Comparison of Thermal Degradation Characteristics of Poly(arylene sulfone)s Using Thermogravimetric Analysis/Mass Spectrometry

LI-HSIANG PERNG

Department of Chemical Engineering, Ta Hwa Institute of Technology, Chung-Lin, Hsinchu 30703, Taiwan, Republic of China

ABSTRACT: Thermal degradation of poly(arylene sulfone)s had been studied by the combination of thermogravimetric analysis/mass spectrometry (TG/MS) with pyrolysis/gas chromatography/mass spectrometry (Py-GC/MS) techniques. Through these two methods, the pyrolysates from poly(ether sulfone) (PES) and polysulfone (PSF) were identified in 11 and 21 sets of evolution curves, respectively, from room temperature to 900 °C. Among these pyrolysates, 12 products from PES and 25 products from PSF were obtained. The major mechanism for both PES and PSF was one-stage pyrolysis involving main chain random scission and carbonization with evolution of SO_2 and phenol as major products. Although the initial thermal stability of PES was lower than that of PSF, the formation of sulfide groups in the condensed phase from PES, through reduction of sulfone group by hydrogen radicals, increased the fire retardation behavior of PES. In PES, the ether and sulfone groups showed similar thermal stability. The thermal stability of functional groups in PSF were in the order of sulfone < ether < isopropylidene group. The scission of the ether group in PSF, with evolution of phenol as the major product, reached maximum evolution amount at the temperature of the maximum thermogravimetry loss of TG (T_{max}). The scission of isopropylidene groups at high temperature (>580 °C) evolved higher mass derivatives that lower the fire retardancy of PSF. By using a simplified kinetic model, PES showed maximum activation energy with a conversion ratio of 0.2–0.3, which implies a high fire retardant effect of sulfide formation in PES. A comparative study with the proposed model and experimental data showed the theoretical pyrolysis curves to be in agreement with the experimental curves for PES and PSF pyrolysis, respectively. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2387–2398, 2001

Key words: PES and PSF pyrolysis; mechanism and kinetic model; Py-GC/MS; TG/MS

INTRODUCTION

Poly(ether sulfone) (PES) and polysulfone (PSF) are amorphous high-performance polymers with high thermal durability used in engineering plastics. They also resist boiling water, organic solvents, chemical corrosion, and ignition, and can be easily adapted for processing. As above, the reason why they have been evaluated recently for the possibility to replace conventional thermally durable materials and components used in aircraft, medical equipment, and automobiles. Al-

though these polymers have a high degree of thermal stability, it is important to understand their degradation because the changes in high-temperature processing may affect the ultimate performance. Therefore, research on their pyrolysis behavior and mechanism will be of paramount importance for processing and performance evaluation.

The thermal degradation of polymers has been used not only for the identification of materials, structure determination, and thermal resistance, but also for the evaluation of the reaction and influence on material strength and toxicity of volatile components. There have been numerous studies evaluating the degradation behavior of poly(arylene sulfone)s in the literature. Danilina et al.[1] used infrared (IR) analysis for the pyrolysates of PES and PSF, along with the change of absorption peaks for 2 h at 470 °C, showing the formation of SO_2 and phenol from the scission of sulfone and ether linkages. Crossland et al.[2] reported the results of thermogravimetry (TG) and pyrolysis/gas chromatography/mass spectrometry (Py-GC/MS) in evaluating the pyrolysis mechanism and pyrolysates of various polysulfones, indicating main chain scission and hydrogen abstraction. However, the relative stability of the different polysulfones could not be postulated because of the lack of quantitative analysis of pyrolysates at different temperature regions. Montaudo et al.[3] used pyrolysis/mass spectrometry (Py-MS) to study the mechanism and product formation of PES pyrolysis. Almen and Ericsion[4] used pyrolysis/gas chromatography/flame ionization detector (Py-GC/FID) and pyrolysis/gas chromatography/flame photometric detector, (Py-GC/FPD) to analyze the evolution of SO_2 from PES and PSF for mechanism and kinetic studies. Ehlers et al.[5] used TG, Py-MS, and infrared spectroscopy (IR) in mechanism and kinetic evaluations of isothermal pyrolysis of PSF and PPS at 250 and 620 °C, respectively. Davies[6] applied Py-MS to determine the kinetic parameters through the change of SO_2 evolution. Levantovskaya et al.[7] studied the isothermal pyrolysis of PSF in vacuum to evaluate mechanism and kinetic parameters through SO_2 evolution, mainly from scission of the sulfone linkage. However, the relationships between mechanisms and kinetics of poly(arylene sulfone)s pyrolysis are not fully clear because of the complexity of the pyrogram.

TG analysis is an excellent tool to study the kinetics of thermal degradation. It provides information on frequency factor, activation energy, and overall reaction order. Unfortunately, it cannot provide enough information on the thermal degradation mechanism because of insufficient capability of evolved gas mixture analysis. The solid residue analysis is limited by the interference of cross-linking of functional groups in the polymer structure and is not ideal for interpretation. Thus, the direct analysis of gas compositions, by continuous monitoring with a real-time thermogravimetric analysis/mass spectrometry (TG/MS) technique, gains more attention in the identification of gaseous products for the mechanism study of pyrolysis. Recently, the development of the TG/MS interface design has made possible a significant breakthrough in stability studies. Such a system has been used in studying the mechanism of poly(ether ether ketone),[8] liquid crystal polymer,[9] polyimide,[10] and fire-retardant additive in polystyrene.[11] The interface system still did not reach the status of ideal and needed more improvement. Up to now, TG/MS has been used mostly in the analysis of small-size molecules, such as CO, CO_2, water, and phenol. The interface system had been modified in my previous study[13] to give high sensitivity and low interference for real-time monitoring of major gas evolution curves in thermal pyrolysis of polymers.

In this study, the real-time evolution curves were obtained by the combination of TG/MS and Py-GC/MS techniques applied to the comparative study of the thermal degradation mechanism and kinetic model for poly(ether sulfone) and polysulfone polymers. In addition, the theoretical pyrolysis curves were calculated from the proposed kinetic model. The correlations of the theoretical and experiment curves are also discussed.

EXPERIMENTAL

Materials

Poly(ether sulfone) polymer (trade name Victrex®) and polysulfone polymer (trade name Udel®) were from ICI Corporation and Union Carbide Corporation, respectively. These commercial grade films had average molecular weights, M_n, of ~1.95 × 10^4 g/mol for PES and ~4.11 × 10^4 g/mol for PSF.

Py-GC/MS Analysis[13]

The Py-GC/MS experiments were carried out using a CDS-2000 Pyroprobe pyrolyzer (Chemical Data System Company) coupled to a HP 5890 gas

chromatograph that was linked to an HP 5972 quadruple mass spectrometer. Sample aliquots (~1.00 mg) were pyrolyzed in a quartz capillary sample holder, using the platinum coil attachment with 5/16" inner diameter (i.d.). The pyroprobes were calibrated to ensure the accuracy of the nominally set temperature. Flash pyrolysis, with helium carrier gas at a flow rate of 50 mL/min and the interface of Py-GC at 250 °C, was used up to 850 °C at a flow rate of 5 °C/ms for identifying pyrolysates from poly(arylene sulfone)s pyrolysis. The GC column was a HP-5MS (30 m × 0.25 mm i.d. with coated film thickness of 0.25 μm). The oven temperature of GC was initially held at 40 °C for 2 min, then programmed to 250 °C at 10 °C/min and held for 5 min, and then programmed to 260 °C at 10 °C/min and held for 10 min. The GC/MS interface was set at 280 °C. Mass spectra were recorded under electron impact ionization energy at 70 eV, and the flow rate was kept constant. The MS detector was scanned from 10 to 400 m/z at a scan rate of 1.8 scan/s. Data analyses were performed with a HP Chem Station G1034 (version 3.00) to match the NIST Mass Spectra Library by comparison.

TG/MS Analysis

The TG/MS experiments were performed with a TG/MS system[13] by coupling a Du Pont TA 2950 analyzer with modified CDS-3500 interface and an HP 5972 quadruple mass spectrometer. The samples (~1.00 mg) were pyrolyzed in the TG, and the evolved gases were led via the CDS 3500 interface to the HP 5972 mass spectrometer to obtain the generation curves of pyrolysates. The interface was a splitter using two deactivated columns of 0.53 and 0.1 mm i.d. capillary tubing, with a length of 30 cm, to split the evolved gases. The operating conditions were as follows: purge gas, helium of 99.9995% purity; temperature setting of the interface, 300 °C; MS range, 10–500 a.m.u.; scan rate, 1.2 scans/s; and two computer systems were used to control TG and MS respectively. For kinetic studies of poly(arylene sulfone)s pyrolysis, the heating rates were set at 5, 10, and 15 °C/min from 30 to 900 °C in He.

RESULTS AND DISCUSSION

Studies of Poly(arylene sulfone)s Pyrolysis by TG/MS and Py-GC/MS

To identify a complicated mixture of ion species by TG/MS, this study attempted to combine the

Table I   Selective Nondisturbance Ion Species in TG/MS Analysis of PES Pyrolysis

Compound	Ion Species, m/z
SO_2	64
Benzene	78
Phenol	94
Diphenylether + diphenylmethane	170
Dibenzofuran	168
Methylbenzene	91
Benzenethiol	110
Diphenyl	154
Dibenzothiophene	184
Chlorobenzene	112
2-Phenoxy-1,1'-biphenyl	246

superior separating and identifying ability of Py-GC/MS to analyze pyrolysates of poly(arylene sulfone)s. Then, the results were used to select nondisturbance specific ion species (m/z) for TG/MS analysis to investigate the real-time evolution curves of pyrolysates.

A typical chromatogram and mass spectra of the pyrolysates obtained by flash pyrolysis of PES and PSF at temperatures up to 850 °C in a helium atmosphere were shown already in a previous publication.[14] The major pyrolyzed gaseous products were identified by Py-GC/MS. The real-time evolution curves from TG/MS were obtained by selecting nondisturbance specific ion species (m/z) except for the pairs of diphenylether + phenylphenol from PES, ethylbenzene + p-xylene, 2-methylbenzene + 4-methylbenzene, diphenylmethane + dibenzofuran, and 4-ethyl-1-phenoxybenzene + 1,1'-oxybis-4-methylbenzene from PSF. Extraction of specific nondisturbance ions from TG/MS analysis resulted in 11 curve sets with 12 pyrolysates from PES and 21 sets of 25 pyrolysates from PSF, except for diphenylsulfide, 1,1'-sulfonylbenzene, and 1,4-diphenoxybenzene from PES as well as 9-phenyl-9H-fluorene, 4-phenoxy-1-(1-phenylmethyl)-benzene and 4-phenoxy-1-(1-phenylethyl)-benzene from PSF. The latter were not found by TG/MS because of condensation or because they were present in only trace amounts. The results are listed in Tables 1a and 1b for PES and PSF pyrolysis, respectively.

The evolution profiles of SO_2, benzene, phenol, diphenylether, and dibenzofuran from TG, differential thermogravimetric analysis DTG, and total ion current (TIC), in the range from room temperature to 900 °C, determined by TG/MS in He at a
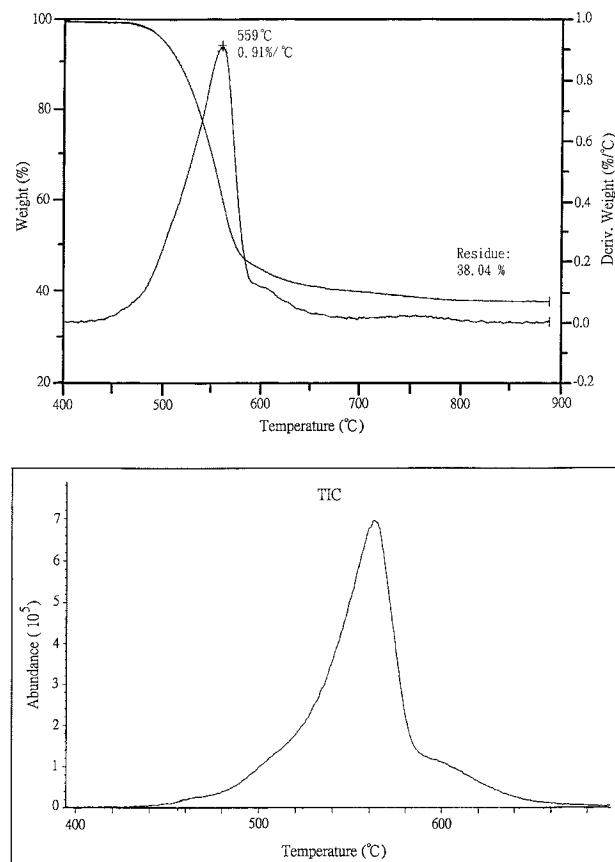
Figure 1 (a) TG/DTG and (b) TIC curves of PES by TG/MS in He at 10 °C/min.

heating rate of 10 °C/min, are shown in Figures 1a and 1b. SO_2 was the dominating pyrolysate in PES pyrolysis, but it was not accompanied by a sulfonic acid derivative. This result indicates main chain scission of sulfone linkages as the primary mechanism of pyrolysis, which had been reported earlier.[1–7] In Figure 2a, SO_2 started to form at 440 °C, maintained slow evolution between 440 and 530 °C, then quickly reached a maximum at ~560 °C, and drastically reduced after 580 °C. The evolution pattern was similar to TIC and DTG curves. The evolution of phenol as the next dominating product was similar to that of SO_2, starting from 480 °C, reaching a maximum at ~560 °C, and decreasing thereafter at ~580 °C, as a result of the main chain random scission of the ether group or hydrogenation of phenoxy intermediates. From the evolution profiles of SO_2 and phenol, the initial evolution temperature of the latter was shown to be 40 °C higher than the former, showing that the bonding energy of the ether linkage is higher than that of

the sulfone linkage.[15] The evolution curves of benzene and phenylether + phenylphenol were similar. They began to evolve ~480 °C; reached maxima around 565 °C, being higher than that of phenol; and still released massive amounts after 580 °C, indicating that these compounds were produced from partially carbonized solid residue. This result was indicated by a similar initial evolution temperature, indicating that these compounds were released after the decomposition of the ether and sulfone groups and reached maximum evolution after massive evolution of SO_2 and phenol. Dibenzofuran began to evolve around 500 °C and reached a maximum around 565 °C, with a lesser quantity after 580 °C, indicating the extensive cyclization of free radicals after massive evolution of SO_2 and phenol.

The evolution curves of methylbenzene, benzenethiol, biphenyl, dibenzothiophene, chlorobenzene, and 2-phenoxy-1,1'-biphenyl are shown in Figure 2b. Benzenethiol and dibenzothiophene began to evolve around 520 and 540 °C, respectively, reached maxima around 580–600 °C, and decreased rapidly after 620 °C. These results indicate that these sulfide compounds formed and were released after the main chain scission. The higher evolution temperature of these compounds could be due to the instability of the sulfide group in the condensed phase, which may decompose from partially carbonized solid residue of PES to release these pyrolysates in maximum amounts around the temperature region 580–620 °C, and thereafter enter the stabilized region. The formation of new sulfide groups[16] in the condensed phase could raise the carbonization effect and improve the thermal stability of PES, indicating the reason for the maximum evolving temperature of SO_2 being similar to that of phenol, as shown in Figure 2a. Methylbenzene, biphenyl, and 2-phenoxy-1,1'-biphenyl began to evolve around 520 °C, reached maxima around 580 °C, and continued to be released after 620 °C, indicating the recombination of free radicals dominated at high temperature. The formation of chlorobenzene could be the release of chlorine contamination from polymerization precursor[17] in the polymer chain ends or side chains. The formation of chlorobenzene was similar to that of SO_2, indicating that evolution of chlorobenzene was accompanied by the scission of sulfone groups.

Pyrolytic Studies of PSF by TG/MS

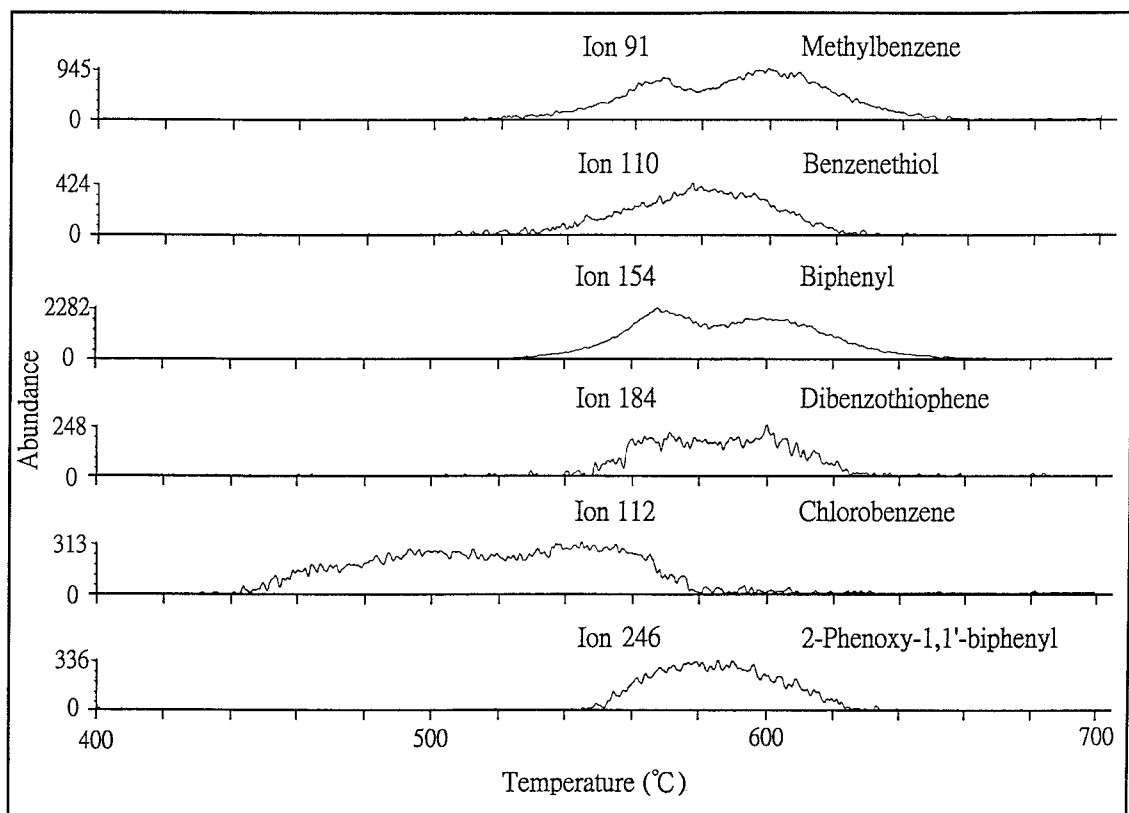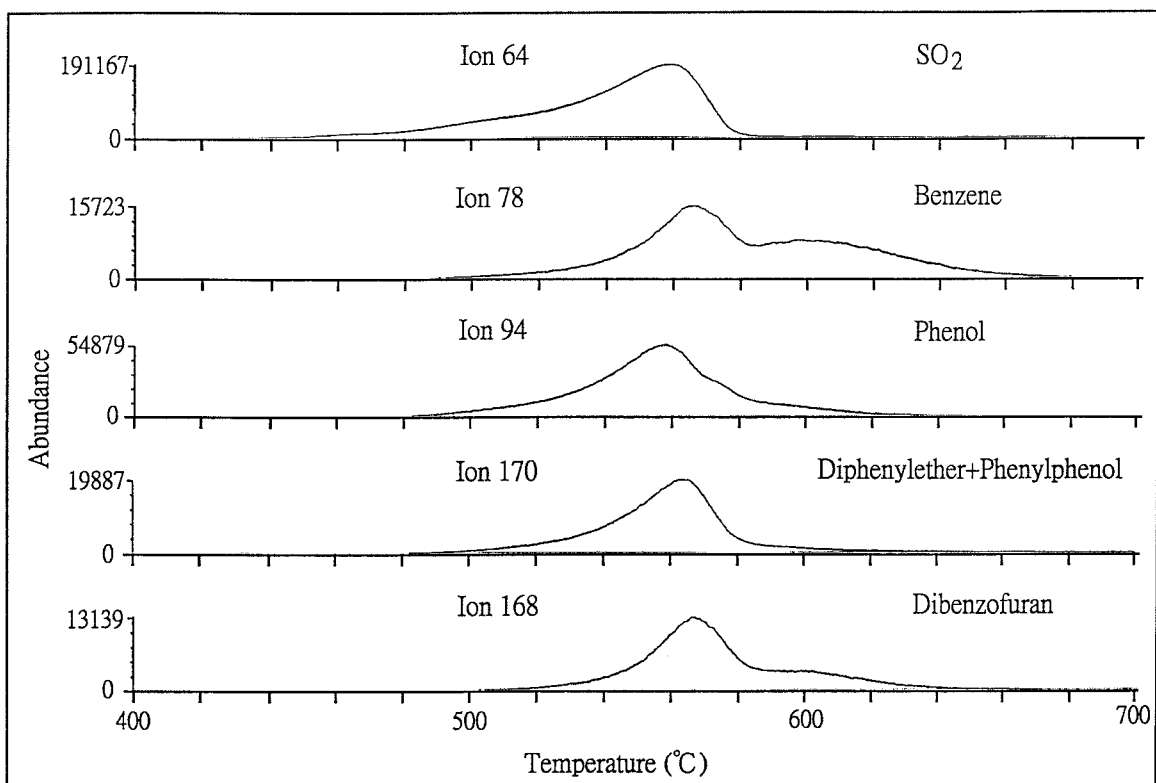The evolution curves of PSF determined by TG, DTG, and TIC, in the range from room tempera-

Figure 2   (a) Change of PES pyrolysis products in TG/MS in He at 10 °C/min: (1) SO_2;
(2) benzene; (3) phenol; (4) diphenyl ether + phenylphenol; (5) dibenzofuran. (b) Change
of PES pyrolysis products in TG/MS in He at 10 °C/min: (1) methylbenzene; (2)
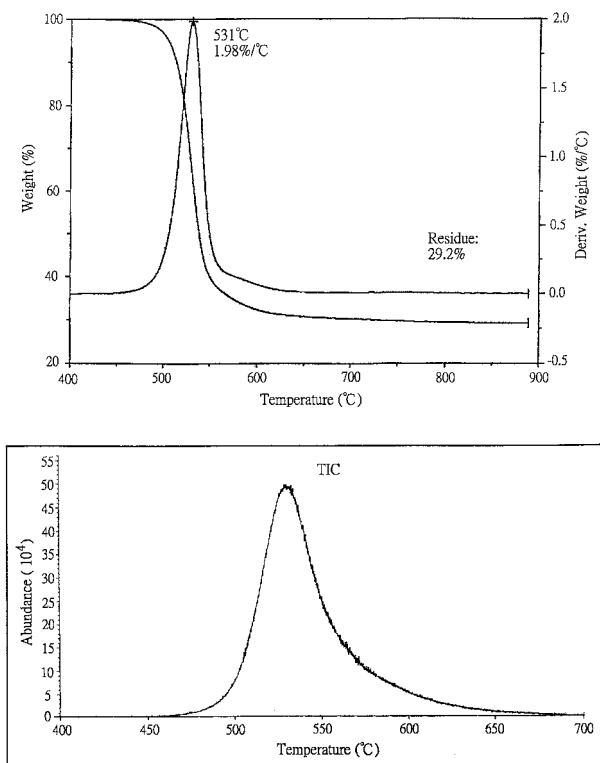benzenethiol; (3) biphenyl; (4) dibenzothiophene; (5) chlorobenzene; (6) 2-phenoxy-1,1'-
biphenyl.

Figure 3 (a) TG/DTG and (b) TIC curves of PSF pyrolysis products in TG/MS in He at 10 °C/min.

ture to 900 °C, with TG/MS in He at a heating rate of 10 °C/min, are shown in Figures 3a and 3b. The evolution curves of SO_2, benzene, phenol, 1-methyl-4-phenoxybenzene, and 4-(1-methylvinyl)-1-phenoxybenzene are shown in Figure 4a. SO_2 was the dominating pyrolysate again, beginning at ~465 °C, reaching a maximum at ~525 °C, and drastically decreasing at ~540 °C. Similarly, phenol as the next dominating pyrolysate began to evolve at ~485 °C, reached a maximum at ~530 °C, and decreased drastically after 600 °C, being similar to TIC and DTG curves. These results indicate that the stability of the sulfone group is less than that of the ether group because of its lower bonding energy.[15] The initial release of 1-methyl-4-phenoxybenzene, at an even higher temperature of ~505 °C, with maximum at ~540 °C and massive release after 580 °C, indicates the stability of the isopropylidene group is higher than those of the sulfone and ether groups. Benzene started at ~465 °C, reached its maximum at ~540 °C and still released massive amounts after 580 °C, indicating that the release of this compound was accompanied by the decomposition of the isopropylidene group.

The evolution curves of compounds containing aryl group are shown in Figure 4b. The evolution curves of naphthalene and 2-ethyl-naphthalene were similar to that of 1-methyl-4-phenoxybenzene, indicating that these compounds were formed through cyclization of free radicals in the latter stage of pyrolysis. The evolution curves of diphenylmethane + dibenzofuran, fluorene, and 4-methyl-dibenzofuran, beginning at ~515 °C, reaching maxima around 560–600 °C, and disappearing after 620 °C, were formed after the release of isopropylidene derivative pyrolysates. This result indicates that these compounds were formed by the cyclization of free radicals, which could be favored in the high temperature region, from partially carbonized solid residues.

Evaluation of Mechanisms

The major mechanisms in the pyrolysis of PES were main chain random scission and carbonization in one-stage reaction regions to release SO_2 from the sulfone group and phenol from the ether group at the temperature of the maximum thermogravimetric loss. The thermal stability of the sulfone group was more fragile than that of the ether group, as shown in Scheme 1.

In this region, the reaction of hydrogen radicals on the sulfone group produced sulfide groups and led to the formation of benzenethiol, diphenylsulfide, and dibenzothiophene at higher temperature, as shown in Scheme 2.

At temperatures >580 °C, the mechanisms shifted to chain transfer with recombination and cyclization of solid residues. The formation of sulfide groups provided strong reducing power on the sulfone group to increase fire resistance, along with the evolution of phenylphenol and 2-phenoxy-1,1'-biphenyl through recombination and cyclization. Dibenzofuran and dibenzothiophene were evolved through cyclization at even higher temperature.

The mechanisms for the pyrolysis of PSF were similar to that for PES, involving the sulfone, ether, and isopropylidene groups to produce SO_2, phenol, and 1-methyl-4-phenoxybenzene as major products. From this result, the stabilities of functional groups were in the order sulfone < ether < isopropylidene. The relatively stable ether group dominated the temperature of maximum thermogravimetry loss rate. The mechanisms are shown in Schemes 3a and 3b.

Subsequent chain transfer led to cyclization and recombination in solid residues along with forma-
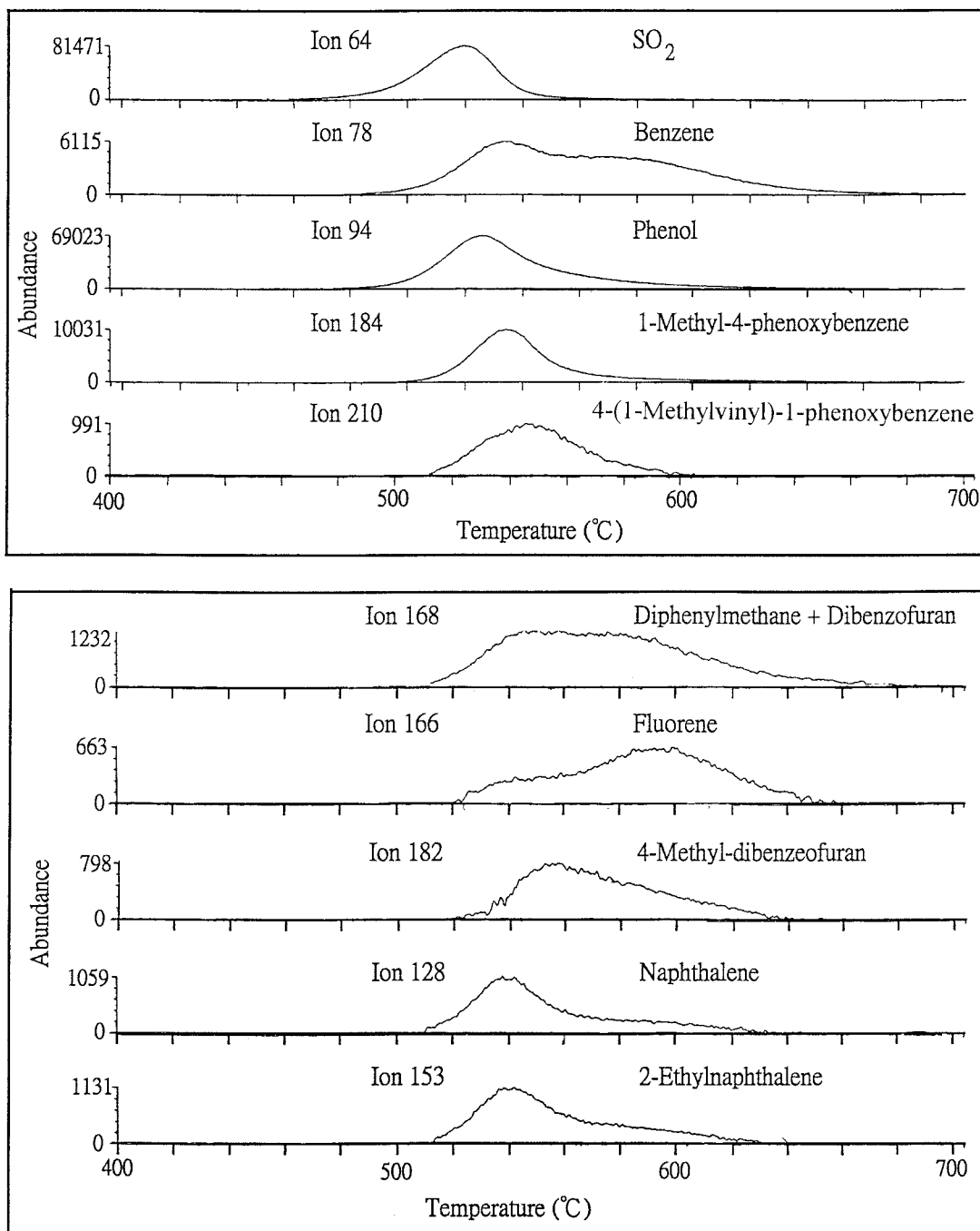
Figure 4 (a) Change of PSF pyrolysis products in TG/MS in He at 10 °C/min: (1) SO_2; (2) benzene; (3) phenol; (4) 1-methyl-4-henoxybenzene; (5) 4-(1-methylvinyl)-1-phenoxybenzene. (b) Change of PSF pyrolysis products in TG/MS in He at 10 °C/min: (1) diphenylmethane + dibenzofuran; (2) fluorene; (3) 4-methyl-dibenzofuran; (4) naphthalene; (5) 2-ethylnaphthalene.

tion of naphthalene, dibenzofuran, and 2-ethyl-naphthalene from partially carbonized residue at >580 °C. The carbonization mechanism became more important at even higher temperatures.

Kinetic Modeling and Parameter Analysis

The TG/DTG curves of PES and PSF, using TG/MS experiments from room temperature to
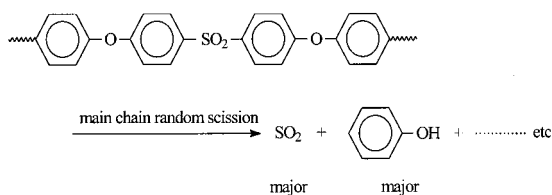
Scheme 1

900 °C, are shown in Figures 1a and 3a, respectively. The maximum pyrolysis rate (r_{max}), maximum temperature (T_{max}), and solid residue at 900 °C were 0.91 wt/°C, 560 °C, and 38 wt% for PES, and 1.98 wt/°C, 530 °C, and 29 wt% for PSF. From the analytical result, the thermal degradation mechanism seems to be considerably complex.

In this study, the Ozawa method[18] was used to calculate the activation energy (E) of PES and PSF at a given degree of conversion (X). That is,

$$E = [R \log(\beta_2/\beta_1)]/\{0.457[(1/T_1) - (1/T_2)]\} \quad (1)$$

where β is the heating rate (°C/min), T is the pyrolysis temperature (K), and subscripts 1 and 2 represent different heating rates or temperatures.

It was possible to calculate the temperature corresponding to a given degree of conversion (X) with different heating rates. The conversion (X) can be expressed as follows: $X = (W_0 - W)/(W_0 - W_f)$, where W_0 is the initial sample weight (g), W is the residual weight at conversion X (g), and W_f is the final residual weight at 900 °C (g).

Then, the apparent activation energy (E) could be calculated by the slope, which can be obtained by plotting the logarithm of heating rate versus the reciprocal of the absolute temperature. A least-squares analysis led to the activation energy values under different conversions, shown in Fig-
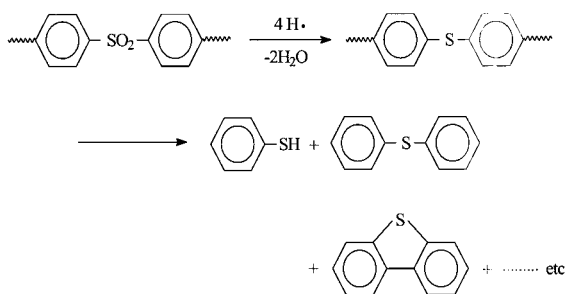
Scheme 2
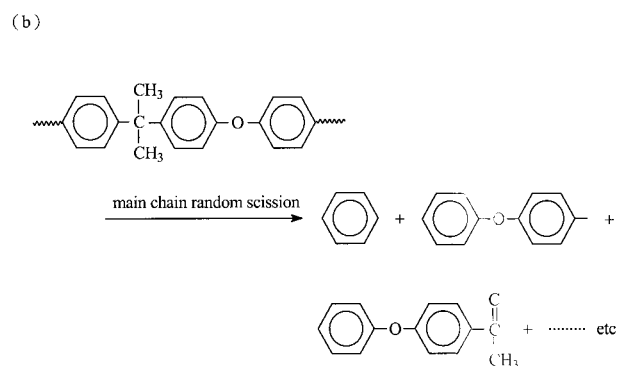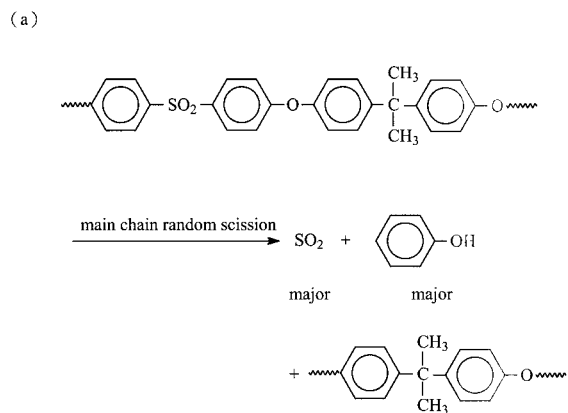
Scheme 3

ure 5, with heating rates of 5, 10, and 15 °C/min, respectively.

The calculated activation energies are shown in Figures 5a and 5b, with only one steady pyrolysis region in the conversion ranges $0.1 < X < 0.7$ for PES and $0.2 < X < 0.8$ for PSF. From analyzing the curve of activation energy under different conversions, PES showed a maximum activation energy region at conversion ratios of 0.2–0.3. This result could be evidence of sulfide group formation in the condensed phase in the temperature region 510–530 °C. When $X > 0.8$, carbonization taking place in the solid residue dominated the mechanism. In PSF, the activation energy decreased in the initial pyrolysis region ($X < 0.2$), and showed a stable activation energy at conversion ratios of 0.2–0.8, indicating that the main chain scission of PSF in the initial stage took place without sulfide formation for radical abstraction to increase the activation energy. For $X > 0.8$, the carbonization mechanism became the major one for pyrolysis in the partially carbonized residue, with rapid increase of activation energy again.
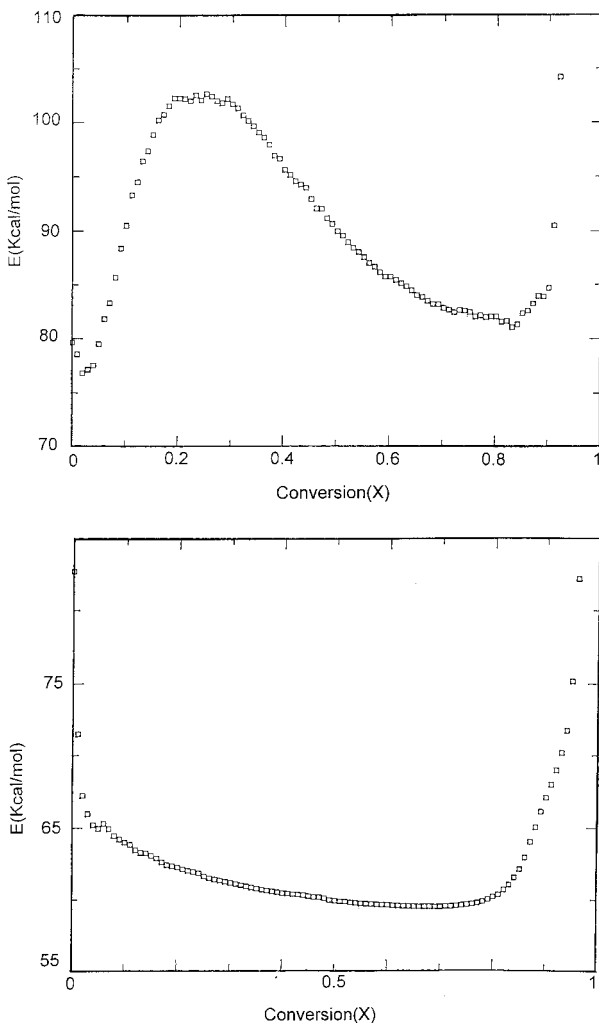
Figure 5 Change of activation energies with conversion of (a) PES and (b) PSF.

the reaction order, and T is the reaction temperature (K).

A straight line with slope n and intercept A was obtained by plotting $\ln[(\partial X/\partial t)/\exp(-E_{av}/(RT))]$ versus $\ln(1 - X)$, as shown in Figure 6, with a reaction order of $n =1.80$ for PES and 1.3 for PSF and pre-exponential factor of $A = 1.30 \times 10^{20}$ min^{-1} for PES and 3.3×10^{16} min^{-1} for PSF. Based on the kinetic parameters and pyrolysis mechanism analysis just described, a simplified one-stage model for both PES and PSF pyrolysis in helium can be proposed as shown in Scheme 4, in which K is the reaction rate constant of pyrolysis, C is the solid residue from carbonization by chain transfer, and V is the pyrolysates for PES and PSF, listed in Tables I and II, respectively, with the evolution of SO_2 and phenol as major products.
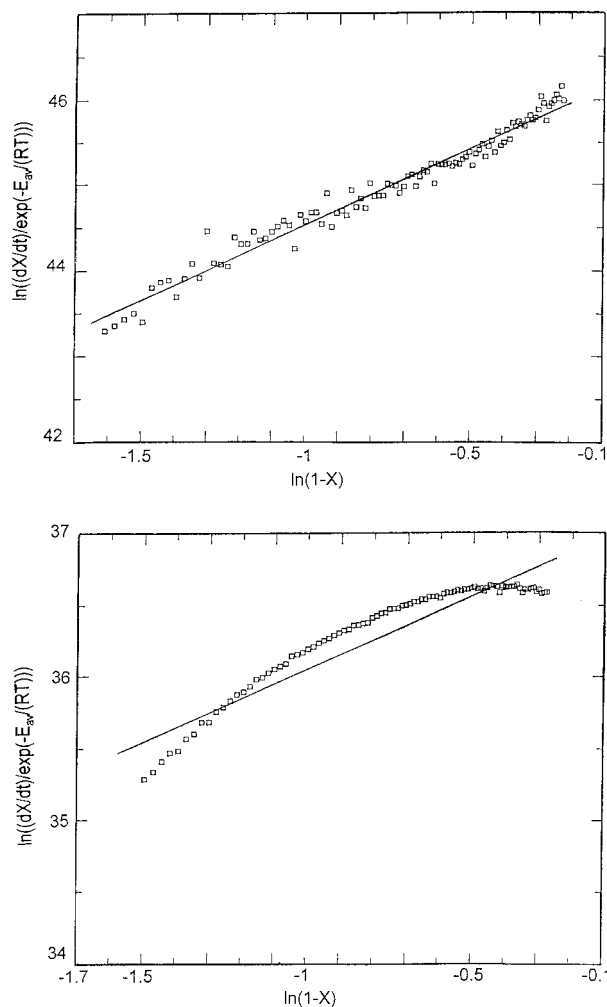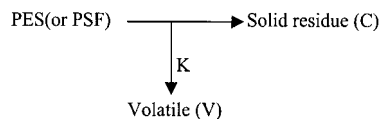
The kinetic parameters were determined by using the arithmetic average activation energy of 77 kcal/mol at $X = 0.1$–0.7 for PES and 60 kcal/mol at $X = 0.2$–0.8 for PSF in this steady region to simplify the pyrolysis model. These values accorded well with those from previous reports[1–6] and met the criteria of Ozawa's method for $RT/E_{av} \ll 1$ in the one-stage pyrolysis region, from which the average activation energy was substituted into the following rearranged equation:[13, 19, 20]

$$\ln[(\partial X/\partial t)/\exp(-E_{av}/(RT))]$$

$$= \ln A + n \ln(1 - X) \quad (2)$$

where E_{av} is the average activation energy (kcal/mol), A is the pre-exponential factor (L/min), n is

Figure 6 Kinetic parameters of (a) PES and (b) PSF pyrolysis in He at 10 7deg;C/min.

PES(or PSF) ——→ Solid residue (C)

K

Volatile (V)

To verify the proposed model, it is necessary to compare the values of residual mass fraction computed by the proposed model with experimental data. The computed values were obtained by substituting the kinetic parameters to the following equation:[19, 20]

$$m = 1 - \left[1 - (1 - n) \frac{ART^2}{\beta E} \right.$$
$$\left. \times \exp\left(-\frac{E_{av}}{RT}\right) \sum (E_{av}, T) \right]^{1/1-n} \quad (n \neq 1) \quad (3)$$

where

$$\sum (E, T) = \sum_{i=0}^{\infty} \left[\left(-\frac{RT}{E_{av}} \right)^i \prod_{j=0}^{i} (j + 1) \right] = 1 - 2\left(\frac{RT}{E_{av}} \right)$$
$$+ 6\left(\frac{RT}{E_{av}} \right)^2 - 24\left(\frac{RT}{E_{av}} \right)^3 + \cdots \quad (4)$$

Table II Selective Nondisturbance Ion Species in TG/MS Analysis of PSF Pyrolysis

| Compound	Ion Species, m/z
SO_2	64
Benzene	78
Phenol	94
1-Methyl-4-phenoxybenzene	184
4-Methylvinyl-1-phenoxybenzene	210
2-Methylphenol + 4-methylphenol	108
4-Ethylphenol	122
p-Vinylphenol	120
4-Isopropenylphenol	121
4-(1-Methyl-1-phenylethyl)-phenol	212
Methylbenzene	92
Ethylbenzene + p-xylene	106
Styrene	104
Diphenylether	170
4-Vinyl-1-phenoxybenzene	196
4-Ethyl-1-phenoxybenzene + 1,1'-oxybis-4-methylbenzene	198
Diphenylmethane + dibenzofuran	168
Fluorene	166
4-Methyl-dibenzofuran	182
Naphthalene	128
2-Ethylnaphthalene	153
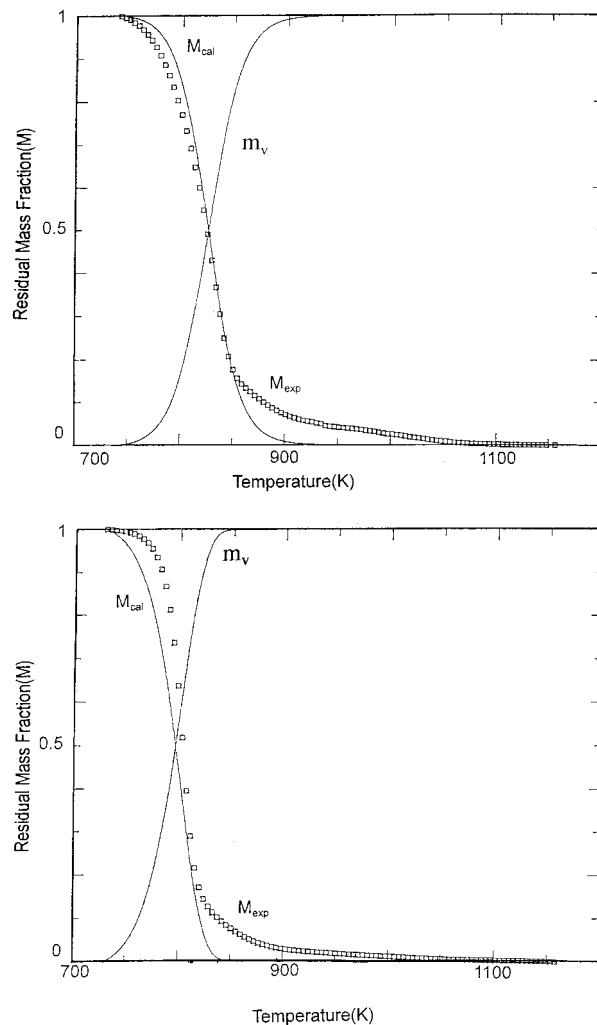
Figure 7 Comparison of theoretical (M_{cal}, m_v) and experimental (M_{exp}) curves of (a) PES and (b) PSF pyrolysis in He at 10 °C/min.

in which F is the weight factor by one-stage pyrolysis region and m_v is the mass fraction of volatiles.

Weighting factors were determined from the TGA programs of PES and PSF in He at a heating rate of 10 °C/min for $F = 1$. By substituting weight factors into eq. 3, theoretical values of residue mass fraction were computed, as shown in Figure 7 for $M_{cal} = 1 - m_v$. In addition, the data from Figures 1a and 3a were normalized and plotted with pyrolysis temperature (K) again. The experimental curve $M_{exp} = 1 - X$ was obtained, as shown in Figures 7a and 7b, and was in good agreement with the computed results of M_{cal} for the proposed model. However, the calculated curve was shifted to a

lower temperature region, showing that the actual thermal stability of PES and PSF could be higher than predicted because the carbonization mechanism gradually became dominant at higher temperature but was not considered in the simplified kinetic model. In addition, the activation energy of PSF pyrolysis for $X < 0.2$, being higher than that for $0.2 < X < 0.8$, was not considered in the simplified model. Thus, the calculated curve was further shifted toward the lower temperature region in the initial pyrolysis in comparison with the pattern of the experimental curve.

CONCLUSIONS

Thermal degradation of poly(ether sulfone) and polysulfone proceeded via one-stage pyrolysis including main chain random scission and carbonization with evolution of SO_2 and phenol as major products. In PES, the ether and sulfone groups had similar stability, which decomposed at the maximum thermogravimetry loss temperature (T_{max}) with maximum rates (r_{max}) being ~560 °C and 0.91 %/°C, respectively. The thermal stabilities of functional groups in PSF were in the order sulfone < ether < isopropylidene group, with the temperatures of maximum evolution amount being around 525, 530, and 540 °C, respectively. The scission of the ether group, with the evolution of phenol as major product, reached its temperature of maximum evolution at the temperature of the maximum thermogravimetric loss (T_{max}). Comparing the results of TG/MS analysis, the initial release temperature of SO_2 for PES was 25 °C lower than that for PSF and the maximum evolving temperature of both SO_2 and phenol for PES was ~30 °C higher than that for PSF. This result indicates that the formation of sulfide groups in the condensed phase of PES might compensate for the comparatively lower thermal stability in the initial pyrolysis and raise the fire retardancy. In PSF, the sulfide formation mechanism did not exist. Furthermore, the initial stability of PES was lower than that of PSF, as shown in the TG curves. The possible causes could be:

1. Low number average molecular weight, M_n, and increased local instability of chain ends and side chains in PES;

2. The higher thermal stability of isopropylidene group in PSF could contribute to its initial stability.
3. The contamination of dichlorodiphenylsulfone in chain ends and side chains of PES structure could lead to evolution of chlorobenzene and SO_2 at the initial pyrolysis temperature.

The evolution of high molecular weight pyrolysates from the isopropylidene group at high temperature for PSF could reduce the yield of solid residue compared with that from PES, which could account for the comparative results from the TG analysis. The kinetic parameters for PES, determined by using the arithmetic average activation energy (77 kcal/mol), are as follows: reaction order ($n = 1.8$) and pre-exponential factor ($A = 1.3 \times 10^{20}$) at $X = 0.1$–0.7. For PSF, the arithmetic average activation energy and calculated kinetic parameters are 60 kcal/mol, $n = 1.3$, and $A = 3.7 \times 10^{20}$ at $X = 0.2$–0.8. Based on these values, the computed TG data from proposed model for PES and PSF were plotted and found to be quite consistent with the experimental results.

REFERENCES

1. Danilina, L.J.; Teleshov, E.N.; Pravednikov, A.N. Polym Sci USSR 1974, 16, 172.
2. Crossland, B.; Knight, G.J.; Wright, W.W. Polym J 1986, 18, 156.
3. Montando, G.; Pugrissi, C.; Sampeni, F. Macromol Chem Phys 1994, 195, 1241.
4. Almen, P.; Ericsion, I. Polym Degrad Stab 1995, 50, 223.
5. Ehlers, G.F.L.; Fischand, K.R.; Powell, W.R. J Polym Sci, Part A-1 1969, 7, 2955.
6. Davies, A. Makromol Chem 1969, 128, 242.
7. Levantovskaya, I.I.; Dralyuk, G.V.; Mochalova, O.A.; Yurkova, I.A. Polym Sci USSR 1971, 13, 7.
8. Day, M.; Cooney, J.D.; Wiles, D.M. J Anal Appl Pyrolysis 1990, 18, 163.

9. Sato, H.; Kikuchi, T.; Koide, N.; Furaya, K. J Anal Appl Pyrolysis 1996, 37, 173.

10. Tsur, Y.; Frelich, Y.L.; Levy, M. J Polym Sci, Part A: Polym Chem 1974, 12, 153.

11. Matuschek, G. Thermochim Acta 1995, 263, 59.

12. Nam, J.D.; Seferis,J.C. J Polym Sci, Part B: Polym Phy 1992, 30, 445.

13. Perng, L.H.; Tsai, C.J.; Ling, Y.C. Polymer 1999, 40, 7321.

14. Perng, L.H. J Polym Sci, Part A: Polym Chem 2000, 38, 583.

15. Cottrell, T.L. The Stength of Chemical Bonds; Butterworth: London, 1958.

16. Yamashita, T.; Kudo, T.; Horie, K.; Maeda, S; Nagata, K. Polym Degrad Stab 1993, 39, 297.

17. Temiraev, K.B.; Shustov, G.B.; Mikitiev, A.K. Polym Sci, Series B 1993, 35(12), 205.

18. Ozawa, T. Bull Chem Soc Jpn 1965, 38, 1881.

19. Chang, C.Y.; Wu, C.H.; Huang, J.Y.; Lin, J.P.; Ying, W.F.; Shih, S.M.; Chen, L.W.; Chang, F.W. J Env Eng (N.Y.) 1996, 122, 1.

20. Lin, J.P.; Chang, C.Y.; Wu, C.H. J Chem Tech Biotech 1996, 66, 1.