High-Resolution Thermogravimetry of Poly(2,6-dimethyl-1,4-phenylene oxide)

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ABSTRACT: The thermal degradation and kinetics of poly(2,6-dimethylphenylene oxide) (PPO) were studied by high-resolution thermogravimetry. The thermogravimetry measurements were conducted at an initial heating rate of $50°C$ min^{-1}, resolution 4.0, and sensitivity 1.0 in both nitrogen and air from room temperature to $900°C$. A two-step degradation process was clearly revealed in air at the temperatures of $430°C$ and $521°C$. The thermal degradation temperatures and kinetic parameters of the PPO appear to be higher in air than in nitrogen, indicative of a higher thermostability in air. The temperature, activation energy, order, and frequency factor of the thermal degradation of the PPO in nitrogen are $419°C$, $100–120$ kJ mol^{-1}, 0.5, and $13–17$ min^{-1}, respectively. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1887–1892, 1999

Key words: poly(2,6-dimethylphenylene oxide); high-resolution thermogravimetry; thermal degradation; degradation kinetics; thermostability

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) as an attractive polymer is characterized by a high glass transition temperature ($T = 212°C$), good thermal and chemical stability, and excellent mechanical properties. Its maximum permanent use temperature is $\sim 200°C$. The PPO is one of the most widely used engineering plastics (as constructional materials and electric components) and also high-performance membrane materials for gas separation and pervaporation.[1] Thermal degradation is of practical importance not only in the processing of the PPO (e.g., extrusion, molding, and welding), but also in use of the PPO products. The thermal degradation and kinetics of the PPO have been studied by a few investiga-tors by a traditional thermogravimetry (TG) at a constant heating rate.[2–5] However, there are few studies on the thermal degradation kinetics of the PPO by a high-resolution TG (High-Res TG) at a variable heating rate that decreases continuously and reversibly with increasing decomposition rate because the High-Res TG is developed recently.

The present article reports thermal degradation characteristics [degradation temperature, T_d; temperature at the maximum degradation rate, T_{dm}; maximum degradation rate $(d\alpha/dt)_m$; and char yield at $600°C$] and kinetic parameters (activation energy, E; decomposition order, n; frequency factor, Z) in nitrogen and air by the High-Res TG. The results obtained are compared with those published earlier.

EXPERIMENTAL

PPO molding and extrusion pellets were purchased from BDH Chemical Ltd (Poole, UK). Pellets contain a small amount of additive that is

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Figure 1   High-Res TG (—), DTG (---), 2DTG (· · ·), and heating rate (– · – ·) curves of
PPO in nitrogen flow at an initial heating rate of 50°C min^{-1} and resolution 4.

insoluble in chloroform. PPO pellets were directly
used to TG measurements without a drying pro-
cess.

High-Res TG experiments were performed in
nitrogen and air of 30 mL min^{-1} using a High-Res

TGA 2950 thermal analyzer (Hi-Res™ TGA) de-
veloped by TA Instruments, Inc. New Castle, DE,
using a high-resolution mode interfaced to the TA
Instruments 2000 controller with a general V4.1
microprocessor. Sample size was 1.3 mg (in nitro-

Figure 2   High-resolution TG (—), DTG (---), 2DTG (· ·), and heating rate (– · – ·) curves of PPO in air flow at an initial heating rate of 50°C min^{-1} and resolution 4.

gen) and 1.2 mg (in air). An initial heating rate and a resolution were fixed at 50°C min^{-1} and 4.0, respectively. Sensitivity was fixed at its default value of 1 in the temperature range of 25–900°C. Thermal degradative and kinetic parameters were derived using the methods described.[6]

RESULTS AND DISCUSSION

High-Res TG, derivative TG (DTG), the second DTG (2DTG), and heating rate for PPO in nitrogen and air are shown in Figures 1 and 2. The high-resolution thermograms exhibiting two-

Table I   High-Res TG Characteristics of PPO

Atmosphere	Heating Rate (°C min^{-1})	$T_d/T_{dm1}/T_{dm2}$ (°C)	$(d\alpha/dt)_m$ (% min^{-1})	$(d\alpha/dT)_m$ (%/°C)	Char Yield at 600°C (wt %)	Ref.
Nitrogen	Variable	419 /425 /530	4.4	5.1	30	This study
Nitrogen	1.7	400 /420 /—	3.2	1.9	32	2
Nitrogen	2.5	400 /405 /—	10.3	4.1	33	3
Nitrogen	2.5	412 /430 /—	3.6	1.5	36	4
Argon	—	406 /430 /—	—	—	—	7
Air	Variable	427 /430 /521	15.6	18.6	13	This study
Air	2.5	315 /400 /—	0.8	0.3	10	4
Air	5	376 /500 /—	3.4	0.7	13	5
Air	—	270 /441 /—	—	—	0	7
Vacuum	3	425 /440 /—	4.9	1.6	32	4

stage degradation process are obtained, whereas only a single-stage degradation was reported by a traditional constant heating rate TG.[2–5] Before the rapid degradation process, a very small weight loss of ~ 3.4% in nitrogen and 5% in air of initial weight in the temperature range from 200° to 400°C in nitrogen and from 270° to 420°C in air took place. The thermal degradation of PPO in nitrogen seems to occur through one major fast degradation stage and a minor subsequent slow degradation stage. Additionally, two shoulder peaks on the major DTG peak in nitrogen are observed. The thermal degradation of the PPO in air occurs through two fast degradation steps, between which there is an another very small slow degradation stage.

The degradation temperature, T_d, the temperature at the maximum weight-loss rate, T_{dm}, the maximum weight-loss rate $(d\alpha/dt)_m$, and $(d\alpha/dT)_m$, and the char yield at 600°C are presented in Table I. Data from the literature are also given in Table I. The T_d and $(d\alpha/dt)_m$ obtained in nitrogen and air in this study are higher than those obtained at the constant heating rates of 1.7–5°C min^{-1} (see refs. 2–5 and 7). It is seen from Table I that the T_d, T_{dm1}, $(d\alpha/dt)_m$, $(d\alpha/dT)_m$, and char yield at 600°C all increase with increasing heating rate in nitrogen and air, except for the results at the variable heating rate in High-Res TG mode in this study.

There is an influence of testing atmosphere on the thermal degradation of the PPO. It is found from Table I that the char yield at 600°C decreases with the variation of atmosphere in the following order:

in nitrogen ≥ in vacuum ≥ in air

It is interesting that the char yield at 600°C determined in nitrogen in this study is exactly the same as the predicted char residue 30 wt % according to the PPO structure.[8] The smallest char yield at 600°C in air is because of thermo-oxidative degradation resulted from oxygen in air. But no regular influence of atmosphere on the degradation temperature and the maximum decomposition rate $(d\alpha/dt)_m$ and $(d\alpha/dT)_m$ is observed. Lower T_d of 315°–427°C for the PPO listed in Table I suggests that the PPO is less thermostable than the bisphenol A polysulfone and polycarbonate, despite their similar aromaticity, possibly due to an easy hydrogen abstraction and formation of a benzyl radical that can initiate rapid degradation of PPO.

As seen in Figures 1 and 2, the weight loss of the first stage of the PPO in nitrogen and air are 40% and 39%, respectively, which are nearly the same as that which corresponds to the exclusive and complete loss of methyl ether groups and hydrogen in the PPO molecules (40%). This seems to show that the thermal degradation of the first stage of PPO results from the abstraction of methyl and ether groups and hydrogen.

Four kinds of plots for the calculation of kinetic parameters of the first-step degradation are shown in Figures 3–6. Kinetic data obtained from Figures 3–6 are summarized in Table II. There are obvious variations in the three kinetic parameters with the mathematical methods used. It is interesting that the E and Z values calculated by Coats–Redfern method are the smallest in the four methods used. The linear correlation coefficient (0.7303– 0.8984) of calculating kinetic parameters by the Coats–Redfern method is also the smallest. These all indicate that the Coats–Red-

Figure 3 Application of the Freeman–Carroll method to High-Res TG data obtained in nitrogen ($\bigcirc$) and air ($\triangle$).

Figure 5 Application of the Friedman method ($\bigcirc$) and the Chang method ($n = 1.0$) ($\triangle$) to the High-Res TG data obtained in air.

fern method may be the worst fit to calculate kinetic parameter based on a High-Res TG curve. It was felt that the better methods for calculating the kinetic parameters on the basis of a High-Res TG curve of PPO are the Freeman–Carroll and Friedman methods, simply due to their larger linear correlation coefficients of 0.9864–0.9998. A great difference of activation energy E and decomposition order n calculated by different methods has been reported.[9] The E and n values for the PPO are 130 kJ mol^{-1} and 1.0 by the Fuoss method and 837 kJ mol^{-1} and 5.0 by the Freeman–Carroll method.

The results in Table II show that the E and Z values in air are at least seven times as large as those in nitrogen. It is reported that the E value

of the PPO could be down to 113 kJ mol^{-1} (see ref. 10). It appears that the E values obtained in this study are in agreement with those reported earlier.[10,11]

Usually, the weakest link in the PPO is the carbon—hydrogen bond in the methyl groups on the phenyl ring, the carbon—oxygen bond between aromatic ring and oxygen atom in the main chain, and the carbon—carbon bond between the aromatic ring and methyl group,[4] as shown in Scheme 1. Thermal degradation of the PPO begins with the cleavage of the ether linkage and simultaneous removal of the methyl groups in the form of methane, with the hydrogen being supplied by other methyl groups and the benzene ring.

Figure 4 Application of the Friedman method ($\bigcirc$) and the Chang method ($n = 0.5$) ($\triangle$) to the High-Res TG data obtained in nitrogen.

Figure 6 Application of the Coats–Redfern method to the High-Res TG data obtained in air at $n = 0.5$ ($\bigcirc$) and in nitrogen at $n = 1.0$ ($\triangle$).

Table II   Kinetic Parameters of Major Thermal Degradation of PPO Calculated by Several Methods

Atmosphere	Freeman–Carroll				Friedman				Chang				Coats–Redfern			
	E[a]	n	Ln Z[b]	r[c]	E	n	Ln Z	r	E	n	Ln Z	r	E	n	Ln Z	r
Nitrogen	118	0.4	17	0.999	112	0.5	16	0.994	104	0.5	14	0.969	98	0.5	13	0.898
Air	809	4.5	137	0.998	750	1.4	126	0.986	811	1.0	137	0.975	332	1.0	54	0.730

[a] E: in kJ mol^{-1}.
[b] Ln Z: in min^{-1}.
[c] r: correlation coefficient.

If the activation energy of the first stage of thermal degradation of the PPO equals the dissociation energy of the carbon—hydrogen bond (325 kJ mol^{-1}), it is found that this activation energy is close to that calculated only by the Coats–Redfern method in air, 332 kJ mol^{-1}, but is much lower than those calculated by other three methods in air and much higher than those calculated in nitrogen. Obviously, there is no simple relationship between the overall activation energy of the first stage degradation and the weakest bond energy of the PPO because of its complex degradation process. As a matter of fact, the first step of the degradation is hydrogen abstraction and formation of a stable benzyl radical. Then, this radical initiates the cleavage in the other linkage just like the ether group.

CONCLUSIONS

The High-Res TG has been used to investigate the thermal degradation of the PPO. The thermal degradation parameters, including degradation temperature, the maximum degradation rate, char yield at 600°C, overall activation energy, degradation order, and frequency factor of the PPO, exhibit a dependency of testing atmosphere. Degradation temperature and activation energy are much greater in air than in nitrogen. The activation energy of the thermal degradation of the PPO obtained in this study is basically in agreement with those reported earlier.

Scheme 1   Bond dissociation energy (kJ mol^{-1}) in PPO.

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