Polymer Bulletin 48, 483–490 (2002)

Polymer Bulletin

Flame retarding mechanism of polycarbonate containing trifunctional phenylsilicone additive studied by analytical pyrolysis techniques

Kenichi Hayashida[1], Hajime Ohtani (✉) [1], Shin Tsuge[1], Koji Nakanishi[2]

[1]Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
[2]Dow corning Toray Silicone Co., Ltd., S&T Div., Ichihara 299-0108, Japan
e-mail hajime@apchem.nagoya-u.ac.jp; Fax +81-52-789-4666

Received: 20 May 2002 / Accepted: 10 June 2002

Summary

The flame retarding mechanism for polycarbonate (PC) by a trifunctional phenyl-rich silicone additive was studied by analytical pyrolysis techniques. In order to clarify the actions of the silicone-based flame retardant for PC substrate during combustion, the change in the chemical structure of the flame retarded PC with the silicone additive (FR-PC) after thermal treatment at 380 ºC was investigated by pyrolysis-gas chromatography (Py-GC) in the presence of organic alkali. On the pyrogram of the thermally treated FR-PC, which exhibited highly insoluble nature, the peaks reflecting the abnormal structures, formed through the reaction between a silyl radical originating from the additive and an ether like oxygen atom in the carbonate linkage of the PC chain accompanied by decarboxylation or Fries rearrangement, were clearly observed in much larger intensity than those on the pyrogram of the thermally treated PC. On the basis of the observed results for the thermally treated FR-PC, it was suggested that the formation of a char barrier on the surface of the FR-PC material was promoted during combustion to reduce the radiant heat of flame and to restrict the diffusion of flammable degradation products into the combustion zone. Thus formed cross-linking structure might surpress the thermal decomposition and confine the movements of the degradation products.

Introduction

Brominated flame retardants have been often added to polymeric materials in practical use because of their extremely high flame retardancy, although the compounds might generate possibly toxic compounds, such as dioxin relatives, during their combustion [1]. Therefore, various non-halogenated flame retardants have been tried to use for some polymeric materials in recent years. Among these, silicone-based flame retardants are noted to generate extremely less amounts of toxic substances even in case of fire [2-4].

The flame retarding behaviour by the silicone additives are of great interest, and several mechanisms leading to their flame retarding effects have been proposed. Kambour et al. studied on the flame retardancy of several silicone-containing block polycarbonates (PCs) [5,6]. They concluded that the char formation was promoted via a chain-building reaction between the thermal degradation products of polydimethylsiloxane and bisphenols [6]. On the other hand, Hshieh demonstrated that the deposited silica-ash formed from silicone-modified organic polymers during their combustion could serve a good insulating layer which reduces the radiant heat of flame, and/or a barrier which restricts both the diffusion of fuels into the combustion zone and the access of oxygen to the unburned fuels [7]. Recently, Iji et al. reported a novel silicone-based flame retardant for PC materials, which consisted of branched chain structure containing trifunctional phenylsiloxane units [8]. They suggested that the superior flame retarding effect of the phenyl-rich silicone resulted from its excellent dispersion in the PC substrate and its rapid movement to the surface of the PC material to form the flame-resistant char barrier during the combustion. However, its chemical change of this flame retarding system during combustion has not been clarified in detail at present.

On the other hand, we have recently characterized abnormal structures such as branching and/or cross-linking structures formed in PC chains during its thermal treatment by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) in the presence of organic alkali, tetramethylammonium hydroxide (TMAH) [9]. On the pyrograms of the thermally treated PC samples, the methyl derivatives of the components, reflecting the abnormal structures, formed through selective cleavages and derivatizations at the carbonate and ester linkages were observed together with those reflecting the main chain and the end groups.

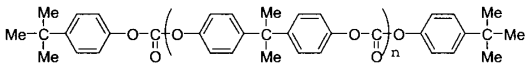
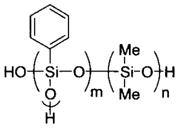
These types of abnormal structures might be also formed in flame-retarded PC materials during the combustion and might lead to the flame retardancy. In this study, therefore, the change in the chemical structure of the silicone-containing flame retarded polycarbonate (FR-PC) after thermal treatment was characterized by pyrolysis-gas chromatography (Py-GC) in the presence of organic alkali, mainly by focusing on the formation of branching and cross-linking structures in the FR-PC sample to develop their flame retarding nature. The observed structural changes were interpreted in terms of the action of the trifunctional phenyl-rich silicone-based flame retardant at the elevated temperature during the combustion of the FR-PC material.

Experimental

Samples

Table 1 summarizes the samples used in this study together with their chemical structures, average molecular weight and flame retardancy data. The silicone-based flame retardant, synthesized by hydrolysis and condensation of trichlorophenylsilane and dichlorodimethylsilane, consisted of 90 mol% of phenylsiloxane and 10 mol% of dimethylsiloxane units, which was proved to contain about 1.1 mol% silanol groups through its ^{29}Si NMR spectrum. The flame-retarded PC (FR-PC) sample was prepared by blending a commercially available bisphenol-A PC, synthesized by the solvent method, with 5 wt% of the flame-retardant at 280 ºC. The oxygen indices (OI) of the control PC and the original FR-PC samples determined by the ASTM method exhibited the superior flame retardancy of the original FR-PC to the control PC. The thermally treated PC and FR-PC were prepared by heating each of them weighing about 1.5 g at 380 ºC for 2 h in an electric oven under a nitrogten atmosphere. Prior to the pyrolysis measurement, all the (FR-)PC samples were cryo-milled into fine

Table 1. Chemical structures of the samples and their number average molecular weight and flame retardancy data

Sample name	Chemical structures or composition	M_n	OI [a]
Control PC		1.3×10^4	26
Silicone-based flame retardant	 m : n = 9 : 1	1.9×10^3	–
Original FR-PC	PC / Flame retardant = 95 / 5 (wt%)	–	35

[a] Volume percent oxygen to just sustain burning mesured by the ASTM test method.

powders with a freezer mill (SPEX, 6750) at liquid nitrogen temperature in order to attain homogenous sampling and the following efficient chemolysis of the samples.

Conditions for Temperature-programmed pyrolysis-mass spectrometry

Temperature-programmed pyrolysis-mass spectrometry (TPPy-MS) measurement system was basically the same as described in the previous papers [10,11] In this system, a temperature-programmable microfurnace pyrolyzer (Frontier Lab, PY-2010D) was directly coupled with a quadrupole mass spectrometer (JEOL, Automass system II) via a deactivated stainless steel capillary (Frontier Lab, UADTM-5N 0.25 mm i. d. x 5 m long) maintained at 300 °C in the oven of a gas chromatograph (Hewlett Packard, HP-5890). About 50 μg of a powdered PC sample was heated in the pyrolyzer from 150 up to 750 °C at a heating rate of 20 °C/min under a helium flow (50 ml/min). Part of the flow (1 ml/min) reduced with the splitter was continuously introduced into the MS.

Conditions for pyrolysis-gas chromatography in the presence of organic alkali

The procedure for reactive pyrolysis-gas chromatography was basically the same as described in the previous papers [9,12]. In this case, the capillary transfer line for TPPy-MS was replaced with a metal capillary separation column coated with polydimethylsiloxane (Frontier Lab, Ultra-Alloy-PY1 30 m x 0.25 mm ID, 0.25 μm film thickness). About 50 μg of a powdered PC sample together with 1.5 μl of a tetramethylammonium hydroxide (TMAH), 25 wt% solution in methanol was put into the pyrolyzer maintained at 400 °C under the flow of helium carrier gas (50 ml/min), to yield the methyl derivatives of the components connected serially through the carbonate (or ester) linkages in the original polymer chain. The column temperature was programmed from 50 up to 300 °C at a rate of 10 °C/min. The peak detection and identification were mainly carried out with the flame ionization detector and the MS, respectively.

Conditions for FT-IR

FT-IR spectra were recorded on a FT-IR microscope (Japan Spectroscopic, Model Jansssen). A powdered PC sample in a potassium bromide disk (1 wt%) was subjected to the IR measurement by co-adding 200 scans at resolution of 1 cm^{-1} with the aperture size of 100 x 100 μm.

Solubility tests of PC samples

About 0.5 g of a PC sample was solubilized into 15 ml of chloroform, the insoluble fraction separated by filtration was dried under a vacuum at room temperature, and then weighed to evaluate the solubility.

Results and discussion

Thermal degradation behaviours of PC samples observed by TPPy-MS

Figure 1 shows the thermal degradation profiles of the phenyl-silicone based flame retardant (a), the control PC (b), and the original FR-PC (c) samples observed by TPPy-MS using selected ion monitoring (SIM) modes. Here, the SIM curves at m/z 78, 44 and 213 mainly represent the evolution of benzene, carbon dioxide and

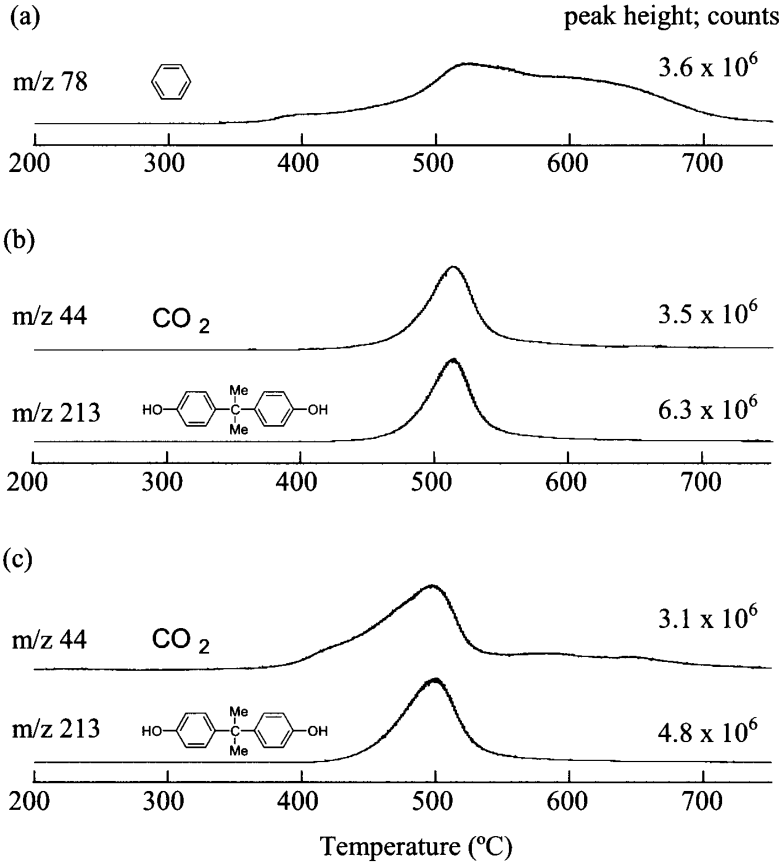


Figure 1. Selected ion monitoring curves measured by TPPy-MS: (a) Silicone-based flame retardant, (b) control PC, and (c) original FR-PC.

bisphenol-A, respectively. As shown in Figure 1(a), benzene is mainly evolved from the silicone-based flame retardant itself over 360 °C. However, almost no silicon-containing species were observed by the TPPy measurement of the flame retardant. This fact suggests that the main chain of the silicone-based flame retardant principally yield condensed and cross-linked structures to some extent with releasing the phenyl substituents in the trifunctional siloxane units during its thermal decomposition [13]. On the other hand, carbon dioxide and bisphenol-A are chiefly evolved in the range between 400 and 600 °C from both the control PC and the original FR-PC. However, the evolution of carbon dioxide for the original FR-PC evidently starts at lower temperatures around 380 °C than that for the control PC above 400 °C suggesting that the carbonate linkages of the PC chain are slightly weakened in the presence of the silicone-based flame retardant to provide some specific changes in the chemical structures relating to the flame retardancy of the FR-PC system. In order to elucidate the structural change in the FR-PC system during its thermal degradation, the thermally treated PC and FR-PC samples at 380 °C, at which the evolution of carbon dioxide was initiated for the original FR-PC, were prepared and subjected to the Py-GC and FT-IR measurements.

Prior to the Py-GC and FT-IR measurements, it was confirmed through the solubility test that the thermally treated FR-PC sample contained about 77 wt% insoluble fraction, while the control PC sample was almost completely soluble in chloroform even after the thermal treatment. The substantial formation of the insoluble fraction

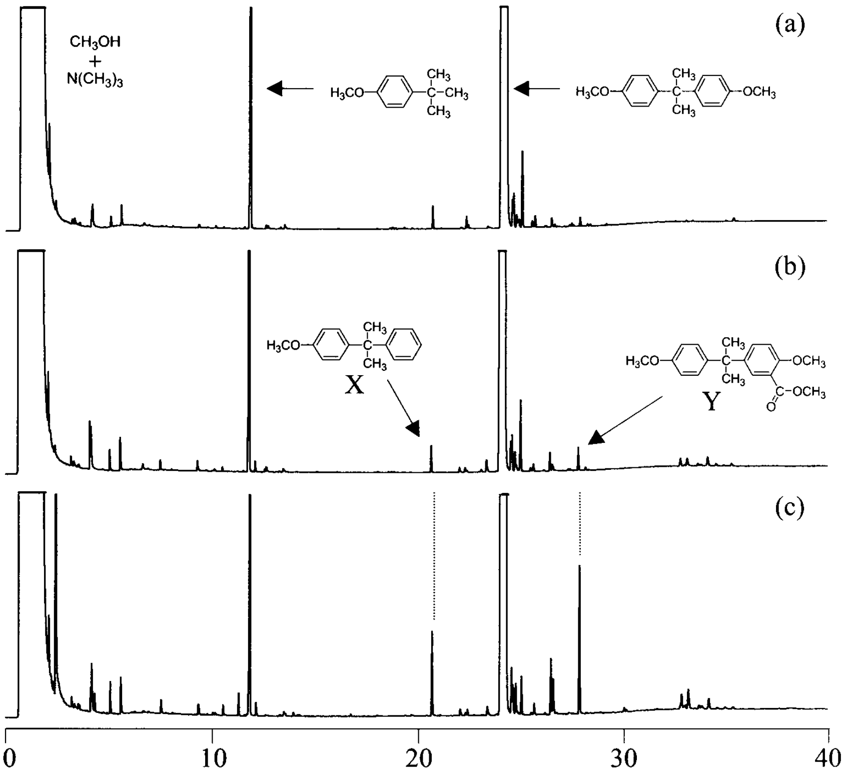


Figure 2. Pyrograms of the PC samples obtained at 400 °C in the presence of TMAH: (a) control PC, (b) thermally treated PC, and (c) thermally treated FR-PC.

indicates that the silicone-based flame retardant should promote cross-linking reactions in the FR-PC system during the thermal treatment although the decarboxylation of carbonate linkages in the PC chain initiates at lower temperature than that for the control PC.

Characteristic products for the thermally treated PC and FR-PC observed by Py-GC in the presence of organic alkali

Figure 2 shows the pyrograms of the control PC (a), the thermally treated PC (b), and the thermally treated FR-PC (c) obtained by Py-GC in the presence of TMAH at 400 °C. On the pyrograms for every PC sample, dimethyl ethers of bisphenol-A reflecting the main chain and *p-tert*-butylanisole reflecting the end group are mainly observed [9,12]. In addition, 2-(4-methoxyphenyl)-2-phenylpropane [X] and 2-(3-methoxycarbonyl-4-methoxyphenyl)-2-(4-methoxyphenyl)propane [Y] reflecting abnormal structures are evidently observed on the pyrogram of the thermally treated PC (b), and more prominently appear on that of the thermally treated FR-PC (c). In the case of the thermally treated PC in the absence of the silicone-based flame retardant, the compound X might be produced through the reactive pyrolysis from a *p*-cumylphenoxy end structure, mainly formed through the scission at a C–O bond in a carbonate linkage during the thermal treatment [14]. Meanwhile, it was reported that the compound Y could be produced from a carboxylic branching structure formed in the thermally treated PC chain through Fries rearrangement at a carbonate linkage [9]. The highly enhanced yields of the compounds X and Y on the pyrogram of the thermally treated FR-PC, therfore, suggest that the formation of the related abnormal structures might be largely promoted in the FR-PC material during the thermal treatment by the function of the silicone-based flame retardant than in the case of the thermally treated PC.

Formation of phenyl silyl ether linkage during thermal treatment of FR-PC confirmed by FT-IR measurement

Figure 3 shows the FT-IR spectra of the original FR-PC before the thermal treatment

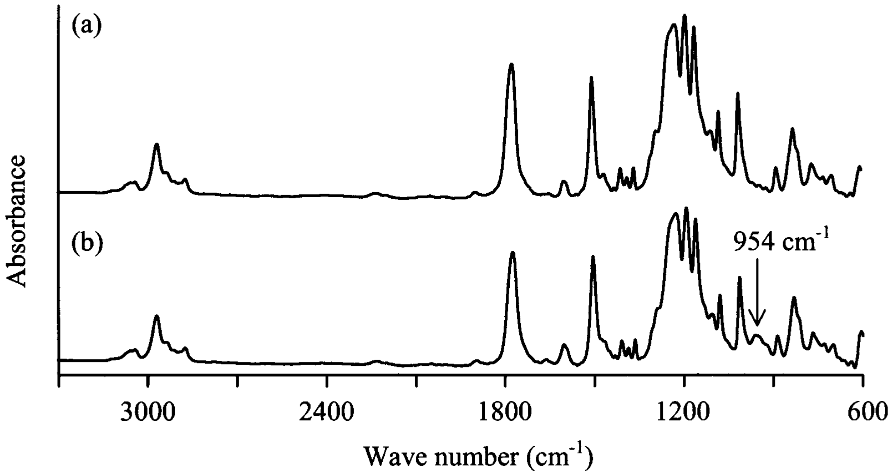


Figure 3. Infrared spectra: (a) original FR-PC, (b) thermally treated FR-PC.

(a) and the thermally treated FR-PC (b). On the IR spectrum of the thermally treated FR-PC, an absorption band which is absent on that of the original FR-PC is observed in the region of 980-900 cm^{-1}. In addition, this band was confirmed to be also absent on the IR spectrum of the thermally treated PC. Since Lipp et al. reported that a Si–O–Ph streching can be observed in the 980 to 920 cm^{-1} region [15], the broad band at around 954 cm^{-1} on the IR spectrum in Figure 5 (b) could be attributed to the presence of phenyl silyl ether linkages formed through the reaction between the silicone-based flame retardant and the PC substrate during the thermal treatment at 380 °C.

Flame retarding mechanism of polycarbonate containing trifunctional phenyl-silicone based additive

On the basis of the observed results mentioned above, the reactions between the PC substrate and the silicone-based flame retardant at the initial stage of the thermal degaradation of the FR-PC system, which might develop the flame retardancy, was speculated. Figure 4 shows a probable formation process of the *p*-cumylphenoxy end structure in the FR-PC system during the thermal treatment, from which the compound X was yielded by reactive pyrolysis. Here, an electrophilic silyl radical produced from the trifunctional siloxane units through the elimination of a phenyl group attacks the ether-like oxygen atom of a carbonate linkage in the PC chain to form a cross-linking structure containing a tetrafunctional siloxane unit, with leaving a carbonyl radical which lead to the *p*-cumylphenoxy end structure through

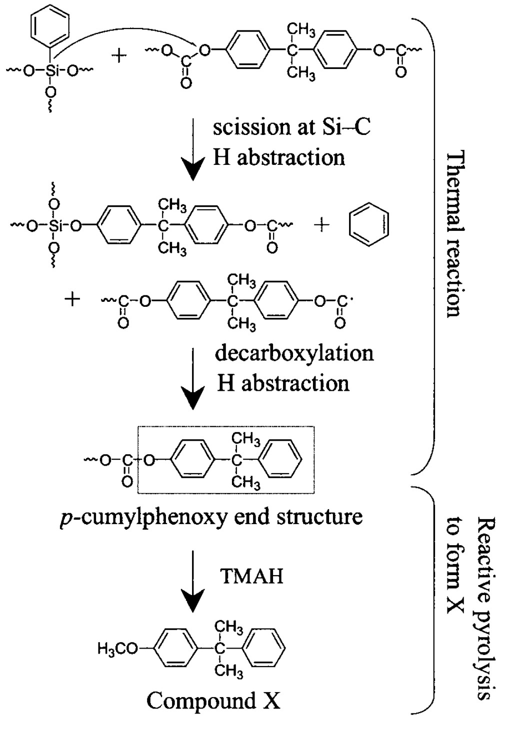


Figure 4. Formation pathway of the *p*-cumylphenoxy end structure and its characteristic product (compound X) for the thermally treated FR-PC.

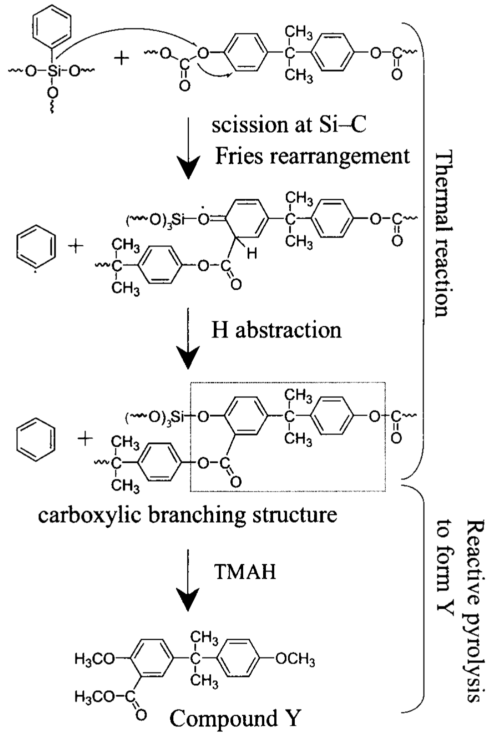


Figure 5. Formantion pathway of the carboxylic branching structure and its characterictic product (compound Y) for the thermally treated FR-PC.

decarboxylation and hydrogen abstraction. Furthermore, Figure 5 shows a possible formation process of the carboxyl branching structure in the thermally treated FR-PC system. In this case, the silyl radical also attacks the ether-like oxygen atom in a similar manner as shown in Figure 4, through simultaneous Fries rearrangement rather than decarboxylation. As the resulting carboxyl branching structure in the PC chain accompanied by the phenyl silyl ether linkage, which might construct stronger cross-linking structures.

So far, it was demonstrated that silicone derivatives containing phenylsiloxane units were to be effective flame-retardants for PC materials through not only its excellent dispersing ability in the PC substrate but also its liability to form a flame-resistant char barrier consisting of the branched silicone and condensed aromatic compounds during combustion [8]. Thus observed results in this work suggest that the formation of the cross-linking structures between the PC substrates and the phenyl silicone-based additives might also play an important role for the flame retardancy of the FR-PC system. At the early stage of the combustion of the FR-PC system, silyl radicals formed through releasing phenyl groups develop the cross-linking structures, which should promote the formation of the char barrier on the surface of the PC material to reduce the radiant heat of flame and to restrict the diffusion of flammable products into the combustion zone. Thus formed cross-linking structure might also suppress the thermal decomposition of the whole material body and confine the movements of the degradation products in the material. These effects would develop synergistically the flame retardancy of the phenylsilicone-containing PC material.

References

1. Bindra SK, Narang RS (1995) Chemosphere 31:4413
2. Frye RB (1984) Preprints Polym Mater Sci Eng Division ACS 51:235
3. Kashiwagi T, Cleary TG (1992) Joint panel Meeting-UJNR Panel on Fire research and Safety 12:267
4. Benrashid R, Nelson GL (1994) J Polym Sci: Part A Polym Chem 32:1847
5. Kambour RP, Klopfer HJ, Smith SA (1981) J Appl Polym Sci 26:847
6. Kambour RP (1981) J Appl Polym Sci 26:861
7. Hshieh F-Y (1998) Fire Mater 22:69
8. Iji M, Serizawa S (1998) Polym Adv Technol 9:593
9. Oba K, Ishida Y, Ito Y, Ohtani H, Tsuge S (2000) Macromolecules 33:8173
10. Sato H, Tsuge S, Ohtani H, Aoi K, Takasu A, Okada M (1997) Macromolecules 30:4030
11. Sato H, Kondo K, Tsuge S, Ohtani H, Sato N (1998) Polym Degrad Stab 62:41
12. Ito Y, Ogasawara H, Ishida Y, Ohtani H, Tsuge S (1996) Polym J 12:1090
13. Sobolevskii MV (1974) Polym Sci USSR 16:840
14. McNeil IC, Rincon A (1991) Polym Degrad Stab 31:163
15. Anderson DR (1974) Analysis of Silicones. Wiley, New York