molecule per positive charge. The absorption edge of the polymer increased from 1.5 to 1.8 eV, indicating that the conjugated sequences had become punctuated by sp^3 carbons formed by an addition reaction, and the infrared spectrum showed a new band at 1300 cm^{-1} due to C–N stretching. We therefore propose that nucleophilic attack of NH_3 on the chains had immobilised the positive soliton charges, as previously speculated,[3] (equation 2). Re-treatment with AsF_5 only restored the conductivity to about 2 S cm^{-1} because of the chemical degradation of the polymer.



(2)

Polythiophene (PT) films were electrochemically prepared as described previously,[4] with counter-ions of BF_4^- or *p*-Tos⁻, the doping levels being about one charge per 3 monomer units. Reaction with 50 torr of NH_3 again led to a very fast loss of conductivity, from 10–50 S cm^{-1} down to 10^{-8} S cm^{-1}. However, in this case there was no shift in the optical absorption edge, compared with the best literature values for electrochemically-undoped PT,[4] a value of 2.2 eV being obtained. The i.r. spectrum of compensated PT–BF_4 showed no C–N vibrations, but there were new bands consistent with the formation of NH_4BF_4;[5] indeed, after a few days this crystalline phase was detectable by *X*-ray diffractometry (XRD) in the relatively amorphous polymer. Furthermore, a non-condensible gas (at 77 K) was evolved from the polymer during the undoping process, and was identified as N_2 by mass spectrometry. We suggest that undoping of PT occurs *via* decomposition of the NH_3, as seen in equation 3.

$$8NH_3 \rightarrow 6NH_4^+ + N_2 + 6e^- \qquad (3)$$

(Unlikely as this may appear, a comparable disproportionation reaction has been identified[6] in inorganic ammonia intercalation complexes.) The electrons produced in equation 3 would serve to compensate the mobile holes on the polymer chain, their place being taken by free NH_4^+ ions. NH_4BF_4 was removed from the undoped PT by Soxhlet treatment with 50% aqueous ethanol or by vacuum sublimation, leaving a high-quality product which was chemically re-doped by AsF_5 or $NO^+BF_4^-/MeNO_2$ to metallic levels of conductivity (50—100 S cm^{-1}).

Polypyrrole tetrafluoroborate (PPy–BF_4), again with about one dopant ion per 3 monomer rings, was grown electrochemically[7] from the monomer in an electrolyte of Et_4NBF_4 and MeCN. Detachable films 5—20 μm thick were found to have a conductivity of 30—40 S cm^{-1}. Ammonia exposure led to a rapid but quite modest reduction in conductivity (Figure 1), which as previously reported,[7,8] could be largely restored by evacuation. Although several groups have suggested the use of this reaction as a basis for an ammonia sensor,[9] it has not yet been properly characterised. We have found the limiting uptake of ammonia to be one NH_3 per BF_4^- dopant. Not

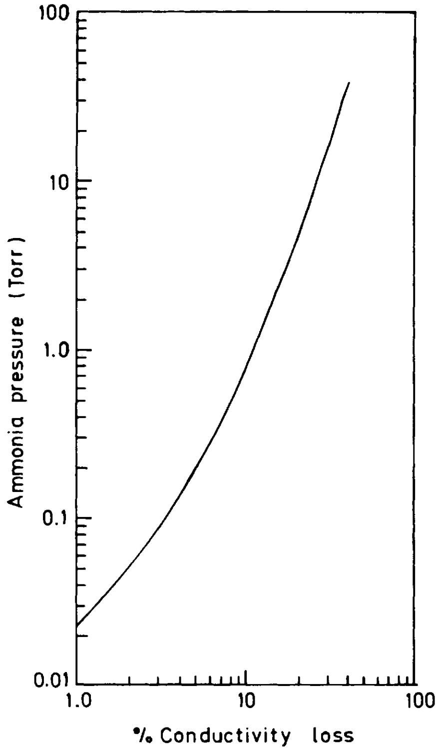


Figure 1. Relative changes in the equilibrated electronic conductivities of PPy–BF_4 films as a function of ammonia pressure.

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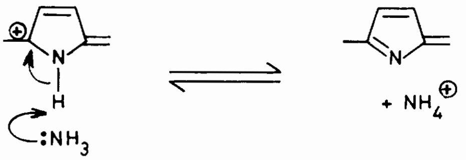
surprisingly, i.r. spectra showed no C–N bond formation, which would be difficult to reverse by pumping, and no NH_4BF_4 could be detected by XRD. Evidently the charge on the PPy backbone is so stabilised that nucleophilic attack or ammonium salt formation cannot be initiated, yet the 'chemical' nature of the NH_3 uptake has been shown by its following a Langmuir, not a Brunauer–Emmett–Teller adsorption isotherm.[10]

The possibility of a weak dative interaction between the NH_3 and the carbon backbone was considered, but it seems unlikely because it would be expected to lead to a lower drift mobility of the positive charges as the NH_3 pressure increases; we have found[10] that only the carrier *concentration* is reduced by ammonia. We have found a very much weaker undoping effect in poly(*N*-methylpyrrole) than in PPy itself; this suggests that charge-removal occurs *via* acid–base chemistry at the N–H proton, as has been observed by Münstedt[11] for PPy with aqueous hydroxide ions. We may propose the proton exchange reaction (equation 4) where the positive charge originally resides at one end of a bipolaron defect.[2] However, a free ammonium ion might be expected to form NH_4BF_4 within a short time, as for PT above, so that there is probably a hydrogen-bonding 'bridge' connecting the two nitrogen atoms involved. For high, sustained pressures of NH_3 (say 100 torr; 48 h), it appears that the ammonium ion does become mobilised, since NH_4BF_4 is then detectable and the undoping is irreversible.



(4)

This work shows that chemical undoping by ammonia gas leads to degradation for p-type PA; preliminary experiments suggest the same is true for poly(phenylene vinylene). On the other hand, the compensation method described above appears useful for the polythiophene family, and it may indeed be more effective and convenient than electrochemical undoping for thick films. The mechanism for polypyrrole is relevant to the practical usefulness of PPy as an ammonia gas sensor; a more detailed report of our study will appear elsewhere.[10]

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