

On the Thermal Degradation of Poly(Styrene Sulfones). VII. Evaluations of Poly(Styrene Sulfone) Thermal Stability Using Invariant Kinetic Parameters

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ABSTRACT: The thermal degradation behavior of poly(styrene sulfone) was investigated by thermogravimetric analysis (TGA) measurement. This study described its thermal stability by applying the invariant kinetic parameter (IKP) method. The thermogravimetric and differential thermogravimetric analyses of different compositions of poly(styrene sulfones) were carried out over the temperature range 100–500°C under nitrogen. The kinetic parameters (preexponential factor and activation energy) of thermal decomposition of poly(styrene sulfone) can be obtained by dynamic measurement of TGA. The IKP method assumes that the kinetic parameters are independent of the experimental conditions. These parameters are computed without any hypothesis on the form of the kinetic degradation function. Invariant activation energies of the degradation of poly(styrene sulfone) show that the thermal stability decreases as the SO₂ content of poly(styrene sulfone) increases due to the thermal instability of the C—S bond. The relation equation, $Ea_{inv} = 237.0 - 290.5X_{SO_2}$, where X_{SO_2} is the molecular fraction of SO₂, was obtained to describe the effect of sulfur dioxide on the thermal stability of poly(styrene sulfone). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1698–1705, 2002

Key words: degradation; thermogravimetric analysis; activation energy

INTRODUCTION

Poly(olefin sulfones) are good candidates for application in microelectronics. They constitute the SO₂ matrix for high radiation-sensitive materials, induced main chain scission, with electron beam used in lithographic masks for the manufacture of integrate circuits on silicon wafers.^{1–3} The analysis of several materials has shown the implication of these materials in composition and aging condition. Thus, there was considerable thermal stability of different composition and under various

conditions of poly(olefin sulfones) used in microelectronics areas. Thus, it is necessary to study the thermal stability of these poly(olefin sulfones), which involves an understanding of their thermal degradation mechanism. Several poly(olefin sulfones), such as poly(acrylamide sulfone),⁴ poly(vinyl chloride sulfone),⁵ and poly(styrene sulfone), were studied in our laboratory.⁶

Thermogravimetric analysis (TGA) has been widely used to investigate the decomposition characteristics of many materials.^{7,8} Numerous investigations have shown that nonisothermal thermogravimetric analysis is a powerful tool to characterize the thermal degradation of polymers. TGA provides a method for thermal stability testing.^{9–11} With proper experimental proce-

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Table I Reaction Condition for Bulk Copolymerization of Styrene and Sulfur Dioxide

Sample No.	Feed Composition ^a [St]/([St] + [SO ₂]) Mole Ratio	Reaction Temp. (°C)	[η] ₀	SO ₂ × 10 ⁻² Mole Fraction	<i>n</i> ^b
PStS-1	2/3	30	0.31	34	1.94
PStS-2	2/3	40	0.28	33	2.03
PStS-3	2/3	50	0.32	27	2.70
PStS-4	2/3	60	0.29	21	3.76
PSt	1.00	50	0.34	0	—

^aAIBN initiator concentration = $6.1 \times 10^{-2}M$.

^b*n*, Styrene moles/SO₂ moles in polymer, determined by elementary analysis.

dures, information about the kinetics of decomposition can be obtained. Kinetic data obtained from thermogravimetric analyses may be used as criteria for the choice of a polymer. The determination of kinetic parameters from data of nonisothermal thermogravimetry is one of the most difficult kinetic problems. Many authors have classified methods of kinetic data analysis into integral, differential, and specified method.^{12,13} These methods were usually applied to study the decomposition of polymeric materials from thermogravimetric data. The present work uses a method developed by Lesnikovich et al.¹⁴ applied to dynamic TGA data for poly(styrene sulfone) decomposition at different heating rates to compute invariant kinetic parameters (IKP). These are independent of the experimental conditions and are computed without making any hypothesis on the form of the kinetic degradation function. So, the values obtained are no longer apparent but real characteristics of the system studied. Moreover, the present method could lead us to compute the distribution of probabilities associated with kinetic functions and then to obtain the degradation mode of the material.

Several compositions of poly(styrene sulfones), which were obtained by copolymerizing styrene and sulfur dioxide under different reaction conditions, were studied in this article. The IKP method is applied in the temperature range that corresponds to the thermal degradation of the poly(styrene sulfone) (i.e., its decomposition in sulfur dioxide and styrene).¹⁵ The aim of this article is to study the effect of the sulfur dioxide content of poly(styrene sulfone) on its pyrolysis by the IKP method.

EXPERIMENTAL

The poly(styrene sulfones) (empirical formula $-(CH_2-CHC_6H_5)_n-SO_2)_x-$) were synthesized

by a free-radical mechanism at various temperatures ranging from 30 to 70°C with different ratios of styrene to sulfur dioxide and *N,N'*-azobisisobutyronitrile (AIBN) as the initiator. Styrene was allowed to react with hydrous sulfur dioxide in a 500-mL Pyrex glass vessel, with constant stirring under high pressure. All polymerizations were carried out to < 10 wt % conversion. The details of the preparation procedure were discussed in previous articles.^{16,17} The viscosities of poly(styrene sulfones) were measured in tetrahydrofuran solutions at 30°C with a Ubbelohde viscometer. The composition of poly(styrene sulfones) was characterized by a Heraeus CHN-S rapid element analyzer. These results are listed in Table I. A Perkin-Elmer 7 series thermal analyzer was used to evaluate the thermal behavior of the poly(styrene sulfones). Thermogravimetric analyses were carried out under nitrogen atmosphere (flow rate 50 cc/min). Sample size of 10 ± 2 mg and four heating rates of 5, 10, 20, and 40°C/min were used.

RESULTS AND DISCUSSION

The Experimental Data of Thermal Degradation of Poly(Styrene Sulfone)

Figure 1 shows the thermogravimetric (TG) and differential thermogravimetric (DTG) curves for the poly(styrene sulfone), sample PStS-3, at various heating rates 5, 10, 20 and 40°C/min. The residual mass after pyrolysis may be expressed by a degree of decomposition, *X*, which is calculated as:

$$X = (W_0 - W)/(W_0 - W_f) \quad (1)$$

where *W*, *W*₀, and *W*_{*f*} are, respectively, the actual, initial, and final weights of the sample. The varia-

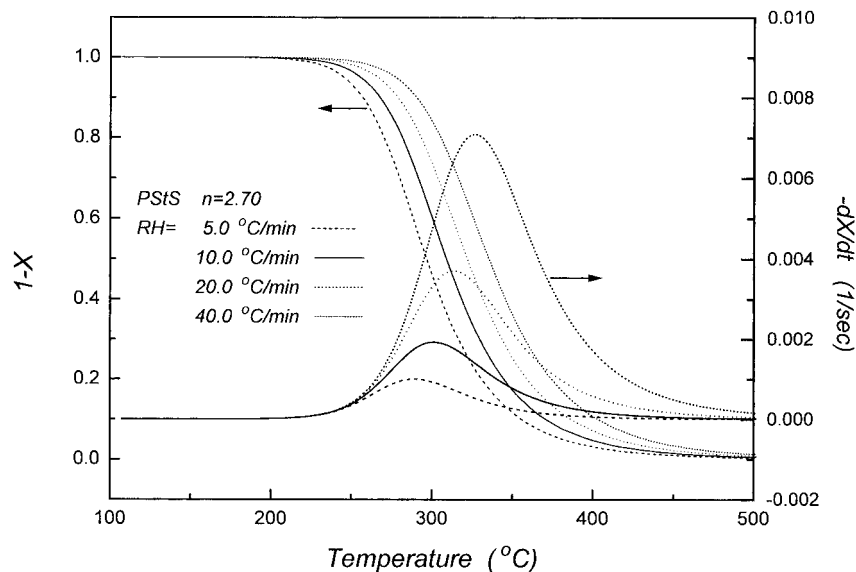


Figure 1 TG and DTG curves of the poly(styrene sulfone), PStS-3, versus heating rates.

tion in X with reaction temperature (T) is shown in Figure 1. Obviously, there is one stage of decomposition over the temperature range of 100–500°C for all four different heating rates investigated. At a lower heating rate, the retention time required for the polymer to a given temperature is longer. This would generally result in a higher conversion. Thus, the residual mass curve with a lower heating rate is to the left of that with a higher heating rate. The differential residual mass after pyrolysis is ex-

pressed by a differential residual mass percentage, dX/dt , shown in Figure 1. The maximum rates of degradation occur at different temperatures for various heating rates. A higher heating rate shifts the rate curve to the higher temperature range and also results in a higher peak rate.

Figures 2 and 3 show the TG and DTG curves for different compositions of poly(styrene sulfone). The variation in degree of decomposition versus the reaction temperature (T) is shown in Figures 2 and 3.

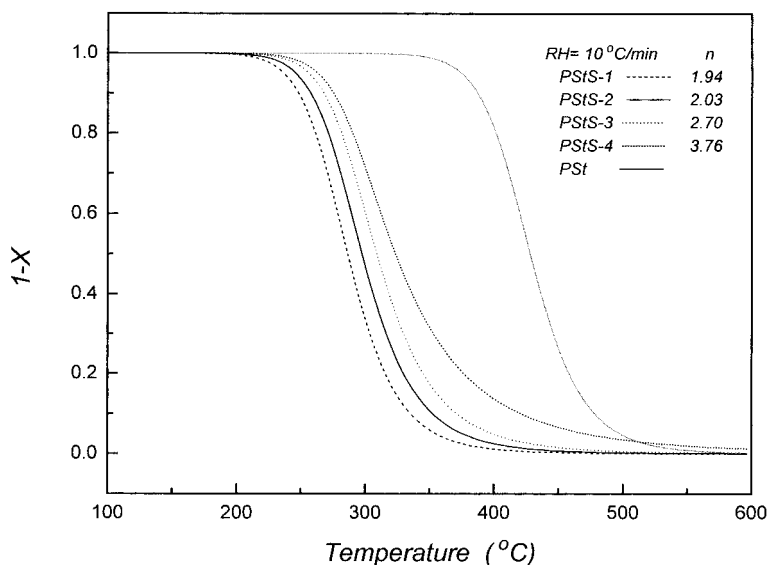


Figure 2 TG curves of the four different poly(styrene sulfones) and one polystyrene system versus heating rates under nitrogen.

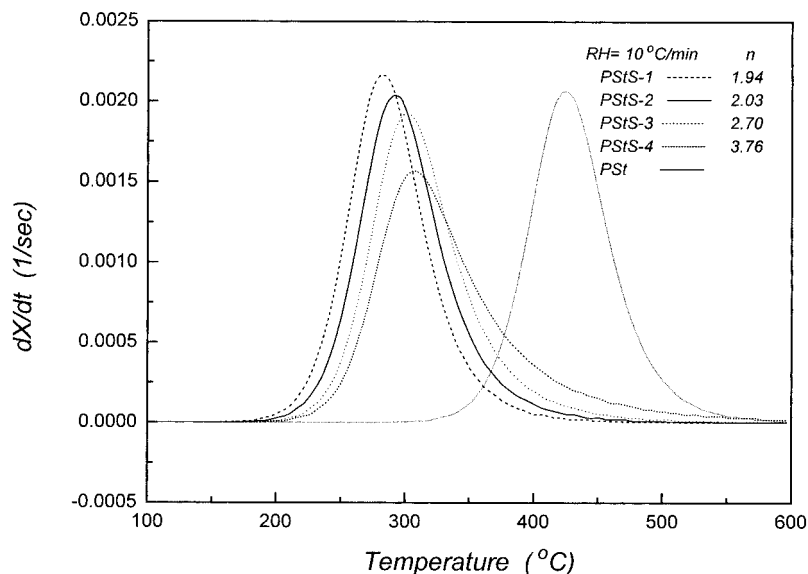


Figure 3 DTG curves of the four different poly(styrene sulfone) systems and one polystyrene versus heating rates under nitrogen.

Obviously, there is one degradation step over the temperature range of 100–500°C whatever the poly(styrene sulfone) investigated. At a higher SO₂ content of poly(styrene sulfone), the retention time required for the polymer to a given conversion is shorter. The maximum rates occur at different temperatures for various compositions of poly(styrene sulfone). A higher SO₂ content of poly(styrene sul-

fone) rate shifts the rate curve to the lower temperature range.

Application of the IKP Method to the Experimental Data

The decomposition rate is assumed to depend only on X and can be described by the following equation:

Table II Kinetic Models Used in the IKP Method¹⁸

Kinetic Models	$f_j(X)$	$g_j(X)$	
Nucleation and nucleus growing	$(1 - X)[- \ln(1 - X)]^{1-n}/n$	$[- \ln(1 - X)]^n$	S1— $n = 1/4$
			S2— $n = 1/3$
			S3— $n = 1/2$
			S4— $n = 2/3$
			S5— $n = 1$
Phase boundary reaction	$(1 - X)^n$	$1 - (1 - X)^1$ $1 - (1 - X)^{1/2}$ $1 - (1 - X)^{1/3}$	S6—Plane symmetry
			S7—Cylindrical symmetry
			S8—Spherical symmetry
Diffusion	X^{-1} $[- \ln(1 - X)]^{-1}$ $[(1 - X)^{-1/3} - 1]^{-1}$	X^2 $(1 - X) \ln(1 - X) + X$ $3/2 [1 - 2/3X - (1 - X)^{2/3}]$	S9—Plane symmetry
			S10—Cylindrical symmetry
			S11—Spherical symmetry
			S12— $n = 1/4$
Potential law	X^{1-n}/n	$X^n (0 < n < 2)$	S13— $n = 1/3$
			S14— $n = 1/2$
			S17— $n = 2/3$
			S18— $n = 3/4$
Reaction order	$(1 - X)^{1-n}/n$	$-(1 - X)^2$ $-(1 - X)^3$	S15—Order 2
			S16—Order 3

Table III Apparent Kinetic Parameters of the Poly(Styrene Sulfone), PStS-3, Obtained for Each Kinetic Function versus the Heating Rates

Heating Rate Function	5°C/min		10°C/min		20°C/min		40°C/min	
	ln A (s ⁻¹)	Ea (kJ/mol)	ln A (s ⁻¹)	Ea (kJ/mol)	ln A (s ⁻¹)	Ea (kJ/mol)	ln A (s ⁻¹)	Ea (kJ/mol)
S1	-1.54	25.48	-1.00	25.52	-0.33	26.07	0.34	26.61
S2	1.44	38.20	1.91	38.20	2.54	38.79	3.15	39.33
S3	7.23	63.60	7.57	63.56	8.10	64.19	8.62	64.81
S4	12.90	88.96	13.12	88.91	13.55	89.63	13.97	90.25
S5	24.07	139.75	24.03	139.58	24.27	140.42	24.49	141.22
S6	24.07	139.75	24.03	139.58	24.27	140.42	24.49	141.22
S7	23.62	138.16	23.57	137.95	23.88	139.04	24.17	140.00
S8	23.47	137.62	23.42	137.37	23.75	138.54	24.06	139.63
S9	55.03	287.37	54.21	286.78	54.07	288.71	53.88	290.51
S10	15.10	98.45	15.23	98.24	15.76	99.50	16.25	100.63
S11	15.33	98.33	15.47	98.12	16.00	99.37	16.50	100.55
S12	-2.11	23.43	-1.59	23.39	-0.82	24.27	-0.08	25.06
S13	0.83	36.03	1.29	35.94	2.01	36.86	2.72	37.74
S14	6.55	61.13	6.88	61.05	7.52	62.05	8.13	63.01
S15	22.96	133.35	22.89	132.97	23.41	134.77	23.89	136.45
S16	22.47	130.13	22.38	129.67	23.04	131.97	23.64	134.10
S17	12.14	86.28	12.34	86.11	12.90	87.24	13.42	88.29
S18	14.92	98.83	15.05	98.66	15.56	99.83	16.04	100.92

$$dX/dt = kf(X) \quad (2)$$

where X is the degree of conversion, $f(X)$ is a certain function of degradation of X , and k is the decomposition rate constant. k can remain a con-

stant and depends upon the temperature. It can be expressed by the equation:

$$k_j = A_j \exp(-Ea/RT) \quad (3)$$

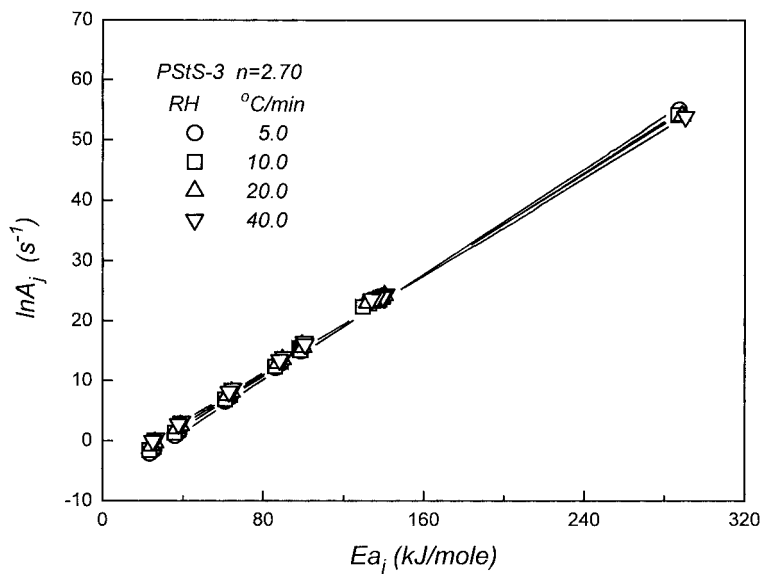


Figure 4 Compensation effect for the poly(styrene sulfone), PStS-3, versus heating rates.

Table IV k_v and T_v Values of the Poly(Styrene Sulfone) versus the Heating Rates

	β_v (°C/min)	$\beta_v = \ln(k_v)$ (k_v : s ⁻¹)	l_v (mol/kJ)	$1/T_v$ (K ⁻¹)
PStS-1	5	-6.628	0.2261	0.001880
	10	-5.984	0.2211	0.001838
	20	-5.309	0.2166	0.001801
	40	-4.660	0.2117	0.001760
PStS-2	5	-6.643	0.2221	0.001847
	10	-5.999	0.2172	0.001806
	20	-5.322	0.2129	0.001770
	40	-4.672	0.2081	0.001730
PStS-3	5	-6.643	0.2181	0.001813
	10	-6.038	0.2134	0.001774
	20	-5.322	0.2092	0.001739
	40	-4.644	0.2050	0.001704
PStS-4	5	-6.755	0.2144	0.001783
	10	-6.112	0.2099	0.001745
	20	-5.387	0.2063	0.001715
	40	-4.645	0.2028	0.001686
PSt	5	-6.615	0.1789	0.001487
	10	-5.964	0.1756	0.001460
	20	-5.241	0.1729	0.001438
	40	-4.541	0.1700	0.001413

where A_j is the preexponential factor (s⁻¹), Ea_j is the activation energy (J/mol), R is constant (J/mol-K), and T is the temperature (K).

Equation (2) can be rewritten by substituting eq. (3) into eq. (2)

$$dX/dt = A_j \exp(-Ea_j/RT) f(X) \quad (4)$$

In the case of a linear heating rate β_v , °C/min, the combination of the above two equations gives the following relationship

$$dX/f_j(X) = A_j/\beta_v \exp(-Ea_j/RT) dT \quad (5)$$

The thermal decomposition of a solid, in heterogeneous process accompanied by release of gaseous products, can usually be characterized by several mechanisms (nucleation, one-, two-, or three-dimensional diffusion, etc.) and consequently by several forms of the function $f(X)$. Thus, it is helpful not to have to assume one function $f(X)$ rather than another one. The IKP method allows such a theoretical approach. The computation of the invariant kinetic parameters and of the probabilities for the degradation functions was carried out from TG curves. In the IKP

method, several functions given in the literature [18 functions $f_j(X)$ reported in Table II] are used.¹⁸

The Coats and Redfern¹⁹ method was used to integrate eq. (5). It leads to the following relation

$$\ln[g_j(X)/T_{iv}^2] = \ln(A_{jv}R/\beta_v Ea_{jv}) - Ea_{jv}/RT_{iv} \quad (6)$$

with $g_j(X) = \int_x^0 1/f_j(X) dX$, i is the data point; β_v is the heating rate, and j is the number of the kinetic function between 1 and 18. Eighteen couples (A_{jv} , Ea_{jv}) per heating rate β_v are obtained.

In this study, this method was carried out for the four different poly(styrene sulfone) samples by using TGA data collected in the decomposition degree range of 0–0.5. As an example, the apparent parameters of the poly(styrene sulfone) sample, PStS-3, obtained for each kinetic function versus heating rates are listed in Table III. The application of the method is based on the study of the compensation effect.²⁰ Indeed, the integration method applied to kinetic function $f_j(X)$ implies significant changes of activation energies and pre-exponential factors. For each function $f_j(X)$, $\ln(A_j)$ versus Ea_j is plotted and, if a compensation effect is observed, a linear relation defined by the following equation is obtained for a given heating rate β_v :

$$\ln A_{jv} = B_v + l_v Ea_{jv} \quad (7)$$

where $B_v = \ln(k_v)$ and l_v is $1/RT_v$. It is shown by plotting $\ln A_j$ versus Ea_j that the compensation effect is observed for each heating rate (Fig. 4) in the case of PStS-3. The values of B_v and l_v (Table IV) are then calculated from the slopes and the intercepts of the straight line obtained. The curves $\ln k_v = f(1/T_v)$ in Figure 5 are straight lines, so the Arrhenius law

$$\ln k_v = \ln A_{inv} - Ea_{inv}/RT_v \quad (8)$$

is followed. Consequently, the values of the invariant activation energy and the invariant pre-exponential factor presented in Table V are calculated from the curves for five different poly(styrene sulfones).

It is clear that, in the temperature range where the thermal degradation of poly(styrene sulfone) occurs, the degradation rate of high SO₂ content PStS is always higher than that of the low SO₂ content PStS. The same result was found in a previous stability classification of the poly(styrene sulfone) versus the chemical composition of

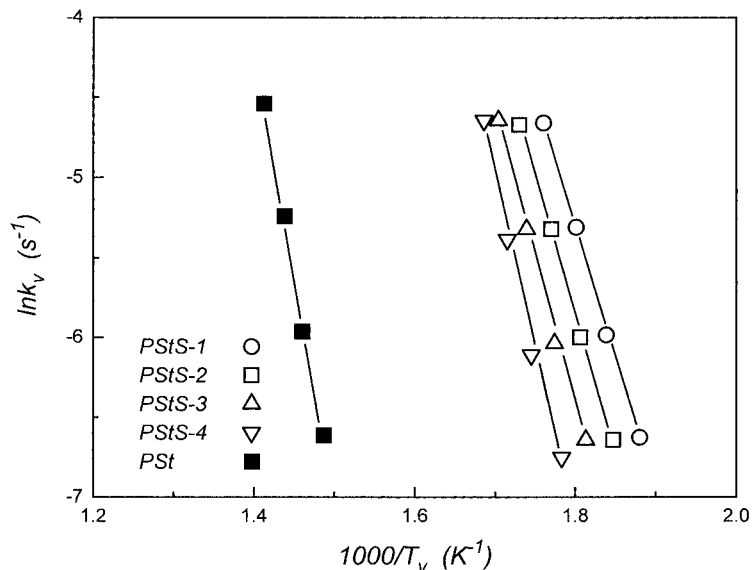


Figure 5 $\ln k_v$ for four different poly(styrene sulfones) and one polystyrene system.

the SO_2 content in the early stage of thermal degradation by determination with pH-meter technique²¹; the higher SO_2 content is less heat resistant than higher styrene content of poly(styrene sulfone). This trend implies that the thermal degradation of the high SO_2 content PStS takes place at a lower temperature than in the case of low SO_2 -PStS. The comparison of the values of the invariant activation energies leads us to conclude that the decrease in thermal stability of the poly(styrene sulfone) is linked with the use of the increase of SO_2 content PStS. The effect of SO_2 content on the invariant activation energy was examined by plotting the molecular fraction of SO_2 as shown in Figure 6. It was found that the invariant activation energy decreases when an increase in the SO_2 content of the poly(styrene sulfone) increases. A linear relationship between the invariant activation energy and the SO_2 content of the poly(styrene sulfone) can apparently be obtained. From this dependence, linear coefficients were evaluated by linear regression analysis. These fits were obtained by the least-squares method. The relation equation, $Ea_{\text{inv}} = 237.0$

$- 290.5X_{\text{SO}_2}$, where X_{SO_2} is molecular fraction of SO_2 , is obtained. From the above relation, it is demonstrated that the higher the SO_2 content is, the lower its thermal stability is.

CONCLUSION

Poly(styrene sulfones) were prepared from different SO_2 molecular fractions in the range of 1.9–3.71. The thermal stability of PStS was investigated by TGA measurement and the kinetic parameters of degradation were evaluated by using the IKP method. The preexponential factor and activation energy of thermal decomposition of different poly(styrene sulfone) samples that can be obtained by dynamic measurement of TGA were $137.7\text{--}182.7$ kJ/mol and $4.0 \times 10^{10}\text{--}1.12 \times 10^{14}$ s^{-1} , respectively. The invariant activation energy of all poly(styrene sulfone) samples is less than that of the polystyrene. Arrhenius plots show that the polymer containing higher SO_2 is the less stable. Invariant activation energies of the degradation of poly(styrene sulfone) shows that the

Table V Invariant Kinetic Parameters of the Poly(Styrene Sulfones) and Polystyrene

Invariant Kinetic Parameters	PStS-1	PStS-2	PStS-3	PStS-4	PSt
A_{inv} (s^{-1})	4.32×10^{10}	6.04×10^{10}	4.26×10^{11}	1.12×10^{14}	2.54×10^{15}
Ea_{inv} (kJ/mol)	137.7	141.7	153.4	182.7	235.5

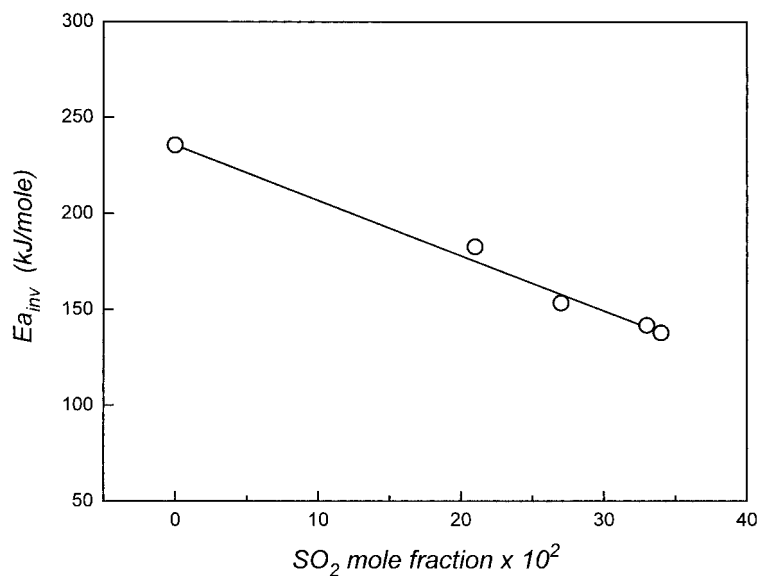


Figure 6 Relationship between invariant activation energy and molecular SO₂ content in poly(styrene sulfone).

thermal stability decreases as the SO₂ content of poly(styrene sulfone) increases, because of the heat instability of the C—S bond. The relation equation, $Ea_{inv} = 237.0 - 290.5X_{SO_2}$, where X_{SO_2} is mole fraction of SO₂, was given for describing the effect of sulfur dioxide on the thermal stability of poly(styrene sulfone).

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REFERENCES

- Matsuda, M.; Iino, M.; Hirayama, T.; Miyashita, T. *Macromolecules* 1972, 5, 240.
- Cais, R. E.; O'Donnell, J. H. *J. Macromol Sci Chem* 1982, A17 (9), 1407.
- Bowden, M. J.; O'Donnell, J. H. *Development in Polymer Degradation-6*; Applied Science Publisher: Barking, U.K., 1985; pp 21-61.
- Yang, M. H. *Polym Degrad Stab* 2000, 68, 451.
- Yang, M. H. *Polym Degrad Stab*, to appear.
- Lin, Y. L.; Yang, M. H.; Wang, J. H. *Polym Test* 1996, 15 (6), 525.
- Nien, K. E.; Yang, M. H.; Chu, T. J. *J Polym Eng* 1997, 17 (1), 23.
- Yang, M. H. *Polym Test* 2000, 19 (1), 85.
- Yang, M. H. *Polym Test* 1998, 17 (3), 191.
- Yang, M. H. *Polym Test* 2000, 19 (1), 105.
- Yang, M. H.; Lin, Y. C.; Chu, T. *J Polym Plast Tech Eng* 1997, 36 (3), 473.
- Nishizaki, H.; Yosida, K.; Wang, J. H. *J Appl Polym Sci* 1982, 25, 2869.
- Marcilla, A.; Beltran, M. *Polym Degrad Stab* 1995, 48, 219.
- Levchick, S. V.; Levchick, G. F.; Lesnickovick, A. J. *Thermochim Acta* 1985, 77, 157.
- Gillham, J. K. *J Appl Polym Sci* 1977, 21, 1159.
- Lin, M. C. M.S. thesis, Cheng Kung University, Tainan, Taiwan, R.O.C., 1983.
- Lee, R. J.; Yang, M. H.; Wang, J. H. *Polym Test* 1999, 18 (8), 601.
- Rose, N.; Bras, M. L.; Bourbigot, S.; Delobel, R. *Polym Degrad Stab* 1994, 45, 387.
- Coats, A. W.; Redfern, J. P. *Nature* 1964, 201, 68.
- Nikoalev, A. V.; Logvinenko, V. A.; Gorbarchev, V. M. *J Thermal Anal* 1974, 6, 473.
- Yang, M. H.; Ou Yang, A. B.; Wang, J. H. *Polym Degrad Stab* 2001, 73 (1), 333.
- Bourbigot, S.; Delobel, R.; Bras, M. L.; Normand, D. *J Chim Phys* 1993, 90, 1909.