Polymer 40 (1999) 2719–2726

polymer

Kinetic study of the thermal and oxidative degradations of poly(arylenether)s containing quinoline units

L. Abate[a,]*, F.A. Bottino[b], S. Calanna[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*

Received 1 June 1998; revised 29 June 1998; accepted 29 June 1998

Abstract

The degradations of five aromatic thermoplastics, in whose repeating units various structures are linked to the same -ArCOQCOAr- moiety (where Ar = 1,4-substituted phenylene and Q = 3,7-substituted quinoline), were performed in dynamic heating conditions in the temperature range 35–950°C, under nitrogen flow and in static air atmosphere. Experiments under nitrogen suggested that degradations started by random chain scissions, to which branching and crosslinking superimposed at higher temperature, with the formation of residues stable up to 950°C; those in oxidative environment indicated that degradations were due to several processes which were simultaneous at low heating rate and that oxidative stages were involved, as supported by the complete weight loss before the overall temperature scanning. The apparent activation energy values associated with the first degradation stage were obtained by the Kissinger method. Results in inert atmosphere suggested that different linkages were involved in the initial chain scission processes of various polymers and that the comprehensive degradation mechanisms were different from those in air. Anomalous double Kissinger straight lines were found for one of the polymers investigated. The results were discussed and compared with those previously obtained for a similar group of aromatic polymers. © 1999 Published by Elsevier Science Ltd. All rights reserved.

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

1. Introduction

Although composites with thermosetting matrices, such as epoxy or phenolic resins, are widely used in the aerospace industry, their brittle nature to impact-initiated failure (due to the highly crosslinked network) and the high production costs of composites based on them, limits their use and drives the industries to examination of thermoplastics. The environmental properties of the available thermoplastics with the desired end-use temperature are limited and researchers have been looking for new advanced thermoplastics. High thermally stable polymers are requested for this purpose because they can be subjected to high temperatures not only in the manufacturing, compounding and processing stage, but also in service or during repair [1–5]. 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 sulphone linkages [6–7]. Recently we started a comparative kinetic study on the degradation of this class of polymers [8–9]. In the last published work we studied four polymers having in the repeating unit the same -ArCOArCOArCOAr- triketone moiety (where Ar = 1,4-substituted phenylene) linked to four different structures (-O-, -OArO-, -OArArO- and -OAr-SO_2ArO-). We determined the apparent activation energies associated with the first degradation stage and we made a stability classification among the various structures [9].

On continuing our studies in this field, in this paper we report a kinetic study on the degradation of another group of thermoplastic polymers, selected according to the identical previously used standard. Moreover, in the repeating units of these polymers the same -ArCOQCOAr- moiety (Ar = 1,4-substituted phenylene, Q = 3,7-substituted quinoline) is linked to the four structures investigated in the previous work [9]. The polymers examined were the following:

1. [-ArCOQCOAr-O-]
2. [-ArCOQCOAr-OArO-]

---

* Corresponding author. Fax: +39-095-7372450; E-mail: labate@ic.ing.unict.it

PII: S0032-3861(98)00518-7

Table 1
Inherent viscosity at 25°C (η_{inh}), glass transition temperature (T_g) and melting temperature (θ_{fus}) of polymers **1**–**5**

Polymer	η_{inh}/dlg^{-1}	T_g/°C	θ_{fus}/°C
1	0.37	182	290, 320
2	0.24	160	295
3	0.25	168	310
4	0.77	220	—
5	0.85	200	280

3. [-ArCOQCOAr-OArArO-]
4. [-ArCOQCOAr-OArSO$_2$ArO-]
5. [-ArCOQCOAr-OAr(CH$_3$)O-]

In polymer **5** the same repeating unit as in polymer **2** is present, apart from a methyl group linked to the phenylene group.

We determined the glass transition (T_g) and melting (ϑ_{fus}) temperatures and the apparent activation energies (E_a) associated with the first degradation stage of the polymers investigated. The comprehensive aim of this work as well as the other ones in the same field is 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.

T_g and ϑ_{fus} values were measured by differential scanning calorimetry (DSC), while thermogravimetry (TG) and differential thermogravimetry (DTG) measurements were used to determine the degradation E_a values.

2. Experimental

2.1. Materials

Polymers were synthesized according to the procedures elsewhere described [6–7] and were used in the form of powder. Samples were dried under vacuum at r.t. and kept in a dessicator under vacuum until use.

2.2. DSC measurements

T_g and ϑ_{fus} values were measured by a Mettler Mod.20 differential scanning calorimeter, coupled with a Mettler TC10A processor. Both heat flow and temperature calibrations were made according to the operating instructions [10], by using the two calibration programs of the TC10A processor.

Table 2
Weight loss (w.l.) (%) of polymers **1**–**5**, under N$_2$ flow, in the temperature range 35–950°C

Φ/°C min^{-1}	1 w.l. %	2 w.l. %	3 w.l. %	4 w.l. %	5 w.l. %
2.5	79.43	85.37	83.84	84.55	81.33
5	59.00	58.11	51.40	59.97	61.72
10	42.44	45.34	42.44	50.93	46.62
15	39.51	48.01	37.86	48.09	41.57
20	39.59	45.50	34.82	45.06	40.71
25	37.82	39.24	37.08	43.41	37.63

Table 3
Temperatures (ϑ) where polymers **1**–**5** reached 100% weight loss in static air atmosphere

Φ/°C min^{-1}	1 ϑ/°C	2 ϑ/°C	3 ϑ/°C	4 ϑ/°C	5 ϑ/°C
1	504.0	504.1	516.4	600.3	483.5
2.5	550.5	553.4	545.3	604.5	516.5
5	592.2	600.1	571.9	653.1	561.3
10	650.4	644.8	621.2	710.5	604.7
15	680.3	655.3	660.1	696.4	655.4
20	731.9	711.9	745.2	764.3	683.6
25	782.2	764.3	769.5	783.7	760.1

Samples of approx. 5–6 mg held in sealed aluminium crucibles, dynamic nitrogen atmosphere (5 l h^{-1}) and the heating rate of 20°C min^{-1} were used in determining both the glass transition and melting temperatures.

2.3. Viscosity measurements

An Ostwald viscometer thermostatted at 25°C was used to determine the inherent viscosities ($\eta_{inh} = \ln\eta_r/C$). Solutions of polymers (0.5 g dl^{-1}) in sulfuric acid were used for measurements.

2.4. TG and DTG measurements

Thermal degradations were performed in a Mettler thermogravimetric analyzer coupled with the same TC 10A processor used for calorimetric measurements. The procedure suggested by the supplier [10] was followed for the temperature calibration of equipment. This method 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.

The degradations were performed in the scanning mode, under a pure N$_2$ flow (20 ml min^{-1}) and in a static air atmosphere. Runs were carried out from 35°C up to 950°C at the various selected heating rates. Samples of 4–6 mg, held in alumina open crucibles were used and their weights were measured as a function of temperature and stored in the list of data of the appropriate built-in program of the TC 10A processor. At the end of each experiment the TG and DTG curves were immediately printed. The weights of sample at the various temperatures were then transferred to a PC and were later used to obtain the degradation curves as plotted here.

3. Results

Inherent viscosities and both the glass transition and melting temperatures of studied polymers were preliminarily determined. The values obtained are reported in Table 1.

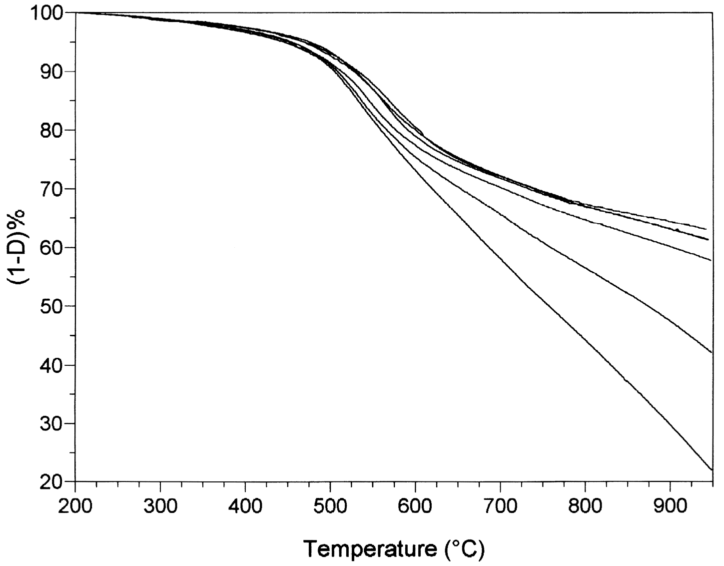

Fig. 1. TG curves under N_2 flow of polymer **1** at the heating rates of 2.5, 5, 10, 15, 20 and 25°C min^{-1} (from left to right).

Polymers were then degraded in both environments described in the Experimental, at heating rates of 2.5, 5, 10, 15, 20 and 25°C min^{-1}. The comprehensive weight losses found in the experiments in inert atmosphere over the complete scanned temperature range are reported in Table 2. Since all polymers completely degraded in oxidative atmosphere, we report in Table 3 the temperatures at which 100% degradation was observed.

3.1. Degradations under N_2 flow

The TG curves from experiments in nitrogen atmosphere showed that, at all heating rates used, our polymers degraded with the formation of a residue stable up to 950°C (Table 2). The DTG curves exhibited an initial broad and irregular decomposition stage at lower temperatures, immediately followed by a continuous and progressive degradation process up to 950°C. The TG curves of polymer **1** at all scanning rates are reported in Fig. 1, in which the percentage of undegraded polymer $(1 - D)\%$ is plotted as a function of temperature, where $D = (W_0 - W)/W_0$, and W_0 and W are the weights of polymer at the starting point and during scanning. In Fig. 2 the DTG curve at $\Phi = 10$°C min^{-1} of polymer **1** is reported as an example. The temperatures of the DTG peak associated with the first degradation stage of various polymers at the different heating rates are reported in Table 4; for all polymers the weight loss corresponding to the first DTG peak was roughly not dependent on the heating rate, and was the greater part of the comprehensive weight loss at higher scanning rates, as supported by the weight loss data of Table 5. Polymer **5**, whose behaviour was qualitatively

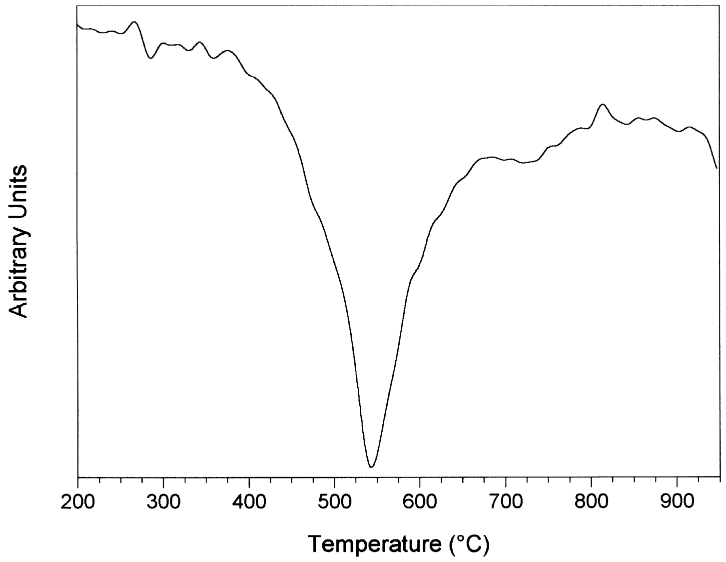

Fig. 2. DTG curve under N_2 flow of polymer **1** at the heating rate of 10°C min^{-1}.

Table 4
Temperatures at maximum rate of weight loss (T_m) for the first degradation stage of polymers **1**–**5** under N_2 flow at various heating rates (Φ)

Φ/°C min^{-1}	**1**T_m/K	**2**T_m/K	**3**T_m/K	**4**T_m/K	**5**T_m/K
2.5	799.0	778.8	n.e.	763.4	639.1
5	807.2	793.2	815.2	775.2	704.1
10	815.9	807.7	828.7	789.2	720.2
15	829.2	817.2	836.2	797.2	729.7
20	837.2	825.2	839.9	804.2	737.1
25	845.1	829.0	846.9	811.9	740.2

n.e., not evaluable.

similar to that of the other polymers, showed lower DTG peak temperatures with lower associated weight losses.

The Kissinger method [11] was selected among the various methods reported in literature [11–14] to determine kinetic parameters by TG and DTG experiments in the scanning mode. The equation obtained by Kissinger is:

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

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 pre-exponential factor, W_m is the weight of the sample at the maximum rate of weight loss and E_a is the apparent activation energy. According to this equation, the E_a values associated with the degradation process can be determined through the linear dependence of $\ln(\Phi/T_m^2)$ on $1/T_m$ at various heating rates. Reliable T_m values (which are the temperatures of the DTG peaks at various used scanning rates) could be determined only for the first degradation stage (Table 4). The least squares treatment of these data according to the Kissinger equation gave single linear regressions for polymers **2**, **3**, **4** and **5**, while a double linear regression was found for polymer **1**. The obtained Kissinger equation coefficients and E_a values are reported in Table 6 and the corresponding straight lines are plotted in Fig. 3.

Since it was not possible to single out reliable T_m values for the degradation processes at higher temperatures, no corresponding kinetic parameter could be determined.

Table 5
Weight loss % of polymers **1**–**5** measured under N_2 flow at the temperature of the first DTG peak at various heating rates (Φ)

	Φ/°C min^{-1}					
Polymer	2.5 w.l. %	5 w.l. %	10 w.l. %	15 w.l. %	20 w.l. %	25 w.l. %
1	15.43	16.00	16.34	17.49	16.90	17.67
2	13.09	16.74	16.04	18.64	19.83	17.03
3	—	14.80	15.49	14.92	12.35	16.42
4	17.41	15.31	14.78	14.15	14.04	15.49
5	7.34	9.26	9.03	8.97	9.36	9.07

3.2. Degradations in static air atmosphere

Degradation experiments performed in an oxidative environment did not show large differences in the thermal behaviour among polymers **1**, **2**, **3** and **5**. At low heating rates a single DTG peak was observed, which at higher scanning rates irregularly broadened and, in some cases, gave origin to a second irregular unresolvable DTG peak. This feature indicated the occurrence of several processes which were simultaneous only at low scanning rates. In all cases samples completely degraded before the overall temperature scanning. The TG and DTG curves of polymer **1** at the heating rates of 2.5, 10 and 20°C min^{-1} are reported as an example in Fig. 4 and Fig. 5.

Polymer **4** showed also at low heating rates two unresolved DTG peaks. The first one increased on increasing the heating rate and that at higher temperature split in two DTG peaks. The TG and DTG curves of polymer **4** at the heating rates of 2.5, 10 and 20°C min^{-1} are reported in Fig. 6 and Fig. 7, respectively.

The apparent activation energies associated with the process at lower temperature were evaluated by the Kissinger method. The T_m values (from DTG peaks) and scanning rates are listed in Table 7.

A double linear regression was also found for polymer **1** in an oxidative environment, while single linear regressions were observed for the other investigated polymers. The linear regression coefficients and E_a values are reported in

Table 6
Regression coefficients and apparent activation energies by the Kissinger equation for the degradations under N_2 flow

Polymer	Φ/°C min^{-1}	a^a	$b \times 10^{-3}$/K^b	r^c	E_a/kJ mol^{-1}
1	2.5–10	54.8 (± 1.6)	53.7 (± 1.3)	0.9997	447 (± 3)
	10–25	13.2 (± 1.6)	19.8 (± 0.5)	0.9994	165 (± 4)
2	2.5–25	23.1 (± 0.5)	27.6 (± 0.4)	0.9995	230 (± 3)
3	5–25	30.1 (± 1.5)	34.2 (± 1.3)	0.9979	284 (± 10)
4	2.5–25	24.7 (± 1.3)	28.3 (± 1.0)	0.9973	235 (± 9)
5	2.5–25	20.0 (± 1.3)	22.2 (± 0.9)	0.9965	185 (± 8)

[a] $a = \ln\left(nRA\frac{W_m^{n-1}}{E_a}\right)$

[b] $b = \frac{E_a}{R}$.

[c] Product moment correlation coefficient.

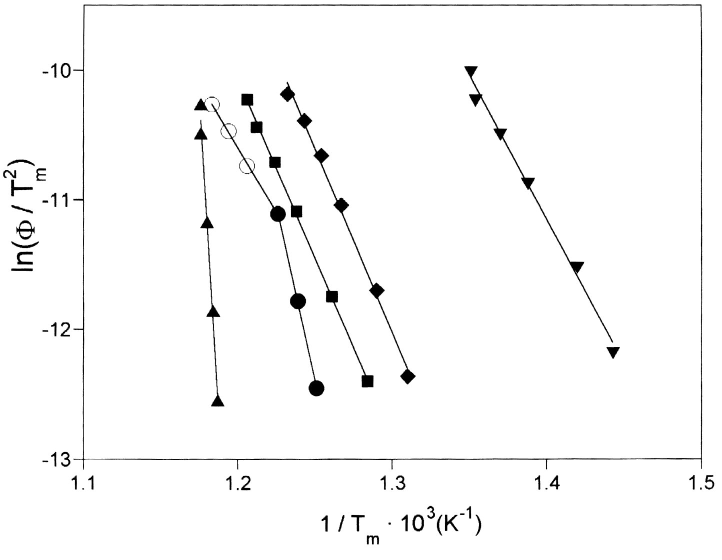

Fig. 3. Kissinger plots for the first degradation stage under N_2 flow of polymers **1** (● for $\Phi = 2.5$, 5 and 10°C min^{-1}; and ○ for $\Phi = 15$, 20 and 25°C min^{-1}), **2** (■), **3** (▲) **4** (◆) and **5** (▼).

Table 8 and the corresponding straight lines are plotted in Fig. 8.

4. Discussion

The unresolved DTG peaks observed in the experiments under N_2 flow indicated that our polymers degraded through two stages in an inert environment. We attributed the stage at lower temperature to random chain scission, which was not a single process, as shown by the broad and irregular DTG peak profiles. The behaviour of polymer **5** suggested that the cleavage of the methyl group was involved in its initial degradation process. The degradation stage at higher temperature could be ascribed to branching and crosslinking processes which superimposed on the initial ones, as supported by the formation of residue stable up to 950°C. The weight loss data reported in Table 2 indicated that at lower heating rates the chain scission rate was higher than branching and crosslinking rates. These results are in agreement with literature reports [15–18] on the thermal degradation of polymers (PEK, PEEK, PES) having structures similar to those of the polymers here studied and with our recently published findings on an analogous group of polymers [9].

The apparent activation energy associated with the first degradation stage decreased in this order: $\mathbf{3} > \mathbf{4} \cong \mathbf{2} > \mathbf{1}$. For polymer **1** the E_a value found for the higher scanning rates was taken into account (see Table 6). The E_a value of polymer **5** was not considered because it is mainly attributable to the cleavage of methyl group involved in the initial

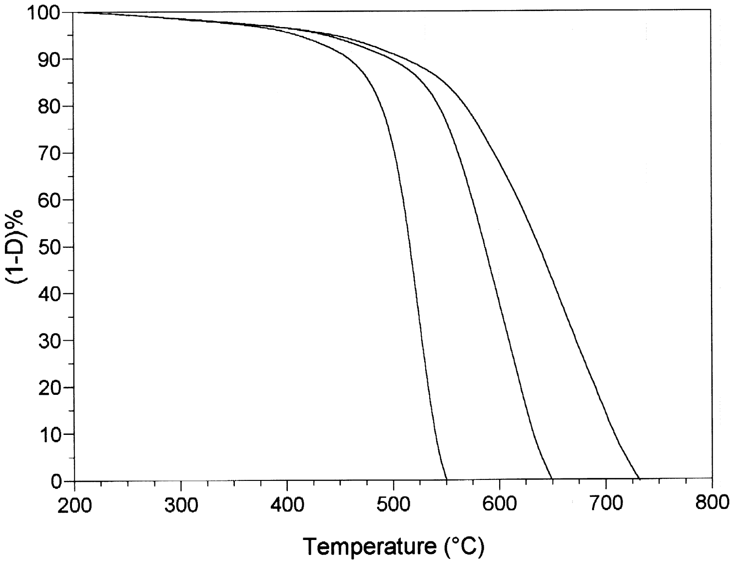

Fig. 4. TG curves in static air atmosphere of polymer **1** at heating rates of 2.5, 10, and 20°C min^{-1} (from left to right).

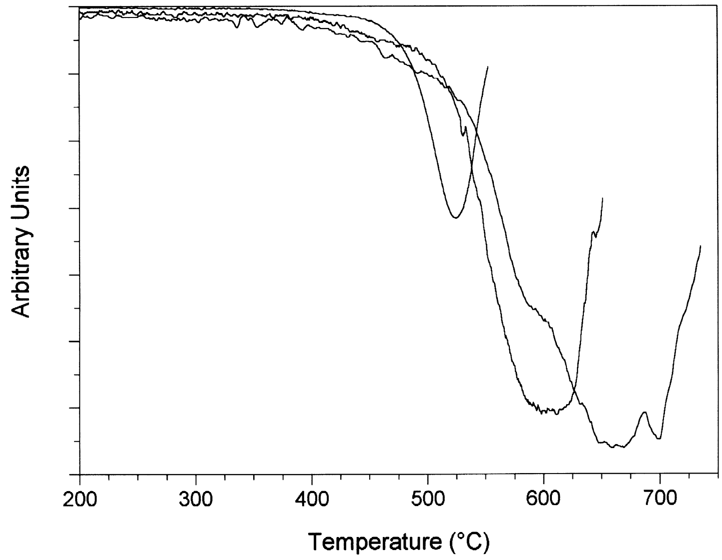

Fig. 5. DTG curves in static air atmosphere of polymer **1** at the heating rates of 2.5, 10, and 20°C min^{-1} (from left to right).

degradation process, as supported by the results shown in Table 4 and Table 5.

The experiments in an oxidative atmosphere indicated that the degradations were due to several processes, which were simultaneous at low heating rates only for polymers **1**, **2**, **3** and **5,** while partially superimposed for polymer **4**. The apparent activation energies associated with the first degradation stage in an air atmosphere decreased in this order: **4** > **3** > **2** > **1**. Also in this case we did not consider polymer **5** and attributed to polymer **1** the E_a value drawn from the experiments at higher heating rates.

Some observations can be made on these results:

1. the E_a values associated with the first degradation stage under nitrogen showed significant differences among the polymers, thus indicating that different linkages were involved in their initial chain scission processes. This behaviour was different from that shown by the previously investigated group of polymers [9], for which very similar E_a values associated with the first degradation stage were found;
2. the E_a values of polymers **2** and **4** under N_2 flow were very similar to those found for the corresponding ones having the triketone moiety [9], thus meaning comparable thermal stability, at least from the kinetic point of view; by contrast, polymer **3** showed a higher E_a value, thus suggesting the occurrence of a kinetically more difficult initial degradation process;
3. the weight loss data of Table 4 and Table 5 indicated that, in inert atmosphere, the chain scission rate exceeded the branching and crosslinking rates only at a low heating rate. This behaviour was similar to that found for the previously studied group of polymers [9];

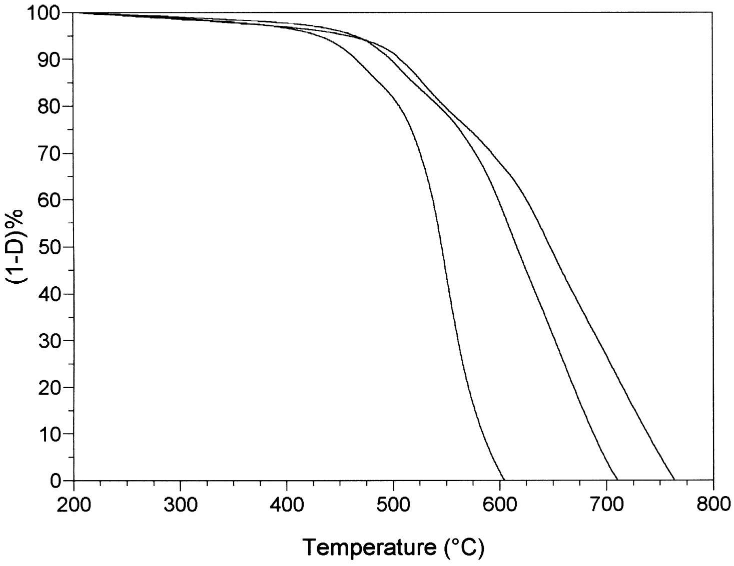

Fig. 6. TG curves in static air atmosphere of polymer **4** at heating rates of 2.5, 10, and 20°C min^{-1} (from left to right).

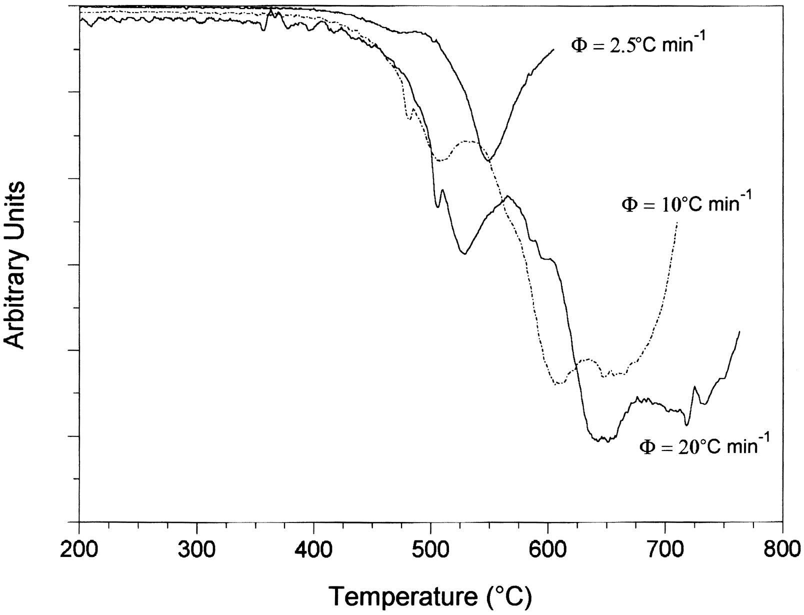

Fig. 7. DTG curves in static air atmosphere of polymer **4** at heating rates of 2.5, 10, and 20°C min^{-1}.

Table 7
Temperatures at maximum rate of weight loss (T_m) for the first degradation stage of polymers **1**–**5** in static air atmosphere at various heating rates (Φ)

Φ/°C min^{-1}	**1** T_m/K	**2** T_m/K	**3** T_m/K	**4** T_m/K	**5** T_m/K
2.5	798.1	788.9	786.3	745.5	777.5
5	865.1	829.9	814.0	761.1	806.4
10	880.6	877.2	842.2	780.6	837.1
15	913.4	905.4	863.2	793.4	860.1
20	937.1	925.9	859.2	802.1	875.1
25	964.4	942.5	866.9	807.5	n.e.

Table 8
Regression coefficients and apparent activation energies by the Kissinger equation for the degradations in static air atmosphere

Polymer	Φ/°C min^{-1}	a[a]	$b \times 10^{-3}$/ K[b]	r[c]	E_a/kJ mol^{-1}
1	2.5–5	2.8 (± 0.3)	12.1 (± 0.3)	0.9997	101 (± 3)
	5–25	− 2.3 (± 0.3)	7.9 (± 0.5)	0.99860	65 (± 1.9)
2	2.5–25	− 0.3 (± 0.2)	9.5 (± 0.3)	0.9995	79 (± 1.2)
3	2.5–15	5.7 (± 0.4)	14.2 (± 0.3)	0.9994	118 (± 3)
4	2.5–25	14.7 (± 0.5)	20.1 (± 0.4)	0.9992	167 (± 3)
5	2.5–20	4.1 (± 0.3)	12.8 (± 0.2)	0.9994	107 (± 2)

[a] $a = \ln\left(nRA\frac{W_m^{n-1}}{E_a}\right)$

[b] $b = \frac{E_a}{R}$.

[c] Product moment correlation coefficient.

4. the observed E_a values in air atmosphere were much lower than the corresponding ones under N_2 flow, thus suggesting a different comprehensive degradation mechanism in which an oxidative stage was involved, as supported by the complete observed weight loss. These values were also considerably lower than the corresponding ones of polymers containing a triketone moiety in the repeating unit. On considering that an oxidative stage is involved in the degradation process, this behaviour could be due to the higher carbon percentage;
5. single Kissinger straight lines were found for polymers **2**, **3**, **4** and **5**, while double linear relationships were obtained for polymer **1** in both inert and oxidative environments. The occurrence of two Kissinger straight lines has been reported in the literature [16,19,20]. We encountered this behaviour in our preceding studies [8,9], but, in this case, the slope of the straight lines at lower scanning rates (and then the corresponding E_a values) was higher than that at higher scanning rates (Figs 3 and 8). In order to explain this behaviour we can only suppose the occurrence at a low heating rate of a different competitive and kinetically more difficult degradation process which superimposes on the initial chain scission process, while it is not possible to attribute it to the slow diffusion of degradation products in the melt.

Acknowledgements

Authors thank the Italian M.U.R.S.T. for financial support.

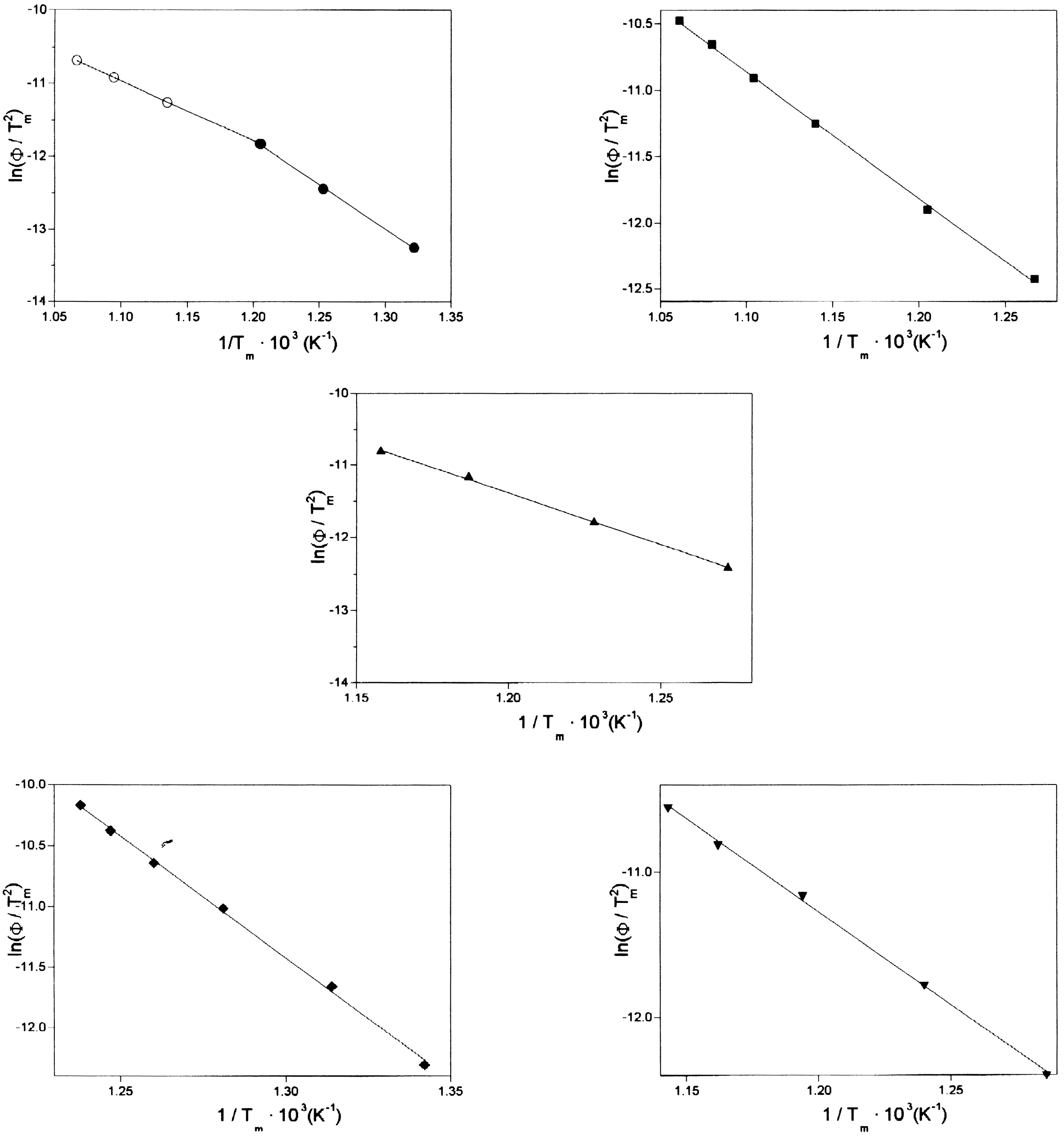

Fig. 8. Kissinger plot for the first degradation stage in static air atmosphere of polymers **1** (● for $\Phi = 2.5$, 5 and 10°C min^{-1}, and ○ for $\Phi = 15$, 20 and 25°C min^{-1}), **2** (■), **3** (▲) **4** (◆) and **5** (▼).

References

[1] Johnson RN, Farnham AG, Clendinning RA, Hale WF, Merriam CN. J Polym Sci A-1 1967;5:2375.

[2] Gabler R, Studinka J. Chimia 1974;28:567.

[3] Cassidy PE. Thermally stable polymers. New York: Marcel Dekker, 1980.

[4] Critchley JP, Knight GJ, Wright WW. Heat-resistant polymers. New York: Plenum Press, 1983.

[5] Staniland PA, Wilde CJ, Bottino FA, Di Pasquale G, Pollicino A, Recca A. Polymer 1976;1992:33.

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

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

[12] Freeman ES, Carroll B. J Phys Chem 1958;62:394.

[13] Doyle CD. J Appl Polym Sci 1961;5:285.

[14] Ozawa T. Bull Chem Soc Jap 1881;1965:38.

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

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

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

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

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

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