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Room temperature dedoping of conducting poly-3-alkylthiophenes

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Thin films of $FeCl_3$ doped polyalkylthiophene (side chain length from 6 to 18) have been automatically dedoped in ambient atmosphere at room temperature. The dedoping rate is dependent upon the side chain length, dopant, ambient lighting and film morphology. The maximum dedoping rate occurred in the first 30 min and dropped off rapidly after one hour. Dedoping is the reversible process of doping, bipolarons being reduced to polarons and then to the neutral state. The production of Fe^{2+} and HCl during the dedoping process indicates that moisture acted as the reducing agent. In other words, bipolarons were reduced by H_2O to polarons. Polarons subsequently disproportionate to bipolarons and neutral polymer or reduced Fe^{3+} to Fe^{2+}. Protons, produced from the oxidition of H_2O, react with $FeCl_4^-$ or $FeCl_4^{2-}$ to produce HCl and iron complexes.

Introduction

The potential applications of conducting polymers in microelectronics have been investigated over the past few decades[1–3] and a significant effort has been made to obtain soluble and processable materials.[4] Enhanced solubilization can be achieved by grafting long alkyl side chains on a polyaromatic backbone as has been demonstrated in polyalkylthiophenes (P3ATs). Polyalkylthiophenes represent a class of conducting polymers that are soluble and processable, and yet retain a degree of the electrical conductivity of the insoluble parent, polythiophene.[5–8] The solubility of polyalkylthiophenes arises from the decrease of attraction between polymer chains and the introduction of favorable interactions between the substituents and the solvent. Unfortunately, side chain substitution also leads to thermal instability of the doped polymer since in P3AT, the doped state has a higher energy than the neutral state. Thermal dedoping appears to be a critical technological problem for the application of P3AT. A considerable number of studies have been made to understand the instability of doped P3AT. It was reported that the dedoping (or conductivity) decay rate depends on the dopant,[9,10] degree of doping and temperature[11] as well as the humidity level of the surrounding atmosphere.[12,13] On the other hand, some studies also showed that the dedoping process also depends on the arrangement of alkyl side chains in the polymer backbone.[14] A reduction of the number of alkyl side chains in a regular way increased the stability towards thermal dedoping.

The dedoping mechanism in P3AT has been explained by the increasing reactivity of the conducting oxidized state towards reducing species, such as water.[9,15] However, Horowitz *et al.*[16] found that the oxidized polymer (in solution) is reduced to the neutral state when acetone was added, but the exact nature of this reaction is still unknown. Most studies have centered on the thermal dedoping process of P3ATs containing $FeCl_4^-$ counter ions. Pei *et al.* believe that thermally activated side chain mobility is the cause for dopant removal from the polymer backbone and that larger dopants will be removed more easily.[17] However, Ciprelli *et al.* discovered that the size of the dopant ions does not appear to be a determining factor in the dedoping process[10] and that the electronic properties of the counter anion play a key role in this process. Nevertheless, it was reported by Abdou *et al.* that for thin films (<1 μm), photochemical dedoping dominates over thermal dedoping under ambient lighting.[18] In addition, solvatochromic behavior was observed for polyalkylthiophene.[19] The solvents used to cast the polymer films affect the packing of polymer chains. Therefore, after doping, the resulting films may have different dedoping rates.

The applications of conducting P3ATs require that we have a thorough understanding of their properties. In order to understand better the nature of the dedoping phenomenon, we investigated the effects of structure regularity, alkyl side chain length, dopant, solvent, and light on the room temperature dedoping of doped P3ATs.

Experimental

Reagents

3-Bromothiophene (stored over molecular sieves), $Ni(dppp)Cl_2$, LDA, Mg, $MgBr_2$, HgO, I_2 and bromoalkanes (with chain length ranging from 6 to 18), were purchased from Aldrich Chemical Co. or other commercial sources and used as received unless otherwise specified. All solvents are HPLC grade and distilled over Na or CaH_2 prior to used (bromoalkanes were distilled over $MgSO_4$).

Preparation of P3AT films

The monomers, 3-alkylthiophenes with a side chain length ranging from 6 to 18, were prepared by a published procedure[20] (Ni catalyzed coupling of the alkyl Grignard with 3-bromothiophene). The purity of monomers was checked by ^1H NMR and found to be >95%. Regio-random P3ATs were prepared by chemical oxidative coupling of the corresponding monomers with $FeCl_3$–$CHCl_3$ according to the procedure described by Sugimoto *et al.*[21] Removal of oligomers and impurities from the obtained polymers was achieved by Soxhlet extraction with MeOH. The dark red neutral P3AT was dried under vacuum. Regio-regular polymers were prepared by a literature procedure.[22] The percentage of HT–HT dyad was measured by ^1H NMR spectroscopy.[23] 25 mg of dried P3AT was dissolved in 2.5 ml of solvent and the solutions were cast onto a silicon wafer or a glass slide. All film thicknesses were between 4750 and 5250 Å.

Doping of P3AT films with solutions of $FeCl_3$ or $AuCl_3$ in dry nitromethane

Chemical doping was performed by dipping the film (cast on substrate) in a nitromethane solution of $FeCl_3$ or $AuCl_3$ for 30 and 60 min, respectively. After oxidation, all films were rinsed several times with nitromethane and dried with N_2. UV–VIS–NIR absorption spectroscopy was used to monitor the doping process. Completeness of doping was judged by the total disappearance of the π–π* transition of the neutral polymer. The degree of oxidation was determined by elemental analysis.

Rate of dedoping

The dedoping process was monitored by UV–VIS–NIR spectroscopy.

Physical measurements

Fourier transform IR spectra were recorded for films on a Si substrate using a Bio-Rad 155 FTIR spectrometer. The thicknesses of the polymer films were measured with a Dektak 3 surface profile measuring system. The scan length is 5 mm and the thickness was calculated from the average of the length scanned. The thickness of films was further calibrated by UV–VIS absorption measurements. UV–VIS–NIR spectra were obtained using a Varian Cary 5E spectrometer in the laboratory atmosphere at room temperature. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) studies were performed with a Hitachi S-800 apparatus at 15 kV. X-Ray photoelectron spectroscopy studies were carried out on a Perkin-Elmer PHI-590AM ESCA/XPS spectrometer system with a cylindrical mirror electron (CMA) energy analyzer. The X-ray sources were Al-Kα at 600 W and Mg-Kα at 400 W. Depth profile secondary ion mass spectra (SIMS) were measured with a SIMS Cameca, ims-4f instrument where a Cs^+ ion gun for sputtering was adjusted to 10 kV acceleration voltage. Gel permeation chromatography analyses were carried out on an Eldex model 9600 HPLC with a UV detector and 30 cm length columns of Waters HT0&HT4 (molecular weight range: 100–600 000). Polystyrene with different molecular weights were used as calibration standards and THF was used as an eluent.

Charge transport measurements

Direct current electrical conductivity measurements of the films on substrates (1.2 cm × 1.2 cm square plate) were performed in the usual four point geometry.[24] The four points on the sample surface were in line at an equal spacing of 2 mm. Each point was adhered to a gold wire electrode. An appropriate current (ranging from 1 nA to 1 mA) was maintained on the two outer electrodes. The floating potential across the two inner electrodes was measured to determine the conductivity.[25]

Results and discussion

Preparation of P3ATs

Regio-random polyalkylthiophenes (P3ATs) with side chain lengths ranging from 6 to 18 were prepared by oxidative coupling of the corresponding monomer using iron(III) chloride as an oxidant. The ratios of HT–HT (head-to-tail to head-to-tail) dyad configuration[23] and molecular weights are listed in Table 1. As shown in Table 1, there is no direct relationship between side-chain length and dyad ratio or molecular weight. Dark red films (thickness: 5000 ± 250 Å) of neutral polymers were cast on glass slides or quartz disks from $CHCl_3$ and THF solutions, then dipped in 0.1 M $FeCl_3$–CH_3NO_2 for doping. After doping, the original broad peak (due to the π–π* transition of the neutral polymer) disappeared, while two broad absorption bands (at λ_{max} *ca.* 800 and *ca.* 1640 nm) grew in. These two peaks are believed to be the optical-induced electronic transitions involving charge-carrying bipolaronic states.[18,26] The peaks at 240, 316 and 368 nm correspond to the absorption of $FeCl_4^-$ which is the counter anion of doped polymers.[27] The time required to completely dope the P3ATs is approximately the same (within 30 min), except for poly(3-octadecylthiophene). The degree of doping determined from elemental analysis is 0.25 which is similar to that reported in the literature.[28–31] The doping time and degree of doping of regio-regular P3ATs are close to those of regio-random polyalkylthiophenes.

Table 1 Molecular weights, $\Delta\lambda_{max}$, HT–HT dyad ratios and average dedoping rate in the 30 min of P3ATs

Side chain length	Molecular weight	$\Delta\lambda_{max}{}^{b}$/nm	HT–HT ratio (%)	Average dedoping rate in the first 30 min
6	4 000	39	53	1.86
7	66 000	32	55	2.88
8	100 000	65	67	5.54
8[a]	4 000	90	96	1.50
10	95 000	28	49	7.77
12	70 000	34	58	5.86
12[a]	4 000	85	98	1.60
14	110 000	35	58	7.08
16	4 000	34	57	6.74
18	3 200	34	48	8.85

[a] Regio-regular polyalkylthiophene. [b] λ_{max}(film) − λ_{max}($CHCl_3$ solution).

Room temperature dedoping of P3AT

The $FeCl_3$ doped P3ATs were stored at room temperature and in ambient lighting. The dedoping of P3AT was monitored by UV–VIS–NIR spectroscopy as shown in Fig. 1(a). It was found that as the dedoping proceeds, the peak at *ca.* 1640 nm (due to charge-carrying bipolaronic states) decreased and a peak at 480 nm (which corresponds to the π–π* transition of the neutral polymer) increased. However, the intensity of the peaks at 264, 310 and 364 (the absorption peaks of $FeCl_4^-$) showed no observable change in the first hour. Interestingly, the peak at *ca.* 800 nm increased initially [with a slight shift of the absorption maximum, as shown in Fig. 1(b)] then decreased as dedoping proceeds. The absorptions of polarons calculated from a theoretical model were 0.18, 1.23 and 1.51 eV.[32] The peak at *ca.* 800 nm (1.7 eV) may be due to the absorption of both polarons and bipolarons. At the beginning of dedoping, bipolarons were reduced to polarons and although the polarons are also reduced to the neutral state, the rate of reduction of bipolarons to polarons is higher than that of reduction of polarons. Thus, the total concentration of polarons initially increases. After the concentration of bipolarons decreased, the production of polarons from bipolarons was slower than the reduction of polarons to the neutral state, and hence the total concentration of polarons decreased.

Effects of the structure and the side chain length on the dedoping rate

In order to eliminate the influence of thickness on the dedoping rate, polymer films with similar thickness (5000 ± 250 Å) were prepared. Since some of the UV–VIS absorption peaks may be difficult to identify during dedoping, the dedoping rate was calculated using the absorption peak at 1640 nm [eqn. (1) and (2)]:

$$R=(I_{1640}-I^{i}_{1640})/I_{1640}\times 100\% \qquad (1)$$

$$v=\mathrm{R}/t_{i} \qquad (2)$$

where R = relative intensity change, v = average dedoping rate within t_i h, t_i = dedoping time/h, I_{1640} = peak intensity at 1640 nm immediately after doping and I^{i}_{1640} = peak intensity at 1640 nm after dedoping for t_i h.

Typical average dedoping rates *vs.* dedoping times of polyalkylthiophene are shown in Fig. 2. The average dedoping rate was very fast in the first 2 h then decreased as dedoping

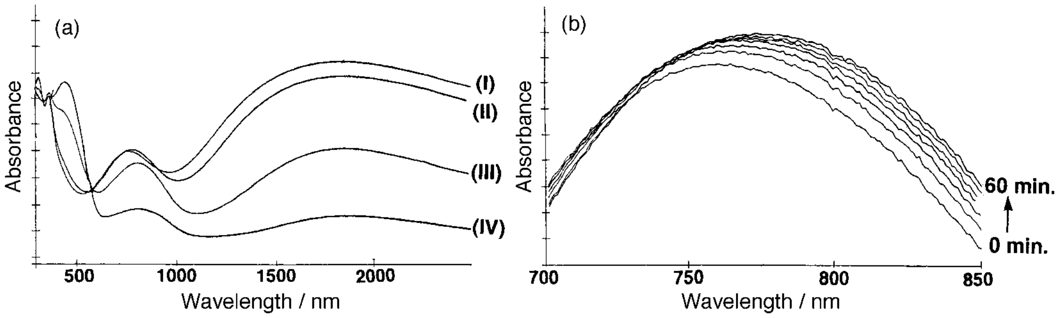


Fig. 1 The UV–VIS–NIR spectra of polyoctadecylthiophene during dedoping: (a) whole spectrum [(I) just doped; (II) after 1 h; (III) after 21 h; (IV) after 250 h], (b) the polaron/bipolaron peak in the first hour.

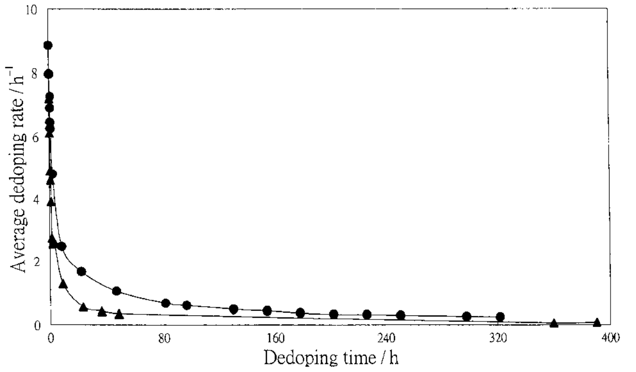


Fig. 2 The average dedoping rate of $FeCl_3$ doped polyoctadecylthiophene cast from (●) $CHCl_3$, (▲) THF solution.

proceeds. The maximum average dedoping rates of P3ATs all occurred during the first 30 min and decreased with increasing time. Table 1 lists the molecular weight, $\Delta\lambda_{max}$ (the difference in absorption maximum between polymer solution and polymer film), HT–HT ratios and average dedoping rate in the first 30 min of P3ATs with various side chain lengths. P3ATs with similar regio-regularity have similar absorption maxima in solution [except for poly(octadecylthiophene)]. The absorption maximum for the π–π^* transition of polymer solutions is blue shifted with respect to the solid state value. This is due to the change in the planarity of conjugated backbone (solid state packing stabilizes the more planar conformation) which in turn depends on the structure regio-regularity of the polymers.[33–35] We found that the shift of the absorption maximum from solution to the solid state film, $\Delta\lambda_{max}$, paralleled the structure regio-regularity. However, the maximum dedoping rate is independent of regio-regularity of regio-random P3ATs. The dedoping phenomenon is the process of reduction of the partially oxidized polymer backbone. One can expect that a high degree of conjugation of the polymer backbone (or better stacking of the polymer chains) will lead to a more stable doped state, and therefore give a low dedoping (reducing) rate. This is well demonstrated in the dedoping rate between regio-regular and regio-random P3ATs (Table 1). Therefore, the independence of the dedoping rate on structure regio-regularity of regio-random polyalkylthiophene indicated that some other factors may have a large influence on the dedoping rate of those polymers.

As expected, the side chain length plays a major role in determining the dedoping rate of P3ATs. In general, the longer the side chain length the higher the dedoping rate. It is believed[18] that the dedoping phenomenon is due to thermally activated side chain mobility, which causes the products (of the dedoping process) to be removed from the polymer backbone. At room temperature, longer alkyl side chains have a higher ability to remove the dedoping products, and therefore lead to a higher dedoping rate.

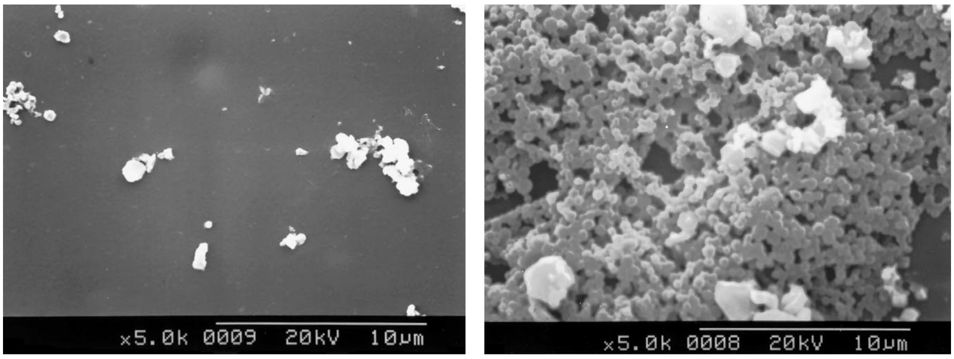
Effects of morphology on the dedoping rate of P3ATs

The dedoping rate was affected not only by side chain length but also by film morphology. It is found that for a given side chain length, the dedoping rate of a polymer film obtained from $CHCl_3$ solution and doped with $FeCl_3$ is higher than that from THF solution and doped with the same oxidant, (Fig. 2) and polyalkylthiophene films cast from different solvents showed different morphologies (Fig. 3). After doping, films obtained from $CHCl_3$ solution had a rather smooth surface, indicating packing of straight polymer chains. By contrast the morphology of doped films obtained from THF solution appear as aggregates of many small polymer balls and fibers. The movement of polymer side-chains and migration of HCl gas (*vide infra*) are easier for polymers with straight chains, therefore films cast from $CHCl_3$ solution have a higher dedoping rate. Furthermore, theoretical calculations have suggested that the stability of doped polythiophenes may be maximized by a favored topology of the dopant molecule.[36] In other words, the dedoping rate will decrease when the steric arrangement of polymer backbone and dopant are favourable. Therefore, the higher stability of doped polyalkthiophene films made from THF solution may result from the fact that these polymer films have suitable steric arrangements to accommodate the $FeCl_4^-$ dopant. In addition, the dissimilar morphology of polymer films obtained from THF and $CHCl_3$ solutions indicated that the interactions between polymer chains of those two types of polymer films are also different. This was displayed by the different energy of polarons and bipolarons in these two types of polymer films as shown in Fig. 4. Polymer films obtained from THF solution have lower absorption energies for the polarons and bipolarons and therefore have a lower dedoping rate.

Effects of light, dopant and moisture on the dedoping rate

Photochemical dedoping of $FeCl_3$ doped P3ATs thin films is known[18] and it is believed that the photolability of the $FeCl_4^-$ dopant is the cause. We studied the dedoping rate of $FeCl_3$ doped P3AT thin films (*ca.* 5000 Å) in the dark and under the ambient lighting at room temperature. It was found that the dedoping rates follow similar time dependent patterns in both environments. However, we did not observe the formation of polymer bound alcohol or cross-linked polymer as seen by Abdou and Holdcroft[2] in the photolyses of P3AT in ambient air. Light as well as temperature and humidity[14] are known to be factors which cause the dedoping of P3ATs. By contrast with the literature report,[2] we found that the dedoping rate of the sample stored in the dark is slightly faster than that in ambient light. The effects of light on the dedoping rate of the polymer films were also independent of the film morphology.

Replacement of $FeCl_4^-$ with a less photolabile dopant, $AuCl_4^-$, decreased the dedoping rate. Nevertheless, the dedoping rates are only 4–15 times lower than for samples doped with $FeCl_3$. This implies that the photolysis of dopant may



(a) (b)

Fig. 3 SEM micrographs of doped (with $FeCl_3$–CH_3NO_2) polyoctadecylthiophene cast from (a) $CHCl_3$, (b) THF solution.

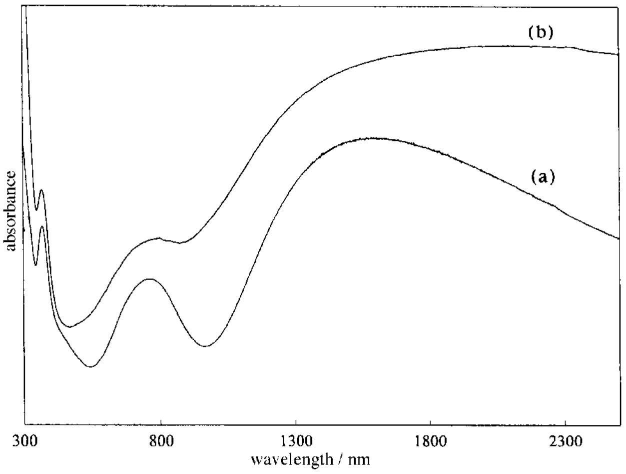


Fig. 4 The UV–VIS–NIR spectra of doped (with $FeCl_3$–CH_3NO_2) polydodecylthiophene cast from (a) $CHCl_3$, (b) THF solution.

not be the major factor for the dedoping of polyalkylthiophene in ambient light.

It was suggested by Ciprelli *et al.*[10] that H_2O was the reducing agent during the dedoping of P3ATs. In order to test the effect of water molecules on the dedoping rate of polyalkylthiophene, the doped films were stored in a glove box (water concentration <1.0 ppm). The dedoping rate of such polymer films was much lower than that of samples in the ambient atmosphere. Unfortunately, since the UV–VIS–NIR spectrometer was exposed to air, the dedoping of P3AT occurred when the UV–VIS–NIR spectra were measured.

Reversibility of the doping/dedoping process: compared to the neutral polymer film, the intensity of the π–π^* transition absorption decreased slightly (and was slightly blue shifted) after total dedoping. This implied that P3AT film degraded slightly during the dedoping process.

Dedoping mechanism

Polyalkylthiophenes in the neutral state are thermodynamically more stable than that in the doped state. In the presence of a large amount of good oxidant, however, the polymer backbone is oxidized. After the removal of oxidant, the polymer has the tendency to reduce back to the neutral state and if a reducing agent such as H_2O is present, the polymer backbone will be reduced automatically. Nevertheless, some contradictions were observed in various studies.[28] In order to understand more about the dedoping mechanism, we studied the products of the dedoping process very carefully. We found that Fe^{2+} and HCl were produced during the dedoping process (the ESCA spectrum showed no observable Fe^{2+} peak in the fully doped P3AT film[37]). The coexistence of Fe^{2+} and Fe^{3+} inside the polymer films was verified by ESCA studies. The results are similar to those reported by Abdou *et al.*[18] The released HCl was detected by pH paper or trapped by an active metal film, such as aluminium foil, and the resultant $AlCl_3$ analyzed by EDS. Depth profile SIMS and ESCA spectra of dedoped P3AT showed that the distribution of the elements is fairly homogeneous through the whole film (Fig. 5). This indicates that during dedoping no significant ion migration or aggregation occurred. Moreover, depth profile Auger studies of P3AT during dedoping (after dedoping for 2 h) showed that although the concentration of Cl is higher on the surface, the Fe concentration was the same throughout the film. Reduction of the polymer backbone was also proved by the decrease in the binding energy of C 1s and S 1s. Detailed ESCA and Auger studies of P3ATs during dedoping will be reported elsewhere.[37]

Moreover, *in situ* UV–VIS–NIR studies showed that at the beginning of dedoping, the peak intensity at *ca.* 800 nm increased in the first 30 min and then decreased (*vide supra*). This indicates that polarons were generated in the dedoping process. Such bipolaron to polaron transformations have been observed in the thermal dedoping of thiophene oligomers.[38] Both polaron and bipolaron peaks disappeared totally after dedoping for 3 months. However, the dedoped P3AT has a room temperature conductivity of 10^{-7} S cm^{-1}, two orders of magnitude higher than the neutral polymer. This increased conductivity may due to a trace amount of polarons and salt impurity in the polymer film. Scheme 1 shows a simple dedoping mechanism derived from the above observations: bipolarons are reduced by H_2O to polarons which then disproportionate[39] to bipolarons and neutral polymer. $FeCl_4^-$ reacts with H_3O^+, produced from the oxidation of H_2O, to form Fe^{3+} complexes and HCl. Polarons or neutral polymer may

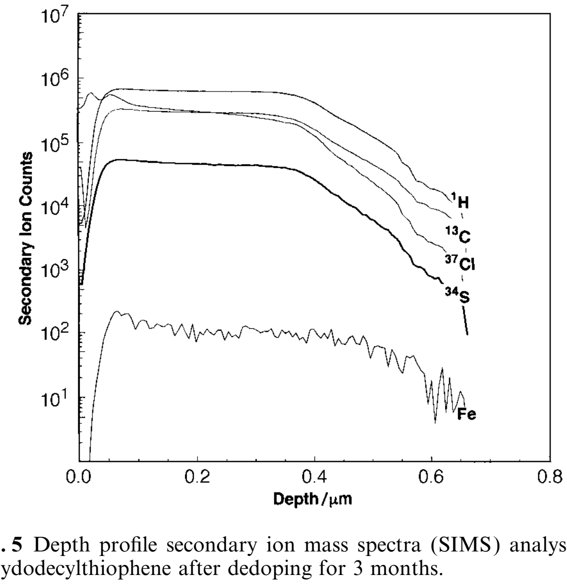
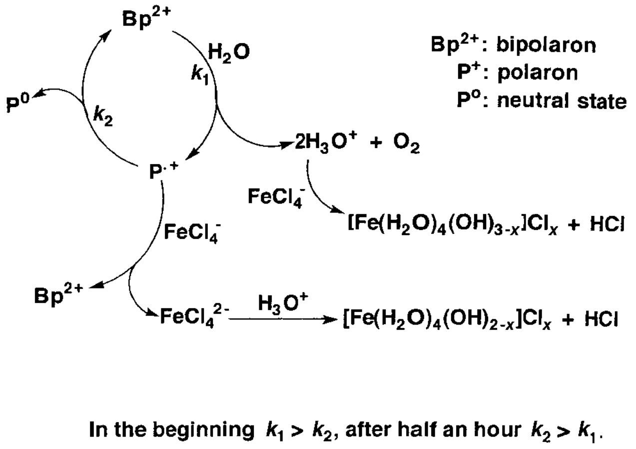


Fig. 5 Depth profile secondary ion mass spectra (SIMS) analysis of polydodecylthiophene after dedoping for 3 months.



Scheme 1 The room temperature dedoping process of polyalkylthiophene.

also reduce some $FeCl_4^-$ to $FeCl_4^{2-}$ which react with H_3O^+ to form HCl and stable Fe^{2+} complexes. The redox reaction between water and the polymer backbone and the release of HCl gas could be the rate determination steps. P3ATs with shorter alkyl side chains form denser films and such films or films with spherical morphology retard the release of HCl and the diffusion of water out of/in the polymer backbone, resulting in a lower dedoping rate. This mechanism also explains why at the start of dedoping, the concentration of $FeCl_4^-$ remains constant and the concentration of polarons increases.

Conclusions

Dedoping of conducting polyalkylthiophene films at room temperature occurred when the oxidized polymer was reduced by water. The dedoping rate depends on the polymer side chain length, film morphology, structure regio-regularity, dopant and light. During dedoping, some Fe^{3+} is reduced to Fe^{2+} and at the same time HCl is produced. The dedoping process involved the conversion of bipolarons to polarons and then to the neutral state. However, since polarons have a relatively low oxidation/reduction potential, (or may be trapped in defect sites), complete conversion to the original neutral state may not occur at room temperature.

Acknowledgments

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