High-Resolution Thermogravimetry of Polyphenylene Sulfide Film under Four Atmospheres

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ABSTRACT: Thermal degradation of polyphenylene sulfide (PPS) film was investigated in air, nitrogen, helium, and argon with different physical and reactive characteristics from room temperature to 790°C by a high-resolution thermogravimetry (TG) at a variable heating rate in response to the changes in the sample's weight-loss rate. In nitrogen and argon, only a single-step degradation process of the PPS was observed, but in helium, a two-step degradation process of PPS was found. Notably, in air a four-step degradation process of the PPS, which was hardly ever revealed by a traditional TG, was found in this investigation. The initial thermal degradation temperature T_d and temperature at the first maximum weight-loss rate T_{dm1} of the PPS increased in the following order: in helium < in nitrogen < in argon < in air. The first maximum weight-loss rate also increased with the variation of atmosphere in the order: nitrogen < air < argon < helium. The char yield at 700°C increased in the order: in air < in helium < in nitrogen < in argon. The activation energy of the major degradation process of PPS calculated based on the high-resolution TG data was very high, increasing in the order: in nitrogen < in argon < in helium < in air. The thermal decomposition parameters of the PPS determined by the high-resolution TG were systematically compared with those by traditional TG at a constant heating rate. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2053–2059, 2002

Key words: polyphenylene sulfide; high-resolution thermogravimetry; thermal decomposition; decomposition activation energy; thermal stability; testing atmosphere

INTRODUCTION

Poly(*p*-phenylene sulfide) (PPS), that is, poly-(thio-1,4-phenylene), is an engineering plastic

prepared by the polycondensation of *p*-dichlorobenzene and sodium sulfide in a polar solvent. PPS is characterized by a combination of useful properties including good melt processability (coating, injection and compression moldings); precision moldability, even with a very small size; outstanding mechanical properties such as high impact strength, toughness, and flexibility; fire retardancy (LOI = 44) and nondripping flammability behavior; good stability to radiation, ultraviolet radiation, and most chemicals; high dielectric strength and low dielectric constant; low

moisture absorption; low coefficient of friction; low-wear property; usually good retention of almost all above-mentioned properties at elevated temperature; and good thermostability.[1,2] PPS exhibits a weight loss of 1.3% after 30 min in air at 400°C.[3] The PPS release coating with good adhesion and hardness finds application in coating cookware for nonstick use, corrosion-resistant and protective coatings for oil field pipes, valves, fittings, couplings, thermocouple wells, and other equipment in both the petroleum and chemical-processing industries. PPS molding articles can be used as sliding vanes, impellers, impeller cases, gauge guards, and seals in corrosive service and as a piston for a nonlubricated gas compressor, and as an electrical insulator such as connectors and coil forms. The thermal degradation of PPS has been studied by a traditional thermogravimetry (TG) at a constant heating rate.[1–7] However, there are no studies on the thermal degradation and kinetics of PPS by a high-resolution TG, especially in helium and argon.

A novel high-resolution TG is a technique to significantly increase the resolution while often shortening the time scale of the experiments. In the variable heating rate mode of high-resolution TG, the heating rate is dynamically, continuously, and inversely varied with the weight-loss rate to maximize resolution, that is, the capacity to separate closely occurring events. For example, the heating rate automatically reduces whenever the weight-loss rate increases but increases whenever the weight-loss rate reduces. Therefore, the heating rate will reach the minimum at the maximal weight-loss rate. The variable heating rate mode provides a choice of resolution ranging from 0 to 8. If the resolution is 0, the heating rate is constant, just like that in the traditional TG mode. If the resolution is greater than 0, the instrument will react to smaller changes in the weight-loss rate. Sensitivity controls the magnitude of response relative to changes in the weight-loss rate. Theoretically, varying the initial heating rate, resolution, or sensitivity can adjust the heating rate and the temperature at the maximum weight-loss rate. High-resolution TG has a greater sensitivity to weight loss than conventional TG. As a result, minor weight losses can be detected during thermal degradation. Moreover, high-resolution TG can quickly achieve reliable degradation temperature and kinetic parameters that may be effectively employed to compare the thermostability and assess thermal lifetime. In this study high-resolution TG was used for the

first time for a systematic investigation of the thermal decomposition temperature, process, and activation energy of PPS in four atmospheres. These results are compared in detail with those reported earlier by traditional TG.

EXPERIMENTAL

Transparent and brown amorphous polyphenylene sulfide (PPS) film (Tedur 9500, M_w = 55,000) with the thickness of 163 μm made by quench melt rolling was obtained by courtesy of Bayer AG, Germany. The PPS referred to as virgin sample is free of fillers, additives, and residual solvents. Before TG measurements, no drying process was performed on the original PPS film. TG analyses were performed under highly pure helium, highly pure nitrogen, highly pure argon, and an air flow of 25 mL/min on a model high-resolution TGA 2950 thermal analyzer (Hi-Res™ TGA; TA Instruments, New Castle, DE), using the high-resolution mode interfaced to TA Instruments 2000 controller with General V.4.1C microprocessor. The sample size was 3.7 mg in helium, 3.7 mg in nitrogen, 4.6 mg in argon, and 5.5 mg in air. The respective initial heating rate and resolution were fixed at 50°C/min and 4.0. The sensitivity was fixed at its default value of 1 in the temperature range of 25–790°C. Thermal degradation temperatures and kinetic parameters were determined using the techniques described previously.[8–19] The degradation temperature T_d was obtained by extrapolation of the initial degradation portion of the TG curve. These data were compared with existing literature values.

RESULTS AND DISCUSSION

Thermal Decomposition Characteristics

The high-resolution thermogravimetry (TG) curves of the PPS in four atmospheres at an initial heating rate of 50°C/min and resolution 4 are shown in Figure 1. The derivative thermogravimetry (DTG) curves are shown in Figures 2 and 3 because they are very useful to exactly determine several degradation parameters and processes. The variations of the weight of PPS with measuring time by using high-resolution thermogravimetry mode in four atmospheres are shown in Figure 4. It is seen that the high-resolution TG technique gives reliable decomposition parameters in
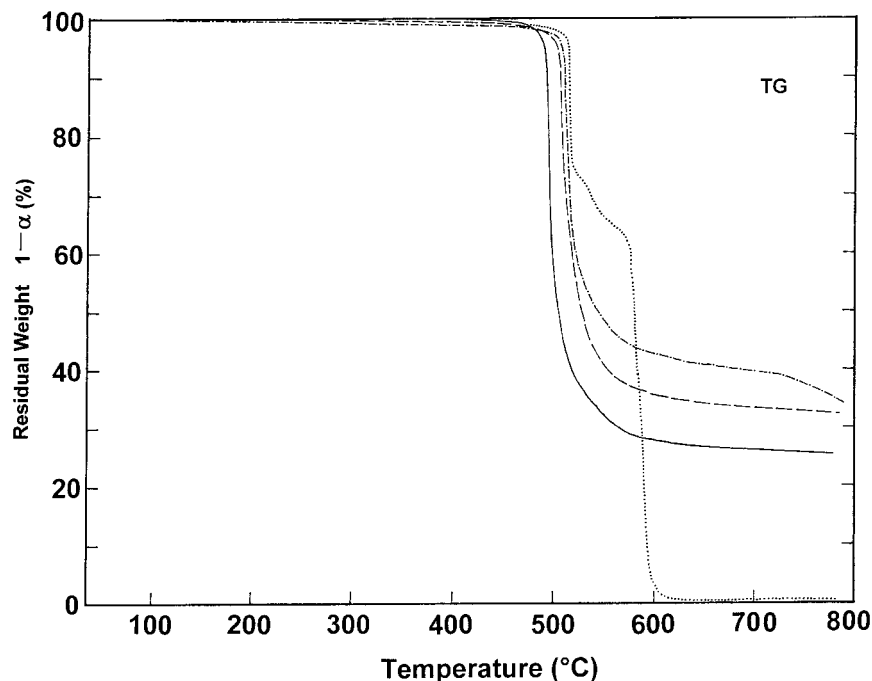
Figure 1   High-resolution TG curves of polyphenylene sulfide (PPS) in helium (—), nitrogen (– – –), argon (– · –), and air (· · ·) at an initial heating rate of 50°C/min and resolution 4.

a short time. Four important decomposition parameters from this study and other studies[1,4–7] are listed in Table I. There is no apparent weight loss until 490°C, indicating that PPS is thermally stable and its moisture content is quite low because PPS was directly examined without any drying process in advance. The thermal degradation of PPS in nitrogen appears to occur through only one fast degradation step, but the thermal degradation in helium and argon takes place through one major and the fastest degradation step first and then one minor and the slowest degradation step. The thermal degradation in air exhibits two additionally subsequent fast degradation stages compared with the thermal degradation in helium and argon. Obviously, the high-resolution TG curve obtained in air really exhibits a higher resolution than that by a traditional TG technique at constant heating rates from 2.5 to 15°C/min because traditional TG curves in air exhibit two or three decomposition steps, as shown in Table I.

The characteristic initial degradation temperature (T_d), the temperature at the maximum weight-loss rate (T_{dm}), the maximum weight-loss rate $(d\alpha/dT)_m$, and char yield at 700°C are given in Table I. There is a strong influence of atmo-

sphere on the thermal degradation of the PPS. The initial thermal degradation temperature T_d and temperature at the maximum weight-loss rate T_{dm1} of PPS increase in the following order: in helium < in nitrogen < in argon < in air. The first maximum weight-loss rate increases with the variation of the atmosphere in the order: in nitrogen < in air < in argon < in helium. The char yield at 700°C increases in the order: in air < in helium < in nitrogen < in argon. The lowest T_d and lowest T_{dm} observed in helium may be attributable to the greatest thermal conductivity of the helium among the four atmospheres (the thermal conductivity is 510 J m^{-1} h^{-1} K^{-1} for helium, 88 J m^{-1} h^{-1} K^{-1} for air, 86 J m^{-1} h^{-1} K^{-1} for nitrogen, and 62 J m^{-1} h^{-1} K^{-1} for argon), given that the testing sample could be heated to the expected temperature more rapidly under more highly conductive helium than under the other three atmospheres. The second lowest char yield at 700°C in helium might be ascribed to the much lower gas density of helium [0.1769 g/mL (STP)] than that of another two inert atmospheres {nitrogen [1.2506 g/mL (STP)] and argon [1.784 g/mL (STP)]} because it is difficult for very light helium to completely replace the residual air inside the sample. This might lead to an occur-
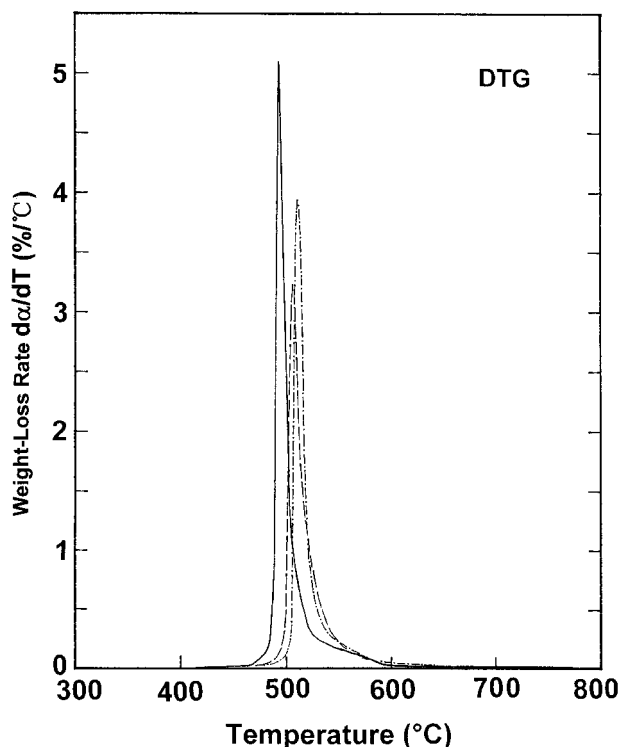
Figure 2 High-resolution DTG curves of PPS in helium (—), nitrogen (– – –), and argon (– · –) at an initial heating rate of 50°C/min and resolution 4.

rence of additionally thermo-oxidative degradation to some extent and finally low char yield.

It appears that the T_d, T_{dm1}, and char yield at 700°C are lower in vacuum than those in the four atmospheres, except that the char yield at 700°C in air is even lower because there is an additionally thermo-oxidative degradation of residual char formed by thermal degradation in air. These suggest the lowest thermostability in vacuum. A possible reason is that the vacuum is a benefit to the evaporation of the gaseous degradation products, leading to the acceleration of the degradation reaction. The T_d values determined by the high-resolution TG in nitrogen and air are usually greater than those by traditional TG but the char yield at 700°C determined in this study in nitrogen and air are generally lower than those at constant heating rates of 2.5–15°C/min. It is interesting that in this study the T_{dm1} in nitrogen is lower and the T_{dm1} in air is higher than corresponding T_{dm1} values obtained by traditional TG at heating rates of 2.5–10°C/min in the literature. Note that the T_d and T_{dm1} values determined by high-resolution TG are lower in nitrogen than those in air, but the T_d and T_{dm1} values determined by traditional TG at heating rates of 2.5–

10°C/min are higher in nitrogen than those in air. It is found that the ratio of average T_d value in air versus average T_d value in nitrogen determined by the traditional TG at heating rates of 2.5–10°C/min listed in Table I equals 0.981, suggesting that the onset of initial bond cleavage is basically thermal in nature and not influenced to any great extent by the presence of oxygen. Nevertheless, PPS exhibits higher thermostability than that of polydimethylphenylene oxide[12] but lower thermostability than that of polyphenylene ether sulfone and polyimide.[13,20]

Thermal Decomposition Process

As can be seen in Table II the weight loss of the first stage of thermal degradation of the PPS in helium, nitrogen, and argon (exclusive of the weight loss in air at variable heating rate in this study) is 42–68 wt %, which is much higher than that (33.3 wt %) which corresponds to the complete loss of sulfur and hydrogen on the benzene rings, indicating that the thermal degradation of
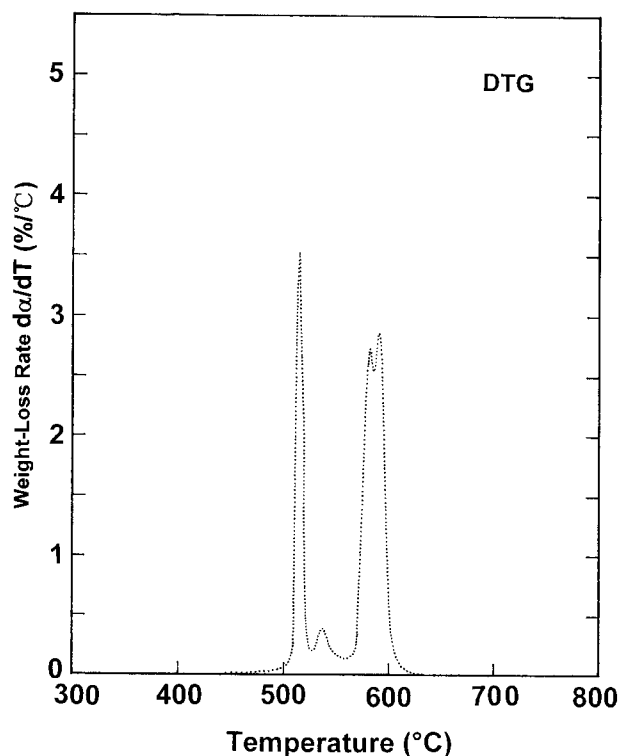

Figure 3 High-resolution DTG curves of PPS in a flowing air (· · ·) at an initial heating rate of 50°C/min and resolution 4.
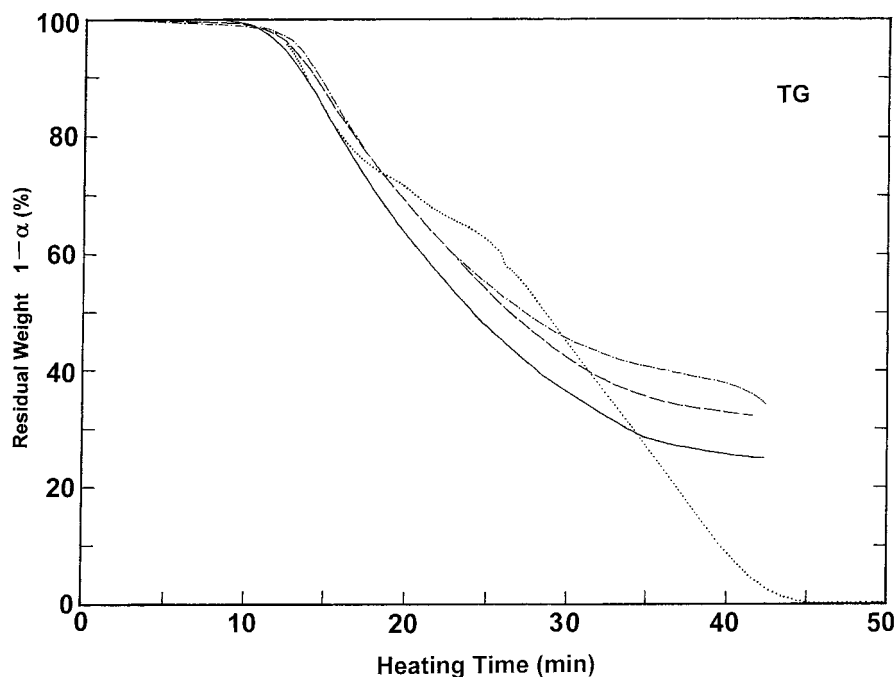
Figure 4 Variation of the weight of PPS with measuring time by using high-resolution thermogravimetry mode in helium (—), nitrogen (– – –), argon (– · –), and air (· · ·) at an initial heating rate of 50°C/min and resolution 4.

PPS is accompanied by the breaking of benzene rings to some extent. The weight loss corresponding to the previous two decomposition steps in air is 35%, which is slightly higher than the complete loss (33.3 wt %) of sulfur and aromatic hydrogen. This might imply that the previous two stages of the thermal degradation of the PPS comprise sulfur and hydrogen abstractions (corresponding volatile products are hydrogen sulfide, hydrogen, benzene, methane, and oxygen uptake with losses of carbon monoxide, water, and sulfur dioxide),[4] and crosslinking between the residual aromatic carbon. The third and fourth stages in air were the degradation of aromatic carbon.

Table I Thermal Degradation Characteristics of Polyphenylene Sulfide

Atmosphere	Heating Rate (°C/min)	$T_d/T_{dm1}/T_{dm2}$ (°C)	$(d\alpha/dT)_{m1}/(d\alpha/dT)_{m2}$ (%/°C)	Char Yield at 700°C (wt %)	Reference
Helium	Variable	492/494/556	5.12/0.15	26	This study
Nitrogen	Variable	503/506/—	3.2/—	33	This study
Nitrogen	2.5	475/497/—	—	41	4
Nitrogen	3	498/536/—	—	38	5
Nitrogen	3	490/540/—	—	43	6
Nitrogen	10	486/500/—	—	—	7
Nitrogen	15	535/557/—	—	58	1
Argon	Variable	507/511/554	3.9/—	40	This study
Air	Variable	512/514/537, 582, 590	3.6/0.4, 2.8, 2.9	0.7	This study
Air	2.5	475/497/639	—	14	4
Air	3	482/517/558, 589	—	0	5
Air	3	477/506/577	—	3	6
Air	15	491/580/—	—	3	1
Vacuum	3	475/495/—	—	26	4

Table II   Temperature Range and Corresponding Weight Loss of Thermal Degradation of Each Step for Polyphenylene Sulfide

Atmosphere	Heating Rate (°C)	Temperature Range (°C) 1st Step/2nd Step/3rd Step	Weight Loss (%) 1st/2nd/3rd	Reference
Helium	Variable	400–535/535–790/—	65/9.5/—	This study
Nitrogen	Variable	180–790/—/—	68/—/—	This study
Nitrogen	15	400–660/660–980/—	42/17/—	1
Argon	Variable	50–542/542–790/—	50/17/—	This study
Air	Variable	150–528/528–560/560–587, 587–790	28/7/30, 34	This study
Air	2.5	340–560/560–900/—	51/35/—	4

Thermal Decomposition Kinetics

Four plots for the calculation of activation energy of the first degradation of the PPS are shown in Figure 5. The kinetic data calculated are summarized in Table III. There is a significant variation in the activation energy with testing atmospheres. The activation energy of the major degradation of PPS calculated by the Friedman method based on the high-resolution TG data is very high and increases in the order: in nitrogen < in argon < in helium < in air. It is apparent that the activation energy values determined by the high-resolution TG in this study are much greater than those (170–200 kJ/mol) determined by traditional TGs.[21,22]

Most polymers contain weak bonds that are expected to break with a higher probability than other stronger bonds. When the thermal energy begins to surpass the bond energies of various bonds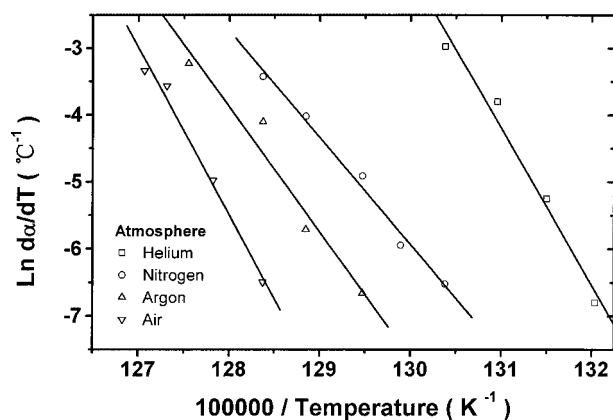 in the PPS chains, a random chain scission takes place and the rate of degradation increases rapidly.[4] It was estimated that the carbon–sulfur bond is the weak linkage. The three bond energies are listed in Figure 6 for reference. From these values, it seems that activation energy values determined by the high-resolution TG in this study are much greater but the activation energy values (170–200 kJ/mol) determined by traditional TGs are lower than the dissociation energy of the weakest bond.

CONCLUSIONS

A high-resolution thermogravimetry was applied to rapidly and successfully investigate the thermal degradation of polyphenylene sulfide. The thermal degradation parameters involving temperature, the maximal degradation rate, char yield at 700°C, and activation energy of polyphenylene sulfide show a strong dependency of testing atmosphere and method. The high-resolution TG and DTG curves of PPS in air actually exhibit much higher resolution than those in helium, argon, and nitrogen, suggesting that the thermal degradation mechanism might be different in the four atmospheres.

Figure 5 Application of the Friedman method to the high-resolution TG data obtained in flowing helium (□), nitrogen (○), argon (△), and air (▽) for the calculation of activation energy of the thermal decomposition.

Table III   Activation Energy of the First Major Thermal Degradation of Polyphenylene Sulfide by High-Resolution Thermogravimetry Calculated by Friedman Technique

Testing Atmosphere	Nitrogen	Argon	Helium	Air
Activation energy (kJ/mol)	1327	1549	1945	2078
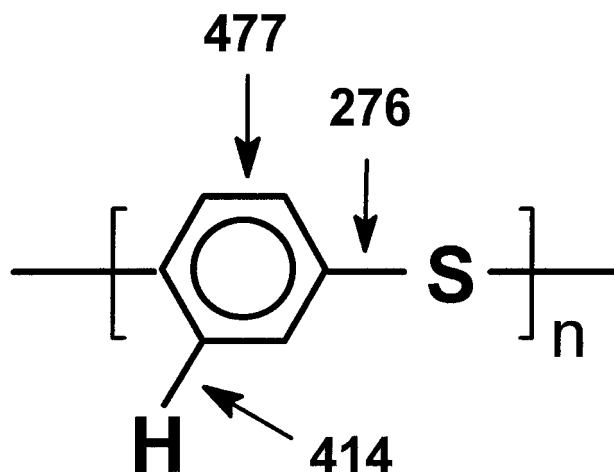
Figure 6 The molecular structure and dissociation energy (kJ/mol) of three types of chemical bonds of PPS.

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