Kinetic study of the thermal degradation of some poly(arylenether)s containing naphthalene units

L. Abate[a,*], S. Calanna[b], G. Di Pasquale[b], A. Pollicino[b]

[a]*Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy*
[b]*Istituto Chimico, Facoltà di Ingegneria, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy*

Abstract

The degradations of five aromatic thermoplastics, containing carbonyl, ether and sulfone linkages and in whose repeating units the $-ArCONaphCOAr-$ moiety (where $Ar = 1,4$ substituted phenylene; $Naph = 2,6$ substituted naphthalene) was present, were performed under N_2 flow in dynamic heating conditions. The obtained results suggested that degradations occurred through random chain scission followed by branching and crosslinking, which partially superimposed with the initial process. The Kissinger method was used to determine the apparent activation energy (E_a) associated with the first degradation stage, and double linear relationships, attributable to slow diffusion of degradation products in the melt, were found in some cases. A thermal stability classification among the studied polymers was made on the basis of the obtained E_a values. This classification was compared with those previously obtained for two analogous groups of thermoplastics and some correlations between thermal stability and polymer chain structure were drawn. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(arylenether)ketones; Poly(arylenether)sulfones; Thermal analysis

1. Introduction

In the last few decades the demand of the aerospace industries has provided the driving force for the development of new high performance materials with low densities to be used in structural applications. Composites with polymer matrix are one class of materials useful in this field, and extensive research has been devoted to the synthesis of organic polymers for use in high temperature applications. The main goal of the research in this area is the preparation of polymers possessing good thermal and oxidative stability, toughness, stiffness and retention of physical properties at high temperature. Most materials of this type are based on aromatic rings incorporated into the main chain. For such polymer systems a balance must be achieved between thermal stability and processability. Thermoplastic polymers, and polyetherketones and polyethersulfones in particular, potentially offer the favourable properties that make them very suitable for such applications [1–5]. One of the most important advantages offered by the thermoplastics over new toughened thermosets in composites' applications is the potential of lower cost manufacturing. Since these polymers must be processed at high temperature, often in excess of 300°C, they are sensitive to degradation and modification

during process. Thermal analysis methods have proved useful not only in defining suitable processing conditions for these polymers as well as useful service guidelines for their application, but also in drawing information on thermal properties–polymer chain structure relationships.

Since thermal stability is connected to both the initial temperature and the rate of degradation of polymers, the determination of kinetic parameters associated with the degradation processes is an interesting topic of research.

Our group is interested in the research of new aromatic thermoplastic polyethers containing carbonyl and sulfone linkages [6,7]. We have in progress a comparative kinetic study on the degradation of this class of polymers [8–10], with the aim to find, if possible, useful correlations between the physico-chemical properties and the structure of polymers, which could be used in designing new polymers having high thermal stability. In particular, we reported in two recent papers the results concerning two different groups of polymers selected according to the following standard: that the repeating unit of the polymers of each group was formed by a same moiety linked to different structures ($-O-$, $-OArO-$, $-OArArO-$, $-OArSO_2ArO-$ and $-OAr(CH_3)O-$). The moiety present in the first group of polymers was the aromatic triketone $-ArCOArCOArCOAr-$ moiety [9], while that present in the second group of polymers was the heterocyclic $-ArCOQCOAr-$ moiety
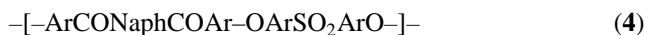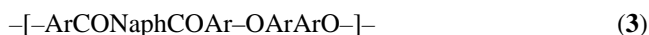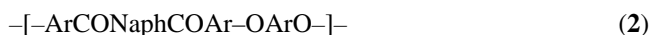
* Corresponding author.

Table 1
Inherent viscosities (η_{inh}), glass transition temperatures (T_g) and melting temperatures (ϑ_{fus}) of polymers **1–5**

Polymer	η_{inh} (dl g^{-1})	T_g (°C)	ϑ_{fus} (°C)
1	0.27	158	346
2	0.32	150	325
3	0.88	195	–
4	0.45	205	–
5	0.52	190	–

[10] (Ar = 1,4-substituted phenylene; Q = 3,7-substituted quinoline).

On continuing our studies in this field, we report here the kinetic study of the thermal degradation of a third group of polymers, selected according to the previously reported standard, in whose repeating units the five over reported structures are linked to the same –ArCONaphCOAr– moiety (Ar = 1,4-substituted phenylene; Naph = 2,6-substituted naphthalene). The examined polymers were the following:

$$–[–ArCONaphCOAr–O–]– \tag{1}$$

$$–[–ArCONaphCOAr–OArO–]– \tag{2}$$

$$–[–ArCONaphCOAr–OArArO–]– \tag{3}$$

$$–[–ArCONaphCOAr–OArSO_2ArO–]– \tag{4}$$

$$–[–ArCONaphCOAr–OAr(CH_3)O–]– \tag{5}$$

The apparent activation energies (E_a) associated with degradation processes were evaluated by thermogravimetry (TG) and differential thermogravimetry (DTG) measurements. Both the glass transition (T_g) and melting (ϑ_{fus}) temperatures were also determined by differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

Polymers were prepared following the procedures described elsewhere [6,7] and were used in the form of powder. Samples were dried under vacuum at room temperature and kept in a dessicator under vacuum until use.

2.2. DSC measurements

The glass transition (T_g) and melting (ϑ_{fus}) temperatures were determined by a Mettler mod.20 differential scanning calorimeter coupled with a Mettler TC 10A processor. Both heat flow and temperature calibrations were performed following the procedures suggested by the supplier and reported in the operating instructions of equipment [11].

Samples of about 5–6 mg held in sealed aluminium crucibles and the heating rate of 20°C min^{-1} under a dynamic nitrogen flow (5 l h^{-1}) were used for the measurements.

2.3. Viscosity measurements

Solutions of polymers in sulphuric acid at the concentration of 0.5 g dl^{-1} were used to determine inherent viscosities ($\eta_{inh} = \ln\eta_r/C$). Measurements were performed by an Ostwald viscometer thermostatted at 25°C.

2.4. TG and DTG measurements

Thermal degradations were performed in a Mettler TA 3000 thermogravimetric analyser coupled with a Mettler TC 10A processor. The temperature calibration of thermobalance was made according to the procedure suggested by Mettler and reported in the users manual of equipment [11]. This procedure is based on the change of the magnetic properties of three metal samples (Isatherm, Nickel and Trafoperm) at their Curie points (142.5, 357.0 and 749.0°C, respectively). The temperature calibration was repeated every month.

Degradations were performed in the scanning mode, from 35 up to 950°C, under nitrogen flow (20 ml min^{-1}), at various heating rates (Φ = 1, 2.5, 5, 10, 15, 20, and 25°C min^{-1}). Samples of 4–6 mg, held in alumina open crucibles, were used and their weights were measured as a

Table 2
Weight loss (w.l.) (%) of polymers **1–5** at the various used heating rates

Φ (°C min^{-1})	**1** w.l. %	**2** w.l.%	**3** w.l.%	**4** w.l.%	**5** w.l.%
1	100.0 (683°C)[a]	100.0 (719°C)[a]	46.02	100.0 (789°C)[a]	100.0 (752°C)[a]
2.5	83.07	100.0 (933°C)[a]	41.70	83.29	84.37
5	69.86	78.07	43.12	71.97	62.73
10	58.23	57.91	37.08	56.86	49.01
15	48.14	59.26	34.67	55.15	45.79
20	44.45	52.13	39.50	50.05	42.04
25	39.42	49.00	37.64	47.51	44.94

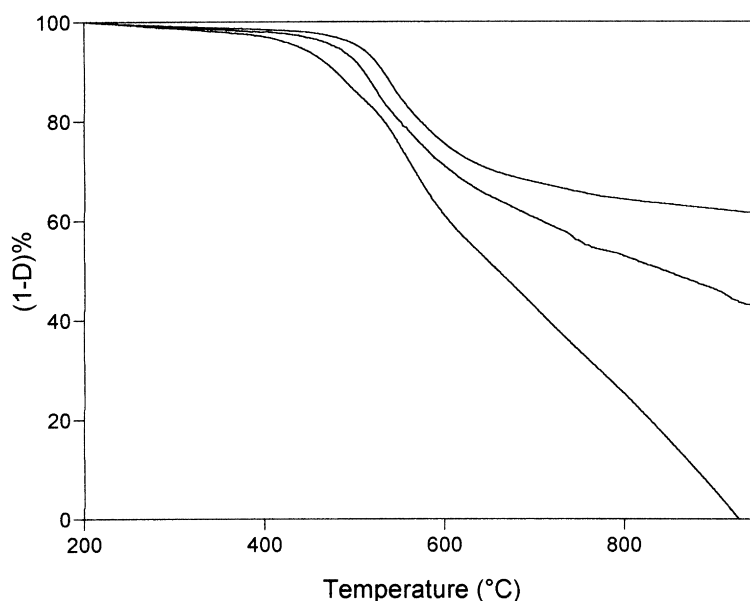[a] Temperature at which 100% weight loss was observed.

Fig. 1. TG curves of the polymer **1** at the heating rates of 2.5, 10 and 25°C min^{-1} (from left to right).

function of temperature and stored in the list of data of the appropriate built-in program of the processor. The TG and DTG curves were immediately printed at the end of each experiment and the weights of the sample at various temperatures were then transferred to a PC. These data were later used to plot the percentage of undegraded polymer $(1 - D)\%$ as a function of temperature, where $D = (W_0 - W)/W_0$, and W_0 and W the weights of the polymer at the starting point and during scanning.

3. Results and discussion

The inherent viscosities of studied polymers were preliminarily determined and the obtained values are listed in Table 1. Both the glass transition and melting temperatures could be determined only for polymers **1** and **2** (Table 1), while for other investigated polymers it was not possible to detect any melting temperature because of their amorphous structure.

The TG curves of degradations showed that all investigated polymers degraded with the formation of residues stable up to 950°C. The percentage of decomposed polymer increased with decreasing heating rate, and the 100% weight loss was observed at $\Phi = 1$°C min^{-1}, apart from polymer **3** (Table 2).

The DTG curves indicated that degradations proceeded through several partially superimposed processes, as supported by the complex shape of the curves. Nevertheless, for polymers **1**, **2** and **4**, the sharp shape of the curves at higher scanning rates suggested that, at these heating rates, various degradation processes were about simultaneous.

For polymer **3** no large difference among the DTG curves at low and high heating rates was evidenced, thus suggesting

that degradation stages were not simultaneous even at high scanning rates.

Also polymer **5** exhibited a behaviour similar to that of polymers **1**, **2** and **4**, but the first DTG peak occurred at lower temperature than other investigated polymers.

The TG and DTG curves of polymer **1** at $\Phi = 2.5$, 10 and 25°C min^{-1} are reported as an example in Figs. 1 and 2, respectively.

The obtained results suggested that polymers **1**, **2** and **4** degraded by an initial random chain scission followed by branching and crosslinking. Nevertheless, the quite sharp DTG peak observed at high heating rates indicated that, in these conditions, the two processes are about simultaneous and that branching and crosslinking rates are comparable with the scission rate, as also supported by the high amount of residue found. By contrast, at low heating rate the scission process was quicker than branching and crosslinking processes and the complete or about complete degradation of polymers was observed. This behaviour was in agreement with some literature reports on polymers having structure similar to that of the polymers here studied [12–15].

Polymer **3** is also degraded by an initial random chain

Table 3
Temperatures at maximum rate of weight loss (T_m/K) for the first degradation stage of polymers **1–5** at the various heating rates used (Φ)

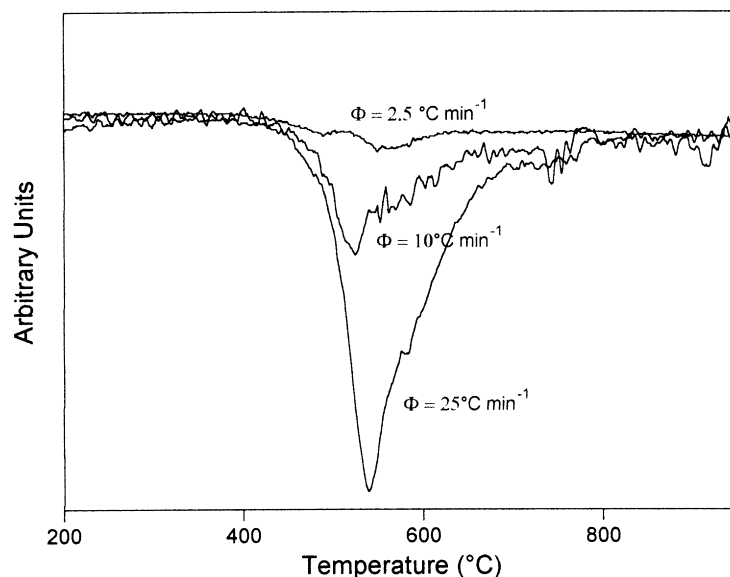| Φ (°C min^{-1})	**1** T_m	**2** T_m	**3** T_m	**4** T_m	**5** T_m
1	736.5	793.2	788.7	770.1	689.3
2.5	760.1	817.3	798.1	788.1	712.1
5	778.0	835.8	805.6	804.1	722.5
10	797.1	850.1	812.1	816.1	738.1
15	803.1	856.0	813.1	826.6	746.6
20	808.1	864.6	817.1	831.6	754.1
25	812.0	868.1	820.1	836.9	759.4

Fig. 2. DTG curves of the polymer **1** at the heating rate of 2.5, 10 and 25°C min^{-1}.

scission followed by branching and crosslinking, but in this case the rate of the first stage was comparable with that of the following stage at all the used scanning rates, in agreement with the high amount of residue obtained at all used heating conditions.

The behaviour of polymer **5** suggested that the cleavage of the bond at methyl group was involved in the initial random chain scission process.

The apparent activation energies (E_a) associated with the first degradation stage of our polymers were determined by the Kissinger equation [16].

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

in which Φ is the heating rate, T_m the temperature at the maximum rate of weight loss, n the apparent reaction order, R the universal gas constant, A the pre-exponential factor and W_m the weight of the sample at the maximum rate of weight loss. Thus, the E_a values were obtained by the slope of the linear relationships between $\ln(\Phi/T_m^2)$ and $1/T_m$. We

used the temperatures of the DTG peaks as T_m values. We could single out reliable T_m values only for the first DTG peak.

The apparent activation energy values associated with the first degradation stage of our polymers were then evaluated by the Kissinger equation, using the data of Table 3. Single linear relationships were obtained only for polymers **4** and **5**, while double linear regressions were found for polymers **1**–**3**. The regression coefficients and the apparent activation energies are listed in Table 4, and in Fig. 3 the corresponding straight lines are plotted.

The occurrence of double Kissinger linear relationships as found for polymers **1**–**3** has been reported in literature [13,17,18] and observed by us in our preceding studies in this field [8–10]. This behaviour has been attributed to kinetically slow diffusion processes. Since O_2 was not present in our experimental conditions, it can only be due to the slow diffusion of the degradation products in the melt, so that, at higher heating rates, the kinetics of process was under diffusion control, in

Table 4
Regression coefficients and apparent activation energies by the Kissinger equation

Polymer	Φ (°C min^{-1})	a[a]	$b \times 10^{-3}$[b] (K)	r[c]	E_a (kJ mol^{-1})
1	1–10	14.9 ($\pm$0.6)	20.7 ($\pm$0.4)	0.9996	172 ($\pm$4)
	10–25	38.3 ($\pm$1.6)	39.4 ($\pm$1.3)	0.9989	327 ($\pm$11)
2	1–5	15.8 ($\pm$0.5)	23.1 ($\pm$0.4)	0.9998	192 ($\pm$3)
	5–25	29.7 ($\pm$1.8)	34.7 ($\pm$1.5)	0.9970	289 ($\pm$13)
3	1–5	60.3 ($\pm$1.2)	58.1 ($\pm$0.9)	0.9999	483 ($\pm$8)
	5–25	88 ($\pm$5)	80 ($\pm$4)	0.9966	665 ($\pm$32)
4	1–25	25.1 ($\pm$0.6)	29.6 ($\pm$0.5)	0.9992	246 ($\pm$4)
5	1–25	20.0 ($\pm$0.3)	22.8 ($\pm$0.2)	0.9997	189 ($\pm$1.9)

[a] $a = \ln(nRA(W_m^{n-1})/E_a)$.
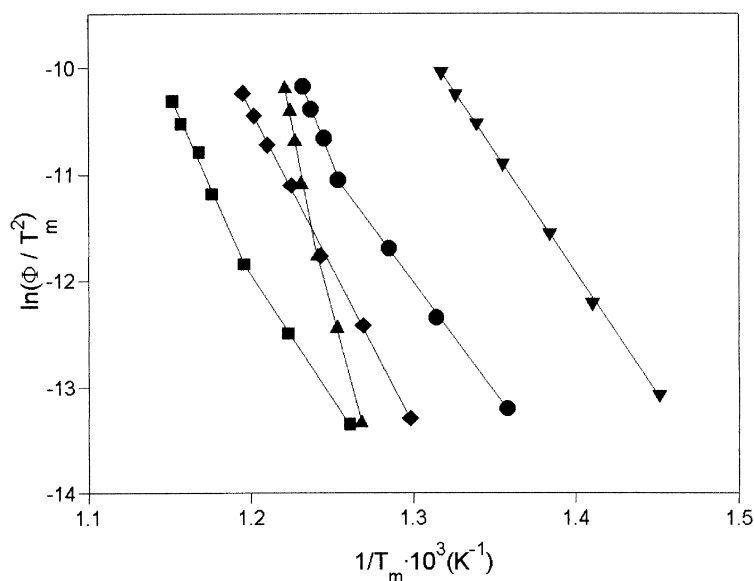[b] $b = E_a/R$.
[c] Product moment correlation coefficient.

Fig. 3. Kissinger plots for the first degradation stage of the polymers: **1** (●), **2** (■), **3** (▲), **4** (◆) and **5** (▼).

agreement with the corresponding high E_a values. As a consequence, we considered true E_a values as those obtained at lower scanning rates.

Some comparisons are possible with the results previously obtained by us for the two analogously selected groups of thermoplastic polymers containing the triketone and the quinoline moieties, respectively [9,10].

From some points of view the polymers studied here behave similarly to those containing the quinoline moiety in their repeating units [10]. In particular:

1. the apparent activation energies associated with the first degradation stage were quite different with each other, thus suggesting that different linkages are involved in the initial degradation process of various polymers;
2. the E_a values of polymers **1** and **5** were practically the same than those of the corresponding ones containing quinoline in their chain. It could indicate that analogous initial chain scissions occur. In particular, the breakage of the methyl group bond seems to be involved in the initial degradation processes of methylated polymers, as supported by the lower T_m values of the first DTG peak;
3. the apparent activation energy obtained for polymer **3**, which was largely higher than those of other investigated polymers analogously to the corresponding one of Ref. [10], could be correlated with the presence of diphenyl group in the repeating unit. By contrast, the E_a value found for polymer **4** was the same as those obtained for both the corresponding polymers of Refs. [9,10]. This finding could indicate that the cleavage of SO_2 group is the controlling process of the kinetics of the first degradation stage for the polymers containing the SO_2 group; and
4. finally, the apparent activation energies associated with the first degradation stage decreased according to this

order: **3 > 4 > 2 > 1**. This classification, in which polymer **5** was not included because its E_a value is mainly attributable to the cleavage of methyl group, is practically the same as that found for the quinoline polymers. By contrast, the trend found for the polymers containing the triketone moiety was very different because appreciable differences were not found among the various polymers. This result could be indicative of the lower thermal stability of the triketone moiety that starts to degrade before the other groups present in the polymer chain, thus suppressing the differences in the E_a values.

The comprehensive results until now obtained seem to indicate that it is possible to draw forecasts about the kinetic parameters of degradation of a polymer on the basis of its structure, but only by comparison with polymers having similar structure.

Acknowledgements

References

[1] Critchley JP, Knight GJ, Wright WW. Heat-resistant polymers, New York: Plenum Press, 1983.
[2] Johnson RN, Farnham AG, Clendinning RA, Hale WF, Merriam CN. J Polym Sci A-1 1967;5:2375.
[3] Hale WF, Farnham AG, Johnson RN, Clendinning RA. J Polym Sci A-1 1967;5:2399.
[4] Gabler R, Studinka J. Chimia 1974;28:567.
[5] Staniland PA, Wilde CJ, Bottino FA, Di Pasquale G, Pollicino A, Recca A. Polymer 1992;33:1976.
[6] Bottino FA, Di Pasquale G, Pollicino A. Eur Polym J 1995;31(1):35.

[7] Bottino FA, Di Pasquale G, Leonardi N, Pollicino A. J Polym Sci (A) 1995;33:843.

[8] Abate L, Calanna S, Pollicino A, Recca A. Polym Eng Sci 1996;36(13):1782.

[9] Abate L, Calanna S, Pollicino A, Recca A. Macromol Chem Phys 1997;198:1437.

[10] Abate L, Bottino FA, Calanna S, Pollicino A. Polymer 1999;40:2719.

[11] Users Manual TA 3000 System. Mettler Instr., AG, Greifensee, 1984.

[12] Hay JN, Kemmish DJ. Polymer 1987;28:2047.

[13] Day M, Cooney JD, Wiles DM. J Appl Polym Sci 1989;38:323.

[14] Kuroda S, Terauki K, Nogami K, Mita I. Eur Polym J 1989;25:1.

[15] Day M, Sally D, Wiles DM. J Appl Polym Sci 1990;40:1615.

[16] Kissinger HE. Anal Chem 1957;29:1702.

[17] Hirata T, Kashiwagi T, Brown JE. Macromolecules 1985;18:1410.

[18] Hill DJT, Dong L, O'Donnell JH, George G, Pomery P. Polym Degrad Stab 1993;40:143.