

# Confirmation of the xanthone structure in thermally treated polycarbonates by reactive pyrolysis-gas chromatography/mass spectrometry

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## Abstract

Reactive pyrolysis-gas chromatography/mass spectrometry in the presence of tetramethylammonium hydroxide was used to confirm the existence of xanthone structures in polycarbonate (PC) samples thermally treated at 300 and 400 °C. The predicted characteristic product ( $M_w = 492$ ) of the xanthone structures was successfully eluted on the resulting pyrogram by use of a deactivated stainless steel capillary column whose temperature was programmed up to 370 °C leading its positive assignment by its mass spectrum. Further, unequivocal identification of the specific product was carried out from the retention index data for the whole main degradation products observed on the pyrograms of the PC samples. Finally, the amounts of the xanthone structures formed in the PC samples are quantitatively discussed. © 2001 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Polycarbonate (PC), mainly comprised of bisphenol A (BPA), is one of the most popular engineering plastics owing to its excellent transparency and mechanical properties. Since PC is often subjected to injection moulding operations at temperatures above 300 °C, causing degradation reactions to some extent, several reports on the study of the thermal decomposition in PC have been published [1–6], and many abnormal structures formed in PC chains during thermal degradation have been elucidated by means of various analytical pyrolysis techniques such as pyrolysis-mass spectrometry (Py-MS) [1] and pyrolysis-gas chromatography (Py-GC) [2], and matrix assisted laser desorption ionization (MALDI) MS [3].

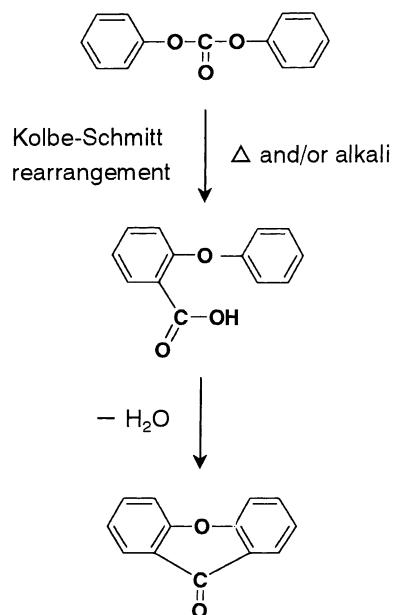
Among these reports, the formation of xanthone-related structures was pointed out by Davis et al., who examined the thermal breakdown of a model compound, diphenyl carbonate, and postulated the rearrangement shown in Scheme 1 to form 2-phenoxy benzoic acid,

which would undergo further intermolecular condensation to give xanthone, found as a product [4]. They also reported that this reaction could be initiated thermally without added alkali, whereas alkali had been known to catalyze this reaction [5]. Then, by extending this mechanism to the PC system, they proposed that the rearrangement of the carbonate group would form a pendant carboxyl group, *ortho* to an ether link, which would undergo further intermolecular condensation to form xanthone structure in the PC chain [6].

The formation of the xanthone-related structures was suggested for the first time by Montaudo et al. [1] through their Py-MS study of thermally treated PC samples. In this report, they suggested that the xanthone structures might be formed by a rearrangement of the carbonate group to cause successive condensation, as shown in Scheme 2. Shortly after this Py-MS report, the same authors [3] confirmed the existence of the xanthone structures by their MALDI-MS investigation of soluble fractions of thermally treated PC samples at 300–450 °C. They also reported that extended heating of PC samples at 400 °C not only increases the amount of PC oligomers containing one xanthone unit but also induces the formation of more-than-one unit along the same chain.

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Scheme 1. Reported formation pathway of the xanthone from diphenyl carbonate.

Recently, the authors have reported work to characterize branching and/or cross-linking structures formed in PC samples during thermal treatment at 300 °C by means of reactive Py-GC/MS in the presence of organic alkali [2]. Although many products reflecting the abnormal structures such as branching and/or cross-linking have been

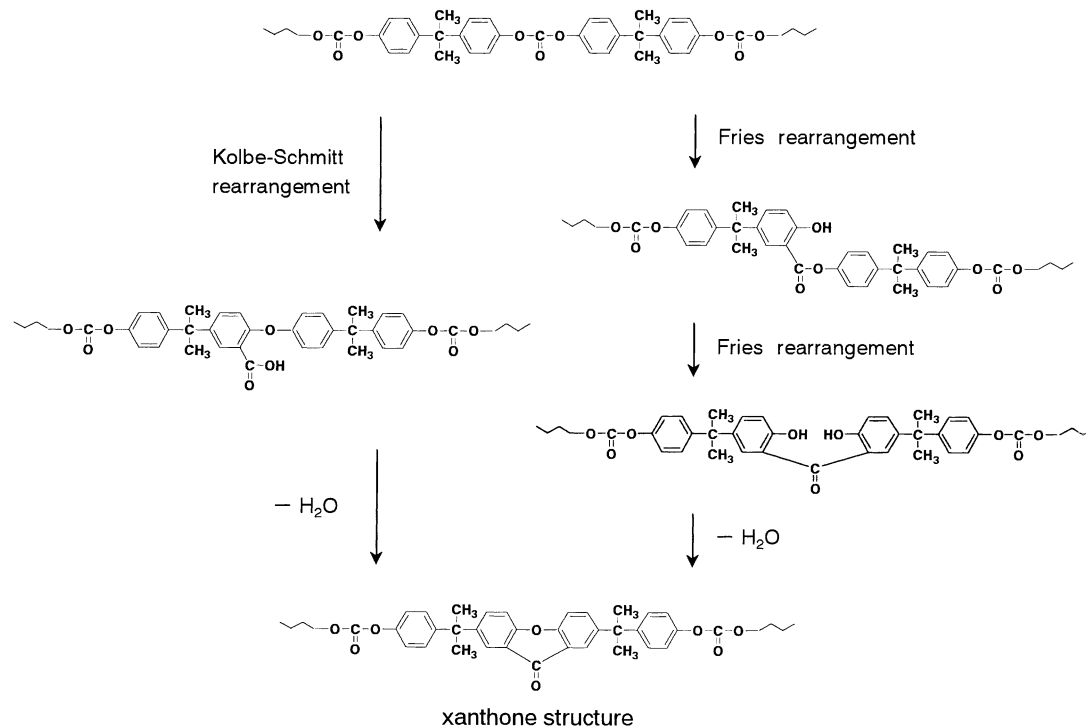
identified, any characteristic products of the xanthone structures were missing from the resulting pyrograms for the thermally treated PC samples.

In this work, the reactive Py-GC/MS technique was extended to confirm the existence of the xanthone structures in thermally treated PC samples at 300 and 400 °C, where the retention index data for the whole main degradation products observed on the pyrograms of the PC samples were effectively used to make unequivocal identification of a specific product related to the xanthone structure in the PC samples.

## 2. Experimental

### 2.1. Samples

A commercially available pelletized PC sample ( $M_n = 1.3 \times 10^4$ ) was thermally treated either at 300 °C for 3 h or 400 °C for 1 h to form two series (A and B) of thermally treated PC samples. The procedures for heating in the presence of atmospheric oxygen and fractionating based on the solubility of the samples were fundamentally the same as described in our previous report [2]. In each series, the thermally treated sample was separated into two fractions based on solubility in chloroform ( $CHCl_3$ ). The PC samples used in this work are listed in Table 1. The series A samples (PC-A or-A') are identical to the samples used in the previous work [2].



Scheme 2. Reported formation pathways of the xanthone structure in the PC chain.

Table 1  
Thermally treated PC samples

Sample code	Heating temperature (°C)	Heating time (h)	Solubility in CHCl <sub>3</sub>
PC-A	300	3	Soluble
PC-A'	300	3	Insoluble
PC-B	400	1	Soluble
PC-B'	400	1	Insoluble

## 2.2. Conditions for Py-GC

The procedure for reactive pyrolysis is basically the same as was described in our previous paper [2]. A vertical microfurnace pyrolyzer (Frontier Lab. PY-2020D), which can heat the interface zone between the pyrolysis chamber and the injection port of GC to the maximum temperature of the separation column to avoid the condensation of the resulting less volatile degradation products in this zone, was directly attached to a gas chromatograph (HP5890) equipped with a flame ionization detector (FID). About 100 µg of a powdered PC sample and 2 µl of a methanol solution (25 wt.%) of tetramethylammonium hydroxide (TMAH, supplied by Aldrich) taken in a platinum sample cup were introduced into the centre of the pyrolyzer, heated at 400 °C under a flow of helium carrier gas. To detect the higher boiling point products, a metal capillary column coated with polydimethylsiloxane immobilized by chemical cross-linking (Frontier Lab. Ultra-Alloy-PY1, 30 m×0.25 mm ID, 0.25 µm film thickness), which can operate at a higher temperature than the fused silica capillary column used in our previous report [2], was used. Thus, the column temperature was programmed from 50 to 370 °C at a rate of 10 °C/min and held for 20 min at 370 °C, which is 70 °C higher than the case for our previous paper [2]. The identification of the peaks on the pyrograms was carried out by use of a Py-GC/MS (Jeol Automass system II) with an electron impact ionization (70 eV) to which the same pyrolyzer was also directly attached.

## 3. Results and discussion

Fig. 1 shows pyrograms of four kinds of PC samples listed in Table 1 by reactive pyrolysis in the presence of TMAH at 400 °C. On the pyrogram for every PC sample, after the elution of trimethylamine and methanol formed from the excess TMAH reagent, the peaks reflecting the abnormal structures formed during the thermal treatment of PC were commonly observed together with those of the main chains and the end groups [2]. On the pyrograms of the samples thermally treated at 300 °C [(A) PC-A and (B) PC-A'], as was reported in our previous paper [2], the whole peaks reflecting the abnormal structures

(peaks 1–7) were more abundantly observed for the insoluble fractions of thermally treated PC [(B) PC-A'] than for the soluble fraction [(A) PC-A]. Basically the same tendency was also found between the samples thermally treated at 400 °C [(C) PC-B and (D) PC-B']. Here it should be noted that by the use of the metal capillary column at the higher oven temperatures up to 370 °C, a peak C, which had not been detected in the recent paper [2], was clearly observed. However, this peak was not observed in the pyrogram of the unheated control PC sample obtained under the same reactive Py-GC conditions. As can be seen in the pyrograms (C) and (D), the peak C and additionally assigned peaks A and B were more intense for the PC samples treated at 400 °C (PC-B and B'). When considering the result report by Montaudo et al. [3] that the oligomers containing the xanthone units were positively detected in the MALDI-MS spectra of the PC samples treated at 400 °C while hardly observed in those at lower temperatures between 300 and 350 °C, these new peaks could be possible candidates for the key products reflecting the xanthone structures.

Before going into further discussion, we speculated a possible degradation product from the xanthone structures formed in a PC sample, through reactive pyrolysis in the presence of TMAH. Fig. 2 shows one of the most probable products [MW = 492] through the reactive pyrolysis of the xanthone moiety formed during the thermal treatment of PC samples at higher temperatures. Similarly, when two successive xanthone units are involved along the chain, the molecular weight of the associated products should be 728. The former product with MW = 492, if any, should appear after ca. 30 min in the pyrograms in Fig. 1 when considering its molecular weight and the retention behaviour of the related products appearing on the pyrograms. Among the three peaks, the peak A should be excluded from the candidates reflecting the xanthone structures owing to its early retention time, ca. 22 min. Actually, this product can be assigned to CH<sub>3</sub>O(C<sub>6</sub>H<sub>4</sub>)C(CH<sub>3</sub>=CH(C<sub>6</sub>H<sub>4</sub>))OCH<sub>3</sub> (MW = 254) from the mass spectrum of peak A, reflecting another abnormal structure generated by the cleavage of an isopropylidene group during the thermal treatment of the PC. Since the peaks B and C observed at about 34 and 40 min, respectively, remain as possible candidates reflecting the xanthone structures judging from their retention time, the mass spectra of those two peaks were carefully examined. From the mass spectrum of the peak B, this product was assigned to be CH<sub>3</sub>O(C<sub>6</sub>H<sub>4</sub>)C(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)O(C<sub>6</sub>H<sub>4</sub>)C(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>)OCH<sub>3</sub> (MW = 466), reflecting the other abnormal structure containing the diphenyl ether moiety formed through the intermolecular CO<sub>2</sub> elimination from the carbonate group reported by Montaudo et al. [1]. Finally, the observed mass spectrum of the peak C which is the last candidate for the key products containing the xanthone

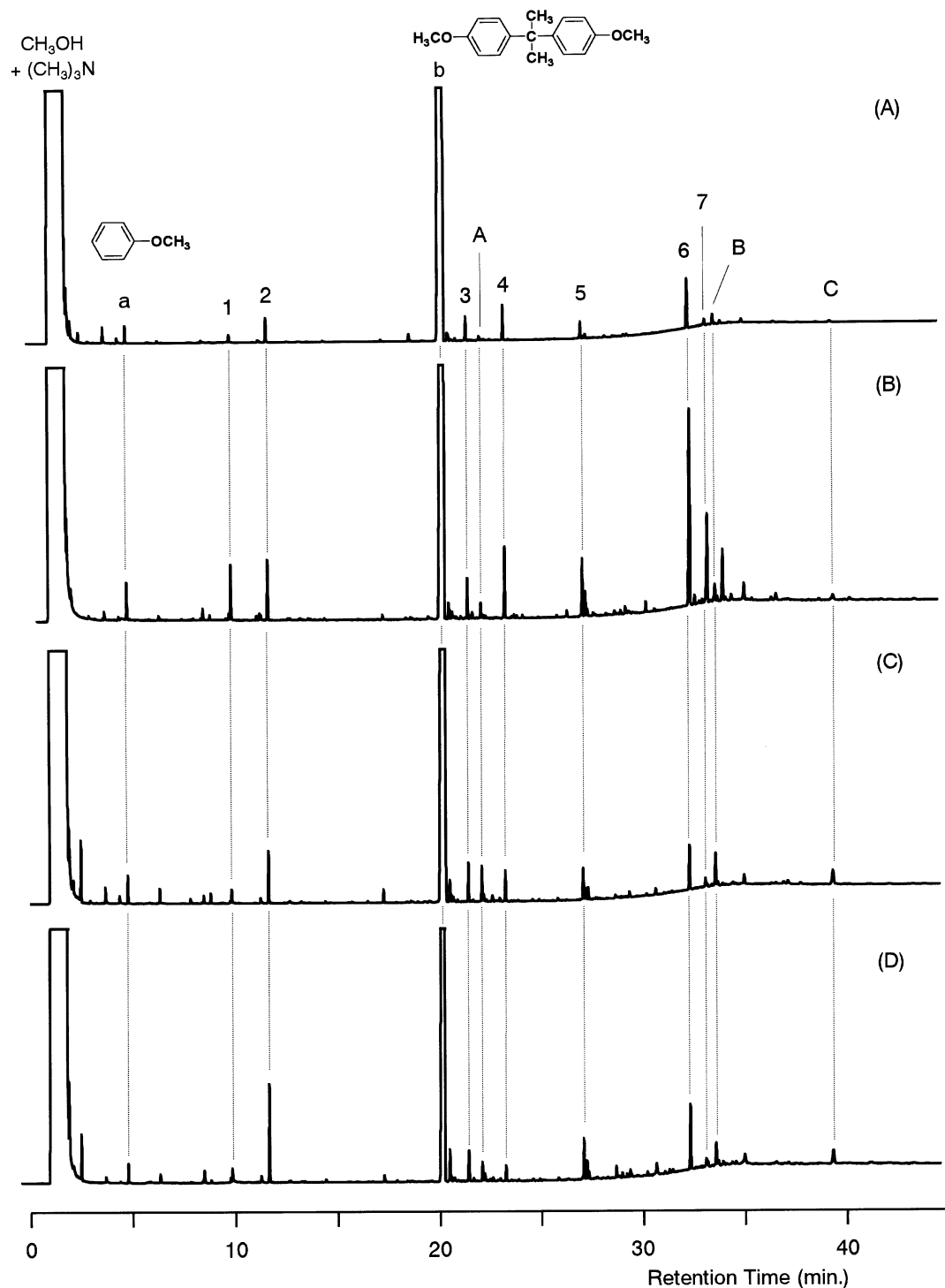


Fig. 1. Pyrograms of four kinds of PC samples listed in Table 1. (A) PC-A, (B) PC-A', (C) PC-B, and (D) PC-B'. Peak numbers correspond to the numbers in Fig. 4.

moiety is shown in Fig. 3. In this spectrum, the molecular ion at  $m/z$  492 and the base peak at  $m/z$  477, mainly formed through the elimination of a methoxy group from an isopropylidene group of the molecule, are clearly observed in addition to various fragment ions such as those at  $m/z$  445, 369 and 149. From this characteristic spectrum, the peak C could be assigned to

the relevant pyrolysis product reflecting the xanthone moiety as speculated in Fig. 2. The fact that the xanthone moiety would not have been formed during the reactive pyrolysis in the presence of TMAH was confirmed by the experimental result that peak C was scarcely observed in the pyrogram of the unheated PC sample under the same reactive pyrolysis condition.

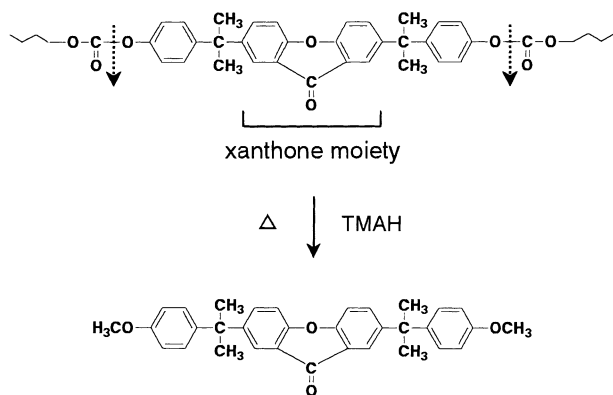


Fig. 2. Possible product through the reactive pyrolysis from the xanthone moiety in the thermally treated PC chain.

In order to make further unequivocal identification of the specific pyrolysis product for the peak C, among the interrelations between the whole related products appearing on the pyrograms, Kovats retention index data for the main pyrolysis products were determined by comparing the retention data for *n*-alkanes obtained by the same separation column through a conventional Py-GC measurement at 600 °C of a polyethylene sample [7]. Fig. 4 shows the relationship between molecular weight and retention index for the main degradation products (peak number: 1–7, a and b, and A, B and C in the pyrograms in Fig. 1) together with the reference data obtained for a xanthone monomer measurement designated by an open square ( $\square$ ). The solid line was obtained by the method of least squares applied to the whole data for the peaks 1–7, and *a* and *b* of which the assignments were reported in the recent paper [2]. Although the data for these products designated by solid circles ( $\bullet$ ) showed almost linear relation, the data for the peaks A, B and C designated by open circle ( $\circ$ ) deviated slightly at higher retention index side when considering their MW. Here, it is very interesting to note that the line connecting the plots of the xanthone monomer ( $\square$ ) and the peak C (broken line) was farthest from the solid line, suggesting that those two products might belong to a different class of homologue. Furthermore, among the pyrolysis products containing more-than-one successive xanthone units, the smallest one with MW = 728 mentioned earlier in the explanation of Fig. 2, if any, would be expected to appear on the pyrogram at about retention index = 6500 plotted as C' ( $\square$ ) in Fig. 4 based on the analogous estimation by use of the extended linear relationship (broken line). However, the peak reflecting this product was not yet positively recognized from the baseline noise on the pyrograms around the expected retention time under the present separation conditions. A further study is currently in progress.

Finally, to make quantitative discussion of the xanthone structures, the relative molar abundances of the

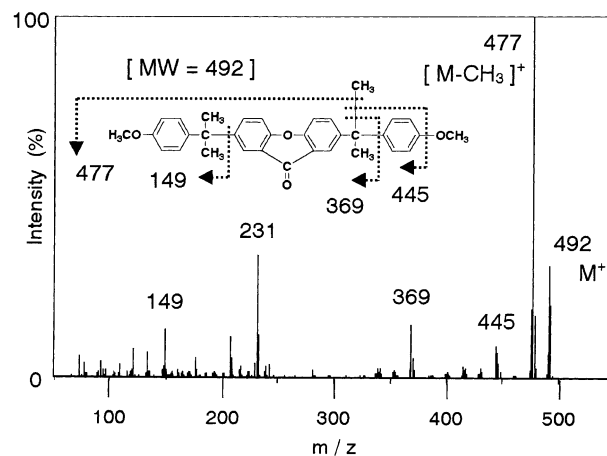


Fig. 3. Observed mass spectrum of peak C.

xanthone moiety in BPA monomer unit base for the thermally treated PC samples determined by Py-GC are summarized in Table 2, together with those by MALDI-MS. The content of xanthone structures (0.11 mol%) for the insoluble fraction (PC-A') was higher than that (0.03 mol%) for the corresponding soluble fraction (PC-A) and a similar tendency was observed for PC-B' and -B. The value (0.31 mol%) observed by Py-GC for the soluble fraction of the thermally treated PC sample at 400 °C (PC-B) shows a fairly large discrepancy from that (2.2 mol%) by MALDI-MS, estimated from the relative intensities of the oligomers containing the xanthone moiety in the partial MALDI-MS spectrum between *m/z* 1000 and 3000. This discrepancy should mostly be attributed to the fact that the MALDI-MS estimation was performed by supposing that the partial spectrum might represent the whole picture of the poly-disperse sample, whereas the Py-GC estimation would reflect the average values of the whole components in the PC samples. The experimental results that the xanthone contents for the other PC samples thermally treated under an inert atmosphere of flowing nitrogen were slightly higher than that for PC samples thermally

Table 2  
Relative molar abundance of the xanthone moiety in monomer units of thermally treated PC samples determined by Py-GC

Sample	Relative molar abundance (mol%)	
	Py-GC <sup>a</sup>	MALDI-MS <sup>b</sup>
PC-A	0.03	— <sup>c</sup>
PC-A'	0.11	— <sup>d</sup>
PC-B	0.31	2.2
PC-B'	0.48	— <sup>d</sup>

<sup>a</sup> Calculated from relative peak intensities on the pyrograms in Fig. 1 or on the MALDI mass spectrum.

<sup>b</sup> Performed by basically same procedure as the reported by Montaudo et al. [3].

<sup>c</sup> Oligomers containing a xanthone moiety were indistinguishable from baseline noise.

<sup>d</sup> Inapplicable because of their insoluble nature.

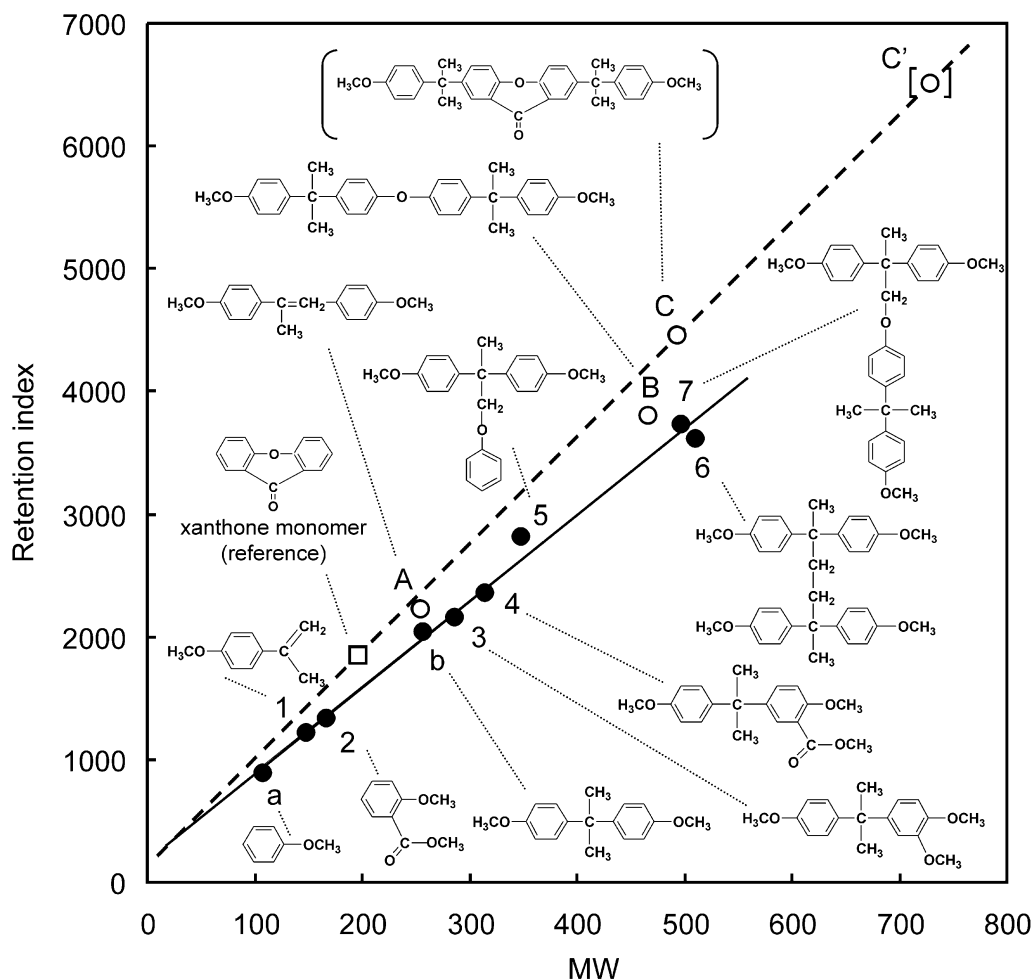


Fig. 4. Relationship between molecular weight and retention index for pyrolysis products observed on the pyrograms in Fig. 1. The solid line was obtained by the method of least square applied for the data designated by solid circles (●) (1–7 and, a and b). The open square (□) and the open circles (○) designate the data for xanthone monomer and for peaks A–C, respectively. The broken line was obtained by connecting the plots of xanthone monomer and peak C. Additional open circle marked as C' (○) is a plot for the product containing two successive xanthone units (MW = 728), whose retention index value was estimated to be ca. 6500 from the extended linear relationship (broken line).

treated under the atmosphere oxygen suggested that in the absence of oxygen the condensation reaction of the carbonate group to form xanthone structure proceeded preferentially to the scission of the carbonate group than is the case under oxygen.

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