

Remarkable thermal stability of BF_3 -doped polyaniline

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We show that the recently synthesized BF_3 -doped polyaniline (PANI) exhibits remarkable stability against thermal aging. Unlike the protonated PANI, which shows rapid degradation of the conductivity on heating in air, BF_3 -doped PANI shows more than an order of magnitude improvement in conductivity. We employ x-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and x-ray diffraction to understand this unexpected phenomenon.

Interesting electrical and optical properties exhibited by conducting polymers make them an attractive choice for various technological applications. However, the use is often limited by a number of crucial technical factors such as the environmental stability. Rapid degradation on exposure to environmental conditions is the primary reason why many of the doped polyacetylene systems, with conductivities nearly as high as that of copper, find less use in applications than doped polyaniline (PANI) with much lower conductivities.^{1,2} The 50% oxidized form of PANI is popular for its environmental stability in both pristine and doped forms. However, at elevated temperatures (above $\sim 75^\circ\text{C}$) the doped PANI suffers significant drop in the conductivity.^{3,4} The process of thermal aging in HCl-doped PANI has been studied extensively and contrary to the previously held hypothesis of thermal dedoping, it was found that the polymer undergoes a chain oxidation followed by chlorination of the aromatic rings, causing a serious disruption in the conjugated network.^{3,5} Since the protonated polymer undergoes irreversible chemical modifications upon heating in air, its conductivity cannot be recovered by redoping.⁶ In several respects, the recently discovered form of highly conducting PANI doped with electron-deficient BF_3 is distinct compared to the usual protonated form of PANI.^{7,8} In particular, a high conductivity in conjunction with its amorphous nature makes this system quite interesting.⁸ However, nothing is as yet known of the environmental stability of this interesting class of compounds. In the present work, we report a detailed investigation of various thermal treatments of BF_3 -doped PANI in order to understand the effect of thermal aging. We find a remarkable thermal stability of BF_3 -doped PANI compared to other doped PANI systems, the thermal treatment in fact leading to an unexpected increase in the conductivity over a wide range of temperature and duration of the treatment.

The sample was prepared⁷ by doping BF_3 into the emeraldine base, synthesized by the chemical oxidation of aniline using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ at $0-5^\circ\text{C}$.⁹ In order to investigate thermal aging in normal atmospheric conditions, powder samples were heated at two temperatures, 100 and 140°C , for different time intervals in an open mouthed ves-

sel; for comparison, heating experiments were also performed in an argon atmosphere. The powder was characterized at different stages of heating using Fourier transform infrared (FTIR) spectroscopy and x-ray photoelectron spectroscopy (XPS). Resistivity was measured by pressing the powder into thin pellets. In certain cases, pellets instead of powders were given the thermal treatment.

Figure 1(a) shows the effect of heating powdered BF_3 - and HCl-doped PANI in air at 100 and 140°C ; we also show the results of heating pellets at 100°C in the same figure. The relative conductivity, defined as the ratio of conductivity of the aged sample to that of the nonaged one, is plotted against the duration of heating. HCl-doped PANI clearly shows a marked degradation upon heating. The conductivity of the powdered samples decreases by orders of magnitude, the higher temperature heating exhibiting a much stronger effect; even the pellet shows a substantial loss in conductivity at 100°C . On the contrary, BF_3 -doped PANI shows an increase of the conductivity in every case, particularly in the short time regime, in certain cases the samples showing more than an order of magnitude improvement. Additionally, beyond the initial stages of heating, the conductivity remains almost the same in spite of prolonged heating in every case.

Various experiments carried out in our work suggest that

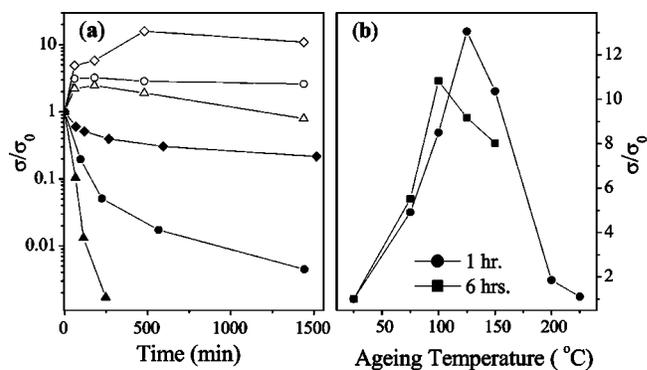


FIG. 1. (a) Variations of the relative conductivities of HCl and BF_3 -doped PANI with the duration of heating. Circles and triangles represent heating of powder at 100 and 140°C , respectively. Diamonds represent heating of pellets at 100°C ; open and closed symbols correspond to BF_3 and HCl-doped PANI, respectively. The data for HCl-doped PANI are taken from Ref. 4. (b) variations of relative conductivities of BF_3 -doped PANI pellets for two different durations of heating in dry Ar as a function of the temperature of heating.

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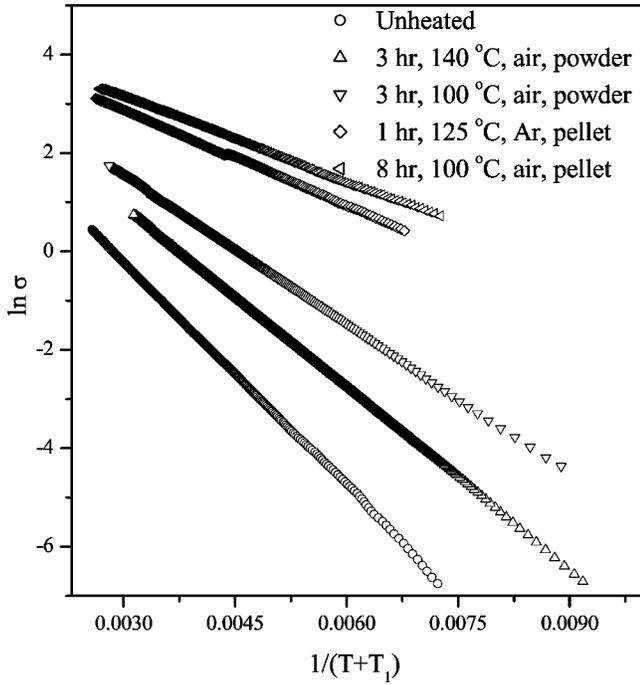


FIG. 2. $\ln \sigma$ plotted against $(T + T_1)^{-1}$, where T_1 in each case is obtained from a least-squared error fitting procedure for $\sigma(T)$ according to Sheng's model.

heating in air or in Ar yields very similar results, eliminating the possibility of any oxidation related influence on the conductivity. Figure 1(b) shows the change in relative conductivity upon heating the pellet in Ar at various temperatures for two different time intervals. We note that the conductivity reaches its highest value upon heating at temperatures close to 125 °C. In fact, among all the heated samples, the highest conductivity (34.2 S cm^{-1}) was obtained upon heating the pellet at 125 °C for 1 h. Furthermore, we observed that annealing the sample at 125 °C for a period as short as 2 min is sufficient to increase the conductivity by an order of magnitude. The experimental data presented in Figs. 1(a) and 1(b) are sufficient to establish the remarkable thermal stability of BF_3 -doped PANI in sharp contrast to protonated PANI and consequently the desirability and efficacy of this recently discovered system, particularly in high temperature applications. In the following, we probe the microscopic origin of this unexpected behavior.

We find that the temperature dependence of conductivity in all BF_3 -doped PANI samples is well described in terms of Sheng's model^{10,11} of fluctuation induced tunneling, leading to $\sigma(T) = \sigma_0 \exp[-T_0/(T + T_1)]$. Figure 2 shows the excellent linearity of $\ln \sigma$ for a number of samples with a variety of treatment, when plotted against $1/(T + T_1)$, where T_1 in each case is determined by a least-squared error fitting procedure. The parameter values obtained from the fit are listed in Table I. Sheng's model views the doped polymer as a heterogeneous system, consisting of large, highly conducting regions separated by thin insulating barriers. In BF_3 -doped PANI, these insulating barriers most probably arise from the grain boundaries. T_0 in the above expression for $\sigma(T)$ defines the average height of the potential barrier between two conducting grains. Table I shows that T_0 and consequently the barrier height decrease significantly and systematically upon

TABLE I. Parameters for the conductivity model. A: before heating, B: powder at 140 °C in air for 3 h, C: powder at 100 °C in air for 3 h, D: pellet at 125 °C in Ar for 1 h, E: pellet at 100 °C in air for 8 h.

	A	B	C	D	E
T_0 (K)	1515	1221	1013	644	578
T_1 (K)	113.4	60.9	64.6	122.4	102.5
σ_0 (S cm^{-1})	75.4	97.5	98.5	122.0	130.8

heating, suggesting a better intergrain connectivity in the heated samples, providing a clue to the understanding of the unexpected improvement of $\sigma(T)$ on heating. Similar evidence is also provided by the x-ray diffraction (XRD) data.

In the case of HCl-doped PANI, it is known that the aging process is initiated at the periphery of the crystalline grains and moves progressively towards its center, transforming the material into an amorphous and poorly conducting phase.³ As prepared BF_3 -doped PANI, however, is known to be already amorphous, despite its high conductivity.⁸ Powder XRD patterns of the heated samples showed complete resemblance with the nonheated sample, suggesting their amorphous nature. It was reported⁸ that the XRD pattern of as-prepared BF_3 -doped PANI, when left in atmosphere for some time, develops a peak at 24.8°, which corresponds to the formation of protonated PANI, as a result of BF_3 hydrolysis; simultaneously, two sharp peaks corresponding to boric acid begin to appear at 14.8° and 28.1°. This suggests that some amount of unreacted BF_3 remains adhered to the as-prepared sample, probably at the grain boundaries, that reacts with moisture in the atmosphere. In contrast, the XRD patterns of the heated samples do not show the above mentioned changes even after being left in atmospheric conditions for a long time. It appears that by heating the sample, it is possible to get rid of this impurity from the grain boundary surfaces and therefore, it must be at least partially responsible for the increase in the conductivity.

The macroscopic conductivity of a multigrain sample is contributed by both the intragrain intrinsic conductivity and the intergrain connectivity. The evidence presented so far establishes only an improved intergrain connectivity in the heated samples. In order to investigate the possibility of changes in the intragrain chemical composition, we carried out a detailed XPS study on BF_3 -doped PANI. Figure 3(a) shows the N 1s spectra of the doped sample prior to (solid circles) and after (open circles) heating at 100 °C. For ease of comparison, we have overlapped the spectrum of the unheated sample (solid line) with that of the heated one. It is evident that the two spectra are essentially identical, establishing identical chemical states for N in both the cases. C 1s spectra, shown in Fig. 3(b), also exhibit identical features for as-prepared and heated samples, once again demonstrated by overlapping the signal from the pristine sample as a solid line on the signal from the heated sample (open circles). This suggests that the thermal treatment does not change the backbone of the doped polymer. However, the B 1s spectrum exhibits a significant decrease in the spectral width upon heating [see Fig. 3(c)]. In order to understand better the spectral changes, we decompose the total B 1s spectrum in each case in terms of component spectra appearing at 193.5 ± 0.05 and 192.4 ± 0.1 eV shown by thin dashed lines, aris-

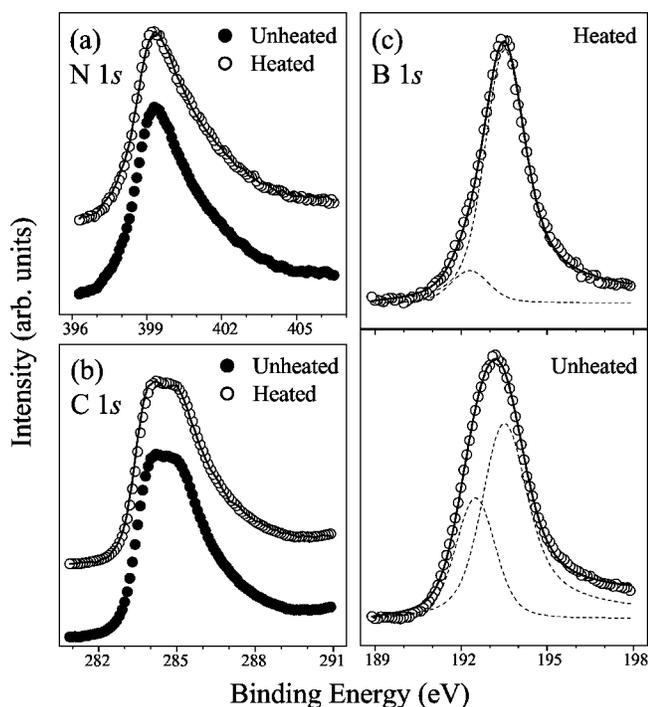


FIG. 3. XPS core-level spectra from BF_3 -doped PANI, before and after heating: (a) N $1s$, (b) C $1s$, and (c) B $1s$. Thin solid lines in insets (a) and (b) represent the spectra of the unheated sample, shifted and overlapped on the spectra (open circles) of the heated samples for comparison. Thin dashed lines in (c) indicate the two boron components obtained from a least-squared-error fit, while the solid lines overlapping the data points are the sum of the two components. Upon heating, the boric acid component decreases from 20% to 5%.

ing from BF_3 reacted to the PANI and traces of boric acid due to partial hydrolysis of unreacted BF_3 near the grain boundary, respectively; the thick lines overlapping the data points are the sums of the two components. The spectral decomposition of B $1s$ spectra clearly establish a strong reduction of the peak at 192.4 eV on heating the sample, leaving the other B $1s$ component arising from the doped BF_3 essentially unchanged. Since the features corresponding to N $1s$, C $1s$, and B $1s$ from the doped BF_3 species remain identical in as-prepared and heated samples, we conclude that heating does not change the chemical composition of the doped polymer; therefore, the changes in the conductivity on heating are primarily due to changes near the grain boundaries, rather than any change within the grains.

We have also characterized the samples at every stage of heating using FTIR spectroscopy. When the sample is heated in air at 140 °C for a prolonged period of time, the spectrum exhibits a few small changes. A small peak begins to appear at 1374 cm^{-1} after about 8 h of heating, growing further in

intensity with continued heating. Although the origin of this peak remains unclear, it is known that this peak is present in the spectrum of undoped PANI and that it diminishes gradually with an increase in the extent of doping,⁷ being present in all partially doped PANI systems. We, therefore, conclude that heating for prolonged periods at a high temperature leads to a slight amount of dedoping; this is consistent with the decrease in the relative conductivity below unity, as observed in the case of BF_3 -doped PANI heated at 140 °C for 1500 min [see Fig. 1(a)]. The fact that no such change is observed in the FTIR spectrum of samples heated at 100 °C, is in agreement with the conductivity results, showing a saturation and suggesting the absence of any significant dedoping at 100 °C. Since, dedoping is found to be the main reason for the decrease in the conductivity on prolonged heating at the higher temperature, we redoped the sample previously heated at 140 °C for 1500 min. The redoped sample showed a 2.6-fold increase in the room temperature conductivity, leading to a value that is close to the highest conductivity observed in the case of heating at 140 °C.

In conclusion, BF_3 -doped PANI shows remarkable stability towards thermal aging. In sharp contrast to protonated PANI, where heating in air causes chemical degradation and a sharp decrease in the conductivity, BF_3 -doped PANI shows a rapid enhancement in conductivity. XPS, FTIR, and XRD results show that heating removes the impurities from the grain boundary regions of the as-prepared samples. Partial dedoping upon heating at 140 °C for long periods causes a small decrease in the conductivity, which could however be recovered upon redoping the heated samples.

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