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# DERIVATOGRAPHIC INVESTIGATIONS OF POLYCARBONATES

*Z. Dobkowski and E. Rudnik*

INDUSTRIAL CHEMISTRY RESEARCH INSTITUTE, WARSAW, POLAND

Derivatographic non-isothermal investigations of the decomposition of PC in air provide useful information on the characteristic decomposition temperatures and the apparent activation energies of the observed steps of decomposition. The following sequence of apparent activation energies of the pyrolysis step was obtained: PC-M>PC-C>PC-A. The values of $E$ for PC-M are the highest, due to shielding of the ester linkages by the ortho-methyl substituents.

**Keywords:** kinetics, polycarbonates

## Introduction

Bisphenol A polycarbonate (PC-A), i.e. poly[oxycarbonyloxy-1,4-phenyl-ene(1-methylethylidene)-1,4-phenylene), is a well-known engineering thermoplastic aliphatic-aromatic polyester resin having an advantageous set of mechanical, thermal and electrical properties, e.g. high impact strength, a relatively high performance temperature of about 130°C in air and self-extinguishing properties. Some of its properties can be improved by chemical modifications, e.g. the introduction of halogen atoms into the aliphatic groups or on the aromatic rings increases the flame resistance, while bulky groups in the ortho position improve hydrolytic resistance.

Important information on the thermal behaviour of modified polymers can be obtained from the methods of thermal analysis, including non-isothermal derivatographic measurements [1–5]. Thus, modified polycarbonates obtained from chloral-derived bisphenol C-2 [6] and from tetramethylbisphenol A [7, 8] were selected for investigations because of their possible applications. Their decompositions in air atmosphere were studied at different heating rates and compared with that of unmodified PC-A. Characteristic temperatures of decomposition were found and the apparent activation energy of decomposition was calculated by using the Kissinger method [9].

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## Theory

The basic kinetic equation for the decomposition of polymers (cf. [2, 4] can be written as

$$\frac{d\alpha}{dt}=k\cdot f(\alpha) \qquad (1)$$

where $\alpha$ is the fractional conversion evaluated from the mass loss, irrespectively of the chemical nature of the volatile or non-volatile decomposition products; hence $\alpha = (m_0-m_t)/m_0$, $m_0$ and $m_t$ being the mass of the polymer sample at the beginning of decomposition, at time 0, and at time $t$, respectively, and $k$ is the rate constant given by the Arrhenius equation

$$k=A\cdot \exp\left(-\frac{E}{RT}\right) \qquad (2)$$

where $A$ is the preexponential factor characterizing the frequency of decomposition events, $E$ is the apparent activation energy of the complex decomposition process, in $J\cdot mol^{-1}$, $R = 8.314\ J\cdot mol^{-1}\cdot K^{-1}$ is the gas constant, and $T$ is the absolute temperature, in K.

In the case of polymer decomposition, it is assumed that the conversion is proportional to the amount of non-decomposed material, i.e.

$$f(\alpha) = (1-\alpha)^n \qquad (3)$$

where $n$ is the reaction order. On combining Eqs (1)–(3), we obtain

$$\frac{d\alpha}{dt}=A(1-\alpha)^n\cdot \exp\left(-\frac{E}{RT}\right) \qquad (4)$$

Differentiation of Eq. (4) and its application to the maximum decomposition rate, $d\alpha/dt$ = max, where $d(d\alpha/dt)dt = 0$, gives

$$\frac{E}{R}\cdot\frac{\beta}{T_m^2}=A\cdot n(1-\alpha)_m^{n-1}\cdot \exp\left(-\frac{E}{RT_m}\right) \qquad (5)$$

where $\beta=dT/dt$ is the heating rate, and the index $m$ denotes the maximum decomposition rate (cf. [9]). Then, with the Kissinger assumption that $n(1-\alpha)_m^{n-1}$ is equal to unity, or for a first order or quasi-first order reaction ($n = 1$), we have

$$\frac{\beta}{T_m^2}=\left[\frac{A}{\frac{E}{R}}\right]\cdot \exp\left(-\frac{E}{RT_m}\right) \qquad (6)$$

Hence, a plot of ln $\beta/T_m^2$ *vs.* $1/T_m$ gives the values of $E$ and $A$.

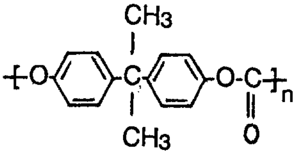
## Experimental

### *Materials*

The following polycarbonates were investigated:

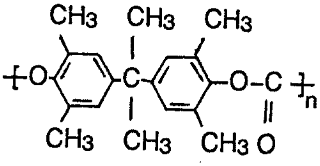
All samples were prepared from phosgene and the respective bisphenols by the interfacial polycondensation method [6–8, 10,11] and used in the form of powder or films without stabilizers. Samples were characterized via the intrinsic viscosity [η] in chloroform at 25°C, using a Schott-Geräte Autoviscometer AVS 400, and via the glass transition temperature $T_g$ at 20 deg/min, using a Perkin Elmer DSC-7 differential scanning calorimeter.

PC-A:



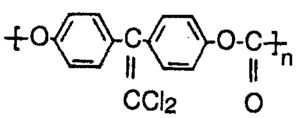
PC from bisphenol A, $T_g$ = 153.0°C, [η] = 102 cm$^3$/g

PC-M:



PC from tetramethylbisphenol *A*, $T_g$ = 181.8°C, [η] = 87 cm$^3$/g

PC-C:



PC from 1,1-dichloro-2,2-di(4-hydroxyphenyl)ethylene, $T_g$ = 164.5°C, [η] = 61 cm$^3$/g

## Derivatographic measurements

A MOM Q 1500 D derivatograph was used for decomposition measurements in air at various heating rates β ranging from 1.25 to 20 deg/min. The characteristics obtained from derivatographic measurements are shown in Fig. 1 on the example of commercial PC-A Sinvet 220, Enichem, Italy (cf. [12). Thus, *T vs. t* gives temperature and the heating rate, the TG curve gives the initial and final temperatures of decomposition $T_{pr}$ at

$\alpha_o = 0$ and $T_{kr}$ at $\alpha = \max$ (in Fig. 1, $\alpha_{max} = 1$), respectively, the DTG curve gives the maximum decomposition rate temperatures $T_{mr}$ and $T_{mu}$ for the first and the second steps of decomposition, respectively, and the DTA curve gives the heat effects during the decomposition process.

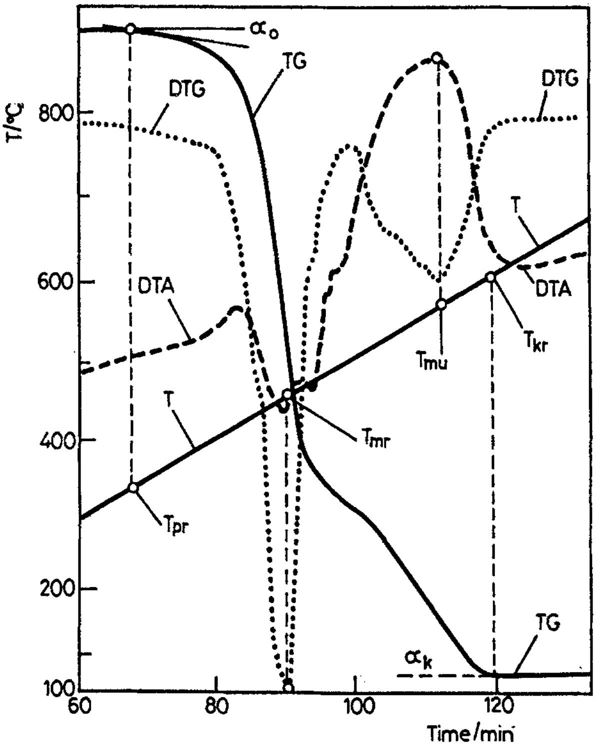


**Fig. 1** Derivatographic characteristics of decomposition. Polymer: commercial bisphenol A polycarbonate (PC-A) Sinvet 220. Conditions: air, heating rate $\beta = 5$ deg/min. Symbols explained in the text

## Results and discussion

It was found from TG, DTG and DTA curves that there are two main steps of decomposition of PC-A, PC-M and PC-C in air (cf. Figs 2–4). The first step, initiated from $T_{pr}$ up to about 450°C, is characterized by $T_{mr}$ and can be described as thermooxidative pyrolysis with a predominance of endothermic scission reactions for PC-A and PC-M, while it is exothermic for PC-C. In the second step, above 450°C up to the final decomposition temperature $T_{kr}$, also characterized by $T_{mu}$, exothermic oxidation reactions prevail. During the decomposition of PC in an inert atmosphere, e.g. in He [13] or in $N_2$ [14, 15], only one decomposition step is observed.

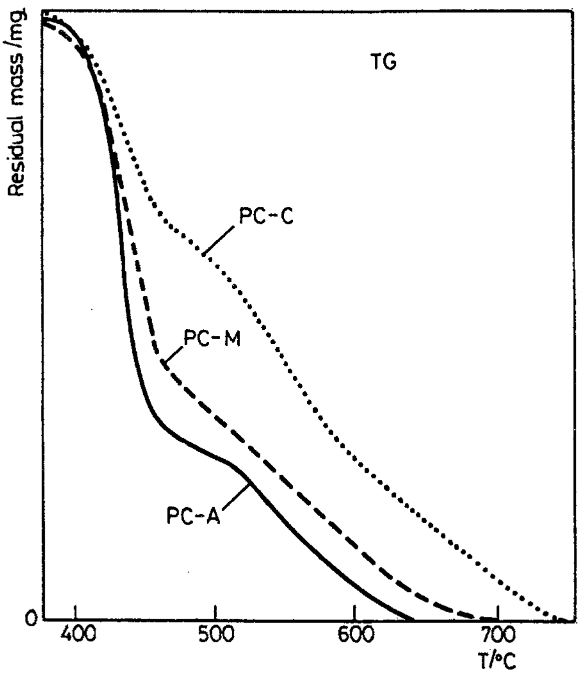


**Fig. 2** TG curves for PC. Heating rate β = 10 deg/min in air

Characteristic temperatures at maximum decomposition rates, $T_{mr}$ and $T_{mu}$, for both decomposition steps are shown in Table 1. From these temperatures and Eq. (6) according to the Kissinger method, the apparent activation energies for each step were calculated, (Fig. 5 and Table 2). The value of $E$ = 115 kJ/mole for PC-A in air is consistent with published results, e.g. $E$ = 107 kJ/mole for isothermal conditions in the temperature range from 250° to 426° [16] or $E$ = 117 kJ/mole in vacuum in the temperature range from 300° to 400°C [17]. Literature data on $E$ for PC-M were not found. The value of $E$ = 158 kJ/mole for PC-C is significantly higher than the published $E$ = 51 kJ/mole obtained in air by the isothermal method [18], but it is similar to the published $E$ = 144 kJ/mole in oxygen [18].

It was found that the apparent activation energy of PC-M is higher than that of PC-AQ (unmodified) or PC-C. In the case of PC-M, methyl groups as substituents on the aromatic rings, in the ortho positions in relation to the ester groups, shield the access of deteriorating agents to the ester linkages. Similar effects have been observed for other types of PC with orthosubstituents,m e.g. methylated PC from di(4-hydroxy-3-methylphenyl)phenylmethane is more stable than its unsubstituted analogue, as measured by

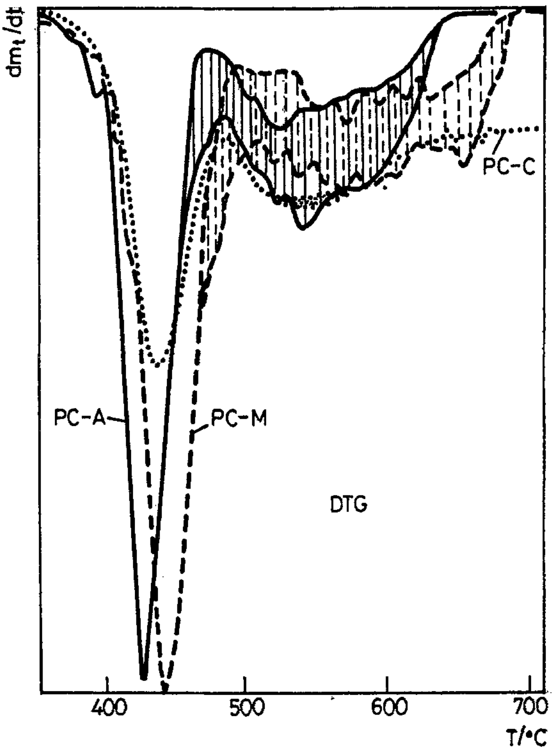


**Fig. 3** DTG curves for PC. Heating rate β = 10 deg/min in air

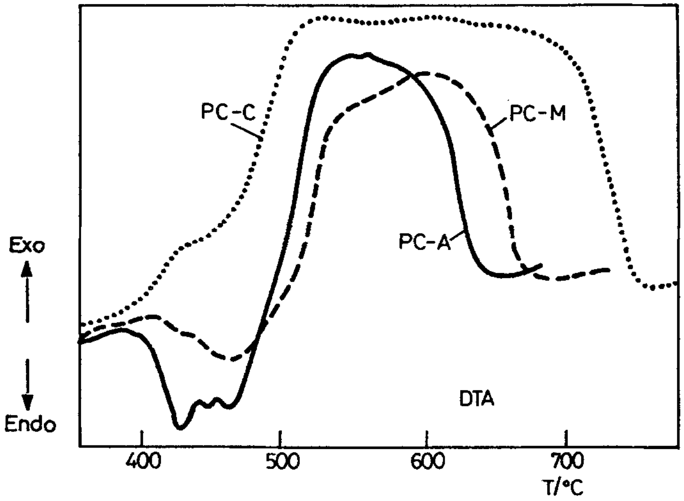


**Fig. 4** DTA curves for PC. Heating rate β = 10 deg/min in air

**Table 1** Characteristic decomposition temperatures of PC

| Polymer | Heating rate β / $deg \cdot min^{-1}$ | Characteristic temperatures, $T$ / K | |
|---|---|---|---|
| | | Pyrolysis, $T_{mr}$ | Oxidation, $T_{mu}$ |
| PC-A | 1.25 | 653 | 702 |
| | 2.5 | 664 | 749 |
| | 5 | 685 | 800 |
| | 10 | 713 | 848 |
| | 20 | 736 | 885 |
| PC-M | 1.25 | 672 | 745 |
| | 2.5 | 686 | 778 |
| | 5 | 703 | 828 |
| | 10 | 716 | 885 |
| | 20 | 735 | 975 |
| PC-C | 1.25 | 662 | 752 |
| | 2.5 | 683 | 783 |
| | 5 | 703 | 828 |
| | 10 | 711 | 885 (broad peak) |
| | 20 | 728 | — (plateau) |

**Table 2** Apparent activation energy of decomposition of PC. The Kissinger method

| Step of decomposition | Polymer | $E$ / $kJ \cdot mol^{-1}$ | $A$ / $min^{-1}$ | Correlation, $r^2$ |
|---|---|---|---|---|
| 1 Pyrolysis | PC-M | 170 | $9.8 \cdot 10^{11}$ | 0.9977 |
| | PC-C | 158 | $1.3 \cdot 10^{11}$ | 0.9694 |
| | PC-A | 115 | $7.7 \cdot 10^{7}$ | 0.9829 |
| 2 Oxidation | PC-M | 58 | $2.2 \cdot 10^{2}$ | 0.9810 |
| | PC-C | 72 | $2.1 \cdot 10^{3}$ | 0.9891 |
| | PC-A | 63 | $9.0 \cdot 10^{2}$ | 0.9821 |

the TG method [19], or PC-C with Cl substituents in the ortho positions exhibits a higher hydrolytic stability than that of unsubstituted PC-C [6, 20].

Considering the resistance against thermooxidative decomposition in air, therefore the following sequence of apparent activation energies of the pyrolysis step is observed: PC-M>PC-C>PC-A.

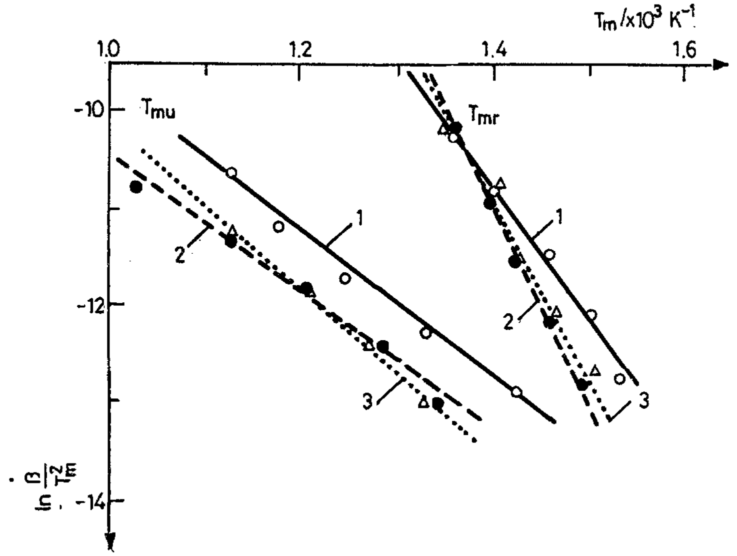


**Fig. 5** The plot of $\left(\frac{\beta}{T_m^2}\right)$ *vs* $\frac{1}{T_m}$ for calculations of *E*.
1. PC-A —o—, 2. PC-M -- • --, 3. PC-C ····Δ····

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**Zusammenfassung** — Derivatographische, nichtisotherme Untersuchungen der Zersetzung von Polycarbonaten in Luft liefern nutzbringende Informationen über die charakteristischen Zersetzungstemperaturen und die scheinbaren Aktivierungsenergien der untersuchten Zersetzungsschritte. Dabei wurde folgende Reihenfolge der scheinbaren Aktivierungsenergie der Pyrolyseschritte beobachtet: PC-M PC-C PC-A. Wegen der Abschirmung der Esterketten durch ortho-Methylsubstituenten sind die Werte E für PC-M am höchsten.