

RADOMIR BOŠKOVIĆ  
TOMICA TOŠIĆ  
LYNNE KATSIKAS  
IVANKA G. POPOVIĆ

Faculty of Technology and  
Metallurgy, Belgrade

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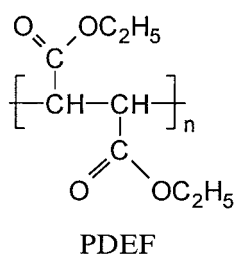
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## THE THERMAL DEGRADATION OF POLY(DIETHYL FUMARATE)

*The kinetics and mechanism of the thermal degradation of poly(diethyl fumarate) (PDEF) were studied by thermogravimetry and analysis of the polymer residue. The characteristic mass loss temperatures were determined, as were the overall thermal degradation activation energies of three PDEF samples of varying molar mass. The dependency of residual polymer molar mass on the degradation time and temperature was established and the kinetic chain lengths of depropagation,  $Z$ , and the number of main-chain scissions per monomer unit,  $s/P_0$ , calculated. A thermal degradation mechanism including de-esterification, random main-chain scission, depolymerization and carbonization is proposed. The thermal degradation of PDEF is compared to the thermolysis of poly(methyl methacrylate) (PMMA) and poly(diethyl itaconate) (PDEI).*

Although thermal degradation studies have been carried out extensively on numerous macromolecular systems, many polymers have yet to be investigated. Polymethacrylates and polyacrylates are examples of commercially relevant polymers that have been studied in detail [1]. The thermal degradation of poly(di-itaconates), versatile engineering materials, has also been studied to a considerable extent [2]. Polymethacrylates and poly(di-itaconates) generally depolymerize when thermally degraded, while only traces of monomer are evolved in the thermolysis of polyacrylates [1]. These examples illustrate the empirical rule that vinylidene type polymers tend to depolymerize, as opposed to vinyl ones that do not or do so only to a minor extent.

The goal of this study was to determine the thermal degradation behaviour of a 1,2-disubstituted vinyl polymer, poly(diethyl fumarate) (PDEF), and compare it to the known thermolysis behaviour of 1,1-disubstituted vinyl, i.e. vinylidene polymers.



Depolymerization, as the major thermolysis reaction in vinylidene polymers is only challenged if there are specific structures in the ester substituents in the monomer unit such as  $\beta$ -hydrogen atoms, halogen atoms or cyclic structures, which can lead to other thermolysis reactions like elimination or side-chain scission. An example of an extreme case is

poly(tert.-butyl methacrylate), which has nine  $\beta$ -hydrogen atoms in the ester substituent of the monomer unit, which quantitatively de-esterifies during thermal degradation [3]. De-esterification becomes a competitive thermolysis pathway when the number of  $\beta$ -hydrogen atoms is greater than two [1].

### EXPERIMENTAL

Diethyl fumarate (DEF) was prepared by the standard esterification of fumaric acid (Aldrich) with ethanol (Zorka). The polymers were synthesised by bulk polymerisation using AIBN as initiator. The polymerisation conditions and average molar masses of the obtained polymers are shown in Table 1.

Non-isothermal thermogravimetric (TG) measurements were performed using a Perkin Elmer TGS-2 instrument at heating rates of 2.5, 10, 20 and 40°/min in the temperature range from room temperature to 600°C in a nitrogen flow (25 cm<sup>3</sup>/min). The overall activation energies of thermal degradation,  $E_a$ , were calculated from the TG data according to the Flynn-Wal method [4].

Sample PDEF-2 was isothermally degraded in the temperature range of 220° to 300°C for up to 30 minutes using a small oven the temperature of which was controlled by a rheostat [5]. The experiments were performed under nitrogen (gas flow rate 46 cm<sup>3</sup>/min). The sample mass was about 80 mg in all cases. The polymer residues were characterised by determining sample mass losses and molar masses by gel permeation chromatography (GPC). A Varian instrument with five columns, a single piston 9010 pump and a RI-4 detector was used for GPC. THF was used as the eluent and narrow molar mass distribution polystyrene samples as calibration standards.

### RESULTS AND DISCUSSION

#### Thermogravimetric analysis

The thermogravimetric (TG) curves of PDEF at different heating rates are shown in Figure 1. It may be

Author address: Prof. dr. Ivanka Popović, Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Yugoslavia, ivanka@elab.tmf.bg.ac.yu

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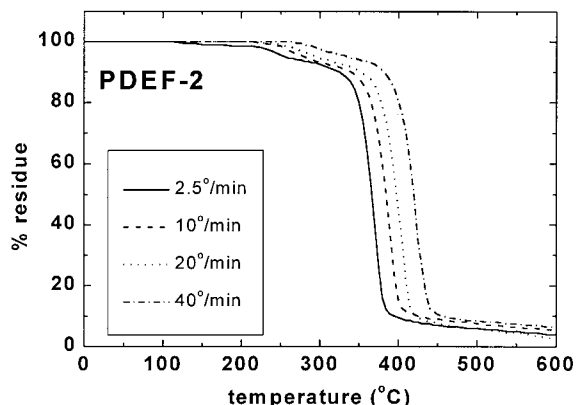


Figure 1. The TG curves of sample PDEF-2 at different heating rates

seen that, after an initial small mass loss of app. 10% occurring over a relatively broad temperature range of over 100°C, extensive mass loss takes place leading to the formation of a carbonaceous residue of about 7% above 400°C. The characteristic mass loss temperatures of three PDEF samples, as well as the amounts of residue at 500°C, are presented in Table 2. It may be seen that there is no relevant effect of molar mass on the shapes of the TG curves in the investigated molar mass range (see Table 1).

Table 1. Polymerization conditions and polymer yields

Sample	Polym. temp. (°C)	[AIBN] (mol%)	Polym. time (h)	Yield (%)	$\bar{M}_n \times 10^{-4}$ (g/mol)	$\bar{M}_w \times 10^{-4}$ (g/mol)
PDEF-1	50	1.0	20.5	4.0	2.09	3.17
PDEF-2	40	0.5	335	25.4	3.86	5.93
PDEF-3	40	0.1	744	22.7	4.56	7.21

Table 2. Temperatures of 10, 15 and 50% mass loss of PDEF and carbon residue at 500°C, heating rate 10°/min

Sample	T <sub>10%</sub> (°C)	T <sub>15%</sub> (°C)	T <sub>50%</sub> (°C)	% residue at 500°C
PDEF-1	355	362	385	7.0
PDEF-2	340	357	385	7.5
PDEF-3	320	355	385	7.0

The differential TG (DTG) curves of PDEF are shown in Figure 2. There is no change in the shape and size of the DTG peaks with increasing heating rate. The values of the DTG maxima are given in Table 2. Comparison of the DTG curves of PDEF and poly(diethyl itaconate) (PDEI), Figure 3, indicates that the major mass loss of PDEF occurs at considerably higher temperatures than in the case of PDEI. However, some volatile evolution is detected in the temperature range in which PDEI degrades. As both polymers have three

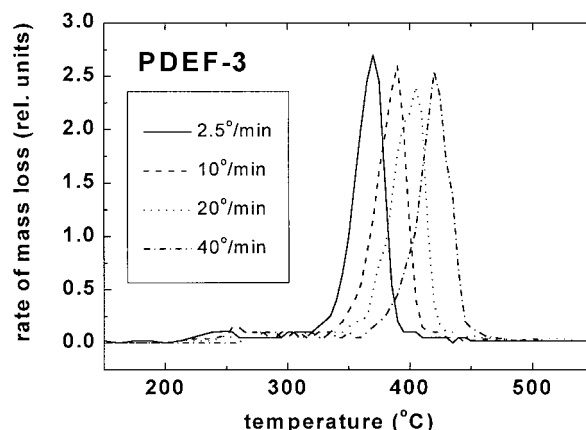


Figure 2. The DTG curves of sample PDEF-3 at different heating rates

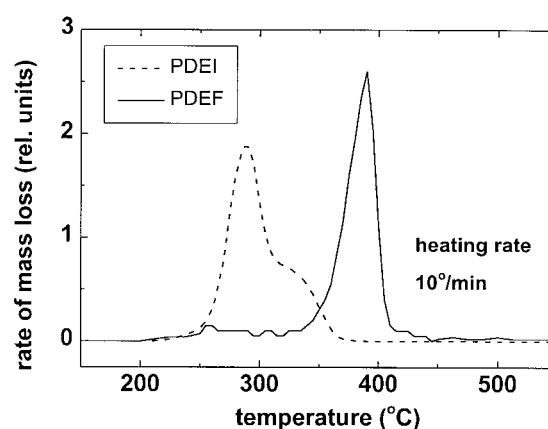


Figure 3. The DTG curves of PDEF and PDEI at a heating rate of 10°/min

β-hydrogen atoms in their respective monomer units, it is possible that some de-esterification occurs during the first stage of PDEF degradation. It has been reported in the literature [6] that ethylene evolution has been detected during the thermal degradation of the monomer DEF at temperatures of 230°C and higher. The major mass loss of PDEF takes place at temperatures that provided sufficient energy for facile scission of C-C or other bonds. The shape of the PDEF DTG curve implies that depolymerization is not or only negligibly initiated by β-scission at unsaturated polymer chain ends.

#### Overall activation energy of thermal degradation

The overall thermal degradation activation energies of the three PDEF samples are presented as a function of mass loss in Figure 4. Their mean values in the range 20 to 80% mass loss are given in Table 3. The obtained values of about 130 kJ/mol compare well to the value for PDEI of  $124 \pm 15$  kJ/mol [7], implying the occurrence of similar phenomena during the thermolysis of both polymers.

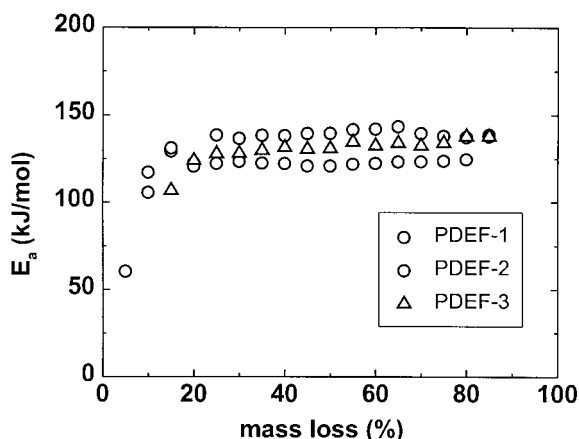


Figure 4. The overall thermal degradation activation energies,  $E_a$ , of PDEF samples as a function of mass loss

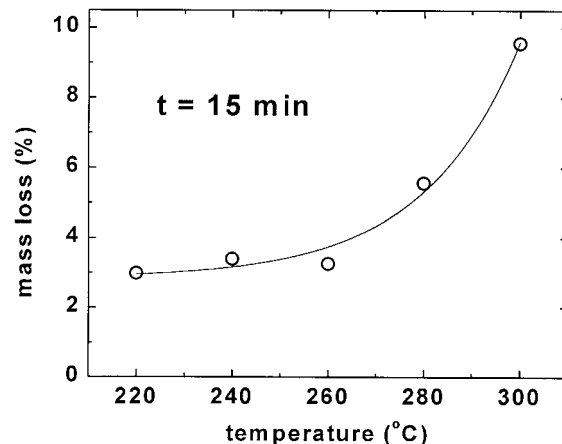


Figure 6. The dependence of the polymer mass loss on degradation temperature at constant degradation time,  $t = 15$  min

**Isothermal thermal degradation studies**

Table 3. Mean thermal degradation activation energies,  $E_a$ , of PDEF samples and temperatures of DTG peak maxima at a heating rate of  $10^\circ/\text{min}$ ,  $T_{DTGmax}$

Sample	$E_a$ (kJ/mol)	$T_{DTGmax}$ (°C)
PDEF-1	$124 \pm 5$	402
PDEF-2	$135 \pm 10$	417
PDEF-3	$130 \pm 7$	415

Sample PDEF-1 was degraded in an inert atmosphere in the temperature range  $220^\circ$  to  $300^\circ\text{C}$  for up to 30 minutes. With increasing mass loss the transparent colourless polymer melts gradually turned yellow and then brown. The dependence of polymer mass loss on degradation time at  $220^\circ$  and  $260^\circ\text{C}$  is presented in Figure 5, while that of mass loss with increasing temperature is depicted in Figure 6.

Slight changes in the molar mass of the polymer are witnessed at  $220^\circ\text{C}$ , corresponding to the gradual small mass loss in the TG curves, Figure 7. A relevant

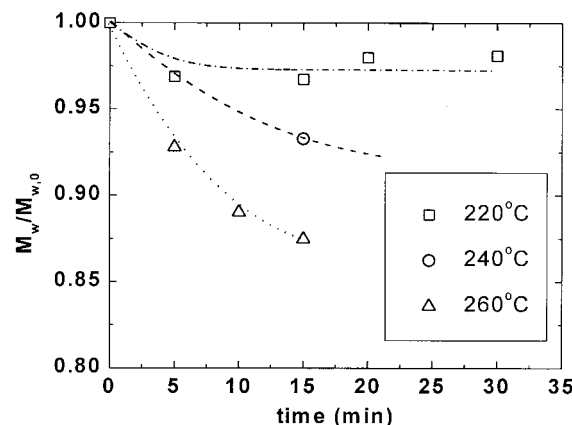


Figure 7. The dependence of the relative molar mass,  $\overline{M}_w/\overline{M}_{w,0}$ , on degradation time at  $220^\circ$  and  $260^\circ\text{C}$

molar mass decrease was registered at  $260^\circ\text{C}$ , Figures 7 and 8.

If it can be assumed that depolymerization does occur during PDEF thermolysis (investigations of the thermolysis volatiles are underway), then the shape of

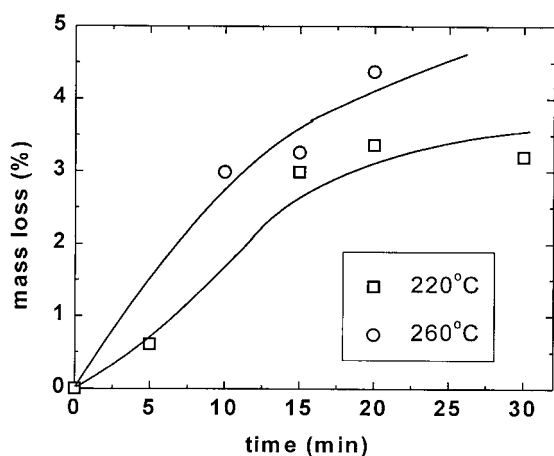


Figure 5. The dependence of the polymer mass loss on degradation time at  $220^\circ$  and  $260^\circ\text{C}$

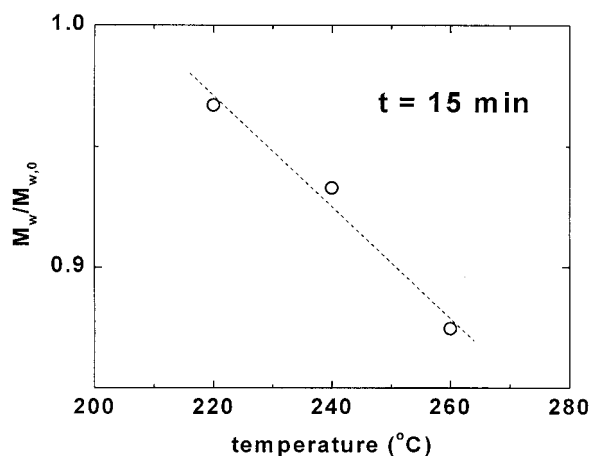


Figure 8. The dependence of the relative molar mass,  $\overline{M}_w/\overline{M}_{w,0}$ , on degradation temperature at constant degradation time,  $t = 15$  min

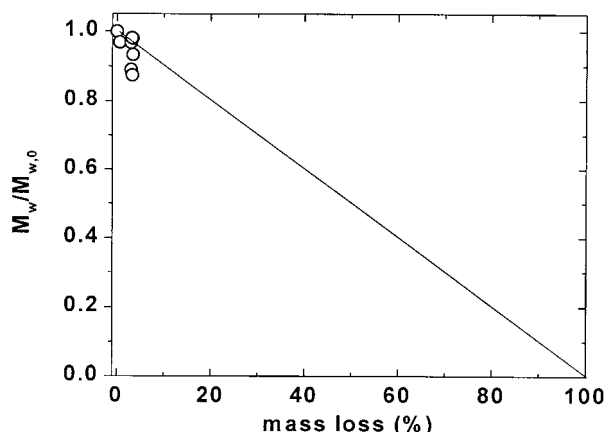


Figure 9. The dependence of the relative molar mass,  $\overline{M}_w/\overline{M}_{w,0}$  on sample mass loss

the dependence of relative molar mass,  $\overline{M}_w/\overline{M}_{w,0}$  on sample mass loss, Figure 9, would imply that the kinetic chain length of depropagation,  $Z$ , is considerably lower than the number-average degree of polymerization of the starting polymer and/or that depolymerization is initiated by random main-chain scission [8].

#### Kinetic chain length of depropagation

The kinetic chain length of depropagation,  $Z$ , may be calculated according to the following equation, assuming that there are no transfer reactions:

$$\frac{W}{W_0} = \frac{P_n^2}{P_0^2} \left( \frac{Z + P_0}{Z + P_n} \right)$$

where  $W/W_0$  is the ratio of the mass of the residue of the starting polymer,  $P_0$  – the initial number-average degree of polymerization and  $P_n$  the number-average degree of polymerization of the residue [9].

The obtained results are presented in Figures 10 and 11. The  $P_0$  of sample PDEF-1 is 121.4, so as predicted in the previous section (Figure 9), the values of  $Z$  are lower than  $P_0$  and they decrease with increasing degradation temperature. This trend may be explained by the occurrence of transfer reactions during degradation and/or reactions blocking depropagation such as anhydride formation after de-esterification.

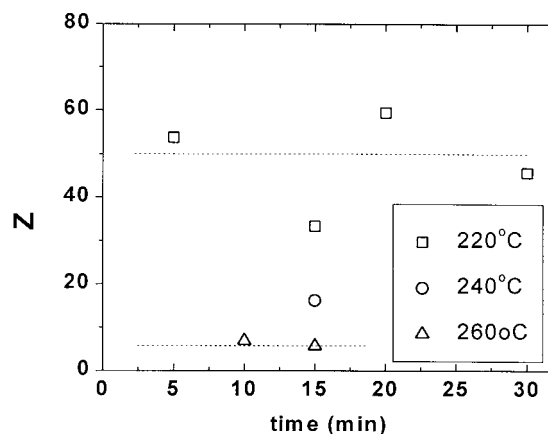
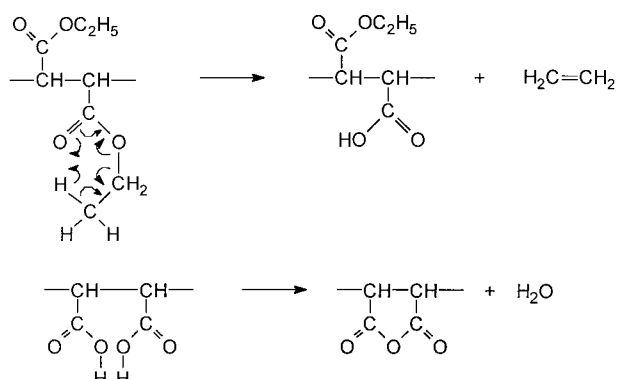


Figure 10. The dependence of the chain length of depropagation,  $Z$ , on degradation time at 220° and 260°C

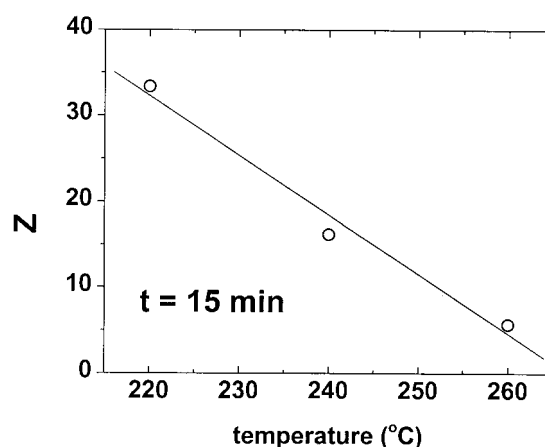


Figure 11. The dependence of the chain length of depropagation,  $Z$ , on degradation temperature at constant degradation time,  $t = 15$  min

For the sake of comparison, Table 4 shows the values of  $Z$  for poly(methyl methacrylate) (PMMA), which are quite high due to unhindered depropagation, and for PDEI, which are very low due to chain transfer to polymer during depolymerization.

Table 4. Values of  $Z$  for PMMA and PDEI

T (°C)	PMMA [9]	PDEI [7]
260	1760	11
280	1630	12
300	1430	20

#### Random main-chain scissions per monomer unit

The number of main-chain scissions per monomer unit,  $s/P_0$ , may be calculated according to the equation (10):

$$\frac{s}{P_0} = \frac{1-x}{P_n} - \frac{1}{P_0}$$

where  $x$  is the amount of thermolysis volatiles, i.e. the sample mass loss.

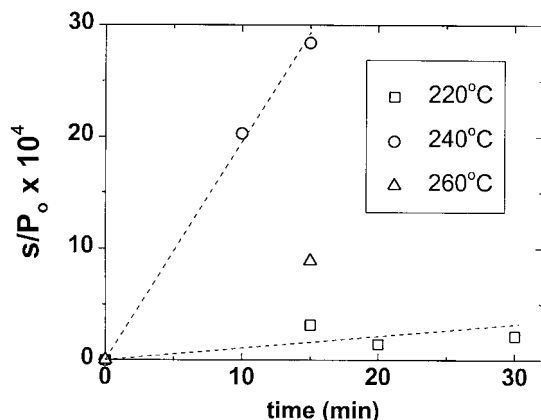


Figure 12. The dependence of the number of random main-chain scissions per monomer unit,  $s/P_0$ , on degradation time at 220° and 260°C

The calculated values are shown in Figures 12 and 13. The exponential increase of  $s/P_0$  with increasing degradation temperature indicates the reasons for the practical problems encountered during the determination of  $s/P_0$  at higher degradation temperatures and longer thermolysis times. The corresponding values of  $s/P_0$  for PDEI are approximately three times lower implying that PDEI is less thermally stable than PDEF as already evidenced by the DTG curves of the two polymers (Figure 3).

#### Proposal of the thermal degradation mechanism

On the basis of the presented results, the following thermal degradation mechanism may be proposed:

At temperatures above 200°C initial de-esterification reactions occur, as well as a few random main-chain scissions enabling depolymerization. As the degradation temperature increases, the frequency of both reactions increases (increase of  $s/P_0$ ). The possibility of two neighbouring ester substituents being de-esterified increases allowing the easy formation of anhydride structures which block depropagation (lower  $Z$  with increasing temperature). With further temperature

#### IZVOD

##### TERMIČKA DEGRADACIJA POLI(DIETIL FUMARATA)

(Naučni rad)

Radomir Bošković, Tomica Tošić, Lynne Katsikas, Ivanka G. Popović  
Tehnološko-metalurški fakultet, Beograd

Kinetika i mehanizam termičke degradacije pol(dietil fumarata) (PDEF) su ispitani termogravimetrijom i analizom polimernog ostatka. Određene su karakteristične temperature gubitka mase, kao i vrednosti ukupne energije aktivacije termičke degradacije tri uzorka PDEF različitih molskih masa. Zavisnost srednje molske mase od temperature i vremena degradacije je uspostavljena i određeni su kinetičke dužina depropagacije,  $Z$ , i broj nasumično raskinutih veza u osnovnom lancu po monomernoj jedinici,  $s/P_0$ . Predložen je mehanizam termičke degradacije PDEF koji uključuje: deesterifikaciju, nasumično raskidanje veze u osnovnom lancu, depolimerizaciju i karbonizaciju. Termička degradacija PDEF je upoređena sa termolizom PMMA i PDEI.

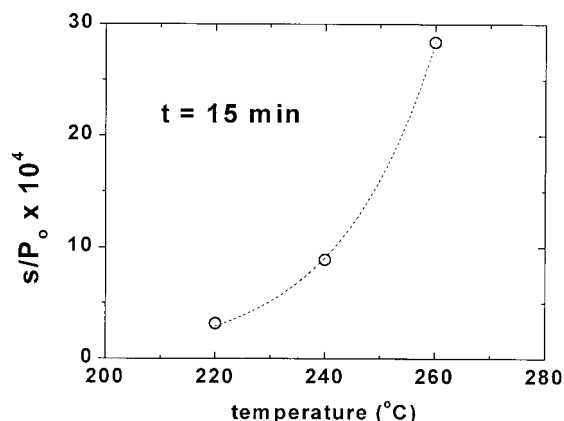


Figure 13. The dependence of the number of random main-chain scissions per monomer unit,  $s/P_0$ , on degradation temperature at constant degradation time,  $t = 15$  min

increase there is sufficient energy in the system for the random scission of both C–C and C–O bonds, which leads to rapid polymer degradation and volatilization. The presence of anhydride structures in the residue favours carbonization reactions at temperatures above 350°C.

This thermolysis mechanism will be verified upon completion of the ongoing thermolysis volatiles analysis.

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