*Macromolecules* **2000,** *33,* 8173−8183

# Characterization of Branching and/or Cross-Linking Structures in Polycarbonate by Reactive Pyrolysis−Gas Chromatography in the Presence of Organic Alkali

**Keishi Oba, Yasuyuki Ishida, Yoshiro Ito, Hajime Ohtani, and Shin Tsuge***

*Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 466-8603, Japan*

*Received April 4, 2000; Revised Manuscript Received August 8, 2000*

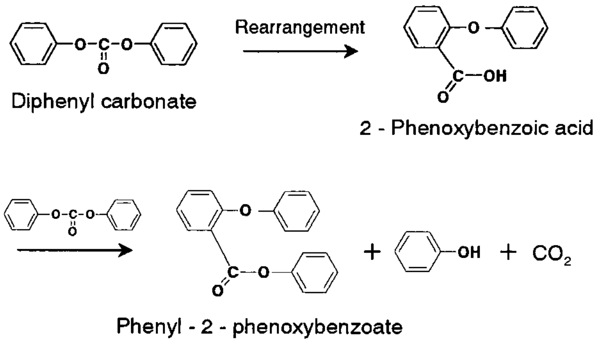
ABSTRACT: The reactive pyrolysis−gas chromatography technique was applied to verify the branching and/or cross-linking structures in an industrially available PC sample and its thermally treated ones through identification of specific pyrolysis products directly reflecting the related abnormal structures. On the pyrograms of the thermally treated samples, the peaks reflecting the abnormal structures such as branching and/or cross-linking were observed together with those reflecting main chain and end groups. Although the formations of these branching and/or cross-linking structures during the thermal treatment of PC had been suggested early, the identification of these pyrolysis compounds by reactive pyrolysis verified the existence of these structures. Furthermore, the fact that some of those characteristic peaks were also observed on the pyrogram of the industrially available PC sample prepared by the melt method indicated that the branching and/or cross-linking reactions would occur to some extent in the industrial polymerization reactor to synthesize the PC by the melt method.

## Introduction

Polycarbonate (PC), mainly comprised of bisphenol A (BPA), is one of the most widely utilized engineering plastics owing to its excellent transparency and mechanical property. PC is synthesized industrially by the solvent method (SM), in which sodium salt of BPA and phosgen are reacted through interfacial polycondensation, and the melt method (MM), in which BPA and diphenyl carbonate are directly reacted through transesterification. The latter MM-PC is known to contain fractions with branching and/or insoluble cross-linking structures to some extent formed under the concomitant relatively higher polymerization temperature (200−300 °C).[1] Characterization of these branching and/or cross-linked structures is important because these structures are closely associated with mechanical properties of the PC materials. However, mainly because of their insoluble nature, their characterization is not an easy task even by spectroscopic methods such as NMR and IR which have been most extensively utilized for soluble polymeric materials.

Davis et al. studied the isothermal pyrolysis of PC in the temperature range 300−400 °C by viscosity measurement for the solution of degraded PC and noticed that polymer undergoes random chain scission when it is thermally degraded in a sealed system,[2] whereas in a continuously evacuated system PC rapidly cross-links to form an insoluble gel through solubility measurement of the products.[3,4] Then, they studied the isothermal pyrolysis of PC using gas chromatography to determine the degradation products of PC in a continuously evacuated system.[5−7] They examined the thermal breakdown of a model compound, diphenyl carbonate, and postulated the rearrangement of diphenyl carbonate to form 2-phenoxybenzoic acid, which would undergo further ester exchange reaction with another diphenyl carbonate to give phenyl-2-phenoxybenzoate found as a product[5] (Scheme 1). Then, by extending this mechanism to the PC system, they proposed a hypothesis that the rearrangement of the carbonate group would form a pendant carboxyl group, ortho to an ether link, which would undergo further ester exchange reaction with another PC chain to form branching structure and/or insoluble gel[6,7] (Scheme 2). However, any pyrolysis products directly reflecting branching and/or cross-linking structures were not identified yet.

**Scheme 1**



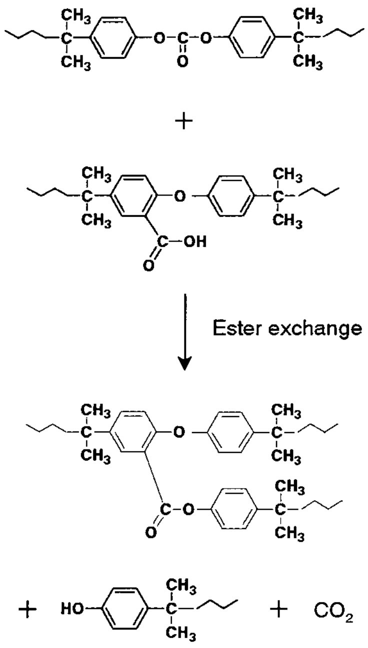
McNeill et al. studied the mechanism of thermal degradation of PC in the temperature range 300−500 °C and the formation processes of branching and/or cross-linking structures mainly using IR spectroscopy and GC−mass spectrometry (GC-MS) techniques by determining the degradation products of PC in a continuously evacuated system.[8,9] They observed BPA, the cyclic dimer of BPA carbonate and various phenols, and proposed the degradation mechanisms for PC through homolysis of the polymer chain and the subsequent reactions of the radicals so formed rather than through ester exchange. For example, the formation of the cyclic dimer of BPA carbonate, which is the major pyrolysis product, was explained by homolytic scission of C−C linkage between the isopropylidene group and the

---

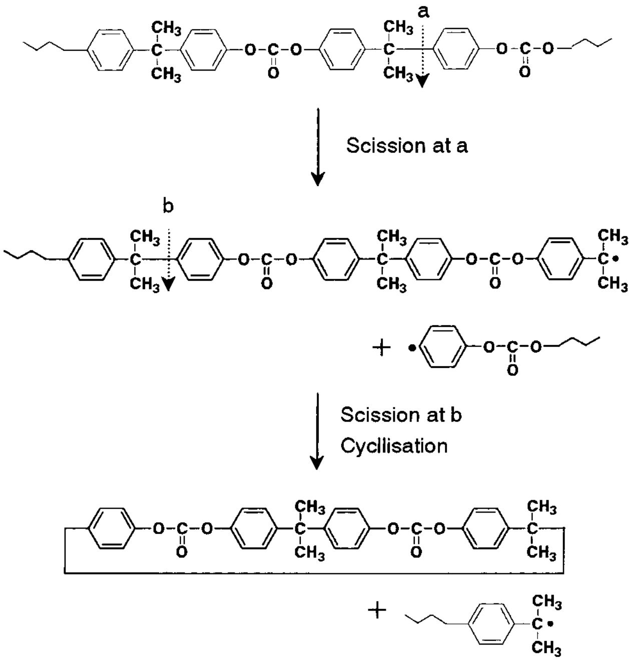
* To whom correspondence should be addressed: e-mail shin@apchem.nagoya-u.ac.jp; Tel +81-52-789-4664; Fax +81-52-789-4666.

10.1021/ma000596a CCC: $19.00

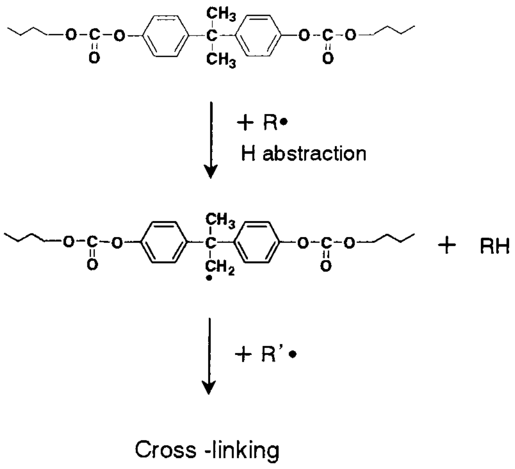
**Scheme 2**



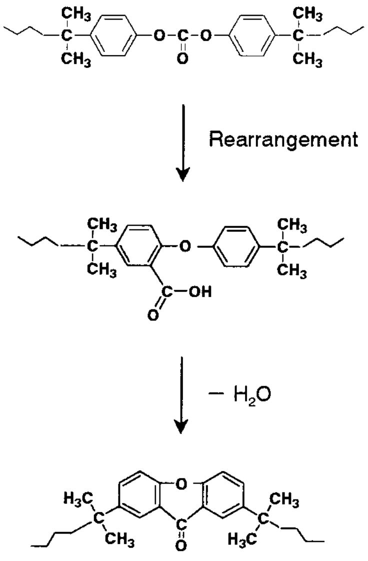
**Scheme 3**



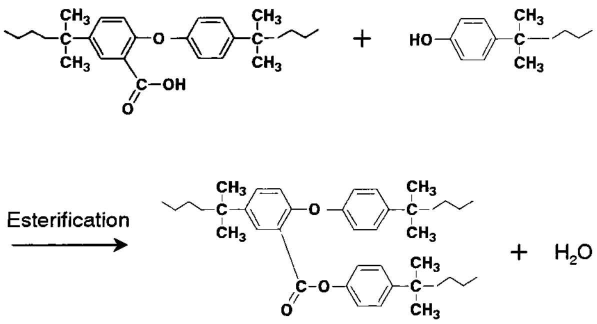
**Scheme 4**



**Scheme 5**



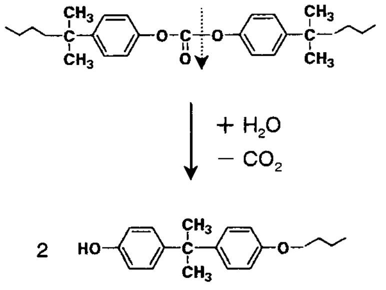
**Scheme 6**



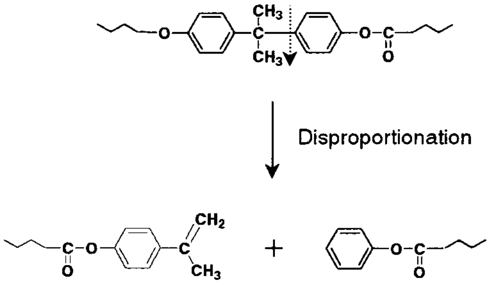
aromatic ring and end-biting reaction of the free-radical end[8,9] (Scheme 3). Furthermore, they speculated H-abstraction by polymer radical ($R^\bullet$) from the methyl group followed by cross-linking reaction of the on-chain polymer radical so formed with another radical ($R'^\bullet$)[8,9] (Scheme 4). However, they did not observe any specific pyrolysis products directly reflecting these branching and/or cross-linking structures.

Montaudo et al. investigated the thermal decomposition processes in PC by pyrolysis−mass spectrometry (Py-MS), during heating from room temperature to 600 or 700 °C by gradual heating at 10 °C/min in a continuously evacuated system.[10−14] On the spectra recorded at the initial stage of the thermal degradation (about 400 °C), they observed mainly BPA and the cyclic oligomers of BPA polycarbonate formed by intramolecular ester exchange processes, unlike the radical mechanism proposed by McNeill et al. On the spectra recorded at higher temperature (500 °C), they observed pyrolysis compounds with xanthone and with other condensed structure units in addition to some kinds of phenols. Thus, they proposed that compounds containing xanthone units were formed by rearrangement of the carbonate group to form a pendant carboxyl group and successive condensation[14] (Scheme 5). Furthermore, they speculated that cross-linking structures might be formed by the further esterification reaction, which would occur between the pendant carboxyl group and phenolic end group of the other polymer chain[12] (Scheme 6). Nevertheless, any specific pyrolysis compounds reflecting those structures were not identified in their

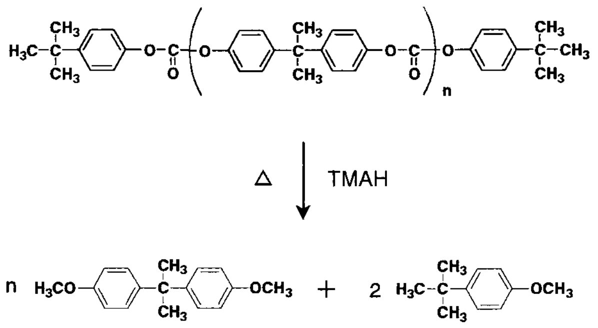
**Scheme 7**



**Scheme 8**



**Scheme 9**



spectra, since those branching and/or cross-linking related structures are contained in the pyrolysis residue mainly as an insoluble gel.

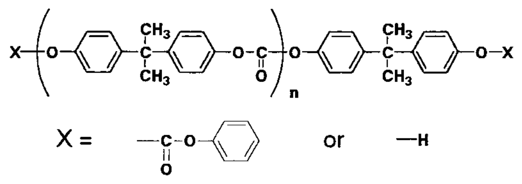
Recently, the same authors investigated the thermal decomposition of PC by heating isothermally at 300, 350, 400, and 450 °C under nitrogen flow and subsequent analysis of the soluble fractions of pyrolysis residue by means of matrix-assisted laser desorption ionization (MALDI) mass spectrometry.[15] On the spectra of the soluble pyrolysis products obtained at 300 and 350 °C, they observed the peaks corresponding to open chain oligomers with phenol end groups, generated by hydrolysis reaction of carbonate groups during heating of PC, as well as the peaks corresponding to cyclic oligomers and open chain oligomers with *tert*-butylphenyl carbonate groups at both ends (Scheme 7). In contrast, in the spectra of the soluble pyrolysis products obtained at 400 and 450 °C, they observed the peaks corresponding to not only PC chains terminated with phenol groups but also PC oligomers bearing a phenyl and/or an isopropylidene group, generated by the disproportionation of the aliphatic bridge of BPA, whereas the peaks corresponding to cyclic and *tert*-butylphenyl carbonate terminated linear oligomers were hardly observed (Scheme 8). Furthermore, in this work they also identified the peaks corresponding to PC oligomers containing xanthone units, which had been confirmed in their previous work.[14] However, any specific products containing branching and/or cross-linking structures were not identified yet, since those products, if any, would be contained in the insoluble fraction not favorable to the MALDI method.

**Table 1. Series of PC Samples**

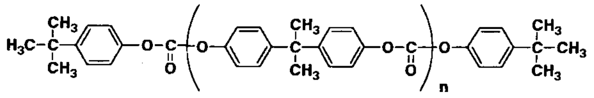
| Sample name | Preparation method | Mn[a] | Mw[a] | Mw / Mn |
|---|---|---|---|---|
| PC-1 | Industrial<br>the melt method | $1.3\times10^4$ | $3.2\times10^4$ | 2.5 |
| PC-2 | Insoluble fraction in $CHCl_3$ for thermally treated PC-1 at 300°C | - | - | - |
| PC-3 | Soluble fraction in $CHCl_3$ for thermally treated PC-1 at 300°C | $1.8\times10^3$ | $1.2\times10^4$ | 6.7 |
| PC-4 | Industrial<br>the solvent method | $2.3\times10^4$ | $5.8\times10^4$ | 2.5 |

[a] Estimated by SEC using polystyrene standards and corrected as described our previous report[18].

PC-1:



PC-4:



Recently, Challinor reported that pyrolysis−gas chromatography (Py-GC) in the presence of organic alkali, such as tetramethylammonium hydroxide (TMAH), was quite effective to the qualitative analysis of various condensation polymers.[16] Applying this technique, the authors have reported that compositional analysis and end group determination of condensation polymers, such as aromatic polyester and PC, were successfully achieved.[17−19] During reactive pyrolysis in the presence of TMAH, the PC polymer chains are decomposed selectively at carbonate linkages to yield quantitatively the methyl derivatives of the components for a given PC sample. For example, a PC sample synthesized by the solvent method is converted into mostly dimethyl ether of BPA together with small amount of *tert*-butylanisole which reflects the end groups (Scheme 9). Thus, this technique has been applied to highly sensitive end group determination of PC homopolymers[18] and to compositional analysis and determination of the end groups of PC copolymers.[19]

In this work, the reactive Py-GC technique was extendedly applied to verify the branching and/or cross-linking structures in industrially available PC and its thermally treated samples through identification of specific pyrolysis products directly reflecting the abnormal structures.

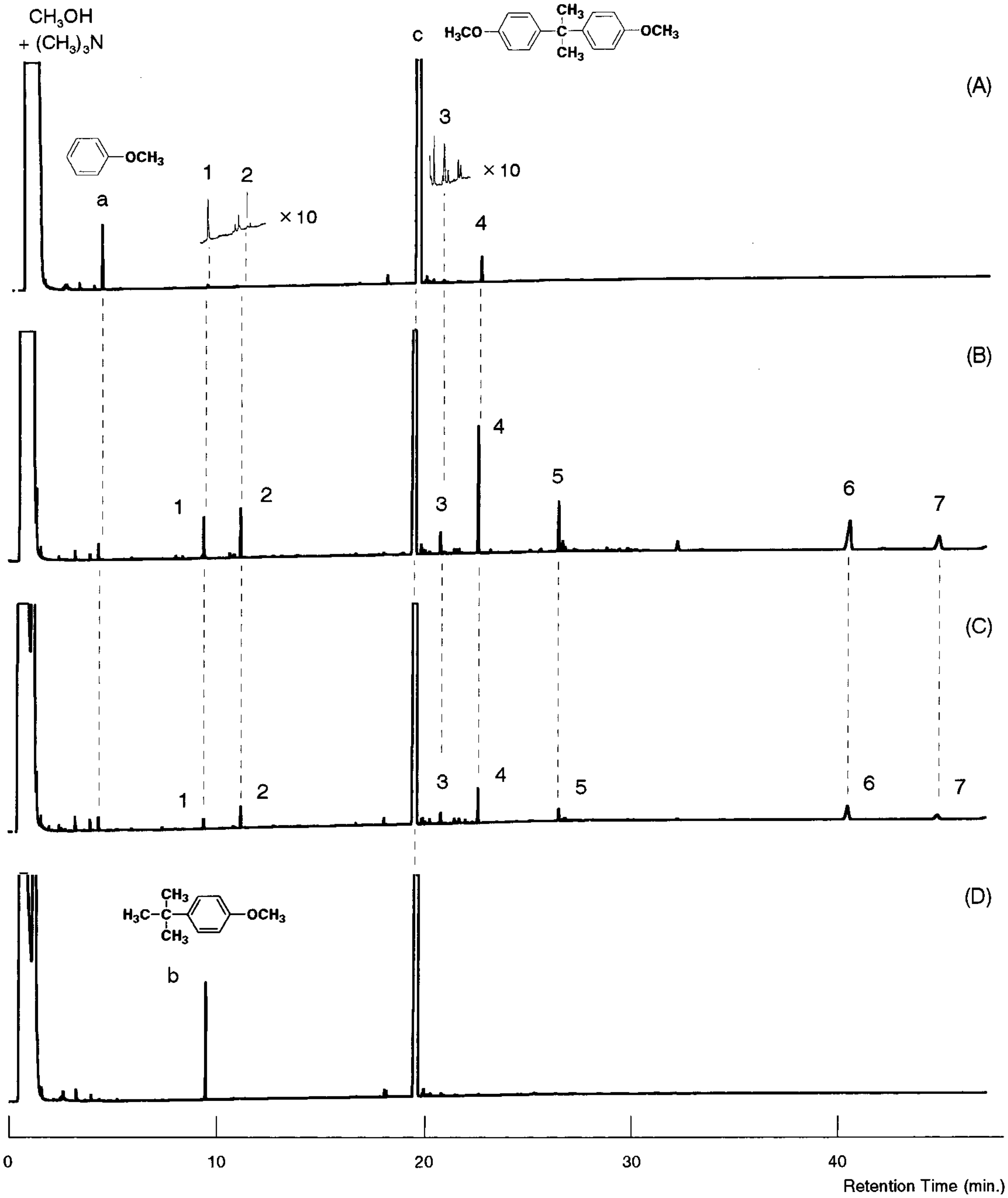


**Figure 1.** Pyrograms of the four kinds of PC samples obtained at 400 °C in the presence of TMAH. (A) PC-1, (B) PC-2, (C) PC-3, and (D) PC-4.

## Experimental Section

**Samples.** An industrially synthesized PC sample by the melt method (PC-1), thermally treated PC-1 samples (PC-2 and -3), and an industrially synthesized PC sample by the solvent method (PC-4) are used in this work. PC-1 and PC-4 are the same samples as used in our previous paper.[18]

An insolubilized PC sample (PC-2) was prepared as follows, assuming that branching and/or cross-linking reactions are occurring to some extent at higher temperatures in the polymerization reactor to synthesize PC by the melt method. After 1.2 g of PC-1 placed in a Pyrex beaker was heated for 3 h at 300 °C in a electric furnace in the presence of atmospheric oxygen, 50 mL of chloroform was added to the thermally treated sample with light brown color. Then, the insoluble fraction [PC-2 (about 0.3 g)] and the soluble one [PC-3 (about 0.8 g)] were separated by use of a glass filter. Both fractions were dried under vacuum at room temperature and cryomilled into a fine powder by a freezer mill (SPEX6750) at liquid nitrogen temperature. The four PC samples used in this work are listed in Table 1 together with their preparation method and average molecular weight data.

**Conditions for Py-GC.** The procedure for reactive pyrolysis is basically the same as was described in our previous papers.[17–19] A vertical microfurnace pyrolyzer (Yanaco GP-1018 improvement type) was directly attached to a gas chromatograph (HP4890) equipped with a flame ionization detector (FID). About 50 $\mu$g of a powdered PC sample and 1 $\mu$L of a methanol solution (25 wt %) of TMAH (Aldrich) taken in a platinum sample cup were introduced into the heated center of the pyrolyzer under the flow of helium carrier gas to proceed selective chemolysis at the carbonate (and the ester/ether) linkages to yield methyl derivatives of the whole components which had been connected serially through the carbonate (and the ester/ether) linkages in the original polymer chain. The relatively low pyrolysis temperature of 400 °C was used to suppress the contribution of random thermal cleavage of the polymer chain at higher temperatures. A fused silica capillary column coated with poly(dimethylsiloxane) immobi-

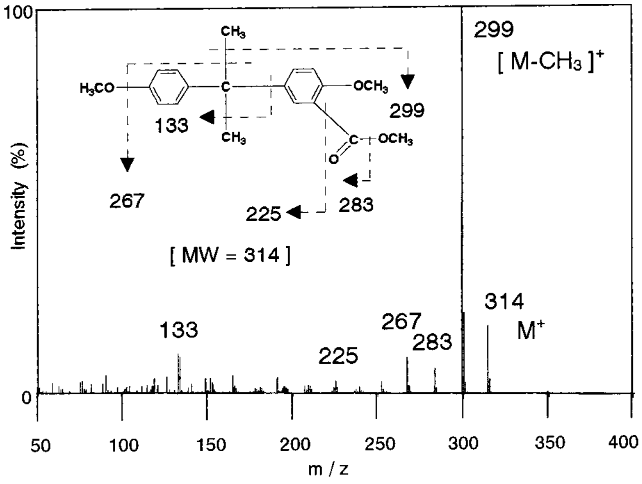


**Figure 2.** Mass spectrum of peak 4.

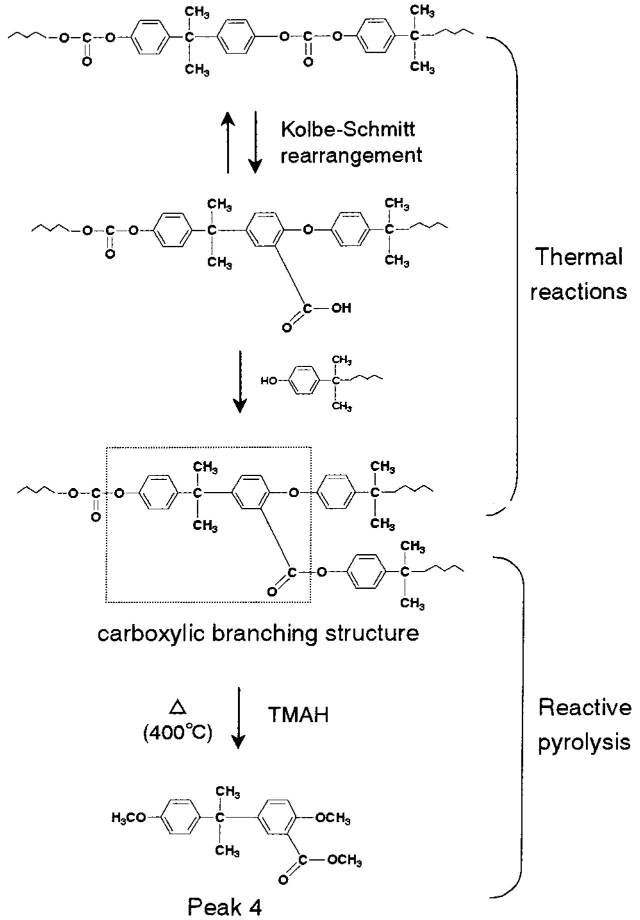


**Figure 3.** Formation pathway of the carboxylic branching structure and its characteristic product (peak 4).

lized by chemical cross-linking (HP Ultra 1, 25 m × 0.2 mm i.d., 0.33 $\mu$m film thickness) was used. The identification of the peaks on the pyrograms was carried out by use of the Py-GC/MS (Shimadzu QP-5050) with an electron impact ionization (70 eV) to which the pyrolyzer (Shimadzu PYR-4A) was also directly attached.

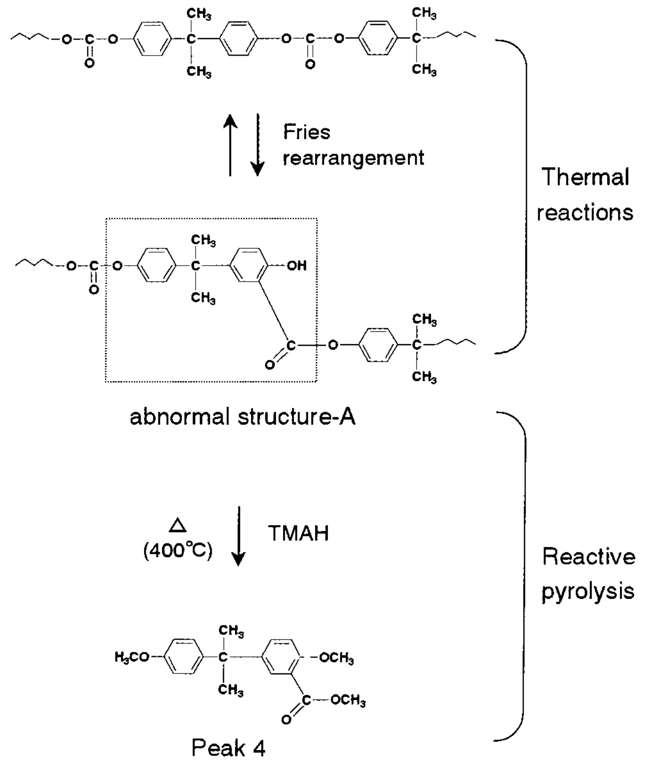


**Figure 4.** Formation pathway of the abnormal structure A and its characteristic product (peak 4).

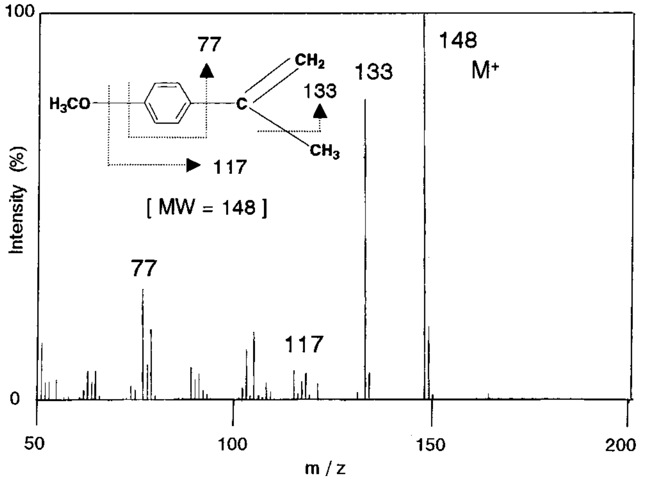


**Figure 5.** Mass spectrum of peak 1.

## Results and Discussion

Figure 1 shows the pyrograms of the four kinds of PC samples listed in Table 1 obtained by the reactive pyrolysis in the presence of TMAH at 400 °C. On the pyrogram for every PC sample, the methyl ether of BPA (peak c) reflecting the main chain and the ethers (peak a and b) reflecting the end groups are clearly observed, after the elution of trimethylamine and methanol formed from the TMAH solution.[18] Among these ethers, anisole (peak a) is commonly formed from the terminal phenoxy group of the melt-method-related PC samples (PC-1, -2, and -3) and *p*-*tert*-butylanisole (peak b) is formed from the terminal *p*-*tert*-butylphenoxy end group in the case of the solvent method PC (PC-4).[18] On the pyrograms of the melt-method-related samples (A, B, and C), peaks 1, 2, 3, and 4 are commonly observed; furthermore, the additional three peaks (peak 5, 6, and 7) are observed only on the pyrograms of the thermally treated PC samples (B and C). Some of these peaks might reflect abnormal structures, such as branching and/or cross-linking structures, formed during the synthesis by the melt method and/or thermal treatment at 300 °C, since these peaks are scarcely observed on the pyrogram of the solvent method PC (D). In the following, identification of those characteristic peaks was carried

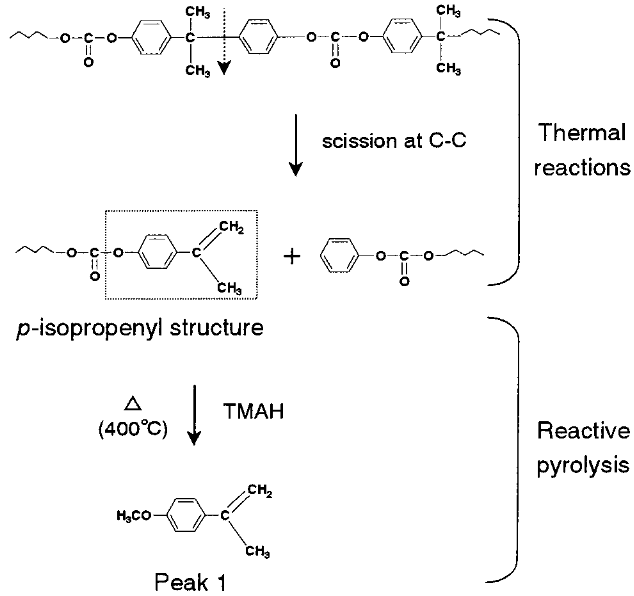


**Figure 6.** Formation pathway of the isopropenyl end group structure and its characteristic product (peak 1).

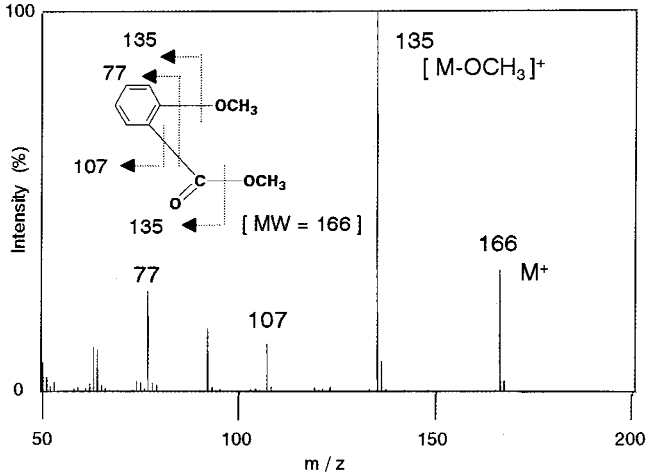


**Figure 7.** Mass spectrum of peak 2.

out mostly by interpreting their mass spectra, and possible abnormal structures constructed in the polymer chains of the melt-method-related PC samples were inductively estimated.

**Carboxylic Branching Structure.** Figure 2 shows the mass spectrum of peak 4 observed in the pyrograms (Figure 1A–C). In this spectrum, the molecular ion at *m/z* 314 and the base fragment ions at *m/z* 299, mainly formed through elimination of a methyl group from a isopropylidene group of the molecule, are observed. In addition, the fragment ions at *m/z* 283 and 267 formed through elimination of a methoxy and both methyl and methoxy groups from the molecule, and the fragment ions at *m/z* 225 and 133, which are characteristic of the dimethyl ether of BPA, are observed. Consequently, peak 4 can be assigned to the dimethyl ether of BPA with a methoxycarbonyl group [MW = 314]. Furthermore, the appearance of this pyrolysis product on the pyrograms suggests that the original polymer samples contained the carboxylic branching structure to some extent. Figure 3 shows the most probable formation process of the carboxylic branching structure through the condensation reaction between the pendant carboxyl group, formed by the Kolbe–Schmitt rearrangement of the carbonate group, and a phenolic end group of the other polymer chain, together with the formation pathway of peak 4 through the reactive pyrolysis of the branching moiety. Although the formation of the carboxylic branching structure during the thermal treatment of a PC was suggested by Davis et al.[6,7] and Montaudo et al.,[12] the clear identification of peak 4 by the reactive pyrolysis strongly supports the existence of the above-mentioned carboxylic branching structure. Moreover, alternative formation pathway for peak 4 is also probable through another abnormal structure (abnormal structure A) generated by the Fries rearrangement. The possible process of this type of rearrangement[14] and the formation root into the product for the peak 4 are shown in Figure 4.

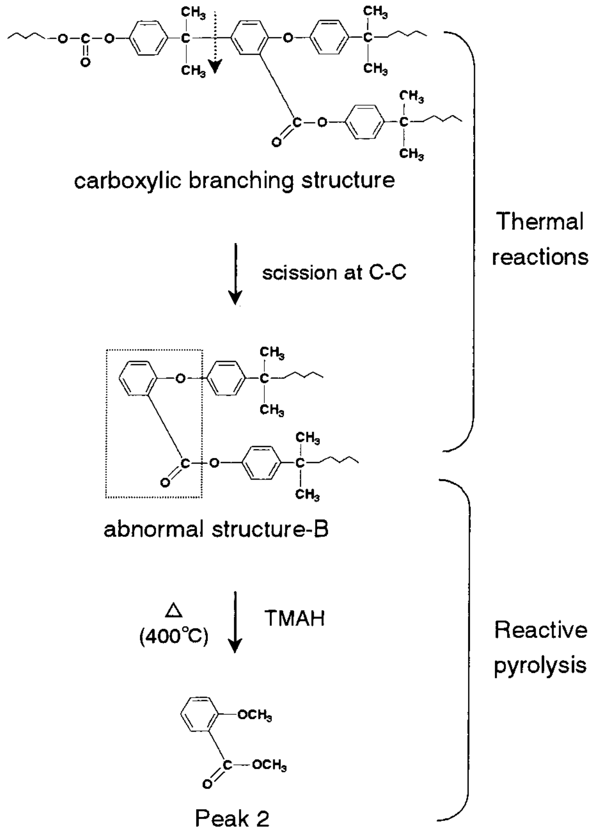


**Figure 8.** Formation pathway of the abnormal structure B and its characteristic product (peak 2).

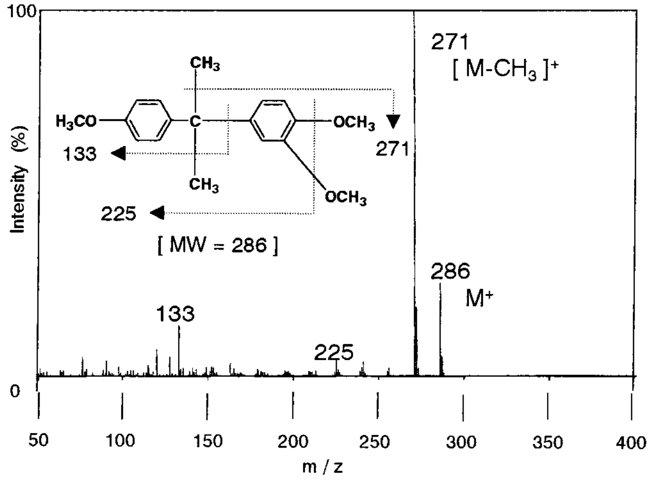


**Figure 9.** Mass spectrum of peak 3.

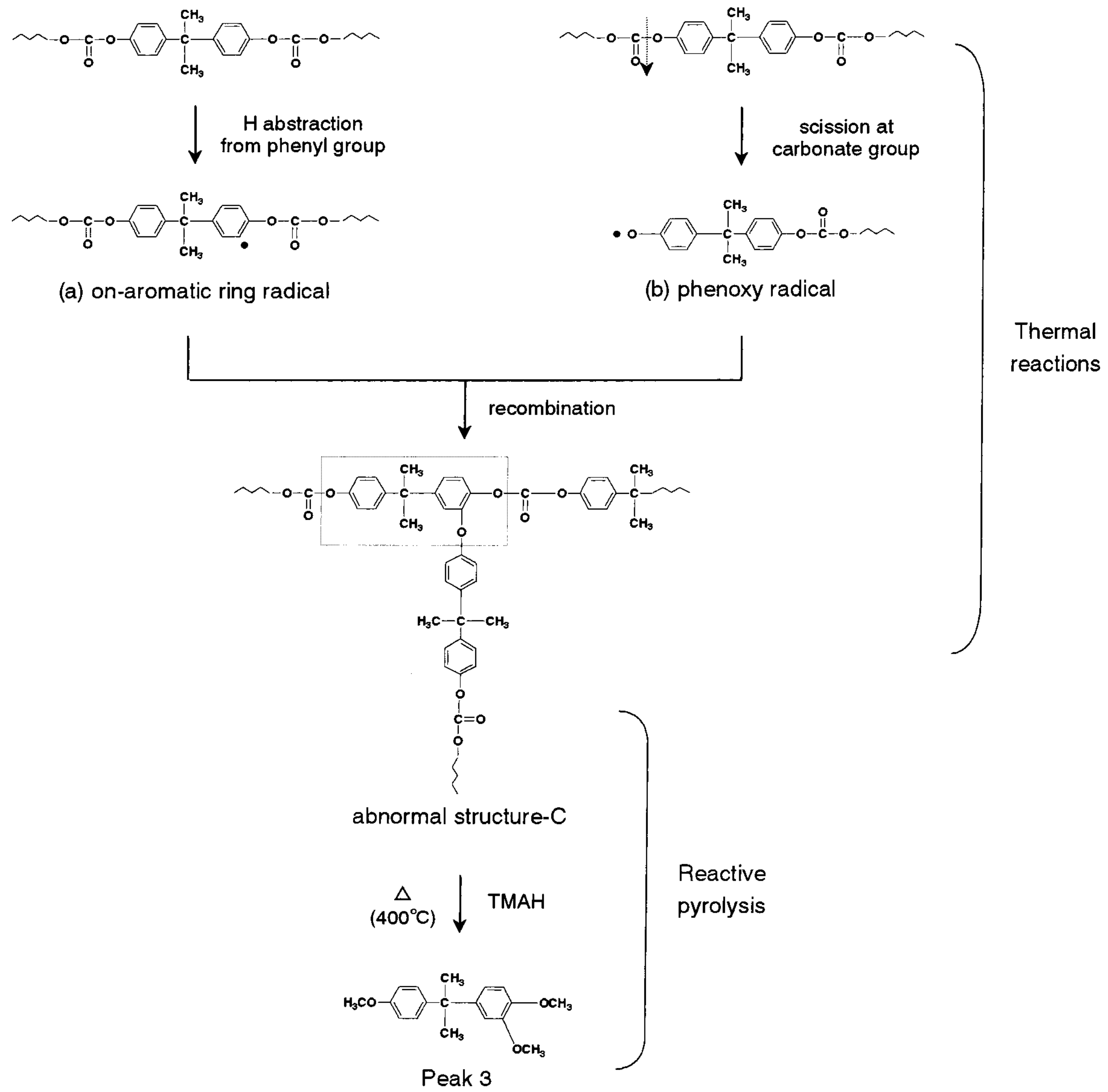


**Figure 10.** Formation pathway of the abnormal structure C and its characteristic product (peak 3).

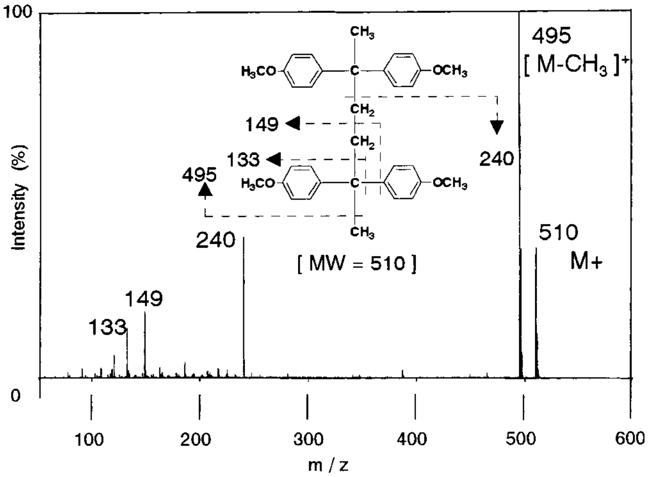


**Figure 11.** Mass spectrum of peak 6.

**Cleavage of Main Chain: Isopropenyl End Group and Abnormal Structure B.** Figure 5 shows the mass spectrum of peak 1 observed in the pyrograms (Figure 1A–C). In this spectrum, in addition to the intense molecular ion at *m*/*z* 148, the fragment ions at *m*/*z* 133 and 117, formed through elimination of a methyl and a methoxy groups from the molecule, respectively, and the ion at *m*/*z* 77, which are characteristic of the aromatic ring, are observed. Thus, peak 1 can be assigned to *p*-isopropenylanisole [MW = 148]. Furthermore, since appreciable cleavage of C–C bond would not occur under the reactive pyrolysis condition, the appearance of this product on the pyrograms suggests that the original polymer samples contained the isopropenyl end group structure to some extent especially in the thermally treated PC samples (PC-2 and -3). Recently, the same phenomenon was also reported through Py-MS and MALDI investigations of PC degradation by Montaudo et al.[14,15] Figure 6 shows the possible formation process of the isopropenyl end group structure through the disproportionation reaction of C–C bond between an isopropylidene group and an aromatic ring, together with the formation pathway of peak 1 through the reactive pyrolysis of the associated end group.

Figure 7 shows the mass spectrum of peak 2 observed in the pyrograms (Figure 1A–C). In this spectrum, the molecular ion at *m*/*z* 166 and the fragment ions at *m*/*z* 135, 107, and 77 are observed, and the latter fragment ions can be attributed to elimination of a methoxy, a methoxycarbonyl, and both of these groups from the

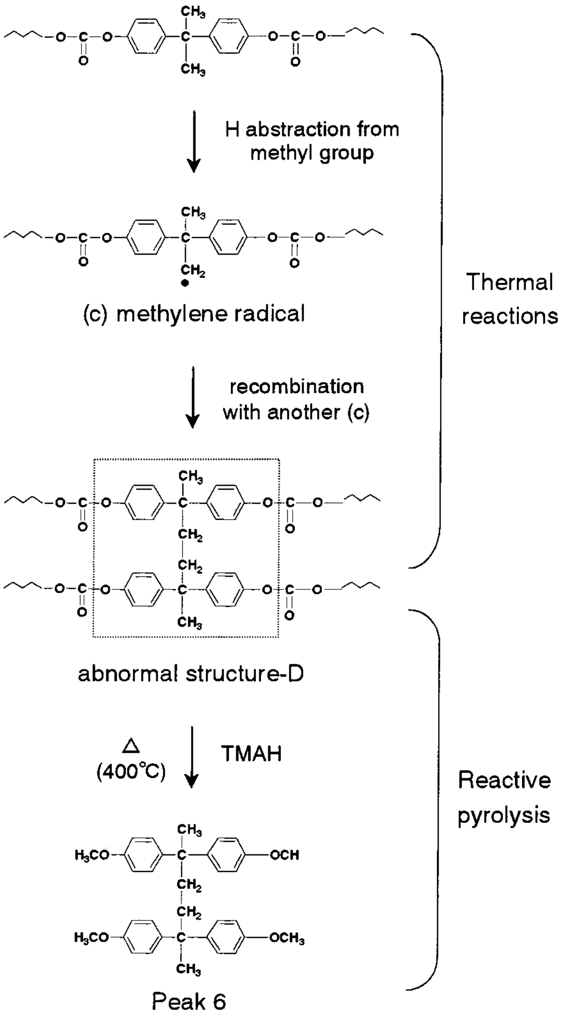


**Figure 12.** Formation pathway of the abnormal structure D and its characteristic product (peak 6).

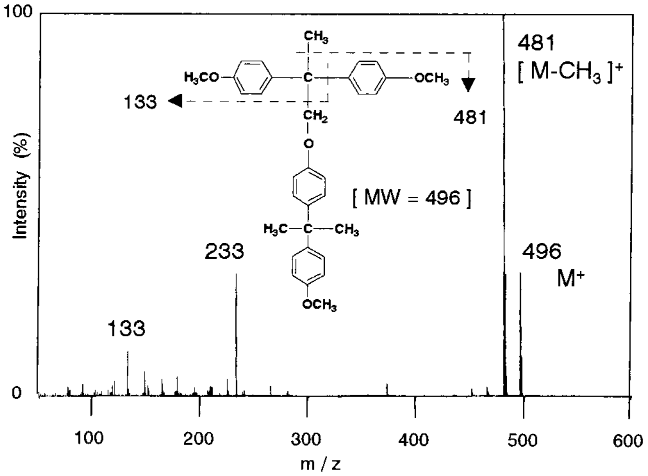


**Figure 13.** Mass spectrum of peak 7.

molecule, respectively. Thus, peak 2 can be assigned to *o*-methoxycarbonyl anisole [MW = 166]. The appearance of this pyrolysis product on the pyrograms suggests that the original polymer contained an abnormal structure (abnormal structure B), which would be formed through the disproportionation reaction of C−C bond neighboring the carboxylic branching structure of which formation pathway was explained in Figure 3. Figure 8 shows the possible formation process of the abnormal structure B through the thermal reaction via the carboxylic branching structure, together with the formation pathway of peak 2 through the reactive pyrolysis of the abnormal structure B.

**Cross-Linking Structure Formed through the Thermal Reaction of Phenoxy and On-Aromatic Ring Radicals: Abnormal Structure C**. Figure 9 shows the mass spectrum of peak 3 observed in the pyrograms (Figure 1A−C). In this spectrum, the molecular ion at *m*/*z* 286, the base fragment ions at *m*/*z* 271, mainly formed through elimination of a methyl group from isopropylidene group of the molecule, and the fragment ions at *m*/*z* 225 and 133, which are characteristic of the dimethyl ether of BPA, are observed. Thus, peak 3 can be assigned to the dimethyl ether of BPA with an additonal methoxy group [MW = 286]. Therefore, the appearance of this pyrolysis product on the pyrograms suggests that the original polymer samples contained another cross-linking structure (abnormal structure C), which would be formed through the recombination reaction of phenoxy and on-aromatic ring radicals, to some extent especially in the thermally treated PC samples (PC-2 and -3). Figure 10 shows the possible formation process of the abnormal structure C through the thermal reactions associated with the on-aromatic ring and the phenoxy radicals, together with the formation pathway of peak 3 through the reactive pyrolysis of the abnormal structure C. Although McNeill et al. proposed the formation of the phenoxy radical by homolysis of a carbonate group during the thermal treatment of a PC,[8,9] the identification of peak 3 by the reactive pyrolysis suggested not only the phenoxy but also the on-aromatic ring radicals might contribute to the formation of another cross-linking structure shown in Figure 10.

**Cross-Linking Structure Formed through the Thermal Reactions of Methylene Radicals: Abnormal Structure D**. Figure 11 shows the mass spectrum of peak 6 observed only in the pyrograms of the thermally treated PC-2 and -3 (Figure 1B,C). In this spectrum, the molecular ion at *m*/*z* 510, the base fragment ions at *m*/*z* 495, formed through elimination of a methyl group from the molecule, and the fragment ions at *m*/*z* 240, 149, and 133, which are characteristic of the dimethyl ether of BPA, are observed. Consequently, peak 6 can be assigned to a dimer of the dimethyl ether of BPA linked through each methyl group [MW = 510]. Furthermore, the fact that this pyrolysis product is observed only on the pyrograms of the thermally treated PC samples suggests that those samples contained another cross-linking structure (abnormal structure D) to some extent. Figure 12 shows the most probable formation process of the abnormal structure D through the recombination reaction between the methylene radicals, formed by H abstraction from a methylene group, together with the formation pathway of peak 6 through the reactive pyrolysis of the branching moiety. Although the formation of the methylene radical and a subsequent cross-linking reaction of the radicals so formed during the thermal treatment of a PC speculated by McNeill et al.,[8,9] the identification of peak 6 by the reactive pyrolysis is the first clear evidence for the existence of the above-mentioned cross-linking structure in the thermally treated PC samples.

**Cross-Linking Structure Formed through Thermal Reactions of Methylene and Phenoxy Radicals and Abnormal Structure Generated from This Structure: Abnormal Structure E and F.** Figure 13

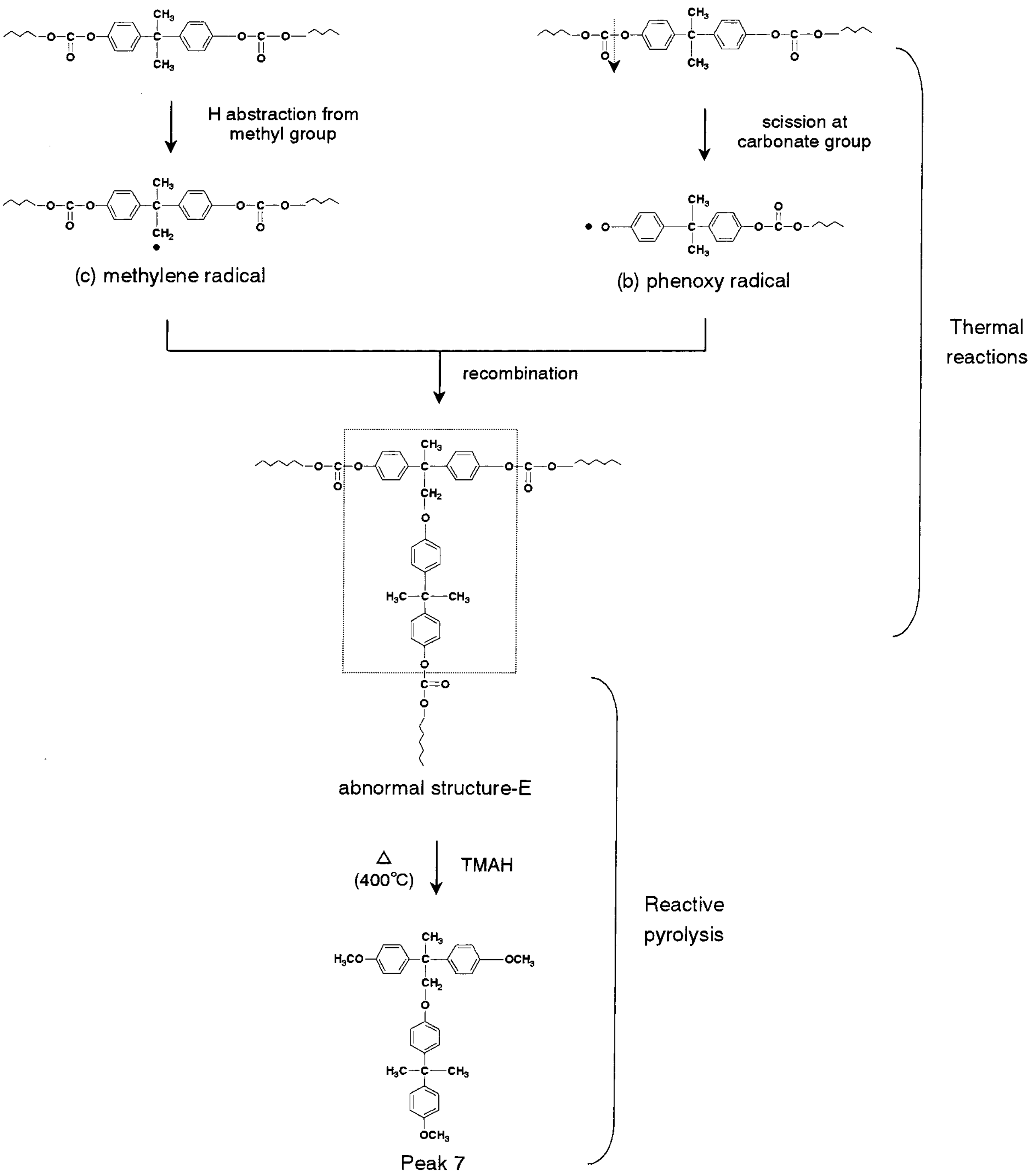
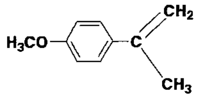
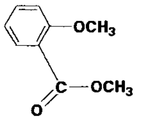
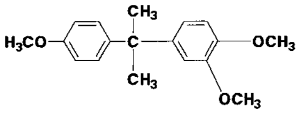
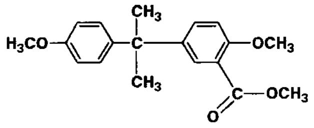
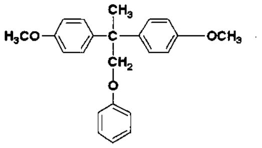
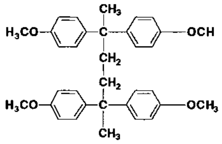
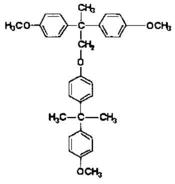


**Figure 14.** Formation pathway of the abnormal structure E and its characteristic product (peak 7).

shows the mass spectrum of peak 7 observed in the pyrograms (Figure 1B,C). In this spectrum, the molecular ion at *m*/*z* 496, the base fragment ions at *m*/*z* 481, formed through elimination of a methyl group from the molecule, and the fragment ions at *m*/*z* 133, which are characteristic of the dimethyl ether of BPA, are observed. Thus, peak 7 can be assigned to a dimer of the methyl ether of BPA linked through methyl and hydroxyl groups of respective molecules [MW = 496]. Therefore, the appearance of this pyrolysis product only on the pyrograms of the thermally treated PC samples suggests that those PC samples contained another cross-linking structure (abnormal structure E), which would be formed to some extent through the recombination reaction of the methylene and the phenoxy radicals. Figure 14 shows the probable formation process of the abnormal structure E, together with the formation pathway of peak 7 through the reactive pyrolysis of the abnormal structure E.

Figure 15 shows the mass spectrum of peak 5 observed in the pyrograms (Figure 1B,C). In this spectrum, the molecular ion at *m*/*z* 348, the base fragment ions at *m*/*z* 333, formed through elimination of a methyl group from the molecule, and the fragment ions at *m*/*z* 133, which are characteristic of the dimethyl ether of BPA, are observed. Thus, peak 5 can be assigned to a dimethyl ether of BPA with a phenoxy group [MW = 348]. The appearance of this pyrolysis product suggests that the thermally treated PC samples contained another abnormal structure (abnormal structure F), which would be formed through the disproportionation reaction of the C−C bond at the abnormal structure E moiety. Figure 16 shows the probable formation process of the abnormal structure F through the thermal

**Table 2. Relative Molar Abundance of the Abnormal Structures in PC Samples**

| Peak No[a] | Structure<br>$C_XH_YO_Z$ MW[b] | Relative abundance ( mol% )[c] | | |
|---|---|---|---|---|
| | | PC-1<br>(MM-PC) | PC-3<br>(soluble fraction) | PC-2<br>(insoluble fraction) |
| 1 | <br>$C_{10}H_{12}O_1$ 148<br>(p-propenyl phenoxy end) | 0.06 | 0.25 | 1.57 |
| 2 | <br>$C_9H_{10}O_3$ 166<br>(abnormal structure-B) | 0.01 | 0.71 | 2.43 |
| 3 | <br>$C_{18}H_{22}O_3$ 286<br>(abnormal structure-C) | 0.05 | 0.21 | 0.56 |
| 4 | <br>$C_{19}H_{22}O_4$ 314<br>(carboxylic structure) | 0.49 | 0.56 | 3.25 |
| 5 | <br>$C_{23}H_{24}O_3$ 348<br>(abnormal structure-F) | - | 0.20 | 1.20 |
| 6 | <br>$C_{34}H_{38}O_4$ 510<br>(abnormal structure-D) | - | 0.48 | 1.85 |
| 7 | <br>$C_{33}H_{36}O_4$ 496<br>(abnormal structure-E) | - | 0.19 | 0.93 |

[a] Peak numbers correspond to those on the pyrograms in Figure 1.

[b] Molecular weight.

[c] Calculated from relative peak intensities on the pyrograms in Figure 1.

reactions via the abnormal structure E, together with the formation pathway of peak 5 through the reactive pyrolysis of the abnormal structure F. The fact that the hydrogen abstraction to generate the methylene radical, which relates to peaks 6 and 7 as well as peak 5, would be mainly attributed to pyrolysis process was confirmed

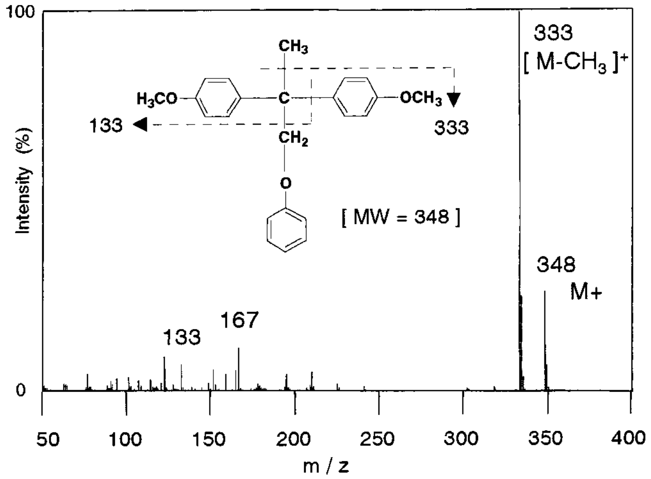


**Figure 15.** Mass spectrum of peak 5.

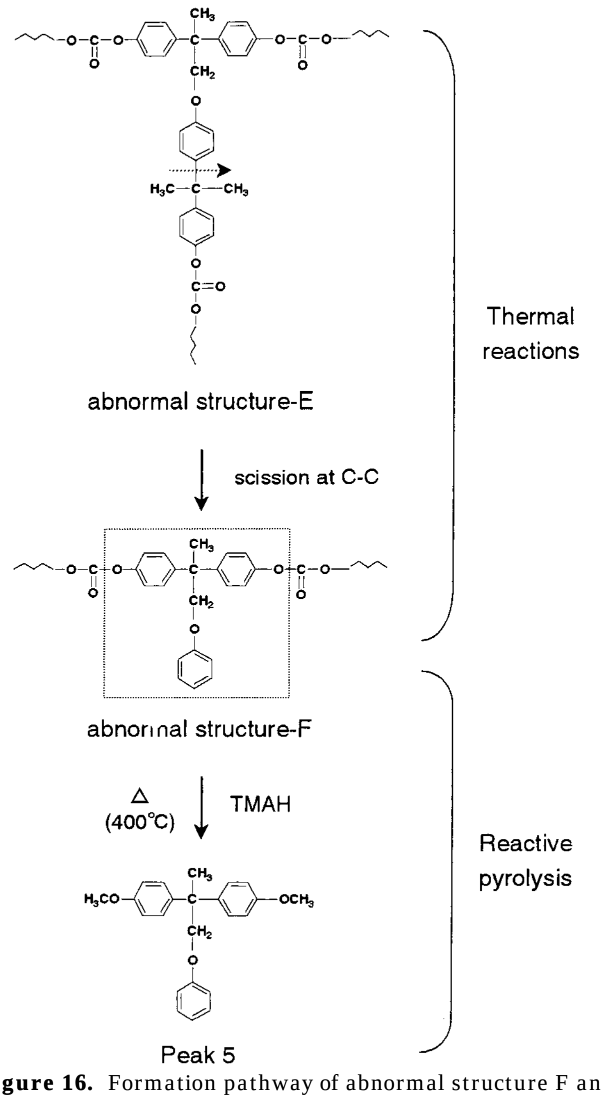


**Figure 16.** Formation pathway of abnormal structure F and its characteristic product (peak 5).

by the experimental results that these peaks were also clearly observed on the pyrograms of the other PC samples thermally treated under inert atmosphere flowing nitrogen.

To make quantitative discussion of the abnormal structures, Table 2 summarizes the relative concentrations of the specific peaks formed from the abnormal structures against that of the BPA formed from the main chain of the melt method-related PC samples. As was expected, the whole abnormal structures were most abundantly observed for the insoluble fraction of thermally treated PC (PC-2), less for the soluble fraction (PC-3) and least for the original PC before the thermal treatment (PC-1). However, it is interesting to note that peak 4 reflecting the carboxylic branching structure amounted to about 0.49 mol % even in PC-1, which suggested that the industrially available PC sample prepared by the melt method would contain about one unit of the branching structure per four chains when considering its number-average molecular weight ($M_n = 1.3 \times 10^4$), provided that the products for peak 4 were exclusively formed from the carboxylic branching structure.

Finally, any specific products containing a xanthone unit, which have been ascertained to form during the thermal degradation of PC by Montaudo et al.,[12,14,15] were missing not only on the pyrogram of the present reactive Py-GC measurement at 400 °C but also on the pyrogram of conventional Py-GC measurement at 600 °C without adding TMAH. These observations suggest that those xanthone-related structures, if any in our tested samples, would undergo hydrolysis into another structure such as the product for peak 4 during the reactive pyrolysis, and those distorted structures might degrade in preference to the ordinary PC structure when pyrolyzing at higher temperatures. Since the other possible reason for the absence of any xanthone-related product in the pyrograms could be attributed to the relatively lower treating temperature at 300 °C when considering the report of Montaudo et al.,[15] further studies for the PC samples thermally treated at higher temperatures than 300 °C are currently in progress with both Py-GC and MALDI-MS measurements.

## References and Notes

(1) Schnell, H. In *Chemistry and Physics of Polycarbonates*; Interscience Publishers: Wiley: New York, 1964; Chapter 3, p 44.
(2) Davis, A.; Golden, J. H. *Makromol. Chem.* **1964**, *78*, 16−23.
(3) Davis, A.; Golden, J. H. *Nature* **1965**, *206*, 397.
(4) Davis, A.; Golden, J. H. *Makromol. Chem.* **1967**, *110*, 180−184.
(5) Davis, A.; Golden, J. H. *J. Chem. Soc. B* **1968**, 40−45.
(6) Davis, A.; Golden, J. H. *J. Chem. Soc. B* **1968**, 45−47.
(7) Davis, A.; Golden, J. H. *J. Macromol. Sci., Rev. Macromol. Chem.* **1969**, *C3*, 49−68.
(8) McNeill, I. C.; Rincon, A. *Polym. Degrad. Stab.* **1991**, *31*, 163−180.
(9) McNeill, I. C.; Rincon, A. *Polym. Degrad. Stab.* **1993**, *39*, 13−19.
(10) Fotti, S.; Giuffrida, M.; Marabvigna, P.; Montaudo, G. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1567−1581.
(11) Montaudo, G.; Puglisi, C.; Samperi, F. *Polym. Degrad. Stab.* **1991**, *31*, 291−326.
(12) Montaudo, G.; Puglisi, C. *Polym. Degrad. Stab.* **1992**, *37*, 91−96.
(13) Montaudo, G.; Puglisi, C.; Samperi, F. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 13−25.
(14) Puglisi, C.; Sturiale, L.; Montaudo, G. *Macromolecules* **1999**, *32*, 2194−2203.
(15) Puglisi, C.; Samperi, F.; Carroccio, S.; Montaudo, G. *Macromolecules* **1999**, *32*, 2194−2203.
(16) Challinor, J. M. *J. Anal. Appl. Pyrolysis* **1989**, *16*, 323−333.
(17) Ohtani, H.; Fujii, R.; Tsuge, S. *J. High Res. Chromatogr.* **1991**, *14*, 388−391.
(18) Ito, Y.; Ogasawara, H.; Ishida, Y.; Tsuge, S.; Ohtani, H. *Polym. J.* **1996**, *28*, 1090−1095.
(19) Ishida, Y.; Kawaguchi, S.; Ito, Y.; Tsuge, S.; Ohtani, H. *J. Anal. Appl. Pyrolysis* **1997**, *40−41*, 321−329.

MA000596A