Macromol. Symp. ***195***, *287–292 (2003)*

Novel Characterization of Branching and/or Cross-linking Structures in Condensation Polymers by Reactive Pyrolysis-Gas Chromatography in the Presence of Organic Alkaline

Shin Tsuge, Hajime Ohtani, Keishi Oba*

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

Summary: The reactive pyrolysis-gas chromatography technique was applied to verify the branching and/or cross-linking structures in an industrially available polycarbonate (PC) sample and its thermally treated one through identification of specific pyrolysis products directly reflecting the related abnormal structures. On the pyrogram of the thermally treated sample, the peaks reflecting the abnormal structures such as branching and/or cross-linking were observed together with those reflecting main chain and end groups. 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 PC synthesized by the melt method.

Keywords: branched; crosslinking; polycarbonates; pyrolysis; pyrolysis-gas chromatography, tetramethyl ammonium hydroxide

Introduction

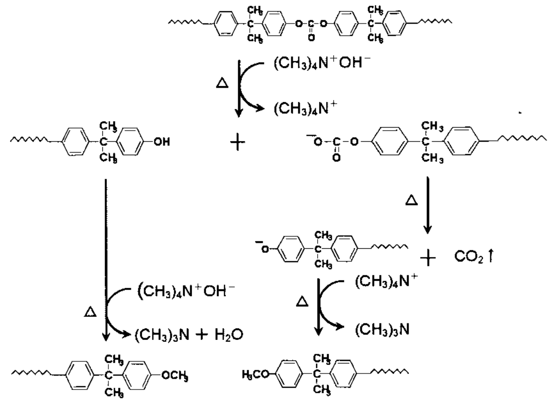
Some condensation polymers are known to contain the fraction with branching and insoluble cross-linking structures to some extent formed concomitantly under relatively higher polymerization temperatures. Furthermore, the condensation polymers are often subjected to injection molding operations at higher temperatures above 300°C causing network formation through the branching and cross-linking to some extent. Among such condensation polymers, 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) and the melt method (MM). The latter MM-PC is known to contain fractions with branching and/or insoluble cross-linking structures to some extent formed under relatively higher polymerization temperatures around 200-300°C. Characterization of these branching and/or cross-linked structures is often requested because these

CCC 1022-1360/00/$ 17,50+.50/0

structures are closely associated with optical and mechanical properties of the PC materials. However, mainly because of their insoluble nature, their analyses are not an easy task even by conventional spectroscopic methods such as NMR which have been most extensively utilized for soluble polymeric materials.

Recently, pyrolysis-gas chromatography (Py-GC) in the presence of organic alkali, such as tetramethylammonium hydroxide (TMAH ; $(CH_3)_4N^+HO^-$), has been reported to be quite effective to the detailed characterization of various condensation polymers. For example, 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 as shown in the Scheme 1.

Applying this technipue, the authors have been successfully achieved compositional analysis and end group determination of condensation polymers, such as aromatic polyester and PC.[1-3] 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.[4-6]



Scheme 1

Experimental Section

Samples: Industrially synthesized PC samples by SM (PC-1) and by MM (PC-2) , and an insolubilized PC sample (PC-3) formed through thermal treatment of PC-2 were used in this work. The thermal treatment of PC-2 weighing ca.1.2 g was carried out in a Pyrex beaker at 300°C for 3 h in an electric furnace in the presence of atmospheric oxygen 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. The insolubilized PC fraction (PC-3) was separated by use of a glass filter from the chloroform solution of the thermally treated PC-2. Table 1 summarizes these PC samples.

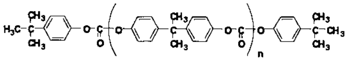
Table 1. PC samples

Sample code	Preparation method	M_n ($\times 10^4$)[a)]	Degree of branching and/or cross-linking structures
PC-1[b)]	Industrial the solvent method	2.3	Low
PC-2[b)]	Industrial the melt method	1.3	Somewhat
PC-3	Insoluble fraction in $CHCl_3$ for thermally treated PC-2 at 300°C	–	Considerable

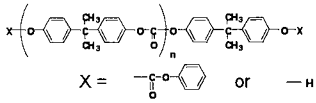
a) Estimated by SEC using polystyrene standards and corrected as described in ref. 2.

b) Chemical structures for PC-1 and PC-2

PC-1



PC-2



Conditions for Py-GC: A vertical microfurnace pyrolyzer (Frontier Lab. PY-2020D) was directly attached to a gas chromatogragh (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 TMAH taken in a platinum sample cup were introduced into the center of the pyrolyzer, heated at 400°C under a flow of helium carrier gas. To observe the higher boiling point products, a metal capillary column coated with polydimethylsiloxane (Frontier Lab. Ultra-Alloy-PY-1, 30 m×0.25 mm ID, 0.25 μm film thickness) was used. The column temperature was programmed from 50 to 370°C at a rate of 10 °C/ min. The identification of the peaks on the pyrograms was carried aut by use of a GC/MS (Jeol Automass system II) to which the same pyrolyzer was also directly attached.

Results and Discussion

Figure 1 shows the pyrograms of the three kinds of PC samples listed in Table 1 obtained by the reactive pyrolysis in the presence of TMAH at 400°C. Table 2 summarizes the characteristic products on the pyrograms identified by Py-GC/MS in order of their retention times, together with their origin. On the pyrogram for every PC sample, the methyl ether of BPA (peak c) reflecting the main chain and the ethers (peaks a and b) reflecting the end groups are clearly observed.[2] On the pyrograms of the MM-related PC samples (B and C), peaks 1-5 are commonly observed, and the additional peaks 6-10 are observed only on the pyrogram for the thermally treated MM-PC sample (C). Some of these peaks might reflect abnormal structures formed during its synthesis and/or thermal treatment at 300°C, since these peaks are scarcely observed on the pyrogram of the solvent method PC (A).

Among these products, peak 5 component can be assigned to the dimethyl ether of BPA with a methoxycarbonyl group. The appearance of this pyrolysis product on the pyrogram of the MM-PC sample (Fig.1(B) for PC-2) suggests that the carboxylic branching structure may be formed to some extent during the polymerization by the melt method. Figure 2 shows the most probable formation process of the carboxylic branching structure formed through the Kolbe-Schmitt and/or the Fries rearrangement of the carbonate group, together with the formation pathway of the peak 5 component through the reactive pyrolysis of the branching moiety.

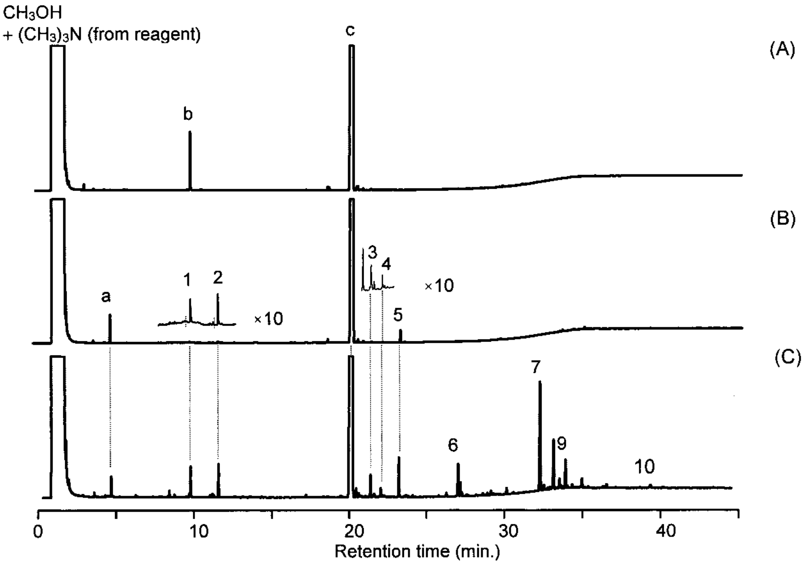
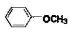
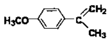
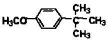
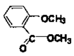
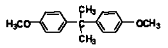
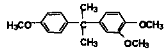
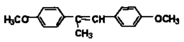
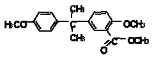
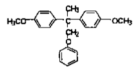
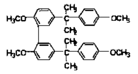
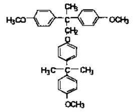
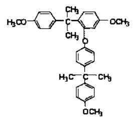
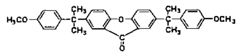


Figure 1. Pyrograms of PC samples obtained at 400°C in the presence of TMAH
(A) PC-1, (B) PC-2, (C) PC-3. Peak numbers correspond to those in Table 2.

In addition, since cleavage of C-C bond would be negligible during the reactive pyrolysis at 400°C, the appearance of peak 1 (*p*-isopropenyl anisole) on the pyrogram of PC-2 (Fig.1(B)) suggests that the MM-PC contained the isopropenyl end group structure formed through the disproportionation reaction of a C(CH_3)-phenylene bond to some extent. This peak was more intensely observed for the thermally treated PC sample (PC-3). In a similar manner, peak 2 reflecting the disproportionation reaction of the C-C bond neighbored by the carboxylic branching structure was observed for the MM-related PC samples (PC-2 and PC-3).

On the other hand, peaks 6-9, which are exclusively observed in the pyrogram of the insolubilized PC (Fig.1(C)), should be derived from other type of branching and cross-linking structures such as CH_2-O (peaks 6 and 8), biphenyl (peak

Table 2. Identification of the characteristic peaks on the pyrograms shown in Figure 1 and their classification

Peak no[a]	Retention time (min.)	Structure	Classification for the corresponding structure in PC chain[b]
a	5.1		I
1	10.1		III
b	10.2		I
2	11.9		III
c	20.5		I
3	21.8		II
4	22.6		III
5	23.6		II
6	27.5		III
7	32.7		II
8	33.6		II
9	34.3		II
10	39.5		III

a) Peak numbers correspond to those on the pyrograms in Fig. 1.

b) I : Main chain or original terminal groups.

II : Branching or cross-linking structures formed during the thermal treatments.

III : Abnormal structures formed during the thermal treatment except for the branching and cross-linking structures.

7) and phenylene-O bridges, formed during the thermal treatment at 300°C. Furthermore, the identification of peak 10 also proved the existence of xanthone structures which had been verified to exist thermally treated PC samples by MALDI-MS.[7]

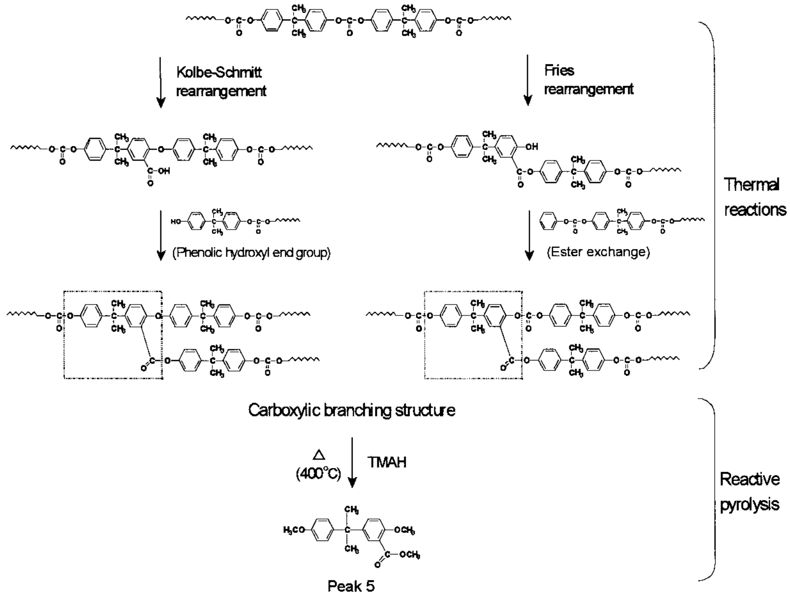


Figure 2. Formation pathway of carboxylic branching structure and its characteristic product (peak 5)

Finally, the contents of the abnormal structures were estimated based on the relative peak intensities of the corresponding peaks. For example, the content of xanthone structure in PC-3 was quantified to be ca. 0.11 mol %. On the other hand, the fact that peak 5 reflecting the carboxylic branching structure amounted to be about 0.49 mol% even for PC-2 suggests that the original MM-PC sample would contain about one unit of the branching structure per four polymer chains when considering its number average molecular weight ($M_n = 1.3 \times 10^4$).

[1] H. Ohtani, R. Fujii, S. Tsuge, *J. High Res. Chromatogr.* **1991**, *14*, 388.
[2] Y. Ito, H. Ogasawara, Y. Ishida, S. Tsuge, H. Ohtani, *Polym. J.* **1996**, *28*, 1090.
[3] Y. Ishida, S. Kawaguchi, S. Tsuge, H. Ohtani, *J. Anal. Appl. Pyrolysis* **1996**, *40-41*, 321.
[4] K. Oba, Y. Ishida, H. Ohtani, S. Tsuge, *Macromolecules* **2000**, *33*, 8173.
[5] K. Oba, H. Ohtani, S. Tsuge, *Polym. Degrad. Stab.* **2001**, *74*, 1711.
[6] K. Oba, Y. Ishida, H. Ohtani, S.Tsuge, *Polym. Degrad. Stab.* **2002**, *76*, 85.
[7] C. Puglisi, L. Sturiale, G. Montaudo, *Macromolecules* **1999**, *32*, 2194.