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CORRELATION OF THERMAL ANALYSIS DATA AND HYDROLYSIS RESISTANCE OF POLYCARBONATES

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Abstract

The initial activation energy at zero conversion E_0 of thermooxidative decomposition has been taken as a measure of thermal stability of polycarbonates (PC) and E_0 has been correlated with the relative hydrolysis rate r_h as a measure of their hydrolyse resistance. It is suggested that both decomposition processes are initiated by the same mechanism, the attack of hydrolytic agent onto ester C–O bonds. The following values of E_0 have been found:

187 (PC-M) > 87 (PC-A) > 43 (PC-C) kJ/mol, and they are correlated with values of r_h being 0.01 (PC-M) < 1 (PC-A) < 4.4 (PC-C). It has been found, using a computer modeling technique, that both E_0 and r_h depend on the minimized energy of conformations.

Keywords: activation energy of decomposition, polycarbonates, rate of hydrolysis

Introduction

It is known fact since years that the life time of bisphenol A polycarbonate (PC-A), i.e. the polyester of carbonic acid and 2,2-di(4-hydroxyphenyl)propane, in humid air is significantly shorter than that one in dry air atmosphere [1, 2]. Similarly, the long life temperature of PC-A is lower in water than that one in dry air, being 60–80°C in water, as compared with 120–130°C in dry air [3]. This can be explained by the fact that the C–O ester bonds of CO_3 groups in PC-A are susceptible to cleavage by hydrolytic agents, including water.

Our recent thermoanalytical investigations of polycarbonates (PC) have been performed in a humid air atmosphere where thermooxidative decomposition of macromolecules can be initiated by a hydrolytic cleavage of ester bonds [4–6]. It has been suggested that the resistance of PC to hydrolysis should be correlated with the resistance to thermooxidative degradation, since the same mechanism of initiation is involved in both cases, i.e. the attack of hydrolytic agent onto the C–O bond [4]. To prove these, three types of PC of different chemical structure have been investigated and the results are presented in this paper. The influence of chemical structure has also been investigated using the computer modeling technique.

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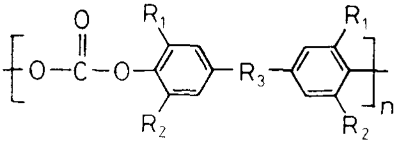
Experimental

Materials

The following PC types of different chemical structures have been investigated:

PC	Ring substituents in *ortho* position $R_1 = R_2$	Bridge groups of bisphenol structure R_3
PC–A	–H	$C(CH_3)_2$
PC–M	$-CH_3$	$C(CH_3)_2$
PC–C	–H	$C=CCl_2$

where the PC unit structure is written as


a)

Essential properties of investigated materials were published elsewhere [3, 5].

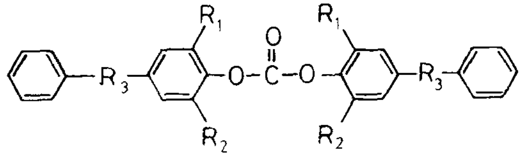
Measurements

Experimental data on the thermooxidative decomposition process of PC in air has been obtained using a MOM Q 1500 D derivatograph for decomposition measurements at various heating rate β ranging from 1.25 to 20 deg/min. Then, from the thermal analysis (TA) characteristics, the values of apparent activation energy E_α of thermooxidative decomposition process at different degrees of conversion α have been calculated using the method of Ozawa [4]. The initial activation energy E_o at the conversion degree 0 has been considered as a parameter characterizing the susceptibility of PC ester bonds to cleavage. The values of E_o can be obtained either by extrapolation of $E_\alpha = f(\alpha)$ to $\alpha = 0$, or (at certain approximation) taking values of E_α at $\alpha = 0.05$ as equal to E_o, or calculating E_o from the initial temperature of decomposition T_{pr} [4, 5].

The relative values of hydrolysis rate r_h as a measure of hydrolytic stability of PC have been taken from literature data, quoted in Ref. [6]. The hydrolysis proceeded in a 10% aqueous NaOH solution at temperature 100°C, as it was described elsewhere [3, 7].

Computer modeling

It has been assumed that the PC ester bond susceptibility to cleavage is influenced, above all, by the nearest substituents in neighbour phenylene rings, as well as by more distant bridge groups between phenylene rings of respective bisphenols. Therefore, the following model molecule has been proposed for computer modeling calculations:



b)

where $R_1 = R_2$ = H or CH_3, and R_3 = $C(CH_3)_2$ or $C{=}CCl_2$ in PC-A, PC-M and PC-C, respectively. Computer calculations have been performed at the Interdisciplinary Computer Modeling Center (ICM) of the Warsaw University, using the CRAY EL 98 computer and the Insight II software of Biosym Technologies. The calculations are based, in principle, on the force field theory [8]. Energies of conformation states of a model molecule have been minimized and minimized energetic contributions calculated according to the BFGS quasi Newton method. A harmonic potential was used for bond energies, and cross term energies were not included. Thus, the following energetic contributions to the total minimized energy can be calculated: bond stretching, angle bending (θ), torsional (φ), and non-bond Van der Waals (repulsive and dispersive) and Coulomb energies [9].

Results and discussion

The values of apparent activation energy E_α, calculated according to the Ozawa method, *vs.* conversion degree α are shown in Fig. 1. Hence, the initial activation energy at zero conversion, E_o for each PC has been found by linear extrapolation of the initial section of the curve, using at least 3 data points. This value has been compared with the respective value of $E_o = E_{pr}$ found from the initial temperature of decomposition T_{pr} (Table 1). It should be noted that the dependence of $\log\beta/T^2$ *vs.* $1/T$ used for calculations of E_{pr} is sensitive to errors in determination of temperature T_{pr} from the TA plots, e.g. an error of about 3% in T_{pr} may cause an error about 15% in E_{pr}. Determinations of E_o from the extrapolation of E_α to zero conversion should be more precise, and such procedure is here recommended. The values of E_α at 5% conversion that can be considered as being E_o are also included in Table 1. All the values of E_o have been compared with the respective published data on the relative rate of hydrolysis r_h, where r_h = 1 for PC-A (Table 1, Fig. 2).

Thus, the correlation of TA and hydrolysis data is evident; the higher is the initial activation energy of decomposition E_o, the higher is the hydrolytic stability of PC, i.e. the lower is the relative hydrolysis rate r_h, according to the following sequence of E_o

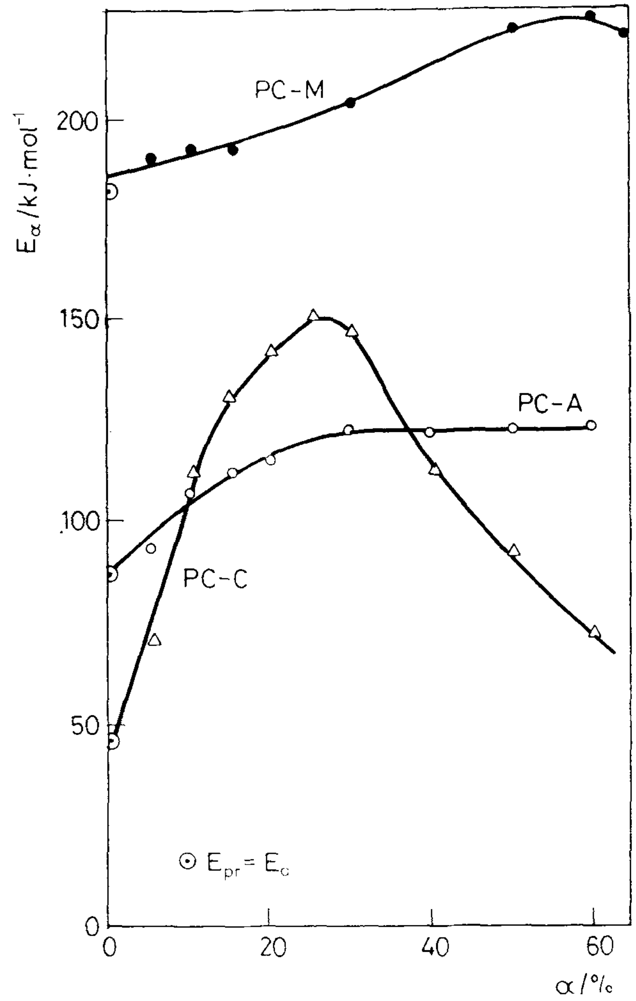


Fig. 1 Apparent activation energy E_α *vs.* conversion degree α

Table 1 Zero conversion activation energy of decomposition E_o *vs.* the relative rate of hydrolysis, r_h

Polycarbonate	PC-M	PC-A	PC-C
r_h	0.01	1	4.4
E_o / kJ·mol^{-1}; acc. to T_{pr}	183.5	73.0	37.6
E_o / kJ·mol^{-1}; acc. to the Ozawa method:			
extrapolation to zero conversion	187.3	87.3	43.1
as E_α at 5% conversion	191.2	94.5	70.0

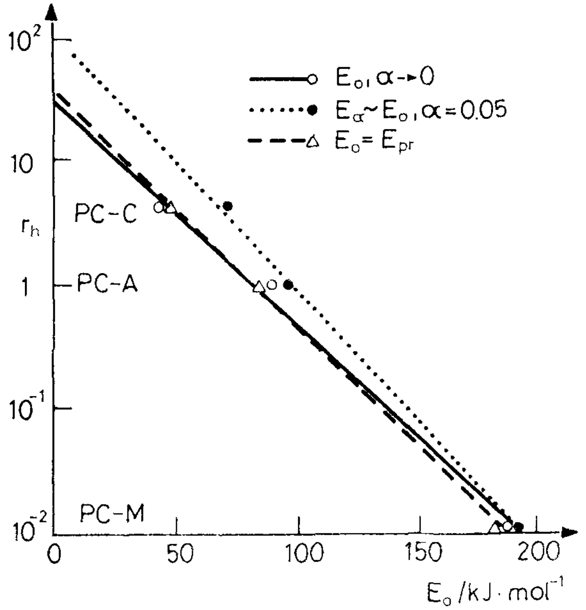


Fig. 2 Correlation of initial activation energy E_0 and relative rate of hydrolysis r_h

Table 2 Energetic contributions at optimized conformation of PC model molecules; energy in kcal/mol

Polycarbonates conformation of CO_3 group	PC–M	PC–A		PC–C
	trans,trans	*trans,trans*	*trans,cis*	*trans,cis*
Total energy	183.90	188.84	190.93	193.96
Bond	51.31	48.67	48.93	38.65
θ	12.38	11.25	12.80	7.14
φ	6.48	6.50	6.50	22.09
Non-bond, total	113.73	122.42	122.10	126.08
Van der Waals	147.12	144.49	144.53	127.54
repulsive	284.56	260.99	262.75	229.34
dispersive	–137.44	–116.50	–118.22	–101.90
Coulomb	–33.39	–22.07	–22.43	–1.45

PC-M > PC-A > PC-C

Another sequence of the activation energies calculated according to the Kissinger method, i.e. PC-M > PC-C > PC-A [5], can be explained by the fact that the maximum decomposition rate, considered for the Kissinger method, is usually obtained at relatively high conversions. The above mentioned sequence is observed for the range of conversions from about 10 to 35%, cf. Fig. 1.

Results of computer modeling calculations, i.e. the optimized conformation of a model molecule and energetic contributions to the minimized total conformational energy for each model compound are shown in Fig. 3 and Table 2, respectively.

Thus, *trans,trans* conformers have been obtained for PC-M and PC-A, and *trans,cis* conformers for PC-A again and for PC-C. In the case of PC-A, the *trans,trans* conformation is preferred over the *trans,cis* conformation by the

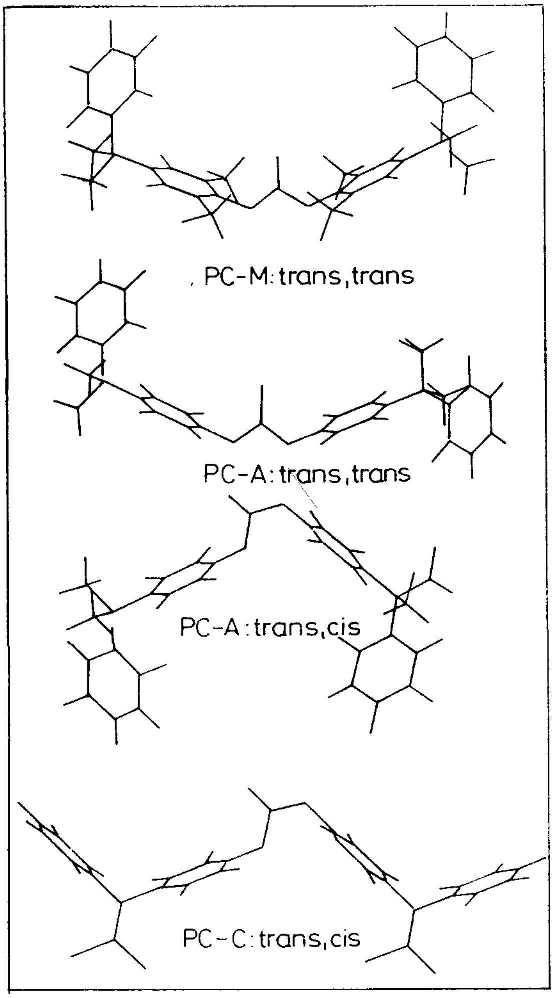


Fig. 3 Conformers of model carbonate molecules at the minimized energy; Computed at 1000 iterations

minimized total energy difference of 1.49 kcal/mol. This is consistent with the value of 1.3 kcal/mol calculated by Williams and Flory [10]. It is observed that all energetic contributions are changed evidently, for some contributions significantly, with the change of bridge structure as for PC-A and PC-C (Table 2). θ and φ energies are at the same level for the same bridge structure in PC-M and PC-A. The plot of E_o and r_h *vs.* the minimized total energy of conformation $E_{conf,\ min}$ for the model molecules is shown in Fig. 4. Both E_o and r_h depends on the minimum conformation energy that is influenced by the ortho-substituents in the vicinity of CO_3 group and by the bridge groups of the bisphenol structure.

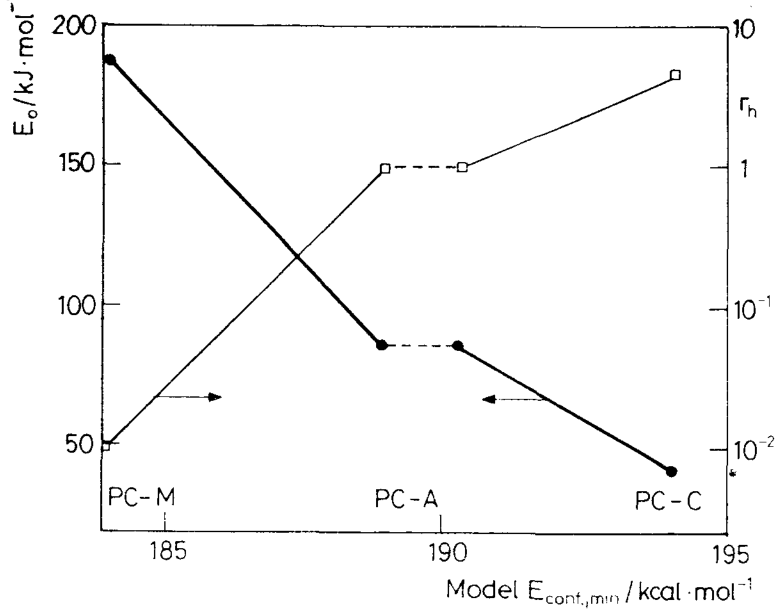


Fig. 4 The initial activation energy E_o and the relative rate of hydrolysis r_h of PC as a function of minimized energy of conformations of carbonate model molecules $E_{conf,\ min}$

Conclusions

It has been found that the initial activation energy E_o of thermooxidative decomposition of PC as a measure of its thermal stability is correlated with the relative rate of hydrolysis r_h as a measure of hydrolytic resistance of PC. The procedure for evaluation of E_o by extrapolation of E_α to zero conversion is recommended. The following values of E_o have been found: 187 (PC-M) >87 (PC-A) >43 (PC-C). The suggestion that the same mechanism of initiation is involved in both processes, i.e. the attack of hydrolytic agent onto the C–O bond, seems to be confirmed.

Moreover, it has been found that the initiation of both decomposition processes depend on the conformation energy which in turn depends on *ortho* substituents shielding the C–O bond, as well as on the more distant bridge groups in the structure of bisphenol. In the case of PC-A, the minima for *trans,trans* and *trans,cis* conformers have been noticed with the energy difference 1.49 kcal/mol that is consistent with 1.3 kcal/mol found earlier by Williams and Flory.

The computer modeling technique can be used for predictions of preferable chemical structures to obtain polymer materials of improved resistance to both thermooxidative and hydrolytic decompositions.

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Zusammenfassung — Die Anfangs-Aktivierungsenergie bei einem Zero-Umsatz E_0 der thermooxidativen Zersetzung wurde als Maß für die thermische Stabilität von Polykarbonaten (PC) und E_0 selbst wurde zur relativen Hydrolysegeschwindigkeit r_h als ein Maß ihrer Hydrolysebeständigkeit korreliert. Es wird behauptet, daß beide Zersetzungsprozesse durch den selben Mechanismus eingeleitet werden, nämlich der Angriff eines hydrolytischen Agens auf die C–O-Bindungen der Estergruppe. Folgende Werte für E_0 wurden gefunden: 187 (PC-M) 87 (PC-A) 43 (PC-C) kJ/mol und diese wurden mit den Werten von r_h: 0.01 (PC-M), 1 (PC-A) 4.4 (PC-C) korreliert. Man fand unter Einsatz einer Computertechnik, daß sowohl E_0 als auch r_h von der Minimalenergie der Konformationen abhängen.