High-Resolution Thermogravimetry of Polyethersulfone Chips in Four Atmospheres

Xin-Gui Li,[1] Hong-Tao Shao,[1] He Bai,[2] Mei-Rong Huang,[1] Wei Zhang[3]

[1]Department of Polymer Materials Science and Engineering, State Key Laboratory of Concrete Materials Research, College of Materials Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China
[2]Tianjin Customs Central Laboratory, the 1st Haibin Wu Road, A Custom Bond Zone of Tianjin Port, Tianjin 300456, China
[3]Department of Macromolecular Science, The Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, China

ABSTRACT: Thermal degradation and kinetics of polyethersulfone (PES) chips were studied in air, nitrogen, helium, and argon from room temperature to 790°C by high-resolution thermogravimetry (TG) at a variable heating rate in response to changes in the sample's degradation rate. In the four atmospheres, a two-step degradation process in air, argon, and helium or a three-step degradation process in nitrogen of the PES were found in this investigation. In particular, the three-step degradation process in nitrogen of the PES revealed by the high-resolution TG was hardly ever observed by a traditional TG. The initial thermal degradation temperature of the PES increases with the testing atmosphere in the following order: air < argon < helium < nitrogen but the activation energy of the first major degradation of PES increases in a different order: argon < nitrogen < helium < air. The degradation temperature, the temperature at the maximum weight-loss rate, the maximum weight-loss rate [$(d\alpha/dT)_{m1}$ and $(d\alpha/dT)_{m2}$], char yield at 790°C, and activation energy of the first major degradation process obtained by the high-resolution TG were compared with those by traditional TG. The PES exhibits the largest $(d\alpha/dT)_{m1}$ and the greatest char yield at 790°C in helium but the largest $(d\alpha/dT)_{m2}$ and smallest char yield in air. A significant dependency of the thermal decomposition of the polymers on the physicochemical properties (density, thermal conductivity, and oxidative ability) of the testing atmospheres is elaborated for the first time. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3631–3637, 2003

Key words: poly(ether sulfones); thermogravimetric analysis (TGA); thermal properties; degradation; activation energy

INTRODUCTION

Polyethersulfone [(PES); poly(oxy-4-phenylenesulfonyl-4-phenylene)] is one of the most widely used and versatile thermoplastic engineering plastics. The very low rate of creep of PES is coupled with a good resistance to failure by static fatigue, high tensile yield strength, and good impact strength, making PES superior in these respects to any other unfilled thermoplastics. PES is particularly resistant to crack initiation and even tough and dimensionally stable after it has absorbed its equi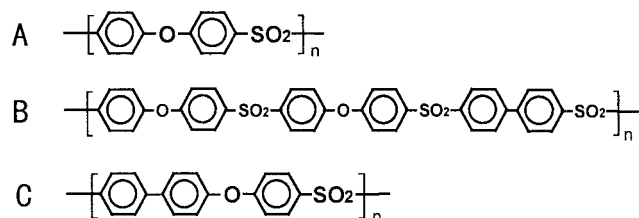librium amount of water. PES also exhibits low flammability (limited oxygen index = 38), low power factor, good permittivity, high resistivity, highly oxidative and thermal stability, and easy melt-processing ability including molding; blow molding; extrusion of sheet, rod, and hollow fiber, and vacuum forming sheet into complex shapes; solvent casting into ultrathin film; and both ultrasonical and solvent welding. PES components can be vacuum metallized, electroplated, and painted.[1] PES is suitable for the production of separation membrane,[2–4] aircraft door frame, automobile parts, electrical and electronic parts, medical equipment, structural adhesive,[1] and composite matrix.[5] PES is marketed by a number of international companies as a class of thermally stable materials. The thermal degradation of the PES has been studied numerous times in the past by traditional thermogravimetry (TG) at a constant heating rate.[6–10] However, there are no studies on the thermal degradation and kinetics of the PES in air and nitrogen by high-resolution TG. In this study, a high-resolution TG was used to investigate thermal decomposition temperature and kinetic parameters of the PES in four atmospheres including

Scheme 1

Figure 1 High-resolution TG curves of polyethersulfone (PES) A in air (· · ·), argon (— · —), helium (– – –), and nitrogen (—) flow at an initial heating rate of 50°C/min and resolution 4.

EXPERIMENTAL

Polyethersulfone (PES) chip, BASF Ultrason E1010 (T_g = 227°C, ρ = 1.337 g/cm^3), was kindly provided by the BASF Co. (Ludwigshafen, Germany). The PES referred to as virgin sample was free of fillers, additives, and residual solvents. Before TG measurements, no drying process was carried out on the original PES chip. The PES has the following molecular structure A. The polyethersulfones B and C with the structures shown in **Scheme 1** are also investigated on the basis of the TG and DTG curves reported in Crossland et al.[6] and Abate et al.[11]

TG analyses were performed under dry air, highly pure nitrogen, highly pure argon, and highly pure helium flow of 25 mL/min on a model high-resolution TGA 2950 thermal analyzer (Hi-Res TGA; TA Instruments, New Castle, DE), using a high-resolution mode interfaced to a TA Instruments 2000 controller with general V.4.1C microprocessor. Sample sizes were 5.6 mg (in air), 4.0 mg (in nitrogen), 4.7 mg (in argon), and 4.2 mg (in helium). 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 a temperature range of 25–790°C. The temperatures and activation energy of thermal degradation were determined using the techniques previously described.[12–29] The degradation temperature T_d was obtained by extrapolation of the initial degradation portion of the TG curve. These data were thoroughly compared with existing literature values.

RESULTS AND DISCUSSION

Thermal degradation characteristics

The high-resolution thermogravimetry (TG) curves of the PES A in air, nitrogen, argon, and helium are shown in Figure 1. The derivative thermogravimetry (DTG) curves are shown in Figure 2 because they are
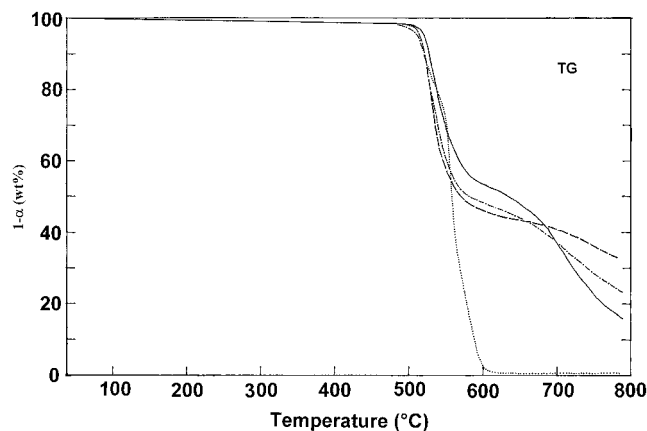
very useful to exactly determine the temperature (T_{dm}) at the maximum weight-loss rate ($d\alpha/dT)_m$ and decomposition step. Variation of the weight of PES A with testing time in four flowing atmospheres at an initial heating rate of 50°C/min and resolution 4 by a high-resolution TG method is shown in Figure 3. It is seen that the TG measurements in a high-resolution mode within a wide temperature range from 25 to 790°C were successfully completed in no longer than 50 min. Four important parameters from this study

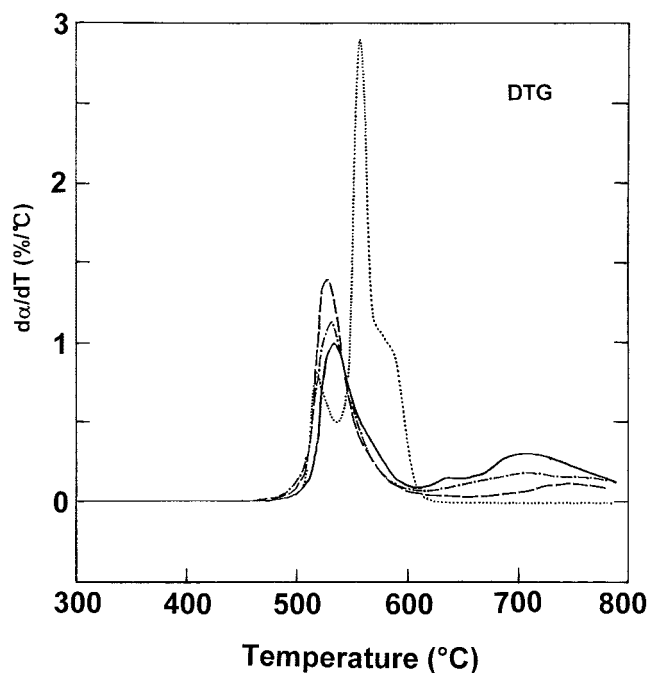**Figure 2** High-resolution DTG curves of the PES A in air (· · ·), argon (— · —), helium (– – –), and nitrogen (—) flow at an initial heating rate of 50°C/min and resolution 4.
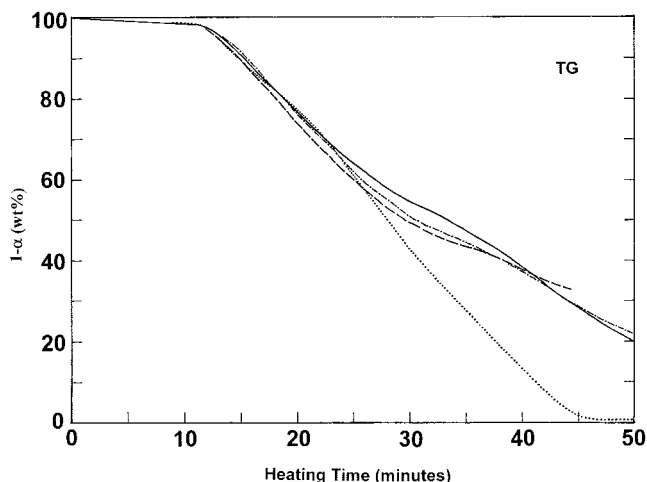
Figure 3 Variation of the weight of PES A with heating time in air (· · ·), argon (— · —), helium (– – –), and nitrogen (—) flow at an initial heating rate of 50°C/min and resolution 4 by a high-resolution TG technique.

and those in the literature.[5–8,10] are listed in Table I. TG curves illustrate no appreciable weight loss until 500°C in the four atmospheres, indicating that the PES A exhibits very high thermostability and quite low moisture content because the PES A was directly examined without drying in advance. In air, the degradation of the PES is essentially complete at 610°C, but in inert atmospheres such as nitrogen, argon, and helium 18–33 wt % of the PES remains at 790°C. The decomposition in air of PES A appears to occur through one relative low thermal degradation step first and then the fastest major oxidative degradation step and finally a subsequent medium degradation step. The thermal degradations in argon, helium, and nitrogen exhibit the fastest major thermal degradation and one (in argon and helium) and two (in nitrogen)

subsequent minor slow degradation stages. The TG curves obtained by the traditional TG method at 2°C/min exhibit two steps in nitrogen and air[6] and thus lower resolution than those by high-resolution TG, as shown in Table I.

The characteristic 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 790°C are given in Table I. The T_d values determined in this study in air and nitrogen are higher than the average T_d determined at constant heating rates of 2–20°C/min. On the contrary, the $(d\alpha/dT)_{m1}$ and char yield at 790°C are lower in this study than those reported in the literature.[6,7] There is an influence of atmosphere on the thermal degradation of the PES A. The T_d of the PES A determined in this study increases with the variation of the atmosphere in the order: air < argon < helium < nitrogen. The T_{dm1} of the PES A determined in this study increases in a different order: air < helium < argon = nitrogen. The T_{dm1}, $(d\alpha/dT)_{m1}$, and char yield at 790°C determined by high-resolution TG all increase in the same order: air < nitrogen < argon < helium.

Obviously, there is the lowest T_d, T_{dm1}, T_{dm2}, and char yield at 790°C in air because of an additional thermooxidative degradation from oxygen in air. These suggest the lower thermostability in air than in inert atmospheres including nitrogen, argon, and helium. In the presence of air, the thermal degradation occurred 2–9°C sooner than in nitrogen, argon, and helium. However, the ratio of T_d in air versus T_d in nitrogen is equal to 0.98, suggesting that the onset of bond cleavage is basically thermal in nature and not influenced to any great extent by the presence of oxygen. Nevertheless, as shown in Tables I and II the PES A exhibits higher decomposition temperatures (T_d and T_{dm1}) and the first maximum weight-loss rate

TABLE I
Thermal Degradation Characteristics of Polyethersulfone (PES) A and C

PES	Atmosphere	Heating rate (°C/min)	$T_d/T_{dm1}/T_{dm2}$ (°C)	$(d\alpha/dT)_{m1}/(d\alpha/dT)_{m2}$ (%/°C)	Char yield at 790°C(wt %)	Reference
A	Air	Variable	510/517/556,576	0.8/2.9	0.8	This study
A	Air	2	509/537/590	1.1/1.3	0	6
A	Air	10	440/455/540	—	3	7
C	Air	2	499/520/540,565	0.6/1.4,1.9	0	6
A	Argon	Variable	512/532/707	1.12/0.2	23	This study
A	Helium	Variable	514/526/749	1.4/0.11	33	This study
A	Nitrogen	Variable	519/532/642,705	1.0/0.15,0.31	18	This study
A	Nitrogen	2	509/537/625	1.1/0.2	35[a]	6
A	Nitrogen	10	517/433/551	—	35	5
A	Nitrogen	20	555/590/—	—	37	8
A	Nitrogen	20	447/579/—	—	36	10
C	Nitrogen	2	462/500/655	0.7/0.2	40[a]	6

[a] The char yield at 660°C.

TABLE II
Thermal Degradation Characteristics of Polyethersulfone B[a]

Atmosphere	Heating rate (°C/min)	$T_d/T_{dm1}/T_{dm2}$ (°C)	$(d\alpha/dT)_{m1}/(d\alpha/dT)_{m2}$[b] (%/°C)	Char yield at 790°C (wt %)
Air	1	494/532/567	0.3/0.16	0
Air	2	496/536/580	0.25/0.25	0
Air	5	511/544/623	0.22/0.18	0
Air	10	523/556/637	0.19/0.12	0
Air	15	536/565/679	0.27/0.10	3
Air	20	528/568/693	0.23/0.08	9
Air	25	544/576/693	0.27/0.07	19
Nitrogen	1	476/511/—	0.31/—	46
Nitrogen	2	479/517/—	0.31/—	43
Nitrogen	5	488/522/—	0.22/—	46
Nitrogen	10	501/533/597	0.24/0.04	46
Nitrogen	15	515/541/600,752	0.24/0.03,0.01	42
Nitrogen	20	512/544/610,759	0.35/0.04,0.01	45
Nitrogen	25	517/549/621,760	0.33/0.05,0.01	44

[a] Their TG and DTG curves were obtained from Abate et al.[11]
[b] Relatively maximum rate of weight loss.

$(d\alpha/dT)_{m1}$ but lower char yield in air and nitrogen than highly aromatic PES B and PES C and bisphenol-A polysulfone when the traditional TG at a constant heating rate was used.[16] If high-resolution TG was used the PES A shows lower T_d in air and nitrogen than that of bisphenol-A polysulfone. Therefore, the order of decomposition temperature of the four poly-(phenylene ether sulfones)[16] is bisphenol-A polysulfone < PES B < PES C < PES A in air and bisphenol-A polysulfone < PES C < PES B < PES A in nitrogen. The presence of the isopropylidene group in bisphenol-A polysulfone accounts for its lowest thermostability. Perhaps, the lower molecular weight of PES B and PES C accounts for their somewhat lower stability regardless of their higher aromaticity.

Additionally, the decomposition temperatures (T_d, T_{dm1}, and T_{dm2}) of the PES B in air and nitrogen increase steadily with an increase in heating rate from 1 to 25°C/min for the TG measurement, as listed in Table II, but the $(d\alpha/dT)_{m1}$ maintains substantially at 0.25%/°C in air and 0.29%/°C in nitrogen. The char yield at 790°C also remains at 45% basically despite the variation of the heating rate. These results suggest

an obvious influence of heating rate on the thermal decomposition features of the polyethersulfones.

Thermal degradation process

As seen in Table III the weight loss of the first stage of thermal degradation of the PES A in four testing atmospheres determined in this study (exclusive of the weight loss at the variable heating rate in air) varies in a narrow range from 48 to 58 wt %, which is larger than that (38 wt %) which corresponds to the complete loss of sulfone, ether group, as well as the hydrogen on the benzene rings in the form of sulfur dioxide, water, and hydrogen. The higher actual weight loss at the first degradation step should be ascribed to the additional weight loss from aromatic carbons. This might imply that the first stage of the thermal degradation of the PES A is primarily an exclusion of sulfur dioxide, dehydration, and hydrogen abstraction, and crosslinking between the residual aromatic carbon.[6,8–10] The second stage was the degradation of aromatic carbon.

TABLE III
Temperature Range and Weight Loss of Thermal Degradation of Each Step for the PES A

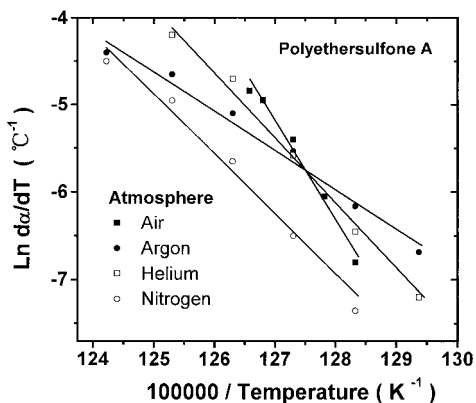| Atmosphere	Heating rate (°C)	Temperature range (°C) 1st step/2nd step	Weight loss (%) 1st step/2nd step	Reference
Air	Variable	100–535/535–573, 573–650	19/52, 29	This study
Air	2	400–563/563–618	58/41/—	6
Argon	Variable	40–614/614–790	53/24/—	This study
Helium	Variable	80–640/640–790	56/12/—	This study
Nitrogen	Variable	100–609/609–653, 653–679	48/6, 32	This study
Nitrogen	2	400–586/586–663	55/11	6

Figure 4 Application of the Friedman method to the high-resolution TG data of PES A obtained in air (■), argon (●), helium (□), and nitrogen (○).

Thermal degradation kinetics

Figures 4–6 illustrate the plots for the calculation of activation energy of the first major degradation of the PES A, PES B, and PES C by the Friedman technique based on the following equation[30]:

$$\ln(d\alpha/dt) = \ln Z + \ln(1 - \alpha) - E/RT$$

where α is the weight loss of the polymer undergoing degradation at time t, R is the gas constant (8.3136 J mol^{-1} K^{-1}), and T is the absolute temperature (K). The plot of $\ln(d\alpha/dt)$ as a function of $1/T$ should be linear with a slope equal to E/R.

The kinetic data calculated are summarized in Table IV. Some activation energies for the three PES samples have been listed for an easier comparison. There are
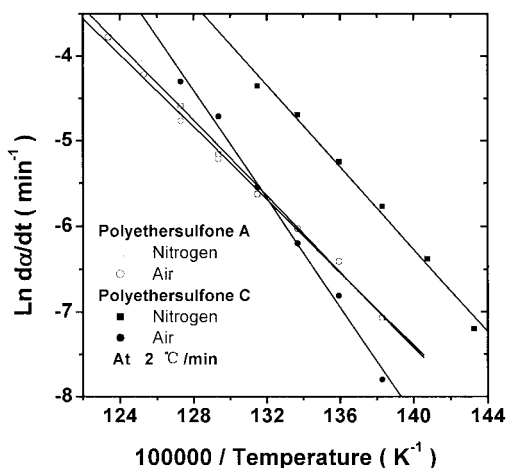

Figure 5 Application of the Friedman method to the traditional TG data of PES A obtained in nitrogen (□) and air (○), and of PES C obtained in nitrogen (■) and air (●) based on the DTG curves from Crossland et al.[6]
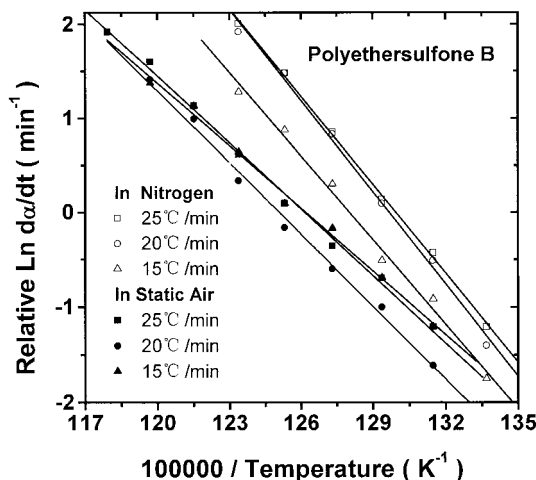

Figure 6 Application of the Friedman method to the traditional TG data of PES B obtained in nitrogen at heating rate of 25°C/min (□), 20°C/min (○), 15°C/min (△), and in air at 25°C/min (■), 20°C/min (●), 15°C/min (▲) based on the DTG curves from Abate et al.[11]

apparent variations with testing atmospheres, suggesting apparent dependency of kinetic feature of the PES on testing atmosphere. An enhancing order of activation energy of the thermal degradation for the PES A in four atmospheres is in argon < in nitrogen < in helium < in air.

On the contrary, the activation energy value for three PES samples seems lower in air than in nitrogen, as shown in Table IV. This opposite phenomenon indicates different decomposition kinetics characteristics in air and nitrogen. Apparently, a considerable difference of the activation energy value for the same PES A is found in the three inert gases. This difference could be attributed to the different density and thermal conductivity of the inert gases. It appears that with decreasing the density of the inert gases from 1.784 g/mL (STP) for argon, and 1.2506 g/mL (STP) for nitrogen to 0.1769 g/mL (STP) for helium, or with increasing the thermal conductivity of the inert gases from 62 J m^{-1} h^{-1} K^{-1} for argon, and 86 J m^{-1} h^{-1} K^{-1} for nitrogen to 510 J m^{-1} h^{-1} K^{-1} for helium, the activation energy values increase monotonically from 380 and 570 to 602 kJ/mol. Therefore, the thermal decomposition of the PES depends significantly on the density and thermal conductivity of the testing atmospheres, besides their reactivity such as oxidative ability from oxygen. Similarly, different activation energy values are also observed for the thermal decomposition of thermoplastic polyimide[28] and polyphenylene sulfide[24] in the four testing atmospheres. This semi-quantitative relationship between the decomposition characteristics of the polymers and the physical properties of the testing atmospheres might be established for the first time.

LI ET AL.

TABLE IV
Activation Energy (kJ/mol) of the First Major Thermal Degradation of Polyethersulfones

PES type	Heating rate (°C/min)	Calculating method	Atmosphere				Reference
			Air	Argon	Helium	Nitrogen	
A	Variable	Friedman	934	380	602	570	This study
A	2	Friedman	177	—	—	185	6 and this study
A	20		—	—	—	159	10
A	Isothermal	Regression	183	—	—	300	6
B	15	Friedman	184	—	—	246	11 and this study
B	20	Friedman	211	—	—	269	11 and this study
B	25	Friedman	196	—	—	260	11 and this study
B	1–25	MacCallum	255	—	—	258	11
B	1–5	Kissinger	646	—	—	735	11
B	5–25	Kissinger	285	—	—	320	11
C	2	Friedman	259	—	—	200	6 and this study
C	Isothermal	Regression	177	—	—	325	6

The activation energies in air and nitrogen determined by the high-resolution TG in this study or calculated by the Kissinger technique in the weight loss of 1–5 wt % are much larger than those determined by traditional TGs. For the activation energy value based on the traditional TG curves by the Friedman technique, the activation energy increases with the variation of polymer sample in the order: PES A < PES B < PES C in air and PES A < PES C < PES B in nitrogen. Note that other calculating techniques give different activation energy values. These imply a dependency of activation energy value on calculating technique.

Most polymers contain weak bonds, which are expected to break with a larger probability than other stronger bonds. When the thermal energy begins to surpass the bond energies of various bonds in the PES chains, a random chain scission occurs and the rate of degradation increases rapidly. It was estimated that the carbon–sulfur bond between the aromatic ring and sulfone group is the weakest linkage and breaks down before the ether group does. The eight bond energies are listed in Figure 7 for reference. From these values, it seems which bond undergoing chain scission could be predictable. The dissociation energy of the C–S bond above-mentioned is 272 kJ/mol, which is slightly higher than the mean activation energy value (257 kJ/mol) in air but slightly lower than the mean

activation energy value (296 kJ/mol) in nitrogen on the basis of traditional TG data. It seems that the first major thermal degradation of the PES is mainly controlled by the abstraction of sulfur dioxide.[6–11]

CONCLUSIONS

A high-resolution thermogravimetry was successfully applied to rapidly investigate the thermal degradation of polyethersulfone in air, argon, helium, and nitrogen. The thermal degradation parameters involving temperature, the maximal degradation rate, char yield at 790°C, and activation energy of polyethersulfone show a dependency of testing atmosphere, testing technique, and its molecular chain structure. The decomposition temperature of polyethersulfone determined by the high-resolution TG in air and nitrogen is higher than that by traditional TG, but the activation energy of the decomposition based on the high-resolution TG data is much higher than that based on the traditional TG data. The high-resolution TG/DTG techniques and procedures described here have been satisfactorily used for a quick investigation of the thermal degradation and its kinetics of several heat-resistance polymers.[15,16,18,24,28] There is a significant relationship between the thermal decomposition characteristics of the polymers and the physicochemical properties of the testing atmospheres.
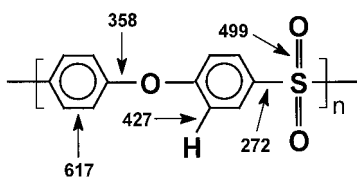
The project was supported by (1) the National Natural Science Foundations of China (20174028); (2) the Foundation of Nano Science and Technology Project of Shanghai China (0259nm022); and (3) the Fund of the Key Laboratory of Molecular Engineering of Polymers of Education Ministry. Fudan University, China. The authors would like to thank Prof. Dr. Yu-Liang Yang (Fudan University) for his valuable help.

Figure 7 The dissociation energy (in kJ/mol) of five bonds in polyethersulfone.

References

1. Leslie, V. J.; Rose, J. B.; Rudkin, G. O.; Feltzin, J. In: New Industrial Polymers; Deanin, R. D., Ed.; ACS Symposium Series 4; American Chemical Society: Washington, DC, 1972; pp. 63–82.
2. Fritzsche, A. K.; Arevalo, A. R.; Connolly, A. F.; Moore, M. D.; Elings, V.; Wu, C. M. J Appl Polym Sci 1992, 45, 1945.
3. Kumazawa, H.; Wang, J. S.; Sada, E. J Polym Sci Part B: Polym Phys 1993, 31, 881.
4. Pham, V. A.; Santerre, J. P.; Matsuura, T.; Narbaitz, R. M. J Appl Polym Sci 1999, 73, 1363.
5. Juangvanich, N.; Mauritz, K. A. J Appl Polym Sci 1998, 67, 1799.
6. Crossland, B.; Knight, G. J.; Wright, W. W. Br Polym J 1986, 118, 156.
7. Archibald, R. S.; Sheares, V. V.; Samulski, E. T.; DeSimone, J. M. Macromolecules 1993, 26, 7083.
8. Bynn, I. S.; Kim, I. C.; Seo, J. W. J Appl Polym Sci 2000, 76, 787.
9. Clark, J. H.; Denness, J. E. Polymer 1994, 35, 2432.
10. Rao, V. L.; Sabeena, P. U.; Rao, M. R.; Ninan, K. N. J Appl Polym Sci 1999, 73, 2113.
11. Abate, L.; Pappalardo, A.; Recca, A. Polym Eng Sci 2000, 40, 1114.
12. Huang, M.-R.; Li, X.-G. J Appl Polym Sci 1998, 68, 293.
13. Li, X.-G.; Huang, M.-R.; Bai, H. Angew Makromol Chem 1998, 256, 9.
14. Li, X.-G.; Huang, M.-R.; Guan, G.-H.; Sun, T. Polym Int 1998, 46, 289.
15. Li, X.-G.; Huang, M.-R. J Appl Polym Sci 1999, 71, 565.
16. Li, X.-G.; Huang, M.-R. React Funct Polym 1999, 42, 59.
17. Li, X.-G.; Huang, M.-R. Polym Degrad Stab 1999, 64, 81.
18. Li, X.-G.; Huang, M.-R. J Macromol Sci Pure Appl Chem 1999, 36, 859.
19. Li, X.-G.; Huang, M.-R. Polym Plast Technol Eng 2000, 39, 317.
20. Li, X.-G.; Huang, M.-R. Polym Test 2000, 19, 385.
21. Li, X.-G.; Huang, M.-R.; Yang, Y.-L. Polym J 2000, 32, 348.
22. Li, X.-G.; Huang, M.-R.; Li, F.; Cai, W.-J.; Jin, Z.; Yang, Y.-L. J Polym Sci Part A: Polym Chem 2000, 38, 4407.
23. Li, X.-G.; Duan, W.; Huang, M.-R.; Yang, Y.-L. J Polym Sci Part A: Polym Chem 2001, 39, 3989.
24. Li, X.-G.; Huang, M.-R.; Bai, H. J Appl Polym Sci 2002, 83, 1940.
25. Li, X.-G.; Huang, M.-R.; Shao, H.-T. J Appl Polym Sci 2002, 86, 1673.
26. Li, X.-G.; Huang, M.-R.; Jin, Y.; Yang, Y.-L. Polymer 2001, 42, 3427.
27. Li, X.-G.; Wang, L.-X.; Huang, M.-R.; Lu, Y.-Q.; Zhu, M.-F.; Menner, A.; Springer, J. Polymer 2001, 42, 6095.
28. Li, X.-G.; Huang, M.-R.; Bai, H.; Yang, Y.-L. Macromol Mater Eng 2001, 286, 421.
29. Huang, M.-R.; Li, X.-G.; Yang, Y.-L. Polym Degrad Stab 2001, 71, 31.
30. Friedman, H. L. J Polym Sci C 1964, 6, 183.