

Thermal Behavior of PES/PEES Copolymers with Different Sequence Distribution: Comparative Study of the Kinetics of Degradation

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ABSTRACT: The degradation of three aromatic thermoplastics copolymers of polyethersulfone (PES) and polyetherethersulfone (PEES) with the same composition but different sequence distribution was performed in a thermogravimetric analyzer in both nitrogen and air environments, in isothermal and dynamic heating conditions. The obtained results suggest that the degradations started by random chain scission under all the experimental conditions. Under N₂ flow, branching and crosslinking were superimposed on the initial process, whereas complete oxidative degradation occurred in air. The apparent activa-

tion energies associated with the first degradation stage were evaluated and correlated with the sequence linkages present in the copolymer chains. The obtained values indicated that the chemical reactions occurring under nitrogen were different from those in air. In addition, a comparison of activation energies of PES/PEES copolymers with different sequence distribution was also reported. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 833–838, 2009

Key words: PES/PEES copolymers; sequence distribution; activation energies

INTRODUCTION

Polyethersulfone (PES) and its copolymers are one of the most widely used and versatile thermoplastic engineering plastics. PES-type polymers are suitable for the production of separation membrane,^{1–3} aircraft door frame, automobile parts, electrical and electronic parts, medical equipment, structural adhesive, and composite matrix.⁴ Copolymers of PES and polyetherethersulfone (PEES) units made either as blocks or as random materials show some improved properties.⁵ Because these materials encounter elevated temperatures at almost every step in the manufacturing, compounding, and processing stages, as well as in service and during repair, thermal stability is also requested. From this point of view, it is important to determine the kinetics of their thermal decomposition and to throw some light on their degradation mechanism. Their thermal degradation of the poly(aryl ether sulfone)s has been studied numerous times in the past by traditional thermogravimetry (TG) at a constant heating rate.^{6–11} However, there are no studies on the thermal degradation and kinetics of the PES copolymers

with the same composition but different sequence distribution in air and nitrogen by TG. In this work, we report our study on the thermal and oxidative degradations of PES/PEES random copolymer (R50), alternative copolymer (A50), and block copolymer (B50), in which three copolymers are proved with the same composition but different sequence distribution. We determined by TG and differential thermogravimetry (DTG) measurements the apparent activation energy values of the degradation for several experimental conditions with the aim to correlate them with the sequence distribution of molecular chain.

EXPERIMENTAL

Materials

PES/PEES copolymers with the same composition but different sequence distribution were synthesized, according to the procedure previously reported,¹² and used in the form of powder. Copolymers were dried under vacuum at room temperature and kept in a desiccator under vacuum until use. Pertinent information on the preparation and properties of the three copolymer samples is given in Table I.

TG and DTG measurements

Thermal degradations were performed in a Mettler TA 3000 thermogravimetric analyzer coupled with a

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TABLE I
Some Properties of Copolymer R50, B50, and A50

Copolymer	Inherent Viscosity (dL g ⁻¹)	T _g (°C)	Randomness ^a	[HQ/DHDPS] ^a
R50	0.45	215.3	1.06	47.1/52.9
B50	0.41	216.1	0.22	51.4/48.6
A50	0.39	215.8	0	50.0/50.0

^a Values were measured by ¹³C NMR in Ref. 12.

Mettler TC 10A processor. The temperature calibration of the thermobalance was made according to the procedure indicated in the users' manual, based on the change of the magnetic properties of three metal samples (alumel, nickel, and trafoperm) at their curie points. For calibration, we used the curie points of 142.5°C, 357.0°C, and 749.0°C for the three metals, respectively, as suggested by the supplier. The temperature calibration was repeated every month.

Degradation experiments were conducted in both isothermal and dynamic heating conditions, using 4–8-mg samples held in alumina crucibles under a pure nitrogen flow (20 mL/min) or in a static air atmosphere. The weight loss of sample as a function of time or of temperature was measured. The degradations in dynamic conditions were made by heating samples from 35 to 850°C at the chosen heating rates. For the experiments in isothermal conditions, samples were quickly heated (40°C/min) from 35°C up to the selected temperature and then maintained at this temperature for 90 min. The weight of samples at the start of isothermal heating was considered the initial one. The difference between this weight and that measured at 35°C was <2% in every case.

RESULTS AND DISCUSSION

Degradation under nitrogen flow

Dynamic experiments in inert atmosphere were first carried out at the various selected scanning rates. In these experimental conditions, polymer degraded with the formation of a residue stable up to 850°C. The TG curves of copolymer A50 are reported in Figure 1 as an example. The corresponding DTG curves (see Fig. 2) showed a first degradation stage at low temperature, immediately followed by another irregular and smaller second stage at higher temperature. To determine the apparent activation energy (E_a) associated with the first degradation stage, we used the Kissinger equation¹³:

$$\ln(\Phi/T_m^2) = \ln(nRAW_m^{n-1}/E_a) - E_a/RT_m \quad (1)$$

where Φ is the heating rate, T_m is the temperature at the maximum rate of weight loss, n is the apparent reaction order, R is the universal gas constant, A is the preexponential factor, and W_m is the weight of the sample at the maximum rate of weight loss. Thus, the E_a value could be determined through the

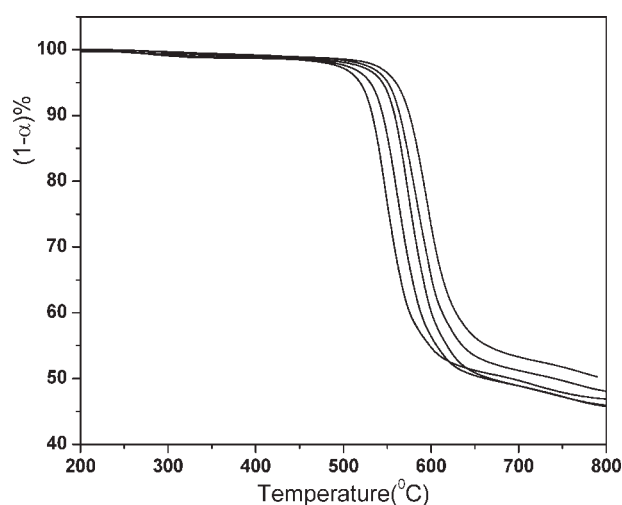


Figure 1 TG curves of copolymer A50 at the heating rates of 2, 3, 5, 10, and 20°C/min under N₂ flow (from left to right).

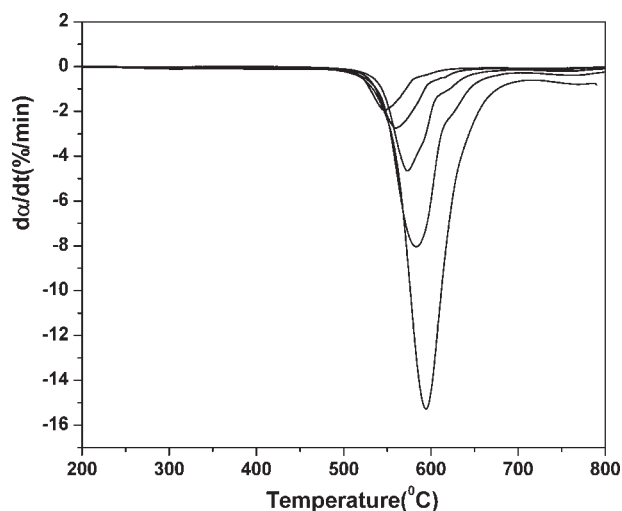


Figure 2 DTG curves of copolymer A50 under N₂ flow at the heating rates of 2, 3, 5, 10, and 20°C/min (from top to bottom).

TABLE II
Temperature at Maximum Rate of Weight Loss (T_m) for
the First Degradation Stage of Copolymers Under N_2
Flow at Various Heating Rates

Φ ($^{\circ}\text{C min}^{-1}$)	R50 T_m (K)	A50 T_m (K)	B50 T_m (K)
2	792.1	822.2	823.5
3	832.3	834.7	825.9
5	854.7	845.9	845.9
10	872.3	856.1	854.7
20	897.6	867.5	859.8

linear dependence of $\ln(\Phi/T_m^2)$ on $1/T_m$ at various heating rates. In Table II, the T_m values of the first degradation stage of the various copolymers (which were the temperatures of the DTG peaks) at the used scanning rates are listed. The results of the measurements performed at $\Phi < 1^{\circ}\text{C/min}$ are not reported because under these conditions it was not possible to identify reliable T_m values. The data of Table II were thus used to evaluate the apparent activation energy associated with the first degradation stage for three copolymers. A single straight line was obtained in all cases (Fig. 3). The corresponding E_a values are reported in Table III. No ki-

netic parameter associated with the second stage of degradation was evaluated owing to the irregular shape of the corresponding DTG curves. In fact, in this case, it was not possible to determine the T_m values.

The isothermal degradations were carried out at five selected temperature. The isothermal degradations proceeded in two stages. In the first one, a high degradation rate was found in every case. By contrast, the trend observed for the second one was dependent on the isothermal temperature. When the temperature was not considerably high, the second degradation stage proceeded at an approximately constant low rate with the formation of a quite stable residue. For the sake of consistency and to compare the calculated kinetic parameters, I used the same set of temperatures for the degradation of three copolymer samples.

To show the behavior of copolymers R50, A50, and B50 in the investigated temperature range, the isothermal degradation curves of copolymer A50 are reported as an example in Figure 4 in which the percentage of undegraded copolymer, $(1 - \alpha)\%$, is plotted as a function of time, where $\alpha = (W_0 - W)/W_0$, and W_0 and W were the weights of the copolymer at

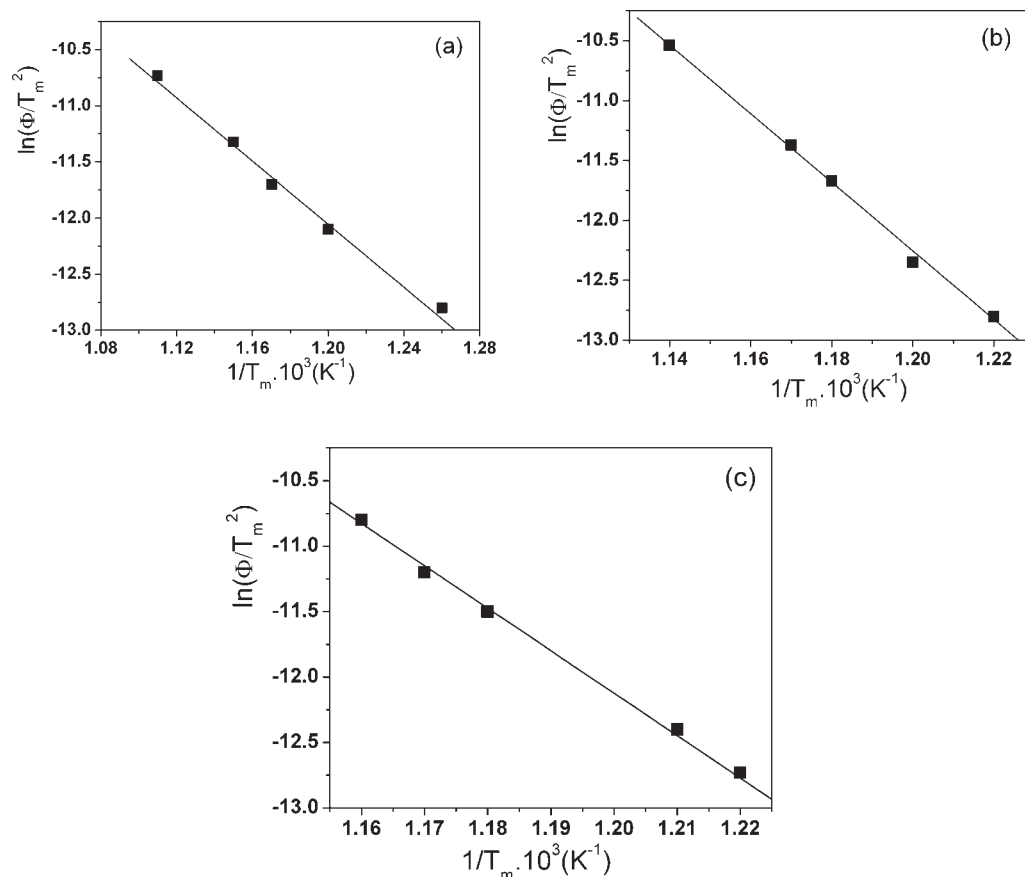


Figure 3 Kissinger plots of copolymers R50 (a), A50 (b), and B50 (c) for the first degradation stage under N_2 flow.

TABLE III
Apparent Activation Energies by Kissinger Equation for the First Degradation Stage Under Nitrogen and Static Air Atmosphere

Copolymer	Under N ₂ Flow, <i>E_a</i> (kJ/mol)	Under Air Flow, <i>E_a</i> (kJ/mol)
R50	178	112
A50	276	194
B50	231	169

the starting point and during the isothermal heating. We used the MacCallum method extensively reported by Hill et al.¹⁴ to determine kinetic parameters from the isothermal experiments. This method is based on the following linear equation:

$$\ln t = \ln[F(1 - \alpha)] - \ln A + E_a/R/T \quad (2)$$

where *t* is the time used to reach a fixed degree of degradation α , and $F(1 - \alpha)$ is a function of the degree of degradation. Thus, the apparent activation energy, E_a could be obtained from the slope of the linear relationship. The E_a values were determined for degrees of degradation $\alpha = 10\%$, 12.5% , 15% , 17.5% , and 20% . Single linear relationships $\ln t = F(1/T)$ at the various selected degrees of degradation were obtained for three copolymers. The corresponding regression coefficients and the evaluated apparent activation energies are reported in Table IV.

Degradations in static air atmosphere

The degradation were then carried out in an oxidative environment. The measurements under dynamic heating conditions, performed at the same heating rates as those under N₂ flow, showed difference among three copolymers. The DTG curves showed in all cases of two degradation peaks. The DTG curves of copolymer A50 are reported as an example in Figure 5. The shape of the DTG curves suggests that the T_m

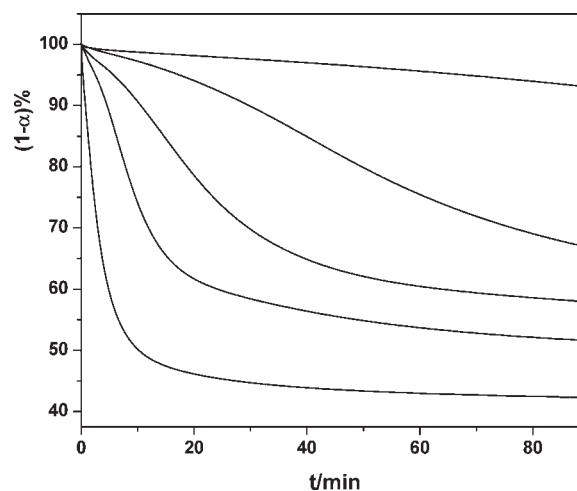


Figure 4 Isothermal degradation curves of copolymer A50 under N₂ flow at 500, 530, 550, 570, and 590°C (from top to bottom).

values for the first degradation stage were associated with the process at lower temperature. These values, which are listed in Table V, were used to evaluate the apparent activation energies for the first degradation stage by the Kissinger equation. Single straight lines were obtained for copolymer R50, A50, and B50. It was not possible to determine kinetic parameters associated with the process at higher temperature.

Three copolymers were then degraded isothermally in static air atmosphere, using the same temperature conditions as under N₂ flow. Under these experimental degradation conditions, qualitative difference was found among three copolymers. Two consecutive unresolvable degradation steps, with total weight loss, were observed in all cases. The isothermal oxidative degradation curves of copolymer A50 are reported as an example in Figure 6. The MacCallum equation was used to determine the apparent activation energies for $5\% < D < 20\%$. The calculated regression coefficients and E_a values are reported in Table VI.

TABLE IV
Regression Coefficients and Apparent Activation Energies by MacCallum Equation for the Isothermal Degradations of the Various Copolymers under N₂ Flow at Several Degrees of Conversion

α %	R50		A50		B50	
	<i>a</i>	<i>E_a</i> (kJ/mol)	<i>a</i>	<i>E_a</i> (kJ/mol)	<i>a</i>	<i>E_a</i> (kJ/mol)
5	–	–	–39.6	284	–30.2	210
7.5	–	–	–46.8	336	–30.8	219
10	–29.6	199	–46.3	334	–29.7	215
12.5	–28.1	188	–43.1	330	–32.2	233
15	–29.2	196	–44.9	332	–30.1	220
17.5	–29.0	191	–45.1	337	–31.3	229
20	–29.4	192	–43.9	340	–29.9	222

$$a = \ln [F(1 - \alpha)].$$

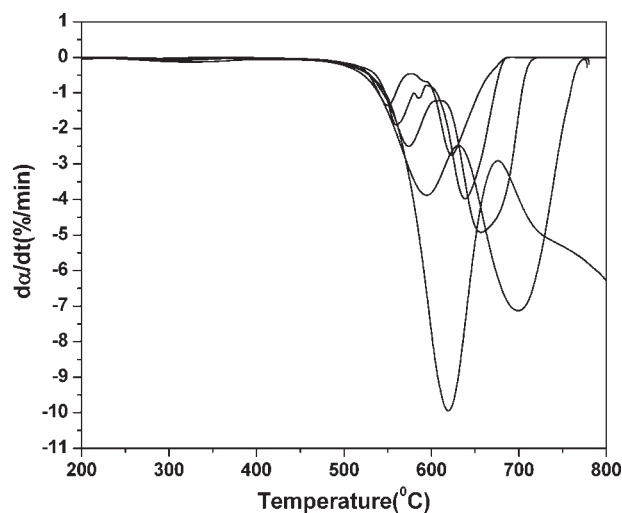


Figure 5 DTG curves of copolymer A50 at the heating rates of 2, 3, 5, 10, and 20 °C/min under air flow (from left to right).

The experiments under N₂ flow showed two degradation stages for three PES/PEES copolymers investigated under both the experimental heating conditions. The DTG curves for the degradations in the scanning mode showed two incompletely resolved DTG peaks, thus meaning the occurrence of partially superimposed processes. We attributed the degradation to random chain scission (first stage) to which branching and crosslinking become superimposed at higher temperature (second DTG peak). This was supported by the large weight loss associated with the first sharp DTG peak, whereas only a small weight loss was associated with the irregular broad second one, with the formation of stable residue. At very low heating rate, only one irregular broad DTG peak was obtained, with 100% weight loss, thus suggesting that under these conditions the chain scission rate exceeded branching and crosslinking rates. These results are in agreement with some literature data, in which the occurrence of the processes of random chain scission, branching, and crosslinking has been observed^{15,16} during the thermal degradation of polymers.

The E_a values associated with the first degradation stage were very different from each other. They

TABLE V
Temperature at Maximum Rate of Weight Loss (T_m) for the First Degradation Stage of Copolymers under Air Flow at Various Heating Rates

Φ (°C min ⁻¹)	R50 T_m (K)	A50 T_m (K)	B50 T_m (K)
2	837.1	823.5	820.8
3	852.3	833.4	822.2
5	862.4	847.2	838.4
10	877.3	867.5	848.6
20	885.1	892.5	858.7

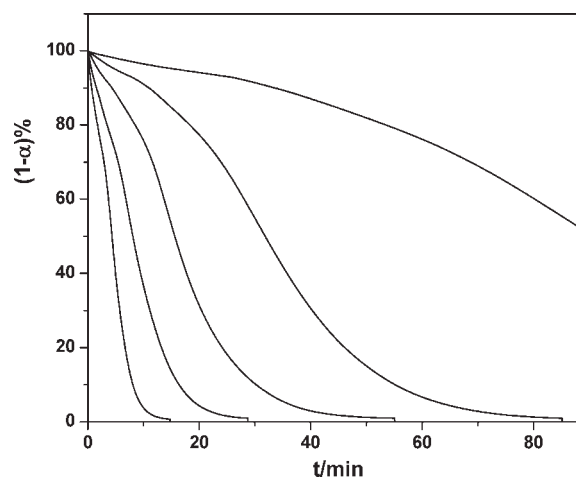


Figure 6 Isothermal degradation curves of copolymer A50 under air flow at 500, 530, 550, 570, and 590 °C (from top to bottom).

decreased according to the order: A50 > B50 > R50. Because the composition of three copolymers is the same, the difference found in the activation energies must be due to the different sequence distribution of molecular chains. The apparent activation energies associated with the first stage of isothermal degradation (5% < α < 20%) essentially kept stable with the increasing degree of conversion. To compare these results with those obtained by dynamic heating, the average apparent activation energies (E_a) were calculated (Table VII). The found values were in good agreement with those of the first degradation stage under dynamic heating conditions, and the same trend was observed, thus meaning the occurrence of the same process for both conditions.

The dynamic experiments in air atmosphere showed that the copolymers degraded in two not well-resolvable steps. The observed E_a values of the degradation stage in lower temperature for copolymer R50, A50, and B50 were considerably smaller than the corresponding ones under N₂ flow. This seems to indicate a different degradation mechanism with a lower activation energy, in agreement with the initial decomposition temperatures; those in air were very much lower than those in nitrogen. Also, because complete weight loss was observed, we think that, in the second degradation stage, the product formed in the first stage undergoes oxidative degradation.

All the observations converge to indicate that a random chain scission is the initial degradation process for three copolymers in both environments studied, followed by branching and crosslinking under nitrogen flow and a progressive oxidative chain degradation in air atmosphere. The different calculated activation energies mean that the initial chain scissions in the two investigated environments are due to different chemical reactions. Another

TABLE VI
Regression Coefficients and Apparent Activation Energies by MacCallum Equation
for the Isothermal Degradations of the Various Copolymers under Air Flow at
Several Degrees of Conversion

α (%)	R50		A50		B50	
	a	E_a (kJ/mol)	a	E_a (kJ/mol)	A	E_a (kJ/mol)
5	–	–	–30.9	217	–	–
7.5	–	–	–30.1	215	–	–
10	–	–	–32.4	221	–25.8	183
12.5	–	–	–31.5	219	–24.9	174
15	–23.3	163	–32.9	224	–24.0	170
17.5	–22.4	158	–27.8	209	–23.7	169
20	–21.6	154	–26.9	204	–23.2	166

$$a = \ln [F(1 - \alpha)].$$

mean that the bond energies of the C–S and C–C bonds in PES copolymers are 272 and 251 kJ/mol, respectively, which are close to the E_v values in nitrogen. Thus, it can be concluded that the first-step thermal degradation of PES copolymers in an inert atmosphere seems to be mainly controlled by the abstraction of sulfur dioxide and methane. The much lower E_v values in air must result from an additional thermal-oxidative decomposition besides thermal decomposition, including branching, and crosslinking. The study of kinetics of degradation of different sequence distribution with the same compositions PES/PEES copolymers showed that alternative copolymer had the higher apparent activation energies than other two kinds of copolymers, because alternative copolymer A50 had a more normalized chain than random and block copolymers.¹⁷ The difference of average thermodegradation apparent activation energies appears to be in different sequence distribution, but the more distinct reason how sequence distribution influences the degradation kinetic has not been drawn at present. The reasonable explanation was that the molecular weight distribution should be narrow for copolymer A50 than copolymers R50 and B50. So, copolymer A50 with narrow molecular weight distribution should be more difficult to decompose. Accordingly, alternative copolymer A50 had the higher apparent activation energies than copolymer R50 and B50.

Although the evaluate method of E_a values of three kinds of copolymers exists uncertainty, the ultima orderliness had not been affected by recheck-

ing the analysis using the Freeman and Carroll method.¹⁸ So, we think that there is a significant relationship between the thermal decomposition characteristics and the sequence distribution of PES copolymers molecular chains.

CONCLUSIONS

These results indicate that the alternative copolymer (A50) is not only stable, but also its thermal oxidative degradation is slower than that for random copolymer (R50) and block copolymer (B50). The experimental evidence suggests that, in both static air and nitrogen flow, the thermal degradation occurs through two stages for three kinds of PES/PEES copolymers.

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TABLE VII
Average Apparent Activation Energies of the Isothermal
Degradations of the Various Copolymers Calculated by
the Values of Tables IV and VI

Copolymer	E_v (N ₂ , kJ/mol)	E_v (air, kJ/mol)
R50	193	158
A50	327	215
B50	221	172