

Thermal degradation kinetics and lifetime prediction of a luminescent conducting polymer

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Abstract: The thermal stability, degradation kinetics and lifetime-prediction of a luminescent conducting polymer, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), are investigated. The derivative thermogravimetry curves indicate a double-stage decomposition process in a nitrogen atmosphere, and a multi-stage decomposition process in an air atmosphere. The apparent activation energy values of MEH-PPV are higher in nitrogen than in air. Activation energies slightly increase and are then approximately stable in nitrogen for the initial mass loss, while the activation energy changes differently with the percentage mass loss in air. The activation energy decreases for the initial mass loss and increases with mass loss when the mass loss is above 30%; beyond 70% it decreases again. The lifetime of MEH-PPV decreases dramatically from 10^6 min to 0.03 min as the temperature increases from 25 °C to 300 °C in air. The lifetime is longer in nitrogen than in air and decreases from 10^{14} min to 2.34 min with increasing the temperature from 25 °C to 300 °C in nitrogen. These lifetime parameters indicate that the service/process temperature has a strong influence on the luminescence of MEH-PPV. The maximum absorption and wavelength at maximum absorption of MEH-PPV decrease with increasing temperature in the visible region.

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Keywords: luminescent conducting polymer; poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV); degradation kinetics; lifetime prediction and absorption behaviour

INTRODUCTION

Polymeric light-emitting devices (LEDs) have attracted a great deal of attention as a result of academic interests and their applications in full-colour flat-panel displays.^{1,2} Extensive studies have been reported on polymeric LEDs with the aim of achieving high brightness and multi-colour emission, and of improving the durability and thermal stability of devices.³ Among the poly(*para*-phenylenevinylene) (PPV)-based luminescent conducting polymers, the dialkoxy derivatives, such as poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), are particularly noteworthy for use in light-emitting layers in polymeric LEDs. The side-group substituents not only render the polymer soluble in common organic solvents, such as xylene and anisole, but also improve the electrical and optical characteristics.^{4–7}

Most work has been focused on two aspects of polymeric LEDs. One is to improve the efficiency of polymeric LEDs by changing materials, electrodes and structures, such as multi-layer structures with

an electron-transporting layer and a hole-transporting layer;^{8–18} The other is to increase the service lifetime of polymeric LEDs through the improvement of existing light-emitting polymers and to develop new light-emitting materials, as well as to investigate failure mechanisms.^{19–24} In fact, the first aspect is related to the luminescence kinetics of materials, while the second is concerned with to the stability of light-emitting polymers.

In MEH-PPV LED investigations, numerous research results showed the built-in potential in MEH-PPV devices to scale with the difference in the work functions of the two metal electrodes.⁸ When the current is plotted as a function of the applied bias, it has a form that suggests trap-limited conduction. The electrons in MEH-PPV have a field-dependent mobility which approaches that of holes under typical operating conditions.⁹ The current scaled with the applied field rather than the voltage with various MEH-PPV layer thickness.¹⁰ A voltage bias applied between the near-field probe and the substrate results in a highly spatially confined electric field studied through measuring the electric field-induced

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Contract/grant sponsor: Area of Strategic Development Fund, The Hong Kong Polytechnic University

(Received 31 July 2002; revised version received 7 March 2003; accepted 24 March 2003)

Published online 5 November 2003

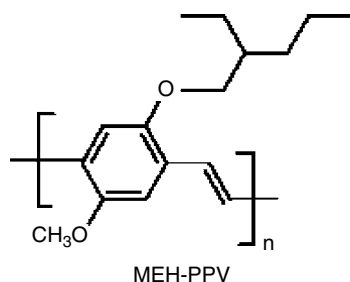
modulation of the near-field photoluminescence of thin films of MEH-PPV.¹³ The emissions from individual MEH-PPV molecules exhibit large-amplitude, discrete intensity fluctuations, which are assigned to excited-state quenching by photo-generated fluorescence quenchers.¹⁴

Some efforts have recently focused on improving the lifetimes of these devices. Thermal decomposition and photo-oxidation degrade the device performance and ultimately limit device lifetime. One of the primary degradation mechanisms in polymeric LEDs is photo- and/or thermo-oxidation of the polymer. This results in the formation of defects which act as exciton dissociation sites, leading to a quenching of photoluminescence, and destroy the properties of the device.^{22–25} The controlled photo- and thermo-oxidation may improve the performance of the devices. A precise understanding of photo-oxidation and thermal decomposition of conjugated polymers during energy transfer (as well as the lifetime prediction of polymers) is, therefore, a necessary step in the optimization of polymeric LEDs.

Thermal stability of polymers is one of the most important properties for both processing and application.^{25–30} Although there have been several papers on photo-oxidation and device degradation,^{22–25} the thermal stability, degradation kinetics and lifetime-prediction of luminescent conducting polymers have not been studied systematically. This paper mainly presents the thermal degradation kinetics and lifetime-prediction of MEH-PPV by dynamic thermogravimetric (TG) and ultraviolet-visible (UV-VIS) behaviour at various temperatures.

EXPERIMENTAL

Poly[2-methoxy-5-(2-ethyl hexoxy)-*p*-phenylenevinylene] (MEH-PPV) material for the study was obtained from American Dye Source, Inc. Its chemical structure is shown below. The glass transition temperature, T_g , is about 67 °C (determined by differential scanning calorimetry i.e., DSC, at 20 °C min⁻¹) and molecular weight, M_w , is 50 000 (gel permeation chromatography, ie, GPC, versus polystyrene standards).



Thermogravimetric (TG) analyses were performed using a Netzsch STA 449C Jupiter instrument

under both air flow (30 ml min⁻¹) and nitrogen flow (20 ml min⁻¹) from 25 to 1000 °C at four heating rates of 2, 5, 10 and 20 °C min⁻¹. Samples (of about 4 mg) were placed in vitreous silica pans. Precision of temperature measurements is ± 1.5 °C.

The MEH-PPV film with a thickness of about 50 nm was spin-coated on a quartz plate. The UV-VIS spectra of MEH-PPV at various temperatures were measured by a Lambda 18 (Perkin-Elmer) UV-VIS Spectrometer.

RESULTS AND DISCUSSION

Thermogravimetric analysis

Thermogravimetry (TG) is the most widely used technique to characterize the thermal decomposition of polymer materials. Figure 1 shows typical TG curves of normalized mass (a) and derivative thermogravimetry (DTG) data of the derivative of mass (b) as functions of temperature for MEH-PPV at a heating rate of 5 °C min⁻¹ in nitrogen and air environments, respectively. It is clear that, while the DTG curves indicate a double-stage decomposition process in nitrogen, a multi-stage decomposition process is found in air.

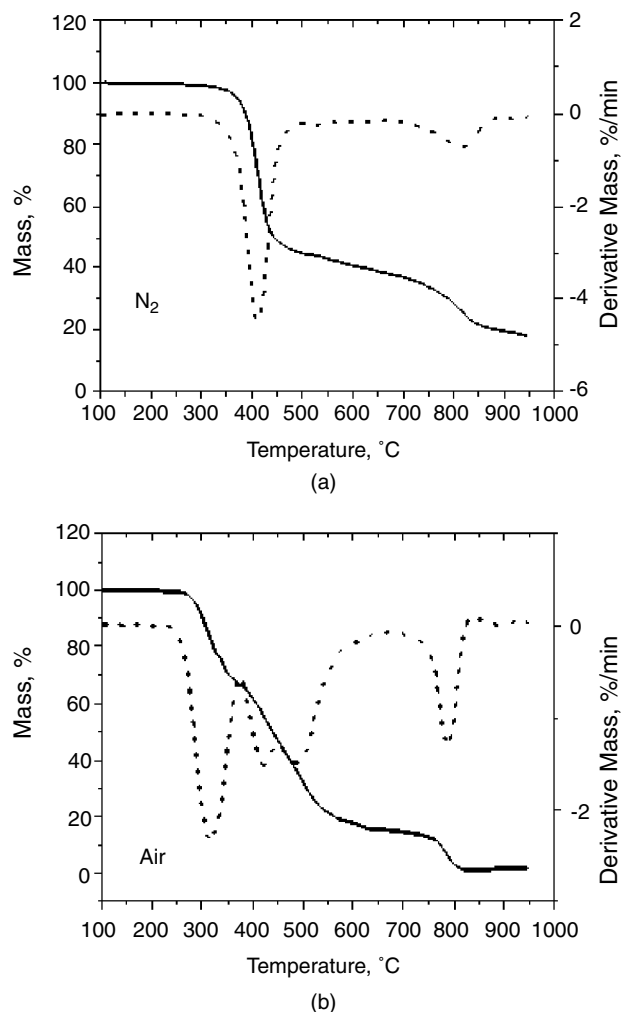


Figure 1. Typical TGA data for MEH-PPV in (a) a nitrogen and (b) an air environment.

The first stage of the degradation reaction in nitrogen was observed around 360 °C and stopped around 450 °C, with a maximum rate at 413 °C. The second stage of the decomposition appears between 450 and 850 °C with a maximum rate of mass loss around 783 °C. The residue mass is about 20% after decomposition. The decomposition behaviour in air is quite different from that in nitrogen. In air, the first stage of degradation reaction begins around 280 °C and stops around 367 °C with a maximum rate at 313 °C. The second and third stages of the decompositions appear between 367 and 462 °C with a maximum rate of mass loss around 412 °C, and between 462 and 650 °C with a maximum rate of mass loss around 478 °C, respectively. The last stage of degradation reaction begins around 650 °C and stops around 813 °C with a maximum rate at 778 °C. This last step, which leads to negligible residue, takes place around 813 °C. This indicates that the degradation mechanisms in nitrogen and air are quite different.

Degradation kinetics

In thermogravimetric analysis, the conversion rate of reaction may be defined as the ratio of actual mass loss to the total mass loss corresponding to the degradation process.

$$\alpha = \frac{M_0 - M}{M_0 - M_f} \quad (1)$$

where, M , M_0 , and M_f are the actual, initial and final masses of the sample, respectively.

The rate of degradation, $(d\alpha/dt)$, can be expressed as functions of temperature and mass of the sample, i.e.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \quad (2)$$

A is the frequency factor, n is the reaction order, E is the apparent activation energy of the degradation reaction, R is the gas constant and T is the absolute temperature. Upon introducing the heating rate, $r = (dT/dt)$, eqn (2) can be modified to

$$\frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{r} \exp\left(-\frac{E}{RT}\right) dT \quad (3)$$

Therefore eqn (3) is the fundamental relationship to determine kinetic parameters on the basis of TG data. The integral form of eqn (3) can be written as

$$g(\alpha) = \frac{A}{r} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{rR} p(x) \quad (4)$$

where $x = \frac{E}{RT}$ and $p(x) = -\int_{\infty}^x \frac{\exp(-x)}{x^2} dx$.

To describe the thermal degradation kinetics, Ozawa³¹ assumed $\log p(x) \approx -2.315 - 0.457x$ or $\ln p(x) \approx -5.330 - 1.052x$ for $20 < x < 60$ for the

non-plateau region of the curves. Equation (4) can be written as

$$\ln g(\alpha) = \ln \frac{AE}{rR} - 5.330 - 1.052 \frac{E}{RT} \quad (5)$$

Here, A and R are constants and, for a particular α or mass loss percentage, $g(\alpha)$ is a constant. Then eqn (5) becomes

$$\ln r = C - 1.052 \frac{E}{RT} \quad (6)$$

where the constant C is given by

$$C = \ln \frac{AE}{g(\alpha)R} - 5.330$$

Hence, the value of E can be computed by Ozawa's method for any particular mass loss, being determined from the linear dependence of the $\ln r$ versus $1/T$ plot at different heating rates for the non-plateau region of the curves.

Figure 2 shows the dynamic TG curves of MEH-PPV in nitrogen and air at heating rates of 2, 5, 10, and 20 °C min⁻¹. The thermal degradation

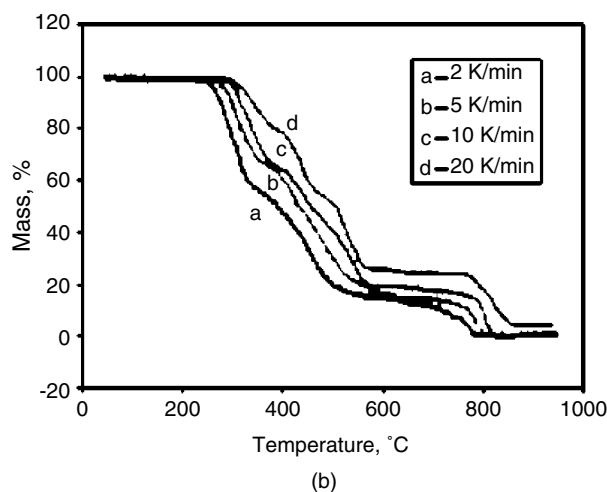
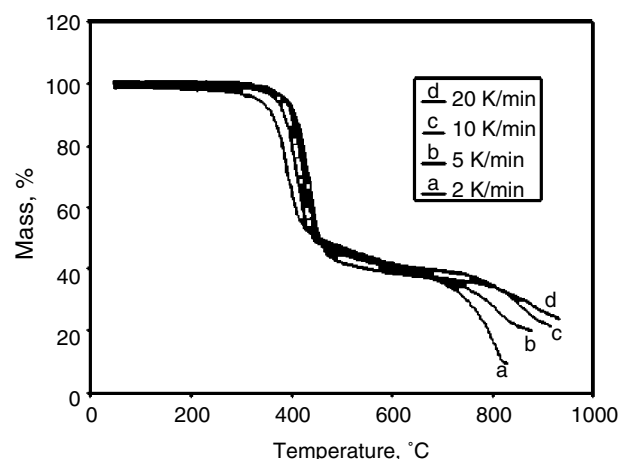


Figure 2. Dynamic TG curves for MEH-PPV at heating rates of 2, 5, 10 and 20 °C min⁻¹ in (a) nitrogen and (b) air.

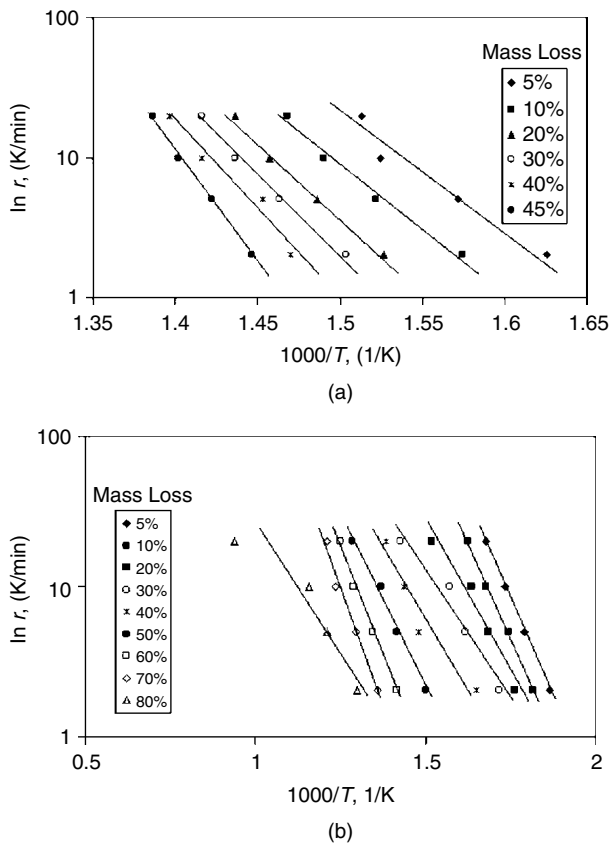


Figure 3. Temperature dependence of $\ln r$ (heating rate) versus reciprocal absolute temperature ($1/T$) for various weight loss in (a) nitrogen and (b) air.

temperatures increase with the heating rate. Based on eqn (6), the relationships between the logarithm of heating rate ($\ln r$) and $1/T$ for different values of mass loss, during the thermal degradation of MEH-PPV in nitrogen and air environment, are shown in Fig 3(a) and (b), respectively. The isoconversional plots are almost parallel straight lines in nitrogen but not in air, which indicates that the multi-stage decomposition process in air is a complex mass loss process with several mechanisms. Figure 4(a) and (b) illustrate that the calculated values of apparent activation energies vary with the percentage of mass loss for the degradation of MEH-PPV in nitrogen and air. The apparent activation energy values are found to be higher in nitrogen than in air. Figure 4(a) shows that the activation energy slightly increases and is then approximately stable in nitrogen for the initial mass loss. A sharp increase in the activation energy is observed around 40% mass loss. The activation energy changes in air are quite different from those in nitrogen: the activation energy decreases for the initial mass loss and increases with mass loss when the mass loss is above 30%; beyond 70% it again decreases. This shows that, in the first step of degradation, the reaction is accelerated once the decomposition starts owing to the decrease of the activation energy. The process of the oxidation of alkyl-substituted PPV has been proposed,²⁵ as shown in Fig 5. Polymer A

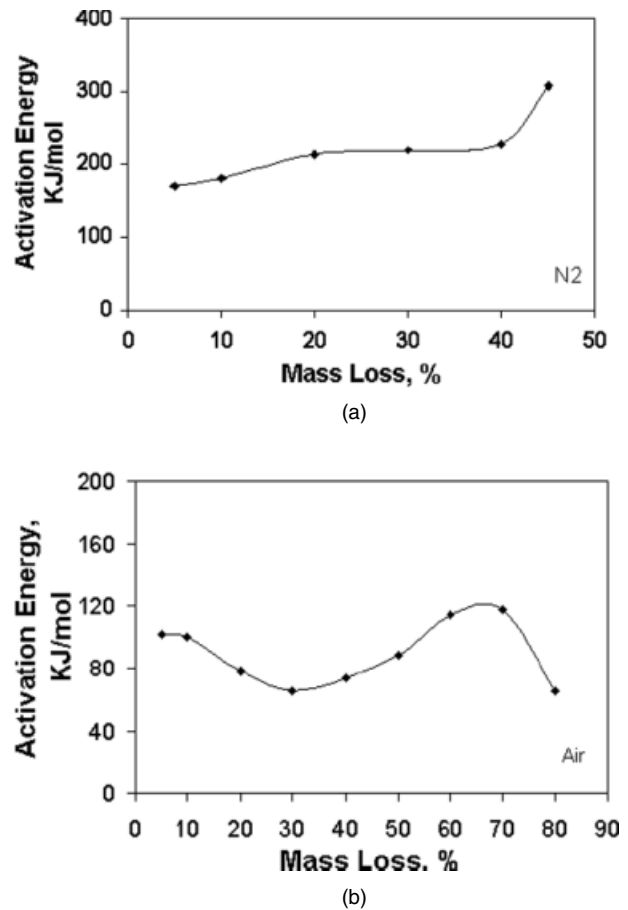


Figure 4. Percentage weight loss dependence of activation energy for the degradation of MEH-PPV in (a) nitrogen and (b) air.

transforms to oxidized product C through an interim peroxide B. In general, the interim peroxide B is unstable and is easily changed to oxidized product C. This oxidation process may be described by the transformation of polymer A to oxidized product C with complex oxidized product such as mixtures through peroxide B during this stage. The 30% mass loss corresponds to a temperature of approximate 350 °C. The decomposition reaction goes into the second stage at 367 °C and above, with increasing percentage mass loss. The oxidized product C thus formed is more stable and requires higher activation energy for its decomposition.

UV-VIS characterization

Figure 6 represents the UV-VIS spectra of MEH-PPV when the temperature reaches different values at a heating rate of 20 °C min⁻¹ in air. The absorption maximum and wavelength at maximum absorption decrease with increasing temperature in the visible region. At the same time, it can be seen from Fig 6 that, at 400 °C, the peak in the visible region dies away and the peak responding to the phenyl group in the UV region still exists. This indicates that, at 400 °C, the polymer A is decomposed into the oxidized product C, which is the main residue left. As the temperature is increased further, the peak in the UV region disappears

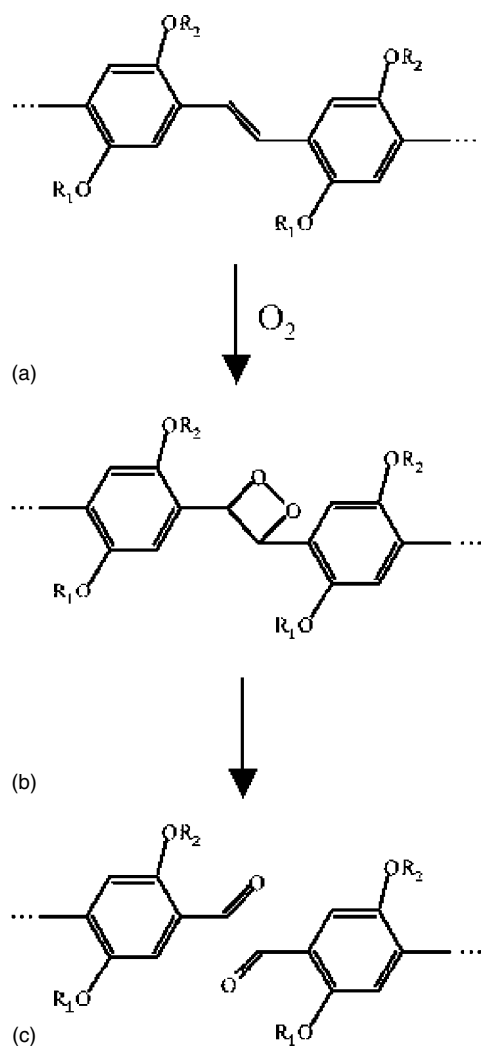


Figure 5. Oxidation process of alkyl-substituted PPV.

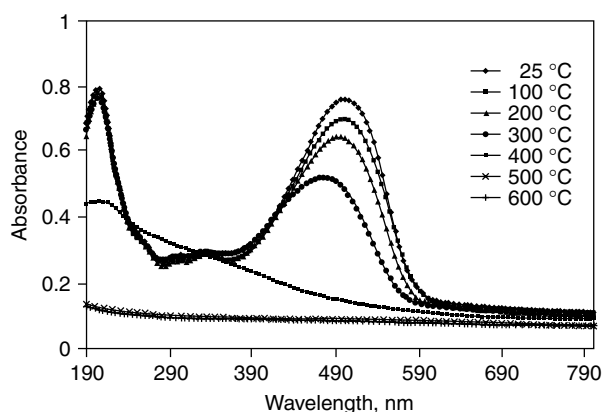


Figure 6. UV-VIS spectra of MEH-PPV for various temperatures at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$.

as a result of further reaction of oxidized product C with oxygen.

Lifetime prediction

The estimated lifetime t_f of a polymer to failure can be defined as the time when the mass loss reaches 5 wt%,²⁹ i.e. $\alpha = 0.05$. From the integration

of eqn (2), the lifetime can be estimated by:

$$t_f = \frac{(1 - 0.95^{1-n})}{A(1-n)} \exp \frac{E}{RT} \quad (n \neq 1) \quad (7)$$

or

$$t_f = \frac{0.0513}{A} \exp \frac{E}{RT} \quad (n = 1) \quad (8)$$

The reaction order value, n , can be obtained directly from the symmetrical index of a derivative thermogravimetry (DTG) peak based on the second Kissinger technique:³⁰

$$n = 1.88 \cdot |(d^2\alpha/dt^2)_L| / |(d^2\alpha/dt^2)_R| \quad (9)$$

where indices L and R correspond to the left and right peak ($d^2\alpha/dt^2$) values (extrema) on the second derivative thermogravimetry (DDTG) curves. The luminescence of a conducting polymer depends on its chemical structure. As one of the primary degradation mechanisms, oxidation results in the formation of defects, leading to the quenching of photoluminescence. When the mass loss (α) of MEH-PPV is 0.04, the corresponding temperature is about $300\text{ }^{\circ}\text{C}$ at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$, the absorption in the visible region decreases, but still exists, as Fig 6 shows. Assuming that the quenching of photoluminescence of MEH-PPV occurs at $\alpha = 0.05$ (corresponding to $320\text{ }^{\circ}\text{C}$), the lifetime can also be estimated by eqn (7).

Figures 7 and 8 show the DTG and DDTG curves of MEH-PPV for the first stage of decomposition at various heating rates in nitrogen and air, respectively. The n values for the first stage of decomposition at various heating rates in nitrogen and air, as well as $\ln A$ values calculated from eqn (2) based on the activation energies at a mass loss of 5%, are listed in Table 1. The average n and $\ln A$ values are 1.74 and 31.72 min^{-1} in nitrogen, respectively, while the respective average n and $\ln A$ values are 1.56, and 22.13 min^{-1} in air. Using these kinetic data and eqn (7), the estimation results of the lifetime values for MEH-PPV in nitrogen and air at a mass loss of 5% and various temperatures are listed in Table 2. It is apparent that the lifetime of MEH-PPV decreases dramatically from 10^6 min to 0.03 min

Table 1. Thermal degradation kinetic parameters of MEH-PPV at a mass loss of 5%

Heating rate ($^{\circ}\text{C min}^{-1}$)	Atmosphere	E_a (kJ mol^{-1})	n	$\ln A$ (min^{-1})
2	Nitrogen	169.27	1.81	31.91
5			1.72	31.41
10			1.70	31.64
20			1.74	31.93
Average			1.74	31.72
2	Air	101.99	1.37	22.15
5			1.67	22.17
10			1.39	22.22
20			1.80	21.97
Average			1.56	22.13

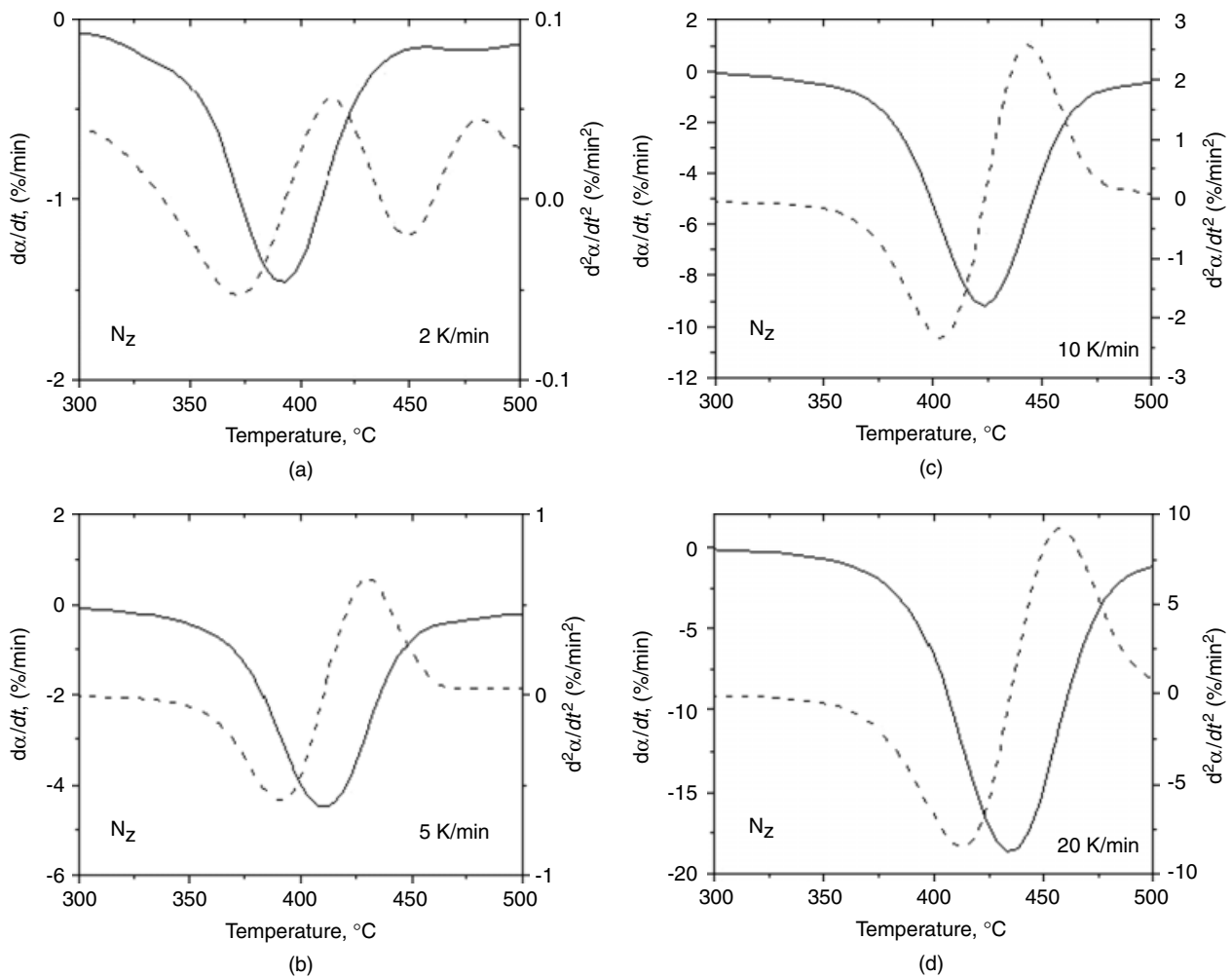


Figure 7. DTG and DDTG curves of MEH-PPV at various heating rates in nitrogen.

as the temperature increases from 25 °C to 300 °C in air. Obviously, the lifetime is longer in nitrogen than in air and decreases from 10^{14} min to 2.34 min with increase in the temperature from 25 °C to 300 °C in nitrogen. These lifetime parameters clearly suggest that the service temperature has a strong influence on the luminescence of MEH-PPV.

CONCLUSIONS

The thermal degradation of MEH-PPV is a double-stage decomposition process in nitrogen and a multi-stage decomposition process in air. This indicates that the degradation mechanisms in nitrogen are quite different from those in air. The apparent activation energy values of MEH-PPV are higher in nitrogen than in air. Activation energies slightly increase and are

then approximately stable in nitrogen until the mass loss reaches 40%. The activation energy decreases initially and then increases when the mass loss is above 30%, beyond 70% it decreases again. The absorption maximum and wavelength at maximum absorption of MEH-PPV decrease with increasing temperature in the visible region. The lifetime of MEH-PPV decreases dramatically with increasing temperature both in air and in nitrogen, but the lifetime is much longer in nitrogen than in air. The lifetime parameters indicate that the service/process temperature has a strong influence on the luminescence of MEH-PPV.

ACKNOWLEDGEMENT

The authors wish to acknowledge the financial support received from the Area of Strategic Development Fund, The Hong Kong Polytechnic University.

Table 2. Estimation values of lifetime of MEH-PPV based on a mass loss of 5% at various temperatures

Atmosphere	Lifetime (min) at temperature				
	25 °C	100 °C	200 °C	300 °C	400 °C
Nitrogen	3.96×10^{14}	4.33×10^8	4.26×10^3	2.34	0.012
Air	9.4×10^6	2.41×10^3	2.32	0.03	1.05×10^{-3}

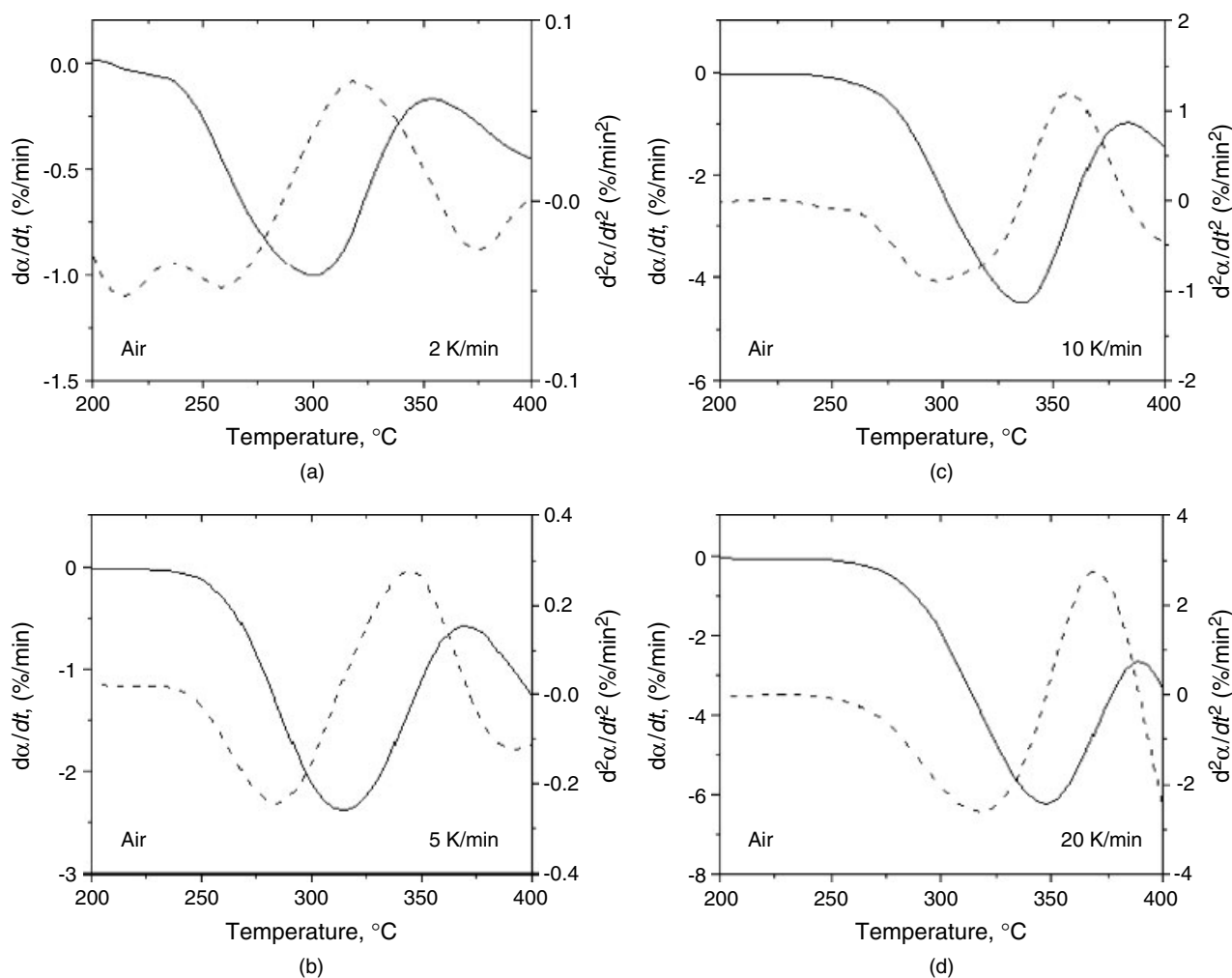


Figure 8. DTG and DDTG curves of MEH-PPV at various heating rates in air.

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