Thermal degradation of bisphenol A polycarbonate

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(Received 3 October 1979; revised 13 February 1980)

Bisphenol A polycarbonate was thermally degraded in a rheometer barrel at temperatures from 300 to 330°C, and samples collected after 20, 40, 60 and 80 min were analysed by gel permeation chromatography. It was obvious that scission reactions occurred, which was evidenced by a significant drop in molecular weight. The number of scissions per molecule was calculated and plotted versus time of heat exposure. These data indicate an activation energy of 112 kJ mol^{-1} (26.7 kcal mol^{-1}) for the degradation reaction. The fracture of macromolecules did not take place randomly, which has been claimed in literature. Degradation experiments carried out in a Du Pont Thermogravimetric Analyser showed quite different results. In this case chain scission was suppressed and crosslinking reactions were promoted. This is in agreement with earlier findings.

INTRODUCTION

Poly[2:2-bis(4'phenylene)propane carbonate], usually referred to as poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene) bisphenol A polycarbonate is one of our most versatile engineering plastics. It has an attractive combination of mechanical properties and good heat stability. Processing is carried out at rather high temperatures in order to decrease the high melt viscosity characteristic of polycarbonate. Like most polyesters it is also susceptible to hydrolysis especially at elevated temperatures. The polymer compound thus has to be carefully predried before processing. Under dry conditions polycarbonate undergoes only limited degradation below 250°C, but injection moulding is often carried out at ~300°C.

The stability of polycarbonate has been the subject of a review by Davis and Golden[1], where the effects of different types of exposure are summarized. Most previous investigations have been concentrated on the degradation reactions caused by high energy radiation, but studies on the thermal degradation have also been reported.

Davis and Golden noticed a decrease in molecular weight during heat exposure in a sealed, evacuated vessel and claimed that the polymer underwent random chain scission[1,2]. Studies were also carried out in continuously evacuated systems and in this case polycarbonate rapidly crosslinked and formed an insoluble gel[1,3−6]. The large discrepancies between the results from these two methods are due to the competition between condensation and hydrolysis reaction as explained by Davis and Golden[1].

Lee[7] emphasized the sensitivity of the carbonic ester towards hydrolysis and alcoholysis:
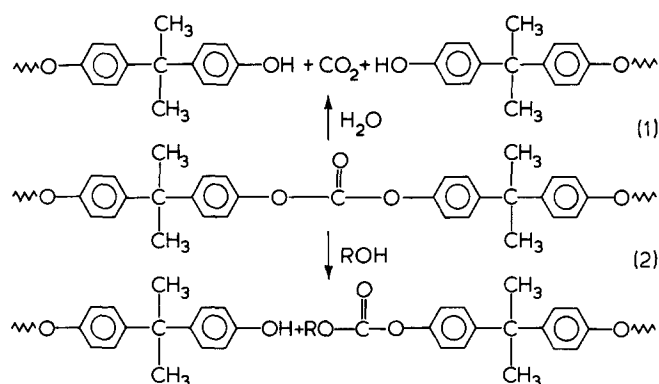
Depolymerization is enhanced by the presence of acidic or basic impurities, which may well be formed in sufficient amounts during the degradation reaction[3,8]. Consequently, hydrolysis results in a decrease in molecular weight.

The most important volatile products collected during polycarbonate degradation are carbon dioxide, phenol and bisphenol A, but smaller amounts of other compounds like carbon monoxide, methane, 2-(p-hydroxyphenyl)-2-phenylpropane, and diphenyl carbonate have also been observed[1,7,9−11]. Davis and Golden[11] determined the rate of gas evolution in an evacuated system at 360°C to be 2×20^{-5} mg mols of gas per gram of polymer per s. The volatiles consisted of 95% CO_2, 3% CO, and 2% CH_4. Phenol was also formed but was collected separately; the amount increased with an increasing moisture content in the sample. The fact that CO_2 is the major product indicates that the carbonate linkage is the most reactive group in the polymer.

Kovarskaya[12] found that scission reactions occurred during processing of polycarbonate, which may lead to

Table 1 Data of investigated polymers

Polymer	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$
Makrofol N	9140	40 600	106 000	4.5
Makrolon 2805	15 100	33 000	53 100	2.2

deterioration of the mechanical properties of the finished part. The effect of moisture was also discussed. The conditions during processing correspond to thermal exposure without removal of volatiles and thus chain scission is expected to take place. The change in melt viscosity has been employed as a measure of the extent of degradation. Lee[7] reported a 50% decrease in melt viscosity after 45 min exposure at 320°C.

In this study we have used gel permeation chromatography (g.p.c.) for the evaluation of the changes in molecular weight during degradation of polycarbonate in a rheometer barrel, which constitutes a good model for processing conditions. It is the purpose of this investigation to study the effect of heat exposure on polymer degradation at static conditions. The results from the corresponding dynamic experiment (extrusion) will be reported on separately.

EXPERIMENTAL

Materials

Two commercial grades of polycarbonate were employed. The samples were supplied by Bayer AG, West Germany. Polymer data are listed in *Table 1*. Makrofol N is polymerized from the melt and exhibits a broad molecular weight distribution (MWD). Makrolon 2805 is prepared by interfacial polymerization, which results in a polydispersity close to two. The methylene chloride employed for the GPC measurements was of analytical grade.

g.p.c.-analysis

A Waters Associates GPC Model 200 was used to obtain molecular weights and molecular weight distributions[13,14]. The experimental conditions were as follows: solvent: methylene chloride; temperature: 25°C; columns: 10^6, 10^5, 10^4, 10^3 Å; sample concentration: 1 mg ml^{-1}; flow rate: 1 ml min^{-1}; injection time: 2 min and sensitivity: 8 times. The GPC was calibrated with polystyrene standards with narrow distributions (Pressure Chemical Co, Pittsburg, Pennsylvania and Waters Associates, Milford, Massachusetts). The concept of a universal calibration proposed by Benoit *et al.* was applied[15]. The intrinsic viscosities of polystyrene standards were measured in methylene chloride at 25°C. From these data the following Mark–Houwink relationship was obtained[13]: $[\eta] = 2.12 \times 10^{-4} \times M^{0.67}$. To transform the universal calibration to polycarbonate calibration the following Mark–Houwink relationship was used[16]: $[\eta] = 1.23 \times 10^{-4} \times M^{-0.815}$.

Thermal degradation

The experiments were conducted using a capillary rheometer model HKR 2000 manufactured by Göttfert Feinwerk Technik, GmbH, Buchen, FRG. The conditions employed correspond to a thermal exposure

without removal of volatile reaction products. Each sample was carefully dried (overnight at 120°C) before it was loaded in small portions into the heated rheometer barrel.

After each loading, the sample was compacted by manual tamping. The filling procedure lasted for about 2 min. The cylinder was then closed by the piston and a small amount of material was extruded through the capillary. The polycarbonate was then stored in the rheometer barrel at preselected conditions.

RESULTS AND DISCUSSION

In a preliminary investigation Makrofol N was heated in a Du Pont Thermogravimetric Analyser. The degradation was carried out in a nitrogen flow and the weight loss was monitored. The results are shown in *Table 2*. A large weight loss was observed at 365°C and a dark insoluble product resulted. In spite of the fact that no weight loss was observed during degradation at 290°C, the product was insoluble in methylene chloride. Experiments conducted on Makrolon 2805 showed quite different results. Samples degraded for 1 h at 255, 275 and 305°C were all soluble in methylene chloride and very small changes in molecular weights were observed. At 305°C a slight increase in molecular weight was detected after 1 h. All other changes were within experimental error. It is obvious that a polycarbonate (Makrofol N), which is polymerized from the melt and exhibits a large $\bar{M}_z$-value, has a high tendency to crosslink under these conditions. As mentioned above the removal of volatile reaction products promotes condensation. The following mechanism has been suggested[1,4-6,10,11]:
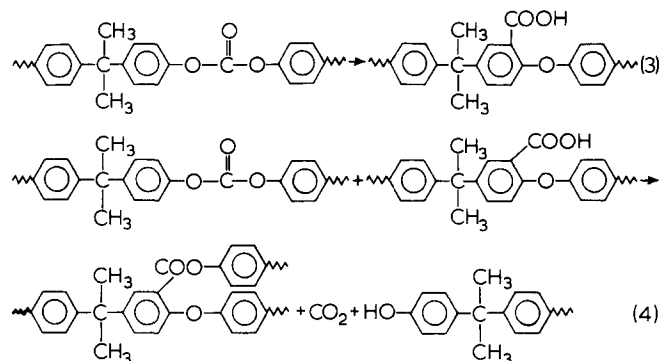
From this introductory study we concluded that experiments carried out in a closed rheometer barrel are better models for the simulation of processing conditions.

Polycarbonate was degraded in a rheometer barrel for up to 80 min. Samples were collected after 20, 40, 60 and 80 min. The experiments were carried out at

Table 2 Degradation of Makrofol N in a thermal analyser

Degradation temperature (°C)	Degradation time (h)	Weight loss (%)	Colour	Solubility
290	1	0	yellowish	insoluble in methylene chloride
350	1	1.6	dark brown	"
365	1	9.5	black	"

Table 3 Molecular weight changes as a result of thermal degradation of polycarbonate in a rheometer barrel

Temperature, (°C)	Degradation time, (min)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$	Scissions per mol/ $\dfrac{\overline{DP}_n^0}{\overline{DP}_n} - 1$
—	—	15 100	33 000	53 100	2.19	—
300	20	15 100	32 900	53 500	2.19	~0
	40	14 200	31 300	50 200	2.21	0.064
	60	14 000	30 700	50 100	2.18	0.075
	80	13 400	29 300	46 700	2.19	0.130
308	20	14 800	31 200	49 600	2.11	0.020
	40	13 600	29 500	46 800	2.16	0.106
	60	13 200	28 900	46 300	2.18	0.140
	80	12 100	27 100	44 200	2.24	0.247
315	20	13 800	30 100	49 000	2.19	0.095
	40	12 400	29 100	47 300	2.35	0.216
	60	11 900	26 400	42 400	2.22	0.269
	80	11 300	25 200	40 900	2.24	0.337
330	20	12 800	30 100	50 000	2.35	0.177
	40	11 100	26 700	44 500	2.40	0.357
	60	10 500	24 500	40 400	2.34	0.440
	80	10 200	23 500	39 400	2.31	0.486
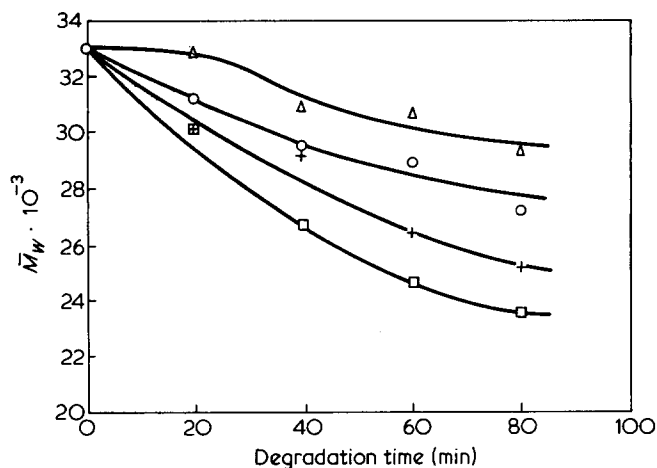
Figure 1 Weight average molecular weight as a function of degradation time: (△) 300, (○) 308, (+) 315 and (▣) 330°C

Figure 2 Molecular weight distributions for polycarbonate: (———) original sample, (— · —) degraded for 80 min at 330°C in a rheometer barrel

300, 308, 315 and 330°C. The changes in molecular weight are shown in *Table* 3 and *Figure* 1. There is a large decrease in molecular weight at the highest degradation temperature (330°C). During 80 min of heat exposure $\bar{M}_n$ decreased from 15 100 to 10 200 and $\bar{M}_w$ from 33 000 to 23 500. At this temperature there was a tendency towards higher polydispersities, whereas at all other temperatures it was almost constant.

In *Figure* 2 a comparison is made between the original molecular weight distribution (MWD) and the one obtained after 80 min at 330°C. MWD was shifted towards lower molecular weights.

Our data indicated the presence of an induction period. This is most clearly demonstrated in *Figure* 3, where the number of scissions per molecule is plotted versus degradation time. At all degradation temperatures — except for the highest one — we observed an induction period. At 300°C there was no significant change in molecular weight after 20 min.

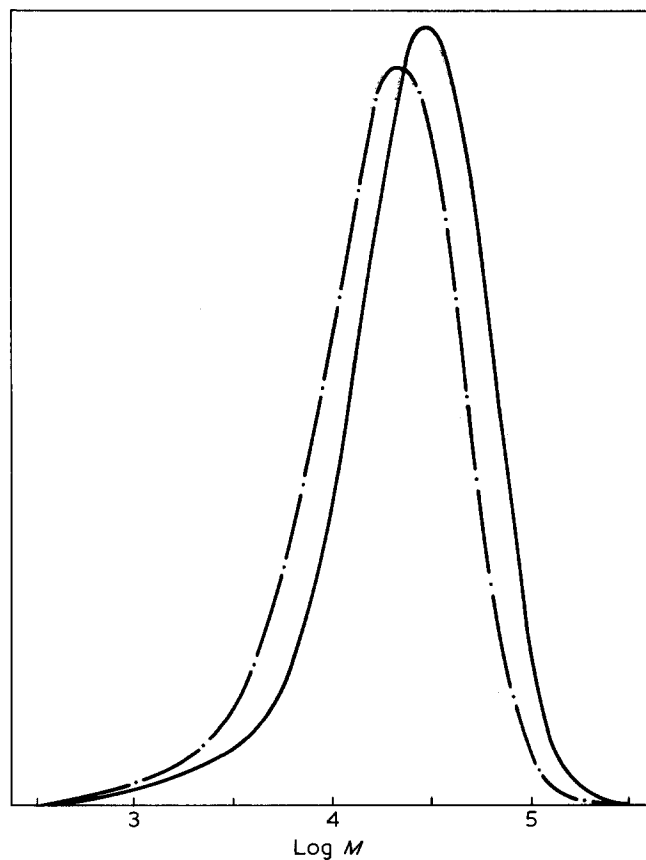A random process would require that the heterogeneity

index $(\bar{M}_w/\bar{M}_n)$ approaches two. This is not the case at 330°C and at the lower temperatures it is difficult to detect the trends. As mentioned above Davis and Golden have studied the thermal degradation of polycarbonate in a sealed evacuated system[1,2]. They claimed that during these conditions polycarbonate undergoes random chain scission. The validity of this statement was tested according to the equation:
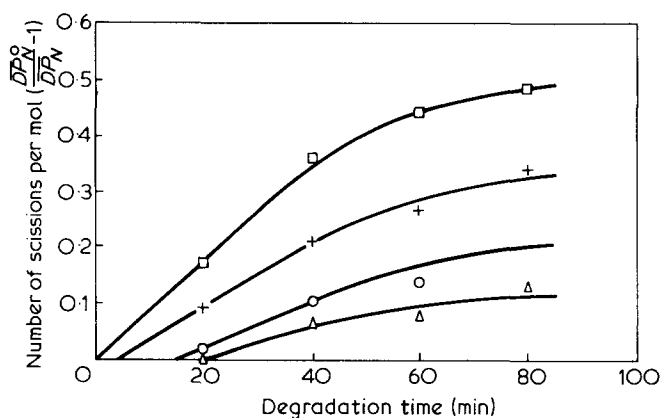
Figure 3 Number of scissions per molecule plotted versus degradation time: ($\triangle$) 300, ($\odot$) 308, (+) 315 and ($\square$) 330°C

$\log [\eta] = -\alpha \log(t + t_0) + C$; $[\eta]$ is intrinsic viscosity, α is the exponent of the Kuhn–Mark–Houwink relationship, $[\eta] = K \cdot M^\alpha$; C is a constant, t is the degradation time, and t_0 is the time required to fracture a molecule of infinite molecular weight to the same number average molecular weight as the original polymer[17]. A linear relationship between $\log [\eta]$ and $\log(t + t_0)$ was taken as a criterion for a random mechanism. Davis and Golden obtained linearity at all temperatures for longer degradation times[2]. However, at the lower temperatures (260–331°C) very few data points were reported, which certainly enlarges the difficulties in making a good prediction of the reaction mechanism. Furthermore, it is not possible to evaluate the data at the initial stages of the degradation. It is also important to note that small deviations from random scission behaviour are very difficult to detect by the above-mentioned procedure.

Our data were carefully analysed according to Scott's method[18], which is based on the fundamental work done by Montroll in 1941[19]. The theoretical model utilizes all available information and includes in essence the increase in chain scission as well as the changes in heterogeneity index. Assuming $\bar{M}_N^0 > 100$ and $\beta < 1$ the relationship may be expressed as follows:

$$\frac{\bar{M}_w}{\bar{M}_w^0} = \frac{2}{\alpha H}\left\{1 - \frac{1}{\alpha}\left[1 - \int_0^\infty \frac{W(y)}{my/\bar{M}_n^0} \cdot e^{-\beta y} dy\right]\right\}$$ (5)

where $\qquad \alpha = \dfrac{\bar{M}_n^0}{\bar{M}_n} - 1$

$\bar{M}_n$ and $\bar{M}_w$ are, respectively, the number and weight average molecular weight after scission, $\bar{M}_n^0$ and $\bar{M}_w^0$ are the corresponding values before scission, α is the number of scissions per initial number average molecule, $W(y)$ is the weight fraction of y-mers initially present, β is the fraction of the bonds (between monomer units) that have undergone scission, and m is the molecular weight of the monomer. Consequently, the relative changes in $\bar{M}_w$ were plotted versus the relative changes in $\bar{M}_n$ and the results were compared with that expected from theory. The theoretical treatment requires that the original MWD can be described by a distribution function. David and

Baeyens-Volant[20] have proposed several criteria that may be used to verify if a given MWD obeys a specific distribution function. For the Schulz–Zimm distributionn (generalized Poisson distribution) $(\bar{M}_n + \bar{M}_z)/\bar{M}_w = 2$ and $1 < \bar{M}_z/\bar{M}_w < 2$. In our case $(\bar{M}_n + \bar{M}_z)/\bar{M}_w = 2.07$ and $\bar{M}_z/\bar{M}_w = 1.61$. The MWD of the undegraded polycarbonate may thus very well be approximated with a Schulz–Zimm distribution.

It was found that all experimental data deviated from the theoretical curve, which implies that polycarbonate did not degrade according to a random scission mechanism. This is in agreement with our results from degradation studies of polycarbonate performed under different conditions[14,21-23].

After one hour of exposure at 300°C every tenth molecule has been broken and at 330°C almost every second molecule was broken after the same time. From the initial slopes of the curves in *Figure 3*, it is possible to determine the degradation rates, r, expressed in number of scissions per mol and min. These data were plotted versus inverse reaction temperature in *Figure 4*. The activation energy for the degradation process is derived from:

$$r = A \cdot e^{-\Delta E/RT}$$

where r = degradation rate, number of scissions mol^{-1} min^{-1}; R = gas constant, cal mol^{-1} K^{-1}; A = constant; T = temperature, K; E = activation energy, cal mol^{-1}. The activation energy determined from the slope in *Figure 4* was found to be 112 kJ mol^{-1} (26.7 kcal mol^{-1}).

Activation energies previously reported are collected in *Table 4*. From thermogravimetric measurements Lee obtained an activation energy of 33 kcal mol^{-1}. The degradation rate was determined as the time to 7% weight loss. This value is significantly higher, but as the experimental conditions are somewhat different, a direct comparison might not be useful. By measuring the rate of gas evolution, Kovarskaya determined an activation energy of 36.5 kcal mol^{-1} in the temperature range between 240°C and 360°C. Davis and Golden[7] also reported an activation energy based on the rate of total gas evolution in the interval 300°C to 389°C. They obtained a value of 28 kcal mol^{-1}, which is closer to our result. However, it is important to note that an activation energy for the scission process in a closed system has not been reported.
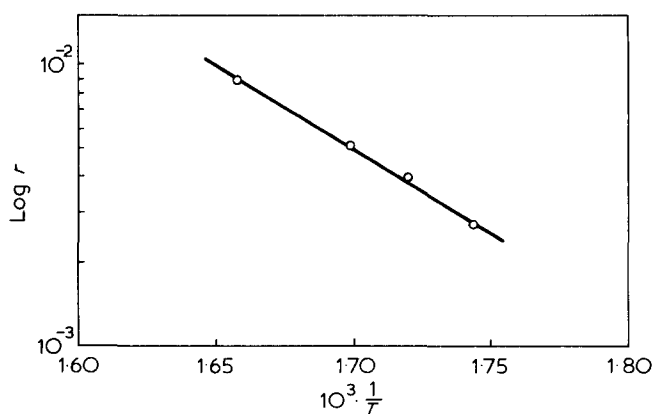

Figure 4 Arrhenius plot for the degradation of polycarbonate in a rheometer barrel

Table 4 Activation energies for the degradation of polycarbonate

Method of detection	Atmosphere	Temperature range (°C)	ΔE kJ mol^{-1}	ΔE kcal mol^{-1}	Ref number
CO_2 evolution	Sealed vacuum	—	88	21	25
Thermogravimetry	"	—	105	25	25
Viscometry	"	360—420	100	23.8	26
"	"	305—400	165	39.5	2
Thermogravimetry	air	465—515	138	33.0	7
Gas evolution	varying concentrations of oxygen	260—300	153	36.5	24
"	continuous vacuum	300—389	117	28	11
Gel permeation chromatography	air (closed rheometer)	300—330	112	26.7	this work

ACKNOWLEDGEMENT

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