High-Resolution Thermogravimetry of Poly(phenylene sulfide) Film under Four Atmospheres

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ABSTRACT: The thermal degradation of poly(phenylene sulfide) (PPS) film is investigated in air, nitrogen, helium, and argon with different physical and reactive characteristics at room temperature to 790°C as ascertained by high-resolution thermogravimetry (TG) at a variable heating rate in response to the changes in the sample's weight-loss rate. Only a one-step degradation process of the PPS is observed in nitrogen and argon, but a two-step degradation process of PPS is found in helium. A four-step degradation process of the PPS, which is hardly ever revealed by traditional TG, is found in this investigation, especially in air. The initial thermal degradation temperature and temperature at the first maximum weight-loss rate of the PPS increase in the following order: helium < nitrogen < argon < air. The first maximum weight-loss rate also increases with the variation of the atmosphere in the order nitrogen < air < argon < helium. The char yield at 700°C increases in the order air < helium < nitrogen < argon. The activation energy of the major degradation process of PPS, as calculated based on the high-resolution TG data, is very high and increases in the order nitrogen < argon < helium < air. The thermal decomposition parameters of the PPS determined by the high-resolution TG are systematically compared with those by traditional TG at a constant heating rate. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1940–1946, 2002

Key words: poly(phenylene sulfide); high-resolution thermogravimetry; thermal decomposition; decomposition activation energy; thermal stability; testing atmosphere

INTRODUCTION

Poly(*p*-phenylene sulfide) [PPS, poly(thio-1,4-phenylene)] is an engineering plastic prepared by the polycondensation of *p*-dichlorobenzene and sodium sulfide in a polar solvent. The 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, flexibility, and fire retardancy (LOI = 44); nondripping flammability behavior; good stability to radiation, UV radiation, and most chemicals; high dielectric strength and low dielectric constant; low moisture absorption; low coefficient of friction; low-wear properties; usually good retention of almost all the 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] As a release coating with good adhesion and hardness it is finding application in coating cookware for nonstick use; corrosion resistant and protective coatings for oil-field pipes, valves, fittings, couplings, and thermocouple wells; and other equipment in 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; as pistons for nonlubricated gas compressors; and as electrical insulators such as connectors and coil forms. The thermal degradation of PPS was studied by traditional thermogravimetry (TG) at a constant heating rate.[1–7] However, there are no studies on the thermal degradation and kinetics of PPS by high-resolution TG, especially in helium and argon. The novel high-resolution TG technique significantly increases the resolution while often shortening the time scale of the experiments. In the variable heating rate mode of the high-resolution TG, the heating rate is dynamically, continuously, and inversely varied with the weight-loss rate to maximize the resolution, which is the capacity to separate closely occurring events. For example, the heating rate is automatically reduced 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 zero, the heating rate is constant, just like the traditional TG mode. If the resolution is larger than zero, 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. Consequently, high-resolution TG can quickly achieve a reliable degradation temperature and kinetic parameters that may be effectively employed to compare the thermostability and assess the 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 PPS film (Tedur 9500, $M_w = 55,000$) with a thickness of 163 μm and made by quench melt rolling was obtained courtesy of Bayer AG. The PPS referred to as a virgin sample is free of fillers, additives, and residual solvents. Before TG measurements, no drying process was performed on the original PPS film. The TG analyses were performed under highly pure helium, highly pure nitrogen, highly pure argon, and an air flow of 25 mL/min on a high-resolution TGA 2950 thermal analyzer (Hi-Res™ TGA; TA Instruments Inc., New Castle, DE) in high-resolution mode interfaced to a TA Instruments 2000 controller with a 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 one in the temperature range of 25–790°C. The 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 TG curves of the PPS in four atmospheres at an initial heating rate of 50°C/min and a resolution of 4 are shown in Figure 1. The derivative TG (DTG) curves are shown in Figures 2 and 3 because they are very useful in the exact determination of several degradation parameters and processes. The variation of the weight of the PPS with measuring time by using the high-resolution TG mode in four atmospheres is shown in Figure 4. It is seen that the high-resolution TG technique gives reliable decomposition parameters in a short time. Four important decomposition parameters from this study and the literature[1,4–7] are listed in Table I. There is no apparent weight loss until 490°C, indicating that the PPS is thermally stable and its moisture content is quite low because the PPS was directly examined without any drying process in advance. The thermal degradation of the PPS in nitrogen appears to occur through only one fast degrada-
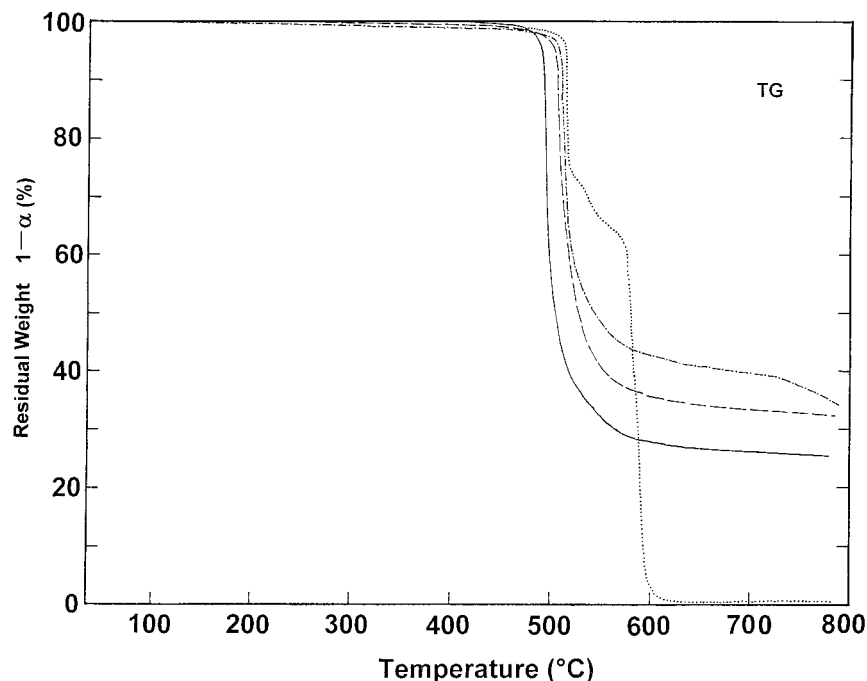
Figure 1 High-resolution TG curves of poly(phenylene sulfide) in (—) helium, (— — —) nitrogen, (— · —) argon, and (· · ·) air at an initial heating rate of 50°C/min and a resolution of 4.

tion step, but the thermal degradation in helium and argon takes place through one major, fastest degradation step first, then one minor, followed by 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 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 T_d, the temperature at the maximum weight-loss rate (T_{dm}), the maximum weight-loss rate ($d\alpha/dT)_m$, and the char yield at 700°C are given in Table I. The atmosphere has a strong influence on the thermal degradation of the PPS. The initial T_d and temperature at the maximum weight-loss rate T_{dm1} of the PPS increase in the following order: helium < nitrogen < argon < air. The first maximum weight-loss rate increases with the variation of the atmosphere in the order nitrogen < air < argon < helium. The char yield at 700°C increases in the order air < helium < nitrogen < argon. The lowest T_d and lowest T_{dm} observed in helium may be due to the greatest thermal conductivity of the
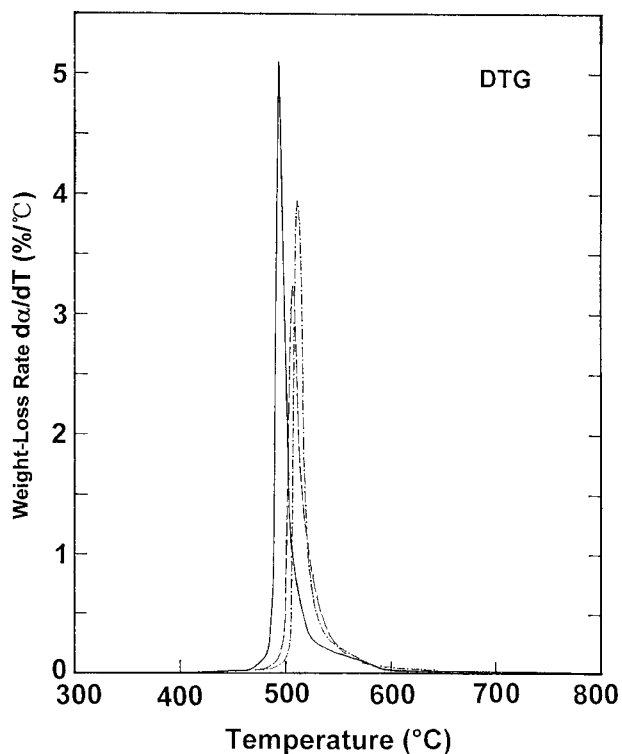

Figure 2 High-resolution DTG curves of poly(phenylene sulfide) in (—) helium, (— — —) nitrogen, and (— · —) argon at an initial heating rate of 50°C/min and a resolution of 4.
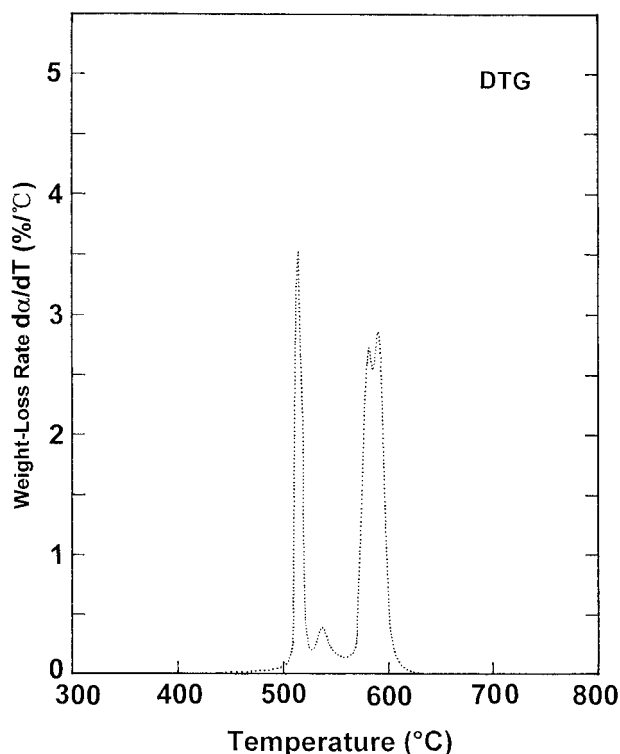
Figure 3 High-resolution DTG curves of poly(phenylene sulfide) in (· · ·) flowing air at an initial heating rate of 50°C/min and a resolution of 4.

helium among the four atmospheres (thermal conductivity = 510 J/m h K for helium, 88 J/m h K for air, 86 J/m h K for nitrogen, and 62 J/m h K for argon), because the testing sample could be heated to the expected temperature more rapidly under more highly conductive helium than under the other three gases. 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 the other 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 occurrence of additionally thermooxidative 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 a vacuum than those in the four atmospheres, except that the char yield at 700°C in air is lower because there is an additional thermooxidative degradation of residual char formed by thermal degradation in air. These suggest the lowest thermostability in a vacuum. A possible reason is that the vacuum benefits 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

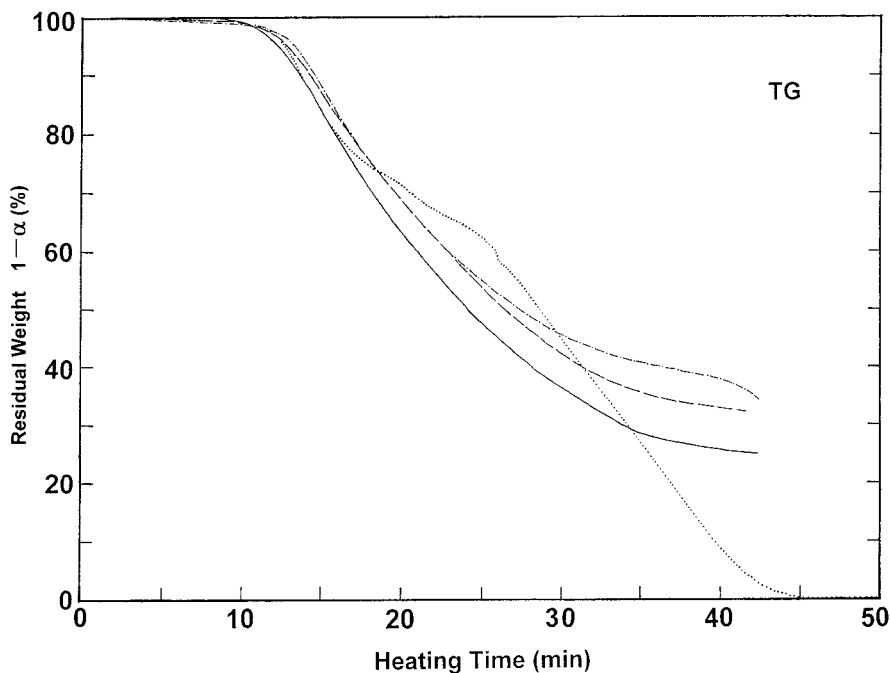**Figure 4** The variation of the weight of poly(phenylene sulfide) with the measuring time by using high-resolution TG mode in (—) helium, (– – –) nitrogen, (· – ·) argon, and (· · ·) air at an initial heating rate of 50°C/min and a resolution of 4.

Table I   Thermal Degradation Characteristics of Poly(phenylene 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 %)	Ref.
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

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 the T_{dm1} in nitrogen in this study is lower and the T_{dm1} in air in this study is higher than the corresponding T_{dm1} 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 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 in air. We found that the ratio of the average T_d value in air versus the average T_d value in nitrogen determined by traditional TG at heating rates of 2.5–10°C/min (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, the PPS exhib-

its higher thermostability than poly(dimethylphe-nylene oxide)[12] but lower thermostability than poly(phenylene 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 the variable heating rate in this study) is 42–68 wt %, which is much higher than that (33.3 wt %) corresponding to the complete loss of sulfur and hydrogen on the benzene rings, indicating that the thermal degradation of 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

Table II   Temperature Range and Corresponding Weight Loss of Thermal Degradation of Each Step for Poly(phenylene sulfide)

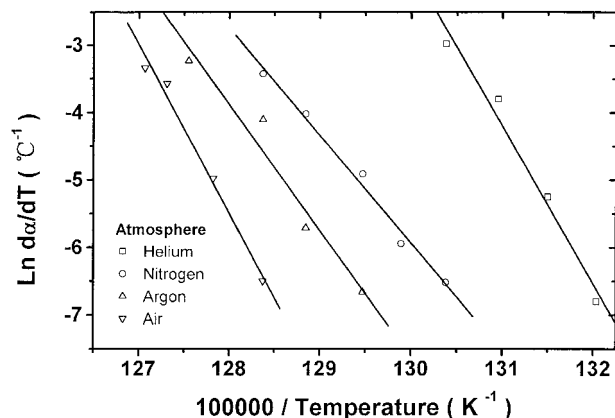| Atmosphere	Heating Rate (°C)	Temperature Range (°C)			Weight Loss (%)			Ref.
		1st Step	2nd Step	3rd Step	1st	2nd	3rd	
Helium	Variable	400–535	535–790	—	65	9.5	—	This study
Nitrogen	Variable	180–790	—	—	68	—	—	This study
Nitrogen	15	400–660	660–980	—	42	17	—	1
Argon	Variable	50–542	542–790	—	50	17	—	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

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 the activation energy of the thermal decomposition.

the thermal degradation of the PPS are 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.

Thermal Decomposition Kinetics

Four plots for the calculation of the activation energy of the first degradation of the PPS are shown in Figure 5. The kinetic data that are calculated are summarized in Table III. There is a significant variation in the activation energy with the 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 nitrogen < argon < helium < air. It is apparent that the activation energy values determined by

Table III Activation Energy of First Major Thermal Degradation of Poly(phenylene sulfide) by High-Resolution Thermogravimetry Calculated by Friedman Technique

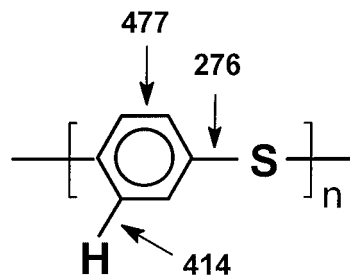|	Testing Atmosphere			
	Nitrogen	Argon	Helium	Air
Activation energy (kJ/mol)	1327	1549	1945	2078

Figure 6 The molecular structure and dissociation energy (kJ/mol) of three types of chemical bonds of poly(phenylene sulfide).

the high-resolution TG in this article are much larger 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, 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 the activation energy values determined by the high-resolution TG in this study are much larger but the activation energy values (170–200 kJ/mol) determined by traditional TGs are lower than the dissociation energy of the weakest bond.

CONCLUSIONS

High-resolution TG was applied to rapidly and successfully investigate the thermal degradation of PPS. The thermal degradation parameters involving the temperature, the maximal degradation rate, the char yield at 700°C, and the activation energy of the PPS show a strong dependency on the testing atmosphere and method. The high-resolution TG and DTG curves of the 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 gases.

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