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Studies on Polythiophene Films Prepared by Electropolymerization

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Abstract: The electrochemical polymerization of thiophene to BF_4^- doped polythiophene using electrochemical cell fitted with a platinum working electrode and ammonium fluoroborate in propylene carbonate electrolyte showed the efficiency of electropolymerization reaching to 100%. The aqueous ammonia is very commonly used as undoping agent for conducting polymers. The work on the undoping of BF_4^- doped polythiophene by dry ammonia was carried out in order to corroborate the mechanism of undoping vis a vis polyacetylene. The work on the mechanism of the dry ammonia undoping of BF_4^- doped polythiophene (PTh^{n+}:nBF_4^-) by dry ammonia is novel in the sense the mechanism is strongly supported by our previous works and the scanning electron micrographs showing the formation of NH_4F crystals. The mechanism of irreversible undoping of BF_4^- doped polythiophene by moisture is also proposed. The scanning electron microscopy showed the surface of the BF_4^- doped polythiophene films produced to be extremely smooth while the beautiful microdendrites composed of globules were formed on the edges of the working electrode. The microdendritic growths of such morphology have also been observed in polypyrrole produced by electropolymerization.

Keywords: Electropolymerization efficiency, scanning electron microscopy, polythiophene, mechanism of undoping

دراسات على أفلام البولي إيثيلين التي يتم إعدادها عن طريق التحليل الكهربائي

الملخص: أظهرت البلمرة الكهروكيميائية للثيوفين إلى بوليثيوفان المخدر ب (ب ف 4-) باستخدام خلية كهروكيميائية مزودة بقطب كهربائي تعمل بالبلاتينيوم وفليوروبورات الأمونيوم في كربونات البروبيلان المنحل بالكهرباء قد أظهرت فعالية البلمرة التي تصل إلى 100%. الأمونياك المائي شائع الاستخدام كعامل غير متجانس لإجراء البوليميرات. تم العمل على إزالة بوليثيوفان مخدرة ب (ب ف 4) بواسطة الأمونيا الجافة من أجل إثبات آلية إلغاء الانزلاق تجاه البولياسيتيلان. يعد العمل على آلية إزالة الأمونيا الجافة في البوليفين ثنائي الميثان المخدر ب (ب ف 4) (ب ت ح ن+: ن ب ف 4-) بواسطة الأمونيا الجافة جديدة في معنى هذه الآلية المدعومة بقوة من طرف أعمالنا السابقة والصور المجهرية الإلكترونية الممسوحة ضوئيا التي تظهر تشكل الكريستال (ن ح 4 ف). تقترح أيضا آلية إلغاء إزالة البوليفين ثنائي ميثيل ب (ب ف 4) بواسطة الرطوبة. المجهر الإلكتروني المسحي أظهر بأن سطح أفلام البوليثيوفان المخدرة ب (ب ف 4) تم إنتاجه ليكون سلسا للغاية، في حين أن روعة الميكرودونديريت المكونة من كريات كانت مشكلة على حواف القطب الكهربائي العامل. كما لوحظت الزيادات الدقيقة في تشكل بوليبيرول ناتج عن البلمرة الكهربائية.

1. Introduction

The conjugated polymers such as polyacetylene (PA), polythiophene (PTh), polyparaphenylene (PPP) etc. show a large increase in their electrical conductivity from insulator through semiconductor to metallic regions on ion-injection by chemical or electrochemical techniques. The conjugated conducting polymers possess the π-conjugated sp^2 hybridized carbon backbone and produced in the *p*-type doped form by chemical or electrochemical polymerization of their monomers. The *p*-type doped forms of such polymers have mobile positive charge carriers (*holes*) generally termed as '*polarons*' and '*bipolarons*' for electrical conduction along the polymer backbone [1, 2].

This is accomplished by removal of electrons from the polymer by an oxidant producing radical cations (holes) on the polymer chain. The movement of the holes on application of voltage causes electrical conduction along the polymer chains provided the electrostatic attraction between the holes and the counter-ions could be overcome by thermal energy or by shielding of charged species. A closely similar is the effect of the interaction between the conjugated polymer chain and reductant which produces electrons on the polymer chain causing electrical conduction by the movement of electrons. This process of great increase in electrical conductivity of conjugated polymers by interaction with oxidant/reductant is called ‘doping’ in an extremely poor analogy to that in conventional inorganic semiconductors [3, 4].

For various reasons, doped conducting polymers needed to be undoped which commonly achieved by reacting them with aqueous or dry ammonia. Ammonia neutralizes or compensates the positive charges on the backbone killing the electrical conductivity of the conducting polymer and therefore this undoping process is also called as electrical neutralization or electrical compensation of conducting polymers. Thus the initial insulating state of the polymer could be regained by reverse process called as ‘undoping’ by chemically or electrochemically neutralizing the charge on the polymer backbone. This process may be perceived as an *n*-type doping of a *p*-type doped polymer in which the undoping reagent neutralizes the electrical charge of the polymer backbone by electron-transfer chemical reaction. The thin films of *p*-type doped polythiophene were found to react rapidly but irreversibly with ammonia and water. The interaction between undoping agents such as ammonia and water with *p*-type doped polythiophene has been examined and the complete mechanism of the undoping process in the form of chemical reactions have been proposed for the first time with the possibility of their use in sensing devices [5. 6-8].

The electrochemical polymerization of thiophene into BF_4^- doped polythiophene (PTh^{n+}:nBF_4^-) films on platinum electrode and the chemistry of ammonia undoping of polyacetylene (PA), polypyrrole (PPy) and polythiophene (PTh) has already been reported [5, 6, 9] while the mechanism of undoping of polythiophene has yet not been discussed to the compeleteness. This prompted us to carry out the experiments on this aspect of undoping of conducting polymers. In short, the 100% electrochemical polymerization efficiency, certain morphological features in the polythiophene films and the formation of NH_4F crystals were observed for the first time. The detailed characterizations of polythiophene studied in this communication have been reported in several other publications of the author.

2. Experimental

An evacuable electrochemical cell with a platinum working electrode and an aluminium counter-electrode was used to produce oxidized polythiophene at a current density of 9–12 mA cm^{-2}. Polythiophene films were washed with dry acetonitrile stored over activated molecular sieves and dried by pumping on a vacuum line for about an hour prior to experimentation. Chemical undoping by moisture and dry ammonia was done in an oxygen-free atmosphere using a specially designed vacuum line fitted with high-vacuum Teflon stopcocks, a Pirani vacuum gauge and a mercury manometer topped with fluorinated oil [5, 6, 9].

3. Results and Discussion

In this communication, some observations *viz*. the efficiency of electrochemical polymerization (E_p) of thiophene, microdendrite formation on the edge of the $PTh^{n+}:nBF_4^-$ films formed during electropolymerization and the effect of pumping on the electrochemically prepared $PTh^{n+}:nBF_4^-$ undoped by dry ammonia are reported for the first time. A complete mechanism for dry ammonia and moisture undoping of polythiophene is also is presented for the first time.

3.1. Efficiency of polymerization

The efficiency of electrochemical polymerization of thiophene (E_p) was calculated using the relation ($E_p = 2W_1/W_2$) where W_1 is the moles of monomer polymerized and W_2 is the moles of electricity passed during polymerization. The efficiency of polymerization was observed to be nearly 100% as evident from the data presented in **Table 1**. Values approaching to 100% for the efficiency of electrochemical polymerization have also been reported by some other workers [10].

Table 1. Efficiency of electropolymerization (E_p) of thiophene in different electrolytes.

Polymer:Dopant (Mol.Ratio)	**Current Passed (mA)**	**Duration of Polymerization (s)**	**Mass of Polythiophene (mg)**	**Efficiency (E_p) (%)**
$PTh^{n+}:nBF_4^-$ (0.1)	29.95	180	2.43	101
$PTh^{n+}:nBF_4^-$ (0.1)	29.95	180	2.35	97
$PTh^{n+}:nClO_4^-$ (0.065)	29.95	190	2.52	100
$PTh^{n+}:nClO_4^-$ (0.065)	29.95	190	2.40	95
$PTh^{n+}:nAsF_6^-$ (0.07)	22.70	230	2.50	100

$PTh^{n+}:nAsF_6^-$ (0.07)	25.70	220	2.65	98
$PTh^{n+}:nAsF_6^-$ (0.07)	29.95	160	2.35	103

3.2. Undoping of polythiophene

It has been observed that polyacetylene doped with AsF_5 ($PA^{n+}:nAsF_6^-$) undergoes undoping by nucleophilic reaction of dry ammonia with the positive charges on the conjugated backbone forming C-N covalent bonds leading to the puncturing in the conjugation and loss of electrical conductivity. In case of electrochemically prepared BF_4^- doped polypyrrole ($PPy^{n+}:nBF_4^-$), low pressures of ammonia undopes the positive charges which could be reversed by pumping indicating that covalent bonds are not formed [5, 6, 9]. The charge neutralization via acid-base chemistry involving $N\cdots H^+\cdots N$ hydrogen bond bridge between the N atom of ammonia and N atom of pyrrole residues holding positive charges was suggested as was observed by Műnstedt [11] for the interaction of polypyrrole with aqueous hydroxide ions. This has led many workers to study the several types of nanocomposites of polypyrrole for sensor applications in the recent years [12-16]. However, an irreversible reaction of ammonia with polypyrrole at higher pressure and prolonged exposure to ammonia similar to that reported for polythiophene was observed.

As has been said earlier, the process of chemical compensation may be treated as *n*-type doping of a *p*-type doped polymer or vice versa in which the polymer passes through an insulation state. Schöllhörn and Zagefka [17] have suggested a redox reaction for ammonia or amine intercalation into layered metal dichalcogenides which has further been supported by the work of Foot and Shaker on ammonia and amine intercalation into $NiPS_3$ and $CdPS_3$ [18]. The disproportionation reaction of ammonia is given here.

$$8\ NH_3 \rightarrow 6\ NH_4^+ + 6e^- + N_2 \qquad (1)$$

In case of electrochemically prepared BF_4^- doped polythiophene ($PTh^{n+}:nBF_4^-$), dry ammonia neutralizes the positive charges on the conjugated backbone of polymer without causing the chemical degradation i.e. the conjugation length of the undoped polythiophene remains unaltered unlike polyacetylene where conjugation length decreases. FTIR spectroscopic and XRD data supported the formation of NH_4BF_4 (sublimes ~230^{o}C) and N_2. In the light of the disproportionation reaction of ammonia, FTIR spectroscopic and XRD data [5, 6, 9], we suggested the mechanism of undoping of $PTh^{n+}:nBF_4^-$ in the following equations.

$$\underset{\text{(Conducting)}}{PTh^{n+}:nBF_4^-} + n\,NH_4^+ + ne^- \rightarrow \underset{\text{(Non-conducting)}}{PTh} + n\,NH_4BF_4 \quad (2)$$

On further pumping on the vacuum line, the undoped polythiophene showed the formation of hexagonal crystals of NH_4F on the surface and embedded in the polythiophene films (**Figure 1**). Similar hexagonal structures on the surface of the electrochemically prepared polythiophene have also been observed by Geetha and Trivedi [20]. By attributing the formation of NH_4F (sublimes ~100°C) to the volatilization of BF_3 (boiling Point -99.9°C) from NH_4BF_4. Therefore, further step into the chemistry of undoping of $PTh^{n+}:nBF_4^-$ may be added as given

$$n\,NH_4BF_4 \rightarrow n\,NH_4F + n\,BF_3 \quad (3)$$

$$n\,NH_4F \rightarrow n\,NH_3 + n\,HF \quad (4)$$

A somewhat similar picture has emerged in the case of moisture undoping of $PTh^{n+}:nBF_4^-$. An analogous disproportionation reaction of water for the chemical undoping of $PTh^{n+}:nBF_4^-$ leading to the formation of HF (Boiling Point ~19.5°C) and BF_3 (Boiling Point -99.9°C) via HBF_4 (Boiling Point ~130°C) was proposed by us as presented here.

$$6\,H_2O \rightarrow 4\,H_3O^+ + 4e^- + O_2 \quad (5)$$

$$\underset{\text{(Conducting)}}{PTh^{n+}:nBF_4^-} + n\,H_3O^+ + ne^- \rightarrow \underset{\text{(Non-conducting)}}{PTh} + n\,HBF_4 + n\,H_2O \quad (6)$$

$$n\,HBF_4 \rightarrow n\,HF + n\,BF_3 \quad (7)$$

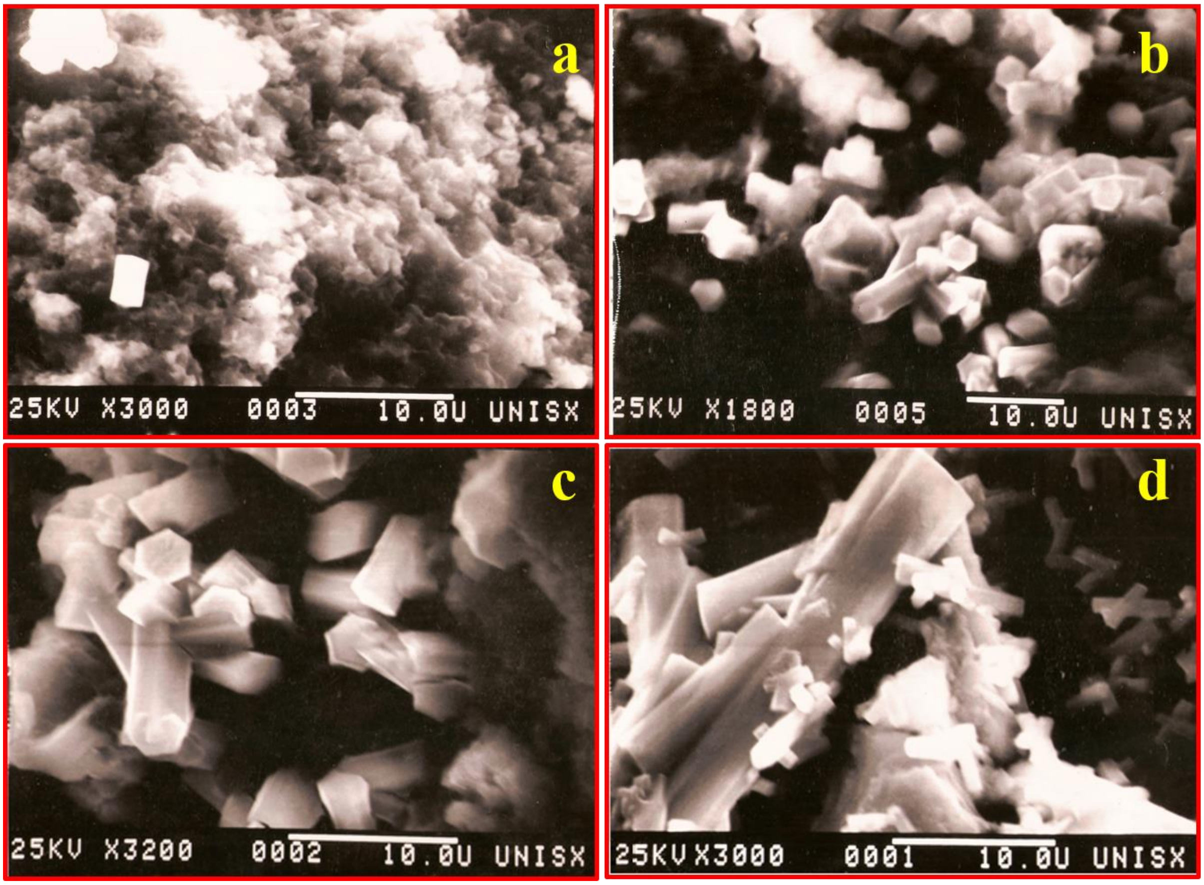

Figure 1. SEM of hexagonal crystals of NH_4F formed during ammonia undoping of PTh^{n+}:nBF_4^- films prepared by electropolymerization.

3.3. Morphological studies

The electropolymerization of thiophene produced PTh^{n+}:nBF_4^- films (thickness 3 micron or less) of very high quality. The scanning electron microscopic studies revealed that the surface of the films was very smooth (**Figure 2**) [21-23].

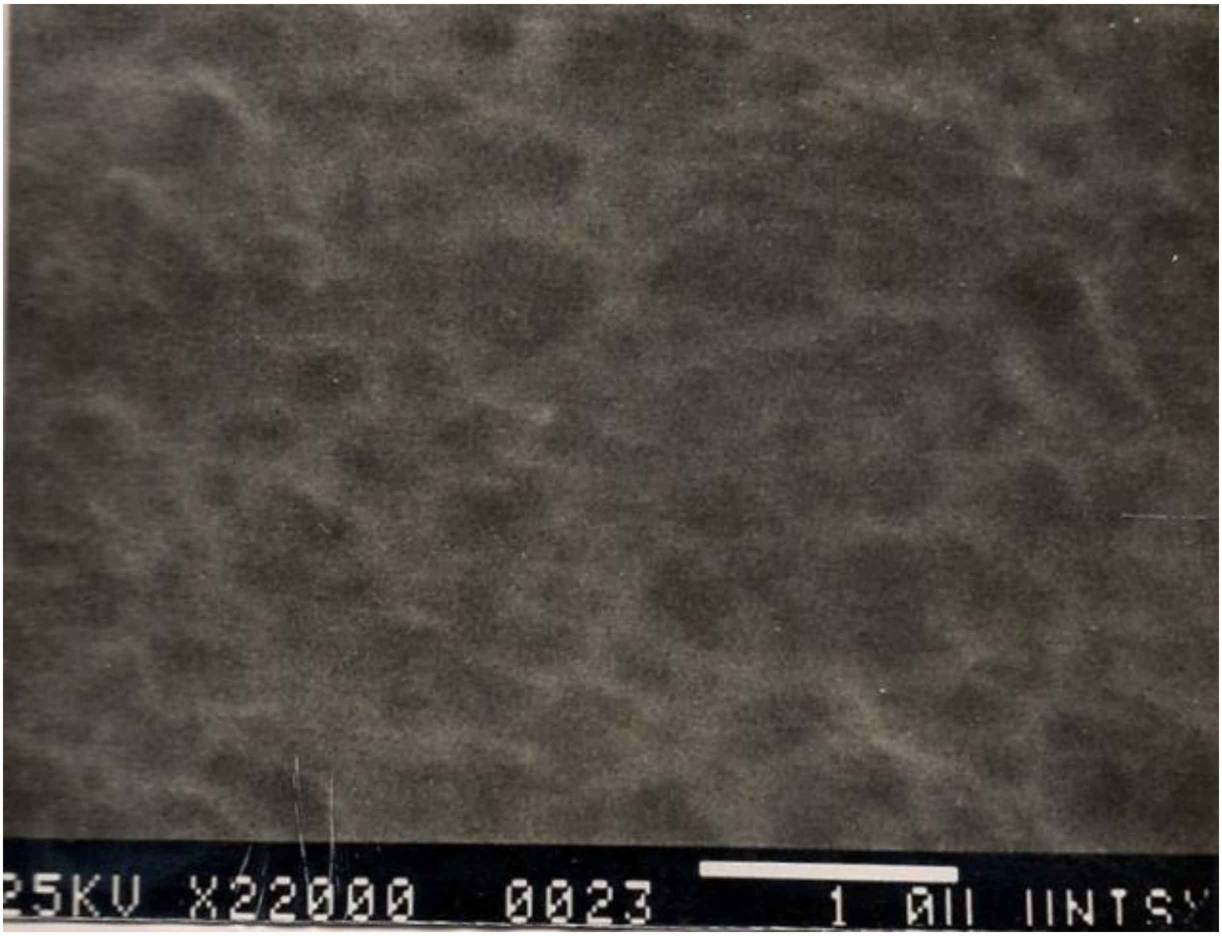

Figure 2. SEM image of the surface of the $PTh^{n+}:nBF_4^-$ films.

At the edge of the films, microdendritic growths of worm-like fibers of different lengths (8-40 micron in diameter) composed of well-organized globules were observed (**Figure 3**). It is typical, where a polymer precipitates after attaining certain threshold chain length into globules forms spherical beads as observed in case of polyethylene [24]. Slightly different types of dendritic growths were observed in polypyrrole during electrochemical polymerization and undoping by others as well [25].

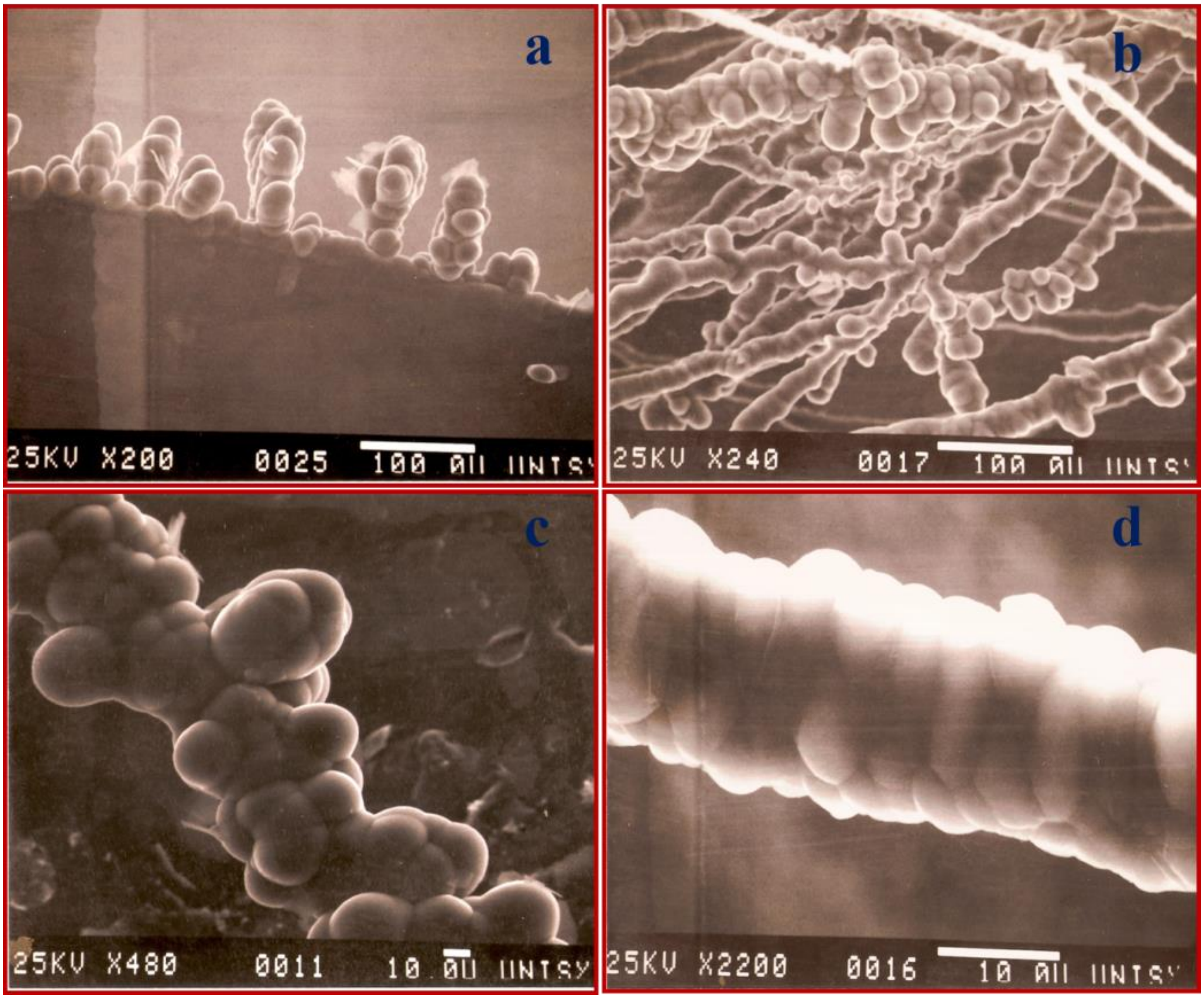

Figure 3. SEM images of the dendritic growths in PTh^{n+}:nBF_4^- films

prepared by electropolymerization in different magnifications.

4. Conclusion

In conclusion, the electropolymerization of thiophene is a highly efficient process which produces high quality thin films of polythiophene. Microdendritic growths of worm-like fibers of different lengths composed of well-organized globules at the edge of the as-prepared polythiophene films. A complete mechanism of dry ammonia undoping of PTh^{n+}:nBF_4^- films is proposed in the light of our previous work and the formation of hexagonal crystals of NH_4F. An analoguous mechanism of moisture undoping of polythiophene is also proposed.

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