ISSN : 0974 - 7486 Volume 7 Issue 5

Materials Science

An Indian Journal

Trade Science Inc.

Short Communication

MSAIJ, 7(5), 2011 [341-343]

Thermal stability study of conducting polyaniline doped with picric acid

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Received: 13th May, 2011 ; Accepted: 13th June, 2011

ABSTRACT

Polyaniline (PANI) was synthesized by chemical oxidation polymerization in the presence of ammonium persulfate as oxidant and different concentration of picric acid. It shows that as the concentration of dopant i.e, picric acid increases it shows higher thermal stability as well as the values of activation energy and Ts increases this indicates the existence of strong interaction at the interface of PANI and dopant.

KEYWORDS

Conducting polymer;
Polyaniline;
Thermal stability;
Picric acid;
Dopant.

INTRODUCTION

Electrically conducting polymers in their pristine and doped states have been the materials of great interest for their applications in modern technologies. The nonlinear response in undoped state whereas a large increase in electrical conductivity in doped state, has attracted many research groups in search of new systems with high conductivities and non-linearity[1]. Besides several other conducting polymers, polyaniline has also been studied extensively, during the last two decades[2,3]. Polyaniline has thus emerged as a potential conductive material due to its comparatively fair environmental stability, ease of preparation and wide areas for its applications such as rechargeable batteries[4,5], electromagnetic interference shielding[6], light emitting diodes[7], display devices[8], biosensors[9] and so on. Inorganic semiconductors like silicon, gallium arsenide have been the backbone of the semiconductor industry for the last four decades. Now a days with the emerging field of conducting polymers along with the advantages of nanotechnology, such organic (semi) conductors are proved very promising materials in electronic, optoelectronic devices, gas sensors etc. Among different conducting polymers, polyaniline (PANI) has occupied the most important place in the family of conducting polymers. The thermal stability of PANI has been investigated by many researchers in present years and the results have shown that PANI base has a very good thermal stability and has higher thermal activation energy whereas PANI doped with protonic acids are significantly less stable[10].

Therefore along with better conductivity, several researchers have shown that thermal stability of PANI could be improved by combining PANI with polystyrene latex[11], multiwalled carbon nanotubes[12], ZnO nanoparticles[13], graphite[14] etc. Along with electrical conductivity, thermal stability of the polymers plays important role to modify the polymer properties to be used for advanced applications.

EXPERIMENTAL

Aniline monomer was distilled under reduced pres-

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sure. Ammonium persulfate (APS), picric acid were used as received. All chemicals were of analytical grade. 0.2M aniline and specific molar quantities of picric acid (0.1M-0.4M) were dissolved in 100 ml deionized water with stirring at room temperature for 30 min. The stirring was then stopped and 50ml aqueous solution of 0.2M APS was added and the reaction was left for 12 hrs. The resulting PANI precipitate was washed with distilled water and methanol several times. Finally the product was dried in vacuum oven at 80^{0}C temperature for 12 hrs.

Thermograms of all samples were recorded on Perkin- Elmer Diamond TGA/DTA in argon atmosphere at a heating rate of 10^{o}C/ min. TGA profile were taken over the temperature range of 30-1000^{o}C.

RESULTS AND DISCUSSIONS

In presence of atmospheric oxygen, the polymers containing low dissociation energy bonds are the most susceptible to oxygen attack whereas polymers containing phenyl group, C-F, fused rings etc. are expected to show higher oxidative stability at elevated temperatures. Another reason for lower thermal stability of polymers than usually expected is due to accidental inclusion of weak linkages in the main chain. While the presence of aromatic moieties in polyaniline will impart a better oxidative stability, the presence of C-N linkages will make it susceptible to oxygen attack. The doped of polyaniline, like other p-type doped conductive polymers, would be expected to be stable to oxygen but will be susceptible to the reaction with doping agent[15]. To understand the thermal stability of polyaniline at different dopant concentration, the thermal study of polyaniline with different concentration of picric acid as dopant were studied and represented in the figure 1.

It has been reported that undoped polyaniline is stable up to as high as 650oC whereas PANI doped with different concentration of Picric acid showed three steps degradation in thermo gravimetric analysis. The first stage weight loss starting practically from room temperature to 150^{o}C corresponds to the loss of water molecules/moisture present in the polymer matrix. The second stage loss, from 150^{o}C to 350^{o}C is associated with the loss of the dopant ion from the polymer matrix (de-doping). The weight loss after 350^{o}C is due to the complete degradation and decomposition of the polymer backbone after the loss of the dopant ion[16]. It has been observed that as the concentration of dopant increases, higher weight loss is obtained in the first step. Second step weight loss related to the loss of dopant ion is also found to be higher in 0.4M concentration as compared to 0.1M concentration. The third and final stage weight loss related to the breakdown, followed by decomposition and degradation of the polymer backbone, is also found to be higher in 0.4M concentration.

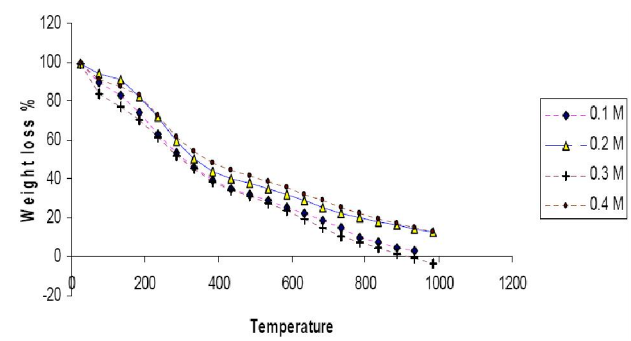

Figure 1 : Shows TGA curves of PANI doped with 0.1M to 0.4M of picric acid

TABLE 1 : Thermogravemetric analysis of weight loss of polyaniline doped with different concentrations of picric acid

Sample(Picric acid) Concentration	First step upto (oC)	Weight loss (%)	Second step (oC) to (oC)	Weight loss (%)	Third step (oC)	Rresidue at 900oC (%)
0.1M	*RT TO 150	10	150 TO 350	32	350	16.42
0.2M	*RT TO 150	13	150 TO 350	35	350	6.39
0.3M	*RT TO 150	19	150 TO 350	37	350	0.961
0.4M	*RT TO 150	23	150 TO 350	41	350	0.948

***RT- Room temperature**

"Sharp - Wentworth method"[17] has been employed for the determination of thermal parameters like thermal activation energy, change in entropy and free energy change of thermal degradation. While calculating these parameters, for the sake of calculations, the central linear region between 400-700^{o}C was considered for all samples which is the main region for polymer degradation. The activation energy (Ea) for the thermal degradation process was calculated using equation,

$$\log [(dc/dT)/(1-c)] = \log A - Ea/2.303\,kT \quad (1)$$

where, c is the fractional weight loss at temperature T, A= α / β, is the pre-exponential factor, Ea can be calculated from the slope of the plot between log [(dc/dT)/ (1-c)] and 1/T.

The values of entropy of activation (ΔS) and the free energy change (G) were calculated using the following Equations[18],

$$\Delta S = 2.303 \log (Ah/ kTs) \quad (2)$$

$$G = Ea - Ts (\Delta S) \quad (3)$$

where, h - Planck's constant, k - Boltzman constant, Ts - Temperature at half weight loss

From TABLE 2, it is observed that the activation energy and the temperature at which half weight loss occurs are higher in 0.4M concentration of PANI doped with picric acid as compare to 0.4M concentration of PANI doped with picric acid. PANI doped with 0.1M degraded half of its original weight at about 577K while this temperature increases to 641K for 0.4M concentration of PANI doped with picric acid.

TABLE 2 : Shows kinetic parameters of PANI doped with 0.1M to 0.4M concentration of picric acid.

PANI-Picric acid Concentration	Ea (KJ/mole)	Δ S (J/K)	G (KJ/mole)	Ts (K)
0.1M	1.43	-14.04	16.47	577
0.2M	58.51924	-28.46	24.45	581
0.3M	101.637	-42.09	28.61	607
0.4M	114.259	-44.49	86.36	641

The temperature at which half weight loss occur is one of the main criteria for the thermal stability of the polymer, we can conclude that PANI doped with 0.4 M concentration of picric acid with is thermally more stable than PANI doped with 0.1 M concentration of picric acid. Also it is observed that, as the concentration of dopant increases in the PANI matrix, the values of activation energy and Ts increases which indicates the existence of strong interaction at the interface of PANI and dopant and increased thermal stability. The negative values of entropy (ΔS) indicates that the polymer has the more ordered structure as the entropy is the measure of disorder, the disorder is less, the structure is more order.

CONCLUSION

A series of polyaniline doped with 0.1M to 0.4M concentration of picric acid have been synthesized by chemical oxidation polymerization method. TGA curves of PANI doped with 0.1M to 0.4M concentration of picric acid shows three significant degradation steps. Increased in thermal activation energy and temperature of half weight loss inferred the thermal stability of higher concentration of PANI doped with picric acid as compared to lower concentration.

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