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Application of model-free kinetics to the thermal and thermo-oxidative degradation of poly(3-hexyl thiophene)

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ABSTRACT

We report here the investigations on the thermal and thermo-oxidative degradation kinetics of a technologically important conducting polymer poly(3-hexyl thiophene) (P3HT) as measured in nitrogen and air medium, respectively. The derivative thermogravimetric results clearly indicate single stage decomposition for thermal degradation while triple stage decomposition is observed for thermo-oxidative degradation. The Vyazovkin model-free kinetics method was applied to calculate the effective activation energy (E_α) of the degradation process as a function of conversion. The E_α values are higher in nitrogen than in air medium. In nitrogen medium, the E_α value remains almost constant up to an extent of conversion, $\alpha = 90\%$. Interestingly, in air medium, the E_α shows an initial minimum, then increase and exhibits a maximum at $\alpha = 45\%$, decreases steadily and plateaus thereafter. This reveals that the degradation mechanism of P3HT in air medium is complex. The model-free isothermal predictions could be of use in correlating the service temperature of this conducting polymer.

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1. Introduction

Conducting polymers such as polyacetylene, polypyrrole, polythiophene, etc., have attracted much attention because of their potential applications in light emitting diodes (LEDs), non-linear optical materials and electrochromic devices [1,2]. During processing and subsequent service life, polymers are exposed to elevated temperatures under different environmental conditions which may initiate various degradation reactions, leading to chain-scission and cross-linking, impaired mechanical properties and ultimately loss of required properties [3]. This becomes a serious concern in polymers used in LED applications as their photoluminescence property gets destroyed. Thus, in the optimization of polymeric LEDs, a precise understanding of the thermal decomposition and lifetime prediction of polymers is therefore, a necessary step.

Poly(3-alkyl thiophenes) are π-electron conjugated polymers that have attracted a lot of interest due to their opto-electronic potentialities [4]. The presence of alkyl side chains not only enhances its solubility in common organic solvents but also decreases its glass transition temperature (T_g) [5,6]. Amongst poly(alkyl thiophenes), poly(3-hexyl thiophene) (P3HT) is an important conducting polymer that has excellent electrical conductivity and electroluminescence properties [1,7,8]. Furthermore, in applications like organic solar cells, diodes and polymeric field effect transistors, P3HT is an often used material because of its low-cost processing and solubility [9–12]. Enhanced service lifetime of P3HT and other derivatives of polythiophenes would improve their efficiency and help in their broad commercialization. For this, prior knowledge on their thermal stability and lifetime in different environments and temperatures is essential. Despite of many opto-electronic aspects that have been studied on P3HT, the thermal decomposition studies performed on this polymer are unfortunately limited only in understanding its degradation temperature [8,13–15].

In the recent years, the model-free kinetics method proposed by Vyazovkin [16–18] has been applied successively to determine the kinetic parameters of the thermal degradation process in many polymers [18–22]. However, there are no literature reports on the kinetic parameters of the thermal degradation process in P3HT using the model-free kinetics. In the present study, using the Vyazovkin model-free kinetics [16–18], we provide the effective activation energy (E_α), the conversion rates and the degradation time as a function of temperature for the thermal and thermo-oxidative degradation of P3HT.

2. Experimental

2.1. Sample preparation

The poly(3-hexyl thiophene) (P3HT) was synthesized chemically by oxidative polymerization using the standard procedure [23]. It was dissolved in chloroform and the solvent was evaporated

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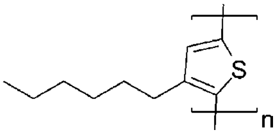
which resulted to a film. The sample was further dried in vacuum for more than 24 h and then used for measurements. The chemical structure of the P3HT is shown below.



2.2. Characterization

Although the main aim of the work is to understand the thermal decomposition kinetics of P3HT using model-free kinetics as applied to its TGA results, we have used different characterization techniques to confirm the nature of the synthesized P3HT. The regioregularity of the P3HT was found by using ^{1}H NMR spectrum in deutrated chloroform ($CDCl_3$) at room temperature with a 400 MHz FT-NMR (Bruker make). The FTIR spectrum was carried out from the films using a FTIR instrument (PerkinElmer RX1). Optical measurements in the solution state were carried out at room temperature with a Varian Cary 500 UV–Vis–NIR spectrophotometer on a quartz cell having path length of 10 mm. The photoluminescence experiments were also done in the solution state using a Varian Cary Eclipse Fluorescence Spectrophotometer. The solution was taken in a 10 mm path length quartz cell and the photoexcitation was done at 448 nm. The emission was detected at right angles to the excitation beam direction. For differential scanning calorimetry (DSC) experiment, DSC Q200 (TA instruments) was employed. Samples of ~6 mg was taken and heated with a heating rate of 10 °C/min.

Thermogravimetric analysis was performed using a TGA (Mettler-Toledo TGA/SDTA 851^e) instrument in the temperature range 30–1100 °C. The instrument was calibrated using a Mettler-Toledo total calibration procedure with respect to the indium and aluminum standards. Samples (~6 mg) for TGA measurements were placed in 70 μl alumina crucibles. The buoyancy effect in TGA has been accounted for by performing empty pan runs and subtracting the resulting data from the subsequent sample mass loss data. The measurements were done using the nominal heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min both in air and nitrogen atmosphere (flow rate in each case was maintained at 50 ml/min). In the temperature program, an initial 10 min isothermal segment allowed the furnace to purge with nitrogen/air and then the temperature was ramped to 1100 °C at the specified heating rate. Mettler-Toledo STAR^e software (ver 9.0) was used to perform the model-free kinetics (MFK) calculations.

2.3. Model-free kinetics

The rate of a thermal or catalytic reaction depends on the extent of conversion (α), temperature (T) and time (t). For each process, the reaction rate as a function of conversion, $f(\alpha)$ is different and must be determined from the experimental data. The dependence of the extent of conversion on temperature is customarily expressed as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where $k(T)$ is the rate constant and $f(\alpha)$ is the reaction model [17]. Depending on the reaction mechanism, the reaction model may take various forms. The temperature dependence of the rate constant is expressed in terms of Arrhenius equation as

$$k(T) = A\exp\left(\frac{-E}{RT}\right) \tag{2}$$

where T is the temperature, R is the gas constant, A is the pre-exponential factor and E is the activation energy.

Substitution of Eq. (2) to Eq. (1) yields

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{3}$$

Generally, the degradation of polymers tends to demonstrate complex kinetics that cannot be described by Eq. (3) alone throughout the whole temperature region [24]. The model-free kinetics method is based on the realization that the activation energy indeed depends on the extent of conversion (α) but they are always same at a particular conversion independent of the heating rate used. Thus, model-free kinetics (MFK) method is also called as an isoconversional method [18]. The kinetic parameters can be calculated using isoconversional methods of Friedman [25,26], Ozawa [27] and Flynn and Wall [28]. But the isothermal predictions based on these methods need the evaluation of kinetic triplet (activation energy E, pre-exponential factor A and reaction model $f(\alpha)$). The advanced integral isoconversional method proposed by Vyazovkin [16–18] allows the evaluation of Arrhenius parameters without choosing the reaction model. The data analysis in this approach follows all the points of conversion from multiple experiments. The main features of this method are given in the following paragraph and more details can be found in a recent review [18].

According to Vyazovkin model-free kinetics method, for a given extent of conversion, the reaction rate is only a function of temperature.

$$\left[\frac{d\ln(d\alpha/dt)}{dT^{-1}}\right]_\alpha = \frac{-E_\alpha}{R} \tag{4}$$

The isoconversional rates in Eq. (4) are determined as the rates to reach a given extent of conversion in several runs performed at different heating programs. The isoconversional method assumes that E_α is constant only at a given extent of conversion and the narrow temperature region related to this conversion at different heating rates [24]. In the model-free kinetics method, the activation energy (E) as a function of the conversion (α) is found. The thermal degradation is carried out at least in three different heating rates (β) and the respective conversion curves are calculated from the measured TG data. For each conversion (α), $\ln(\beta/T^2)$ is plotted against $1/T_\alpha$ that results to a straight line with slope ($-E_\alpha/R$), thus providing the activation energy as a function of conversion [17,18]. This plot enables to explore lifetime prediction of the polymer under study and the mechanisms of the thermally stimulated processes.

2.3.1. Isothermal predictions

Kinetic computations are used to simulate the variation of extent of conversion (α) vs. time (t) for a constant given temperature (T_{iso}) [18,29]. The obtained kinetic parameters are generally used to predict the maximum usable temperatures, to estimate the lifetime of polymers and the optimum processing conditions. Such isothermal predictions are called model-free predictions. The reliability of such predictions has been well documented in literature [18,19,21,24,30].

3. Results and discussion

First we report the nature of the synthesized P3HT as verified from various techniques. The ^{1}H NMR spectrum of P3HT in the 2.4–3.0 ppm region is shown in Fig. 1A. The NMR spectrum displays two signals at 2.81 and 2.56 for the methylene protons of hexyl substituent nearest to the thiophene ring [23,31]. The head–tail (HT) content was estimated from the ratio of the area of peaks at 2.56 ppm (HH) and 2.81 ppm (HT) in the NMR spectrum [23]. Using this assignment, we obtained a HT content of ~85% for our P3HT. The FTIR spectrum (Fig. 1B) shows the main essential spectral features of P3HT. The absorption peak at 3055 cm^{-1} is due to aromatic C–H stretching and the peaks at 2924 cm^{-1} and 2852 cm^{-1} are due

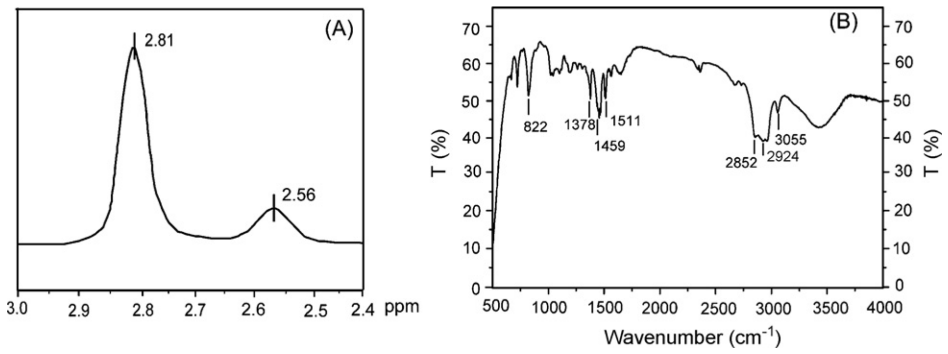


Fig. 1. (A) NMR spectrum of P3HT in $CDCl_3$ solution (0.01 mg/ml) and (B) FTIR spectrum of P3HT film.

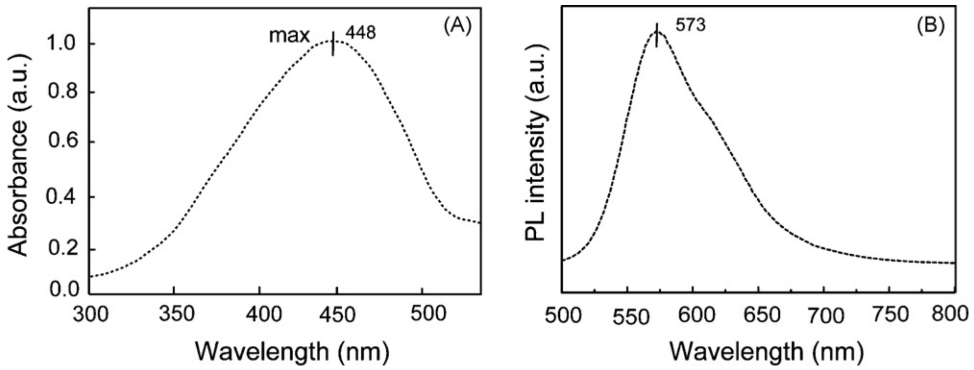


Fig. 2. (A) UV–vis spectrum of P3HT in chloroform solution (0.01 mg/ml) and (B) photoluminescence spectrum of P3HT in chloroform solution (0.005 mg/ml).

to CH_2 asymmetric and symmetric stretchings respectively [14,32]. The FTIR spectrum also displays the 1511 cm^{-1} and 1459 cm^{-1} peaks that are due to thiophene ring stretching [32] and 1378 cm^{-1} peak due to methyl deformation [31]. The peak at 822 cm^{-1} is due to C–H out-of-plane bending vibration of the thiophene ring [14].

The UV–Vis spectrum was taken in chloroform solution (0.01 mg/ml) that gives a broad absorption spectrum with a maximum wavelength of absorption λ_{max}, at 448 nm due to the π–π^* transition of the thiophene ring (Fig. 2A) [33]. Fig. 2B shows the solution-state photoluminescence (PL) spectrum of P3HT (0.005 mg/ml) which displays a clear photoluminescence intensity with maximum at ca. 573 nm [14,33].

The DSC plot of P3HT film is shown in Fig. 3 which exhibits an endothermic transition at ca. 193 °C with an enthalpy of fusion 3.6 J/g in close agreement with its reported value [8].

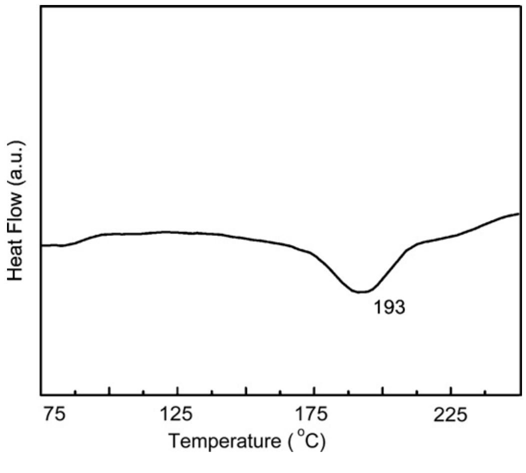


Fig. 3. The DSC plot of P3HT film.

Thermogravimetry is the most widely used technique to characterize the thermal decomposition of polymers. Fig. 4 shows the typical TG curves of normalized mass and derivative thermogravimetry (DTG) data of the derivative mass of P3HT at a heating rate of 20 °C/min in (A) nitrogen and (B) air media, respectively. The DTG curves illuminate that the decomposition process in nitrogen is single-step while, it is triple stage in air medium.

Thermal decomposition reaction of P3HT in nitrogen medium was observed at ca. 460 °C and ends at ca. 525 °C with the maximum rate of degradation at ca. 498 °C. The residual mass is ca. 30% after degradation. The decomposition behaviour of P3HT in air medium is different from that in nitrogen. The first stage of decomposition in air is mild and starts at ca. 285 °C and ends at ca. 340 °C with a maximum rate of mass loss around 311 °C. This decomposition is followed by a significant degradation step which occurs between 410 °C and 510 °C with the maximum mass loss at ca. 474 °C. The final decomposition step leads to a negligible residue (<5%) that commences almost instantaneously after second stage and ends at ca. 690 °C with the maximum mass loss at ca. 583 °C.

Earlier study on the thermal decomposition of this polymer has shown single-step decomposition in nitrogen medium in agreement with our results [8]. But, in air or oxygen medium, P3HT and related polymers have shown two stage decomposition in contrast to three stage decomposition in the present case [2,3,13–15]. The first decomposition was attributed to cleavage of the alkyl chains while the second one was explained as due to thermo-oxidative decomposition of the polymer backbone [2,3,13,15].

Following this, we attribute the degradation in nitrogen to be mainly due to the cleavage of the hexyl chain attached to the aromatic thiophene backbone. The maximum decomposition temperature in air at ca. 474 °C could be due to scission of the alkyl side chain. At high temperature of ca. 583 °C, oxidation is accelerated and the pyrolysis of the aromatic backbone of the polymer chains is ignited [13,15]. The oxidation of the sulphur atom in the backbone

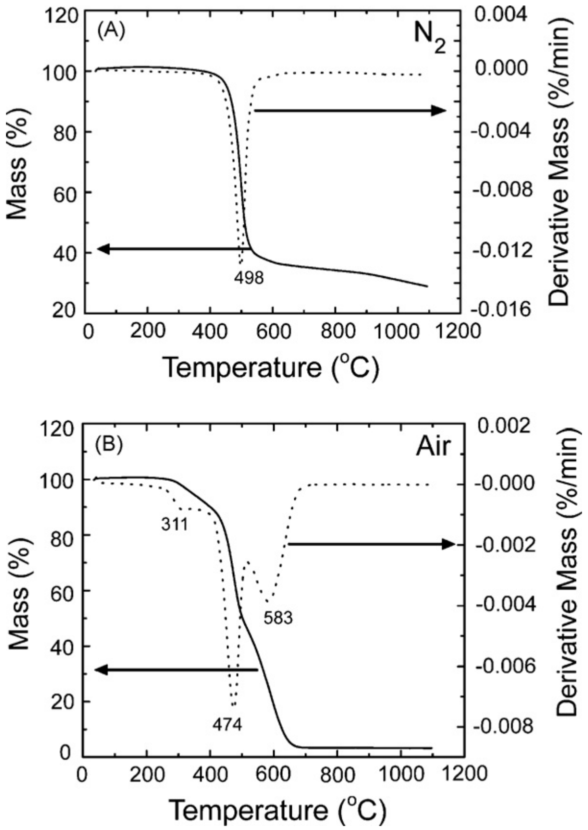


Fig. 4. Typical thermogravimetric data with heating rate 20 °C/min for P3HT in (A) nitrogen and (B) air medium.

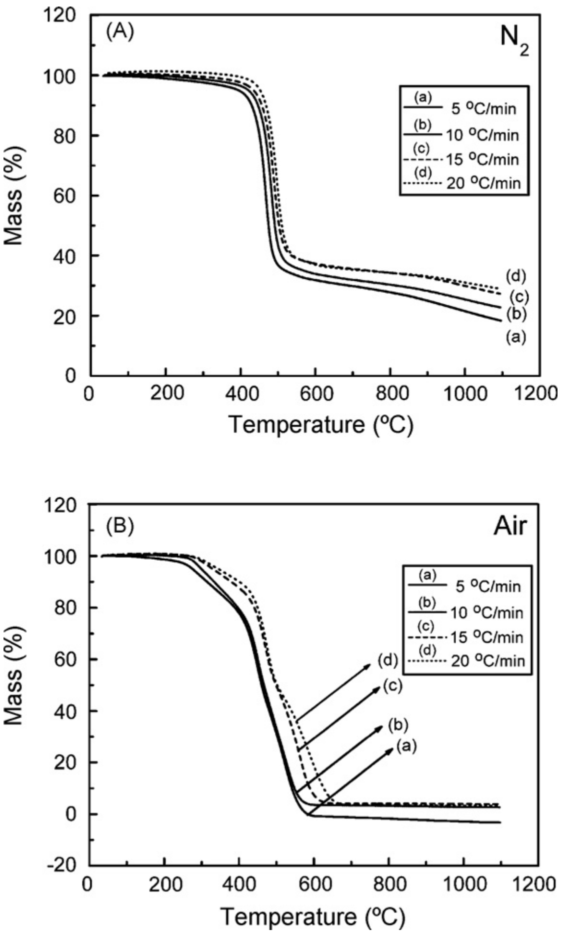


Fig. 5. Thermogravimetric curves for P3HT at a heating rate of (a) 5 °C/min, (b) 10 °C/min (c) 15 °C/min and (d) 20 °C/min in (A) nitrogen and (B) air medium.

thiophene ring would result to sulfoxides, sulfones which are then decomposed to sulfonate esters [34]. Although the origin of the first decomposition maximum at ca. 311 °C is not clear, it could be suggested as due to the cleavage of more vulnerable alkyl chains. This suggestion is based on the wide temperature range (285–460 °C) reported for the first decomposition by various authors [13–15].

Beyond 800 °C, the TGA plot obtained in air medium remains stable whereas the curve obtained in nitrogen medium shows a mild gradual decrease (Fig. 4A and B). The TGA measurements conducted in nitrogen and air have shown similar trends at high temperatures (after the main degradation steps) for poly[1,4-bis-(3-alkyl-2-thienyl)phenylene] and poly[(3-alkyl thio)thiophenes] [3,35] in agreement with the present results. Although the DTG curve gives no clear indication to attribute this mild decrease to a step change, it reflects that the obtained residue is less stable at this high temperature. Previous thermal degradation study on poly(3-octyl thiophene) using pyrolysis mass spectrometer resulted to main products such as hexane, heptane, hydrogen sulphide (H_2S), low molecular weight hydrocarbons and carbon disulfide (CS_2) [36]. Amongst these, CS_2 was observed only at high temperature (ca. 800 °C) [36]. Thus, in the present case for P3HT degradation in nitrogen medium, one could expect the breakage of the thiophinic ring (after the main degradation step) and the formation of CS_2. The gradual elimination of this product (mainly) could be the reason for the steady decrease observed in TGA curve after 800 °C (Fig. 4A).

Fig. 5 shows the TG curves of P3HT in (A) nitrogen and (B) air at a heating rate of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min. The onset decomposition temperatures in nitrogen medium are 423 °C, 437 °C, 447 °C and 460 °C at the heating rates 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min respectively. The corresponding onset decomposition temperatures in air are lower and observed at 257 °C, 271 °C, 277 °C and 285 °C. The thermal degradation temperatures increase with the heating rate in agreement with the thermal decomposition data reported in other polymers [37,38]. The char yield at 800 °C in nitrogen medium is 18–29% while it is less than 5% in air medium at all the four heating rates.

Fig. 6A and B shows the plot of percentage of conversion vs. time for P3HT in nitrogen and air medium respectively obtained from model-free kinetics data. From these plots, it is clear that the time for degradation of P3HT decreases considerably as a function of temperature. At 400 °C, in nitrogen medium, P3HT needs ca. 100 min to degrade 43% of the initial mass and for the same time in air medium 92% of the initial mass is degraded. These observations clarifies that the degradation mechanism of P3HT in nitrogen and air medium is different, as pointed out earlier.

Since the thermal degradation of polymers usually involves multiple steps characterized by different activation energy values, the relative contribution of these steps to the overall degradation rate changes with both temperature and extent of conversion. This means that the effective activation energy (E_α) determined from TGA data should be a function of these two variables. The dependence of E_α on the extent of conversion for the thermal degradation process of P3HT in nitrogen and air medium is shown in Fig. 7A and B. In nitrogen medium, the E_α value remains almost constant around 200 kJ/mol (Fig. 7A). This means that the degradation process involves single-step kinetics and is in agreement with the degradation pattern observed (Fig. 4A). Also, the obtained activation energy of P3HT are comparable to the value of 222 kJ/mol reported for a highly regioregular poly(3-dodecyl thiophenes) (P3DT) in nitrogen medium [2]. However, in air medium, the variation of E_α with the extent of conversion reveals the exis-

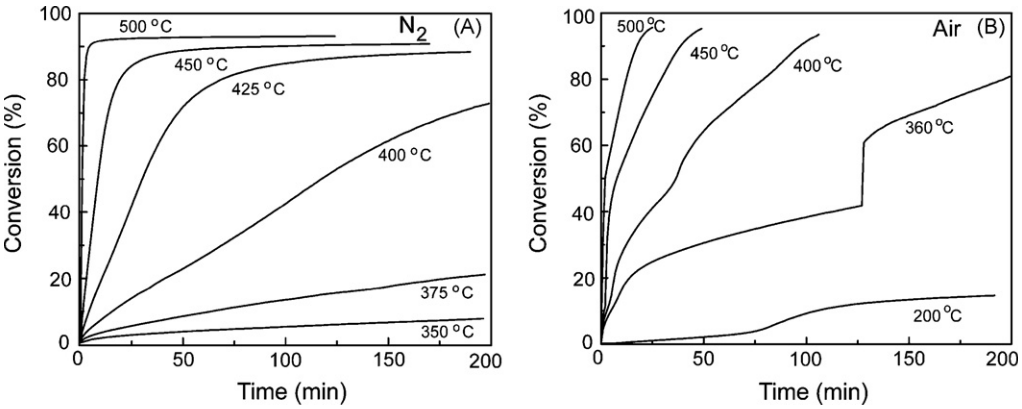


Fig. 6. Extent of conversion of P3HT as a function of time at different temperatures in (A) nitrogen and (B) air medium.

tence of a complex reaction mechanism (multi-step kinetics) and that P3HT degradation in air cannot be adequately described by a single E_α value (Figs. 4B and 7B). In air medium, thermal degradation occurs via three stages. In the first stage ($\alpha < 0.15$), the E_α value is about 50–90 kJ/mol. Degradation starts with the cleavage of the most vulnerable alkyl tails at this conversion stage. Once all the weak links have given way to initiation, the mass loss is controlled by the cleavage at the stronger links [24]. Thus, for higher conversions ($0.15 < \alpha < 0.45$), the effective activation energy shows an increase from ~50 kJ/mol to 155 kJ/mol. This high increase of E_α reveals that greater energy is required for the breakage of strong linkages. Once the main chain-scission occurs, the effective activation energy decreases to ~90 kJ/mol ($\alpha < 0.65$) and remains almost constant thereafter. From the present results, it is clear that the polymer is more stable in nitrogen medium compared to air. Also, even at high temperatures (800 °C and above), the residue obtained in nitrogen medium is higher (ca. 25%) as compared to residue in air medium (<5%). These clarify the reason for higher activation energy in nitrogen as compared to air medium.

Further, we have estimated the temperature of the degradation process of P3HT predicted by model-free data, providing the time required to the degradation reaction, as summarized in Tables 1 and 2 for nitrogen and air medium respectively. For instance, to achieve 10% degradation in nitrogen, it is necessary to expose P3HT at 408 °C for 10 min whereas to achieve the same degradation for the same time in air 313 °C is sufficient. If one examines what happens at 90% of conversion, it is clear that in nitrogen medium the sample needs to be exposed at 486 °C for 10 min whereas a temperature of 539 °C is essential in air medium for the same period of time.

Generally, the degradation of polymers in inert medium like nitrogen needs high temperature than in air medium [3,18]. But,

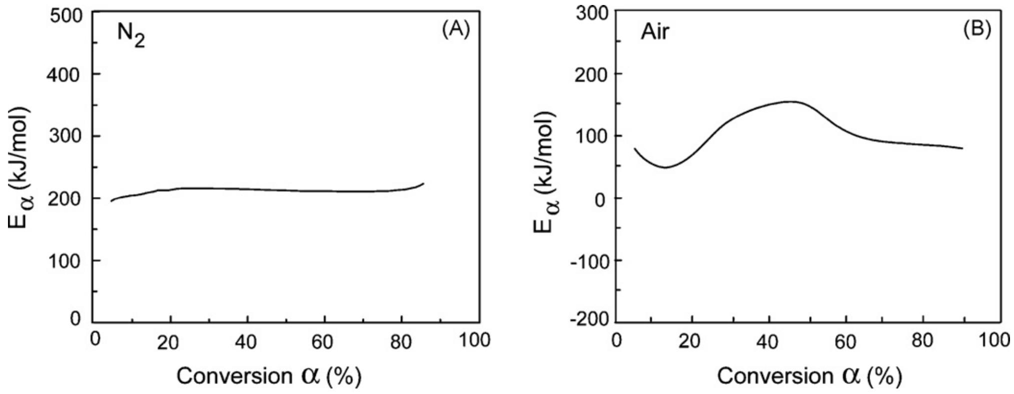


Fig. 7. The dependence of effective activation energy on the extent of conversion for the degradation of P3HT in (A) nitrogen and (B) air medium obtained using model-free kinetics of TGA data.

Table 1
Isoconversion parameters for P3HT in nitrogen medium.

Time (min)	Conversion (%)								
	10	20	30	40	50	60	70	80	90
10	408.3	425.9	435.5	441.8	446.7	451.3	456.3	463.5	485.6
20	395.4	413.0	422.3	428.3	432.9	437.3	442.1	449.1	474.0
30	388.2	405.6	414.8	420.7	425.1	429.3	434.0	441.0	467.4
40	383.1	400.5	409.6	415.3	419.7	423.8	428.4	435.3	462.8
50	379.2	396.6	405.7	411.3	415.5	419.6	424.1	431.0	459.3
60	376.1	393.4	402.4	408.0	412.1	416.1	420.6	427.5	456.4
70	373.2	390.7	399.7	405.2	409.3	413.3	417.7	424.5	454.0
80	371.2	388.4	397.4	402.8	406.9	410.8	415.2	422.0	452.0
90	369.2	386.4	395.4	400.8	404.8	408.6	413.0	419.8	450.1
100	367.4	384.7	393.6	398.9	402.9	406.7	411.0	417.8	448.5

Table 2
Isoconversion parameters for P3HT in air medium.

Time (min)	Conversion (%)								
	10	20	30	40	50	60	70	80	90
10	313.1	376.4	406.6	424.1	440.9	466.3	490.7	512.9	539.1
20	274.5	342.8	385.0	404.5	418.4	434.0	452.7	471.0	490.9
30	254.2	324.7	372.9	393.6	405.9	416.4	432.1	448.6	465.3
40	240.7	312.5	364.7	386.0	397.3	404.4	418.3	433.4	448.1
50	230.6	303.4	358.4	380.3	390.7	395.4	407.9	422.1	435.3
60	222.7	296.1	353.4	375.6	385.5	388.2	399.6	413.1	425.2
70	216.2	290.1	349.2	371.8	381.1	382.3	392.8	405.7	416.9
80	210.8	285.1	345.6	368.5	377.4	377.2	387.0	399.4	409.8
90	206.0	280.6	342.5	365.6	374.1	372.8	382.0	394.0	403.7
100	201.9	276.8	339.7	363.0	371.2	368.9	377.5	389.2	398.4

polymers like poly(methyl methacrylate) have shown improved thermal stability in air as compared to nitrogen medium [39]. The interesting feature from this isoconversional results is that beyond 50% of conversion, to effect the change during the initial period of time (10–20 min), higher temperature is needed in air medium than in nitrogen. This result illustrates that the existence of incongruity in thermal behaviour of polymers at any stage during its thermal degradation, could be found with the use of model-free kinetics.

4. Conclusions

For the first time, we have applied model-free kinetics to understand the thermal degradation of P3HT. The thermal degradation of P3HT involves single-step decomposition in nitrogen while three stage decomposition has been observed in air. The degradation mechanism of P3HT in air is quite different from that observed in nitrogen. The value of effective activation energy (E_α) of P3HT is higher in nitrogen than in air. In nitrogen, the E_α value remains almost constant at ca. 200 kJ/mol. But, in air medium, it starts to decrease from 90 kJ/mol, shows a minimum at 15% of conversion, then increase up to 45% of conversion and exhibits a gradual decrease thereafter to saturate close to the initial value. The present results are expected to be of help in correlating the service temperature and luminescence property of P3HT.

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