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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.

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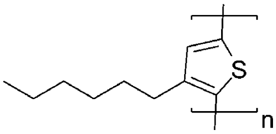
which resulted to a film. The sample was further dried in vacuum for more than 24 h and then used for measurements. The chemical structure of the P3HT is shown below.



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