Thermal Decomposition Behavior and Flame Retardancy of Polycarbonate Containing Organic Metal Salts: Effect of Salt Composition

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ABSTRACT: This report describes the thermal decomposition behavior and the formation to investigate the flame-retardant mechanism of organic metal salt in polycarbonate. Moreover, the flame retardancy of the polycarbonate with the addition of various kinds of organic metal salt was evaluated, and the difference in flame retardancy was considered. The decomposition of organic metal salt in polycarbonate during combustion promotes the decomposition of polycarbonate as a catalyst and the formation of a char layer on the surface that inhibits the supply of flammable gas and heat transfer. The flame retardancy is related to the final decomposition temperature of organic metal salt, and it is highest when it is close to the maximum decomposition temperature of polycarbonate. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2131–2139, 2004

Key words: polycarbonate; flame retardance; thermogravimetric analysis; organic metal salt; degradation

INTRODUCTION

Polycarbonate has excellent mechanical properties and flame retardancy and is used for various applications. However, for electron and electric applications, where high flame retardancy is required, the flame-retardant technologies of polycarbonate have been developed.[1–7] One technology is to add a little organic metal salt such as potassium trichlorobenzene sulfonate.[8] This organic metal salt promotes decomposition of polycarbonate and inhibits combustion by generating incombustible carbon dioxide and forming a char layer at the burning surface. Ballistreri et al.[8] showed clearly that the thermal decomposition process of polycarbonate was changed by adding potassium trichlorobenzene sulfonate and the char layer formation was promoted. Furthermore, they reported that the char layer formed at the burning surface acted as a heat-insulating material and therefore inhibited the heat transfer from flame zone to the bulk. Recently, Takeda et al. showed that potassium perfluorobutane sulfonate changes the decomposition process of polycarbonate similarly, and this process is more effective for the flame retardancy of polycarbonate.[9] Moreover, Uozumi and Hatashi reported that Nafion, which chemically combines the sulfonic acid group with fluororesin, contributes to accelerate the rate of decarboxylation of polycarbonate and increase the amount of char layer.[10] Van Krevelen reported the relationship between the char content and the oxygen index and the tendency for flame retardancy to improve with the amount of combustion residuals.[11] For example, although the limited oxygen index (LOI) of polyolefin that does not generate combustion residual is about 18, the LOI of PPS with 70% combustion residual is 45. However, in our research and the report of Wang et al.,[7] although the amount of combustion residuals of the polycarbonate decreases upon adding the organic metal salt, the LOI increases.

This report describes the thermal decomposition behavior and the char formation to investigate the flame-retardant mechanism of organic metal salt in polycarbonate. Moreover, the flame retardancy of the polycarbonate with the addition of various kinds of organic metal salt was evaluated, and the difference in flame retardancy was considered.

EXPERIMENTAL

Materials

Polycarbonate used in this study was Toughlon FN1900A (trade name from Idemitsu Petrochemical Co., Ltd.), a bisphenol A-type polycarbonate with a viscosity-average molecular weight of 19,000 and melt flow index 20 g/10 min (conditions: 300°C, 1.2 kg). The organic metal salts were potassium perfluorobutane sulfonate (KFBS), its derivatives, potassium *p*-

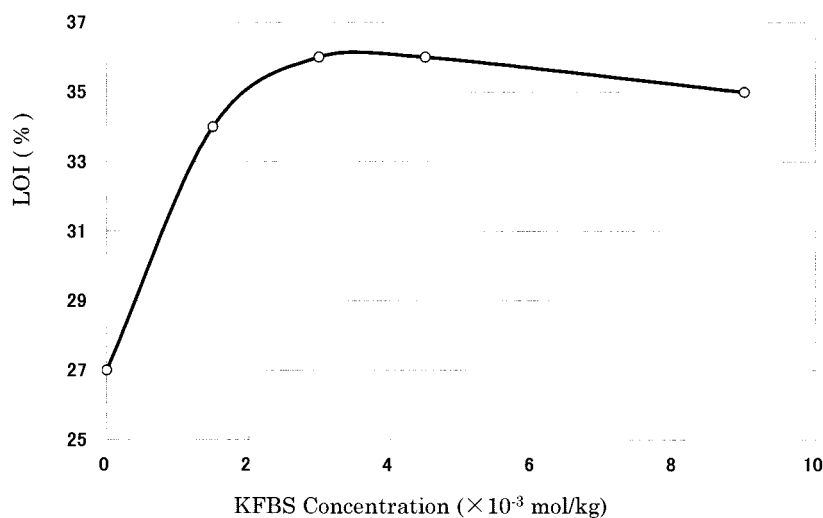*Correspondence to:* A. Nodera (akio.nodera@ipc.idemitsu.co.jp).

Figure 1 LOI values as a function of KFBS concentration.

toluene sulfonate (KTS) produced by Dainippon Ink and Chemicals, and potassium diphenylsulfone sulfonate (KSS) produced by UCB.

Using a 50-mmφ single-screw extruder at a cylinder temperature of 280°C and screw speed of 80 rpm, mixtures of polycarbonate and organic metal salt were melt-kneaded and extruded into pellets. The resulting pellets were dried at 120°C for 5 h and then injection-molded at an injection temperature of 280°C into test pieces for measurement of flame retardancy.

Limited oxygen index

LOI measurements were performed according to the JIS K7201 method (ignition flame, 15–20 mm), using a candle-type flammability tester (Toyo Seiki seisakusho). The sample bars with 3-mm thickness were made by injection molding and conditioned for 1 week at 23°C and 50% relative humidity.

Thermogravimetric analysis

A Perkin-Elmer thermal analyzer TGA-7 was used to determine the weight loss during thermal degradation of pure polycarbonate and the mixtures with organic metal salts. Experiments were carried out on 10 mg of sample under nitrogen and furnace heating rate of 20°C/min up to 700°C. In combustion, oxygen is consumed in the gas phase, and so degradation and char formation in the solid phase would be generated in a nonoxygen atmosphere.

Pyrolysis-gas chromatography-mass spectrometry

Pyrolysis was performed within the double shot pyrolyzer (Flonter Lab PY2020D). Pyroprove was directly connected to a gas chromatograph (Thermo

Quest Trace GC2000). Pyrolytic conditions were as follows: temperature 550°C, time 90 s. A 80/100 mesh chromosorb W column was used for pyrolysis product separation with a temperature program allowing a 5°C/min heating rate from 50 to 300°C. Identification of the pyrolysis products was achieved by GS-MS, with the pyrolyzer directly interfaced to a gas-mass spectrometer (Thermo Quest Finnigan Polaris).

RESULTS AND DISCUSSION

Flame retardancy of potassium perfluorobutane sulfonate

The LOI values as a function of KFBS concentration are shown in Figure 1. Figure 1 shows that a slight addition of KFBS causes a sensible LOI increment in polycarbonate, and the LOI value of the polycarbonate containing 3–4.5×10^{-3} mol/kg KFBS seems to saturate at 36. When the content of KFBS to 9×10^{-3} mol/kg, the flame retardancy decreases slightly. This
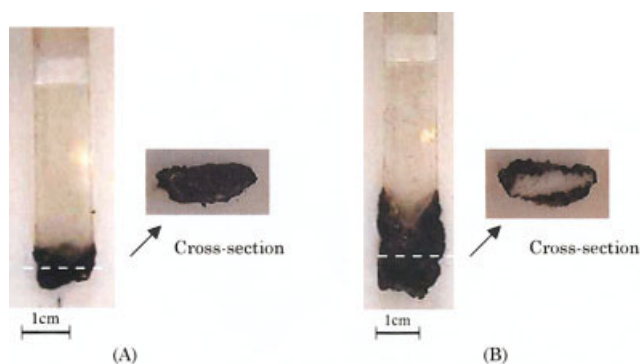

Photo 1 Char formation of pure PC (A) and PC containing 9.0×10^{-3} mol/kg KFBS (B) with LOI tester under 40% oxygen in combustion for 20 s.

TABLE I
Rate of Char Formation on the Surface and Conceptual Shapes with Different Contents of KFBS

Amouts of KFBS ($\times 10^{-3}$ mol/kg)	0	1.5	3.0	4.5	9.0
Velocities of forming char on the surface (cm/s)	0.05	0.07	0.10	0.12	0.13
A cross-sectional conceptual shapes	■ ———————————————————————→ ▭				

behavior of KFBS is similar to that of KSS although the concentration is different.[8] It is thought that formation of the char layer from polycarbonate inhibits combustion, so the rates of char formation with an LOI tester under 40% oxygen were measured (Photo 1, Table I). The same samples as for LOI measurements were used. The rate of char formation was determined by measurement of the maximum char length in combustion for 20 s. The rate increased with the addition of KFBS to polycarbonate, and KFBS promoted the charring formation of polycarbonate. The cross-sectional conceptual shapes of these combustion samples are also shown in Table I. When polycarbonate containing KFBS was burned, the char layer was formed only on the surface and the inside was not carbonized. The tendency became strong as the amount of KFBS increased. Thermogravimetric analysis (TGA) curves of all samples are depicted in Figure 2. The number in parentheses is the amount (%) of residue at 650°C. KFBS causes thermal destabilization and the initial temperature of weight loss decreases as the amount of KFBS increases. On the other hand, the amounts of thermal degradation residue at 650°C are the almost same and do not depend on the amount of KFBS.

Figure 3 shows the rates of weight loss on the temperatures in TGA. It is clearly shown that all the maximum rates of polycarbonate containing $1.5–4.5 \times 10^{-3}$ mol/kg KFBS are higher than that of polycarbonate containing no KFBS and the temperature of the maximum rate decreases as the amount of KFBS increases. Moreover, the maximum rate seems to be saturated at more than 3×10^{-3} mol/kg KFBS. The high flame retardancy of polycarbonate containing KFBS is not caused by an increase in carbonization, but by the formation speed of char layer on the surface. KFBS promotes the char layer on the surface by quickly decomposing PC, and when the rate of decomposition reaches the maximum, LOI no longer increases. Furthermore, when the char forms at extremely low temperature, the flame retardancy decreases since the flame spreads easily on the surface.

Influence of an alkali metal in the salts on flame retardancy

The flame retardancy of different alkali metals in perfluorobutane sulfonate was investigated. In addition to potassium salt, lithium perfluorobutane sulfonate
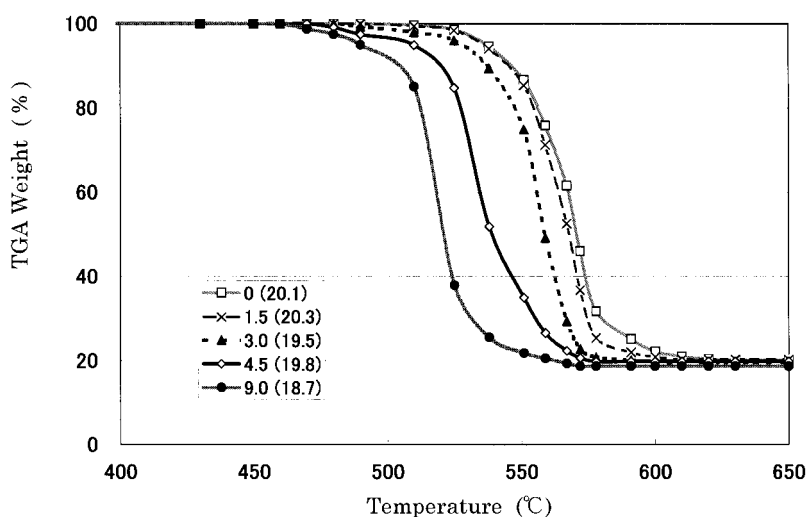

Figure 2 TGA curves of polycarbonate containing the different concentration of KFBS; numbers in parentheses show the amount of residue.
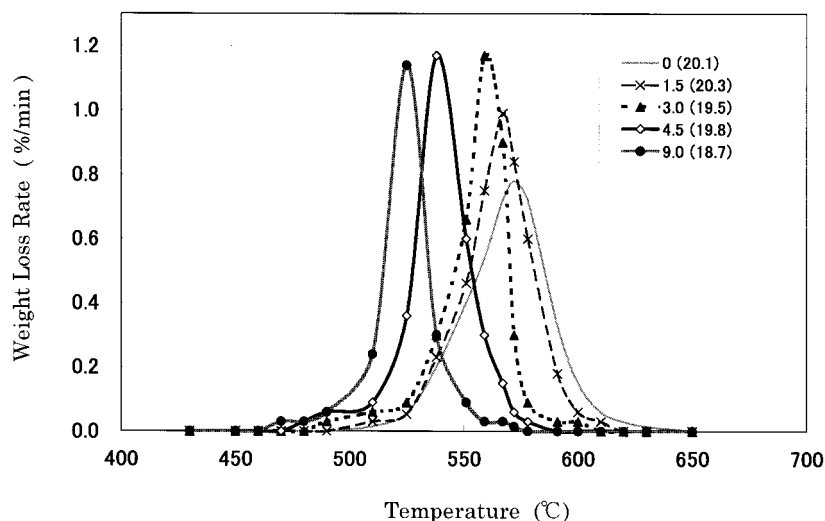
Figure 3 Weight loss rate and the amount of residue for polycarbonate containing different concentration of KFBS on temperature by TGA; numbers in parentheses show the amount of residue.

(LiFBS), sodium perfluorobutane sulfonate (NaFBS), and cesium perfluorobutane sulfonate (CsFBS) were evaluated. The LOI values as a function of alkali metal perfluorobutane sulfonate concentration are shown in Figure 4. The maximum LOI value of CsFBS is 36, and CsFBS shows high flame retardancy like KFBS. But the maximum LOI values of LiFBS and NaFBS are 31–32 and the increments are less than that of KFBS. Their rates of weight loss for polycarbonate with 4.5×10^{-3} mol/kg of alkali metal on the temperatures in TGA are shown in Figure 5. The numbers in parentheses are the amounts (%) of residue at 650°C. Compared with KFBS, the maximum rate of CsFBS increases slightly, and the temperature of the maximum rate is the almost same as that of polycarbonate containing KFBS. The maximum rates of NaFBS and LiFBS are lower

than that of KFBS, and the temperatures become lower. The maximum loss rate tends to increase with the molecular weight of alkali metal. The amounts of the thermal residue were the almost same in the different kinds of metals. It is thought that the flame retardancy of LiFBS in polycarbonate is poor because the temperature and rate of polycarbonate degradation are lower.

Influence of an organic structure in the salts on flame retardancy

The flame retardancy of different structures in potassium salts was investigated. Potassium perfluorooctane sulfonate (KFOS) and potassium perfluoromethane sulfonate (KFMS) as perfluorocarbons,
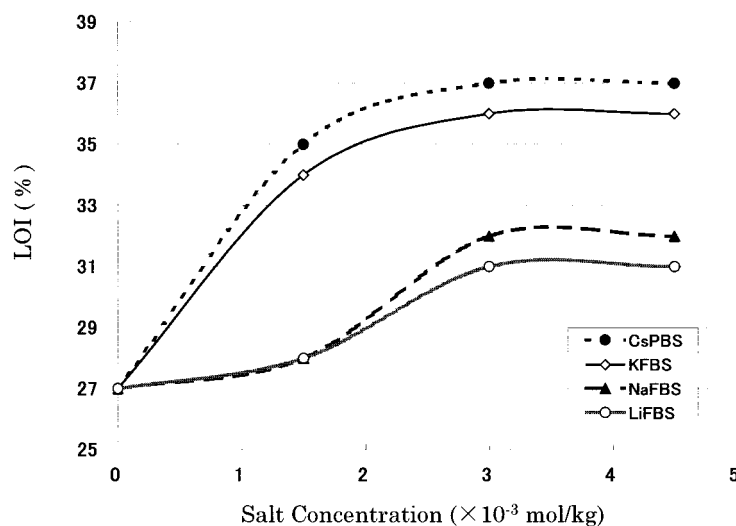

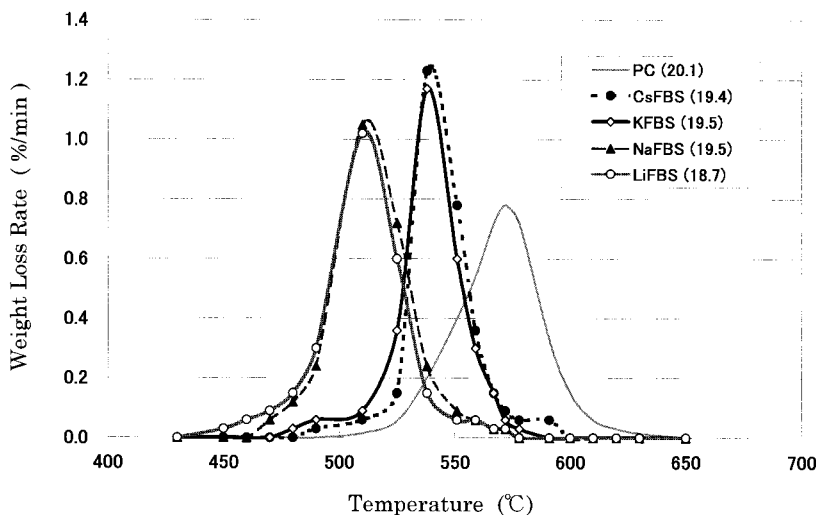**Figure 4** LOI values as a function of CsFBS, KFBS, NaFBS, and LiFBS concentration.

Figure 5 Weight loss rate and the amount of residue for polycarbonate with 4.5×10^{-3} mol/kg of CsFBS, KFBS, NaFBS, and LiFBS on temperature by TGA; numbers in parentheses show the amount of residue.

having different chain length, and KTS and KSS as hydrocarbons were evaluated. The LOI values as a function of alkali metal concentration are shown in Figure 6. The LOI values of all salts were saturated at $3-4.5 \times 10^{-3}$ mol/kg. The LOI of KFMS was 41 and was higher than that of others. The LOI tended to increase as the chain of fluorocarbon became long. In the hydrocarbons, the LOI of KTS did not show a high value although the LOI of KSS was 38. Their rates of weight loss for polycarbonate with 4.5×10^{-3} mol/kg of alkali metal on the temperatures in TGA are shown in Figure 7. The numbers in parentheses are the amounts (%) of residue at 650°C. The maximum rate of KFMS increased to 1.26 wt %/min and shifted to high temperature near polycarbonate containing no organic salt. The maximum rate of KTS was lowered like that of LiFBS. Regardless of the structure the

amounts of the thermal residue were the almost same as for polycarbonate containing no salt.

Flame-retardant mechanism of organic salt in polycarbonate

Figure 8 shows the relationship between LOIs and maximum loss rates for evaluated samples. As the loss rate increases, the LOI tends to increase. It is thought that the formation rate of char layer also contributes to flame retardancy since the amount of thermal residue does not change. The short time of degradation in polycarbonate is effective to generate a char layer on the surface before degradation temperature at the inner layer. Figure 9 shows the relationship between LOIs and temperatures of maximum loss rate in the polycarbonate containing 4.5×10^{-3} mol/kg salt
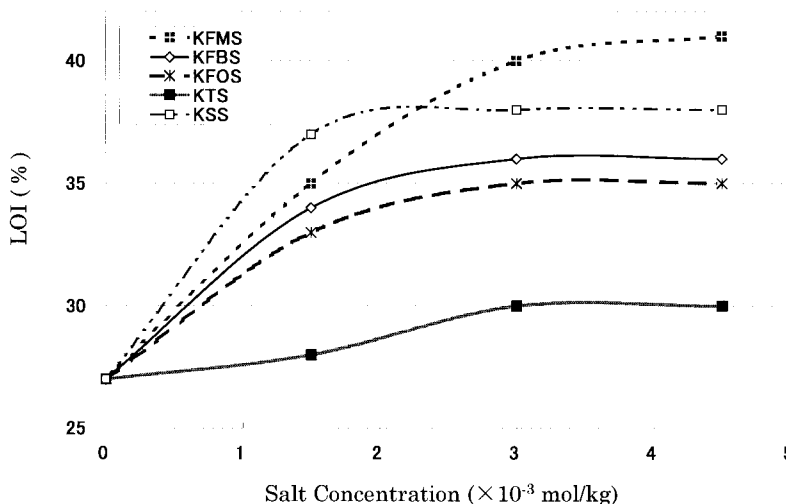

Figure 6 LOI values as a function of KFOS, KFBS, KFMS, KTS, and KSS concentration.
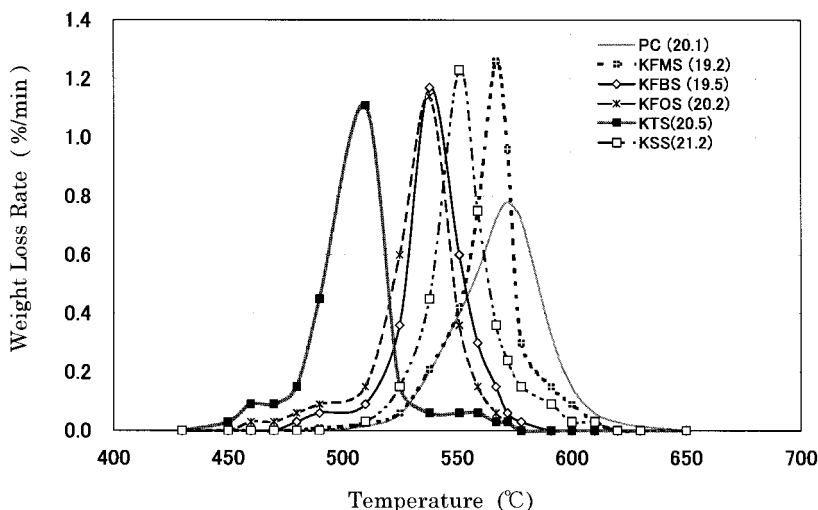
Figure 7 Weight loss rate and the amount of residue for polycarbonate with 4.5×10^{-3} mol/kg of KFOS, KFBS, KFMS, KTS, and KSS on temperature by TGA; numbers in parentheses show the amount of residue.

reaching the maximum LOIs. As the temperature increases, the LOI increases proportionally although the maximum rate tends to decrease at low temperature. The lower degradation temperature causes the earlier ignition and the spread of flame, and so flame retardancy would decrease. It is thought that flame retardancy at small-case fire tests such as LOI and UL94 increases when the loss rate is faster and the temperature is close to that of polycarbonate.

Based on such a result, the difference in flame retardancy in the kind of metal salt is considered. First, the thermal decomposition behavior of the metal salt itself was investigated. The TGA curves of all salts are depicted in Figures 10 and 11. For comparison, the data of polycarbonate containing no additive are included in Figures 10 and 11 as well. Experiments were carried out under nitrogen and a furnace heating rate

of 20°C/min up to 700°C. The initial loss temperatures of all organic metal salts are lower than that of polycarbonate. The initial loss of LiFBS, NaFBS, and KTS began with a lower temperature, but the initial loss of KFMS was a high temperature near the polycarbonate. From Table II, it is seen that all the polycarbonate samples containing the organic metal salt decompose after the initial decomposition of organic salt. But initial decomposition products from the organic salt are hardly thought to decompose polycarbonate since there is the large difference of initial loss temperature between salt and polycarbonate such as in the cases of LiFBS and KTS. On the other hand, the final loss (the point reaching to residue + 2%) temperature of the organic salts is coincident with the temperature of maximum loss rate of polycarbonate. That is, when decomposition of the organic salt advances to some
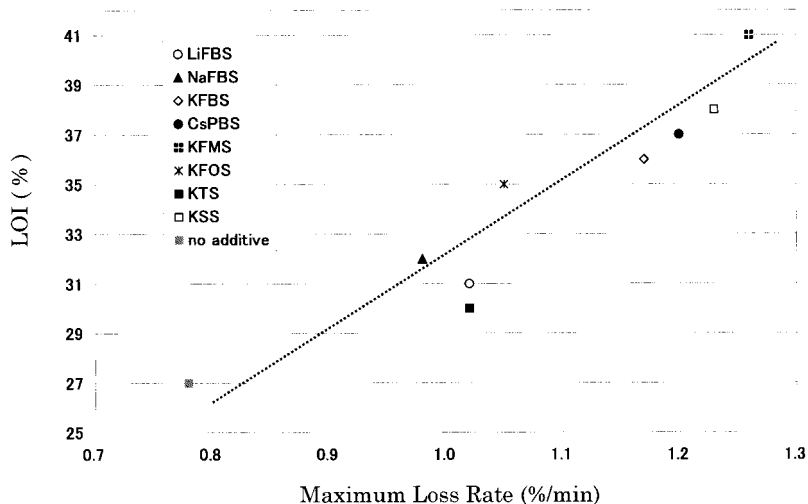

Figure 8 Relationship between LOIs and maximum loss rates in this study.
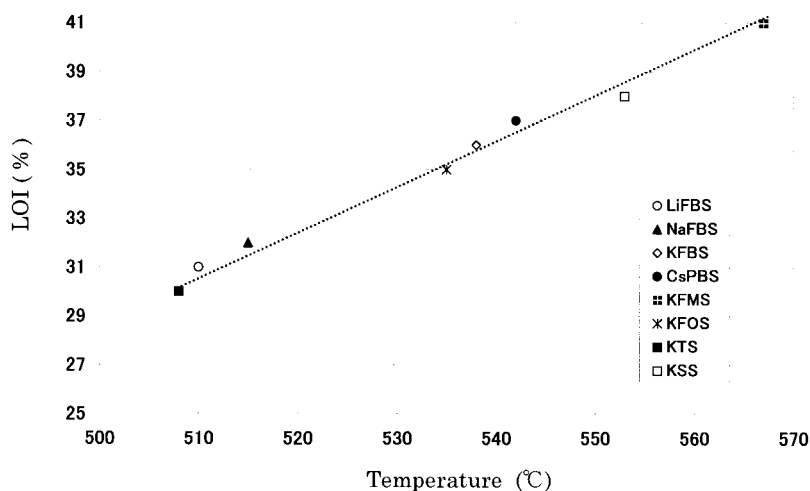
Figure 9 Relationship between LOIs and temperatures of maximum loss rate in the polycarbonate with 4.5×10^{-3} mol/kg salt in this study.

extent, the decomposition rate of polycarbonate with an organic salt is the highest. Consequently, the organic salt with a higher final loss decomposition temperature has higher flame retardancy for polycarbonate (Fig. 12). However, the organic salts with decomposition temperature far beyond polycarbonate are assumed to be ineffective in flame retardancy.

Next, the decomposition mechanism of polycarbonate with organic metal salt is considered. Table III shows the amounts (%) of gases generated from pure polycarbonate and polycarbonate with the organic metal salt at 550°C obtained by pyrolysis GC-MS. The amount (%) was determined by a relative area from the GC trace. It is thought that 550°C is close to the combustion temperature at which both polycarbonate and organic metal salt are decomposing. The ratio of bisphenol A increases by adding the organic metal to

polycarbonate and is not dependent on the kind of salt although their flame retardancy is different. In combustion, the decomposition behavior of polycarbonate by LiFBS, KFBS, and CsFBS is the almost same and only the temperature differs. Intermolecular-exchange and isomerization reactions with hydrolysis generate bisphenol A as a decomposition product and their reactions are promoted by alkaline substances acting as catalyst.[8,12,13] It is supposed that an organic metal salt would generate alkaline substances by thermal decomposition under water. In this study, it is thought that the organic metal salt in polycarbonate decomposes similarly and accelerates the decomposition of polycarbonate. Generally, fluorocarbon has higher thermal stability than hydrocarbon, and so fluorocarbon salts have high decomposition temperature. Moreover, it is expected that the diphenylsulfone
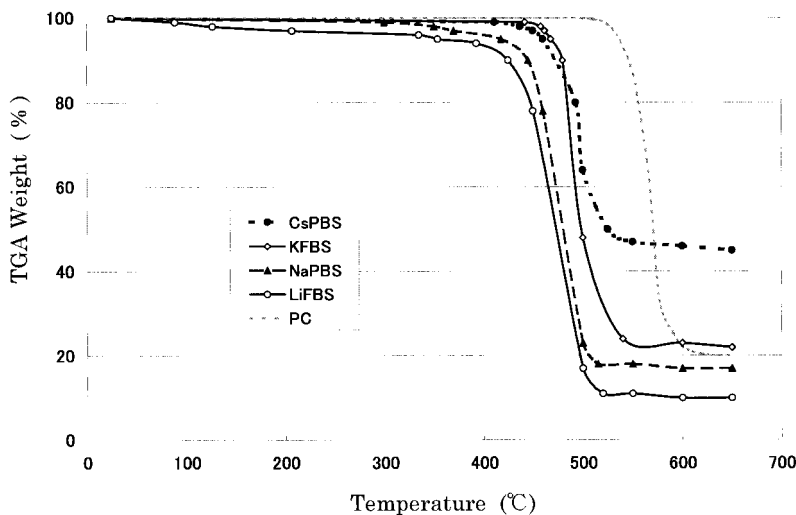

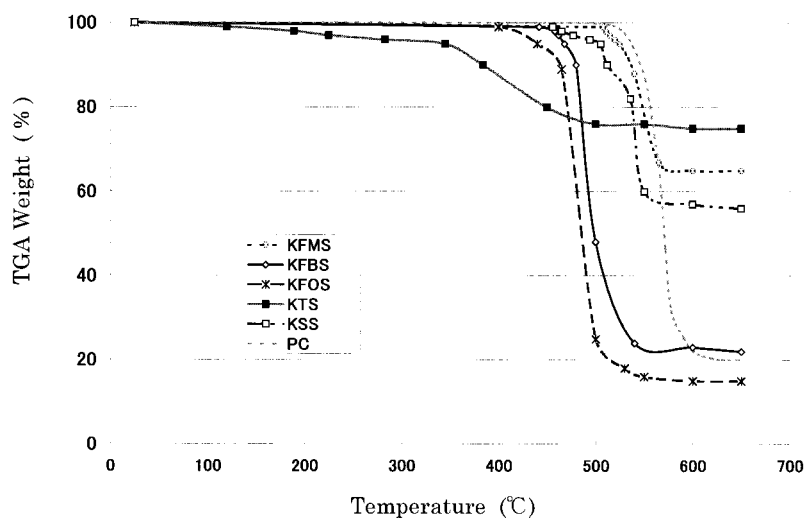**Figure 10** TGA curves of CsFBS, KFBS, NaFBS, and LiFBS.

Figure 11   TGA curves of KFOS, KFBS, KFMS, KTS, and KSS.

structure would have good thermal stability. The organic metal salt having organic structure with high thermal stability shows high decomposition temperature. Another reason is the difference of hydration in the organic metal salts because water has a great influence on the decomposition of the salt. The water absorption (humidity 85%, 12 h, measurement by weight change) of LiFBS, NaFBS, KFBS, and CsFBS is 8.6, 1.2, 0.1, and 0%, respectively, and the salt of a larger water absorption has early decomposition. The

TABLE II
5 wt % and Final Loss Temperatures of the Organic Metal Salts, 5 wt % Loss and Maximum Rate Temperatures, and Maximum LOI of Polycarbonate Containing 4.5×10^{-3} mol/kg Salt

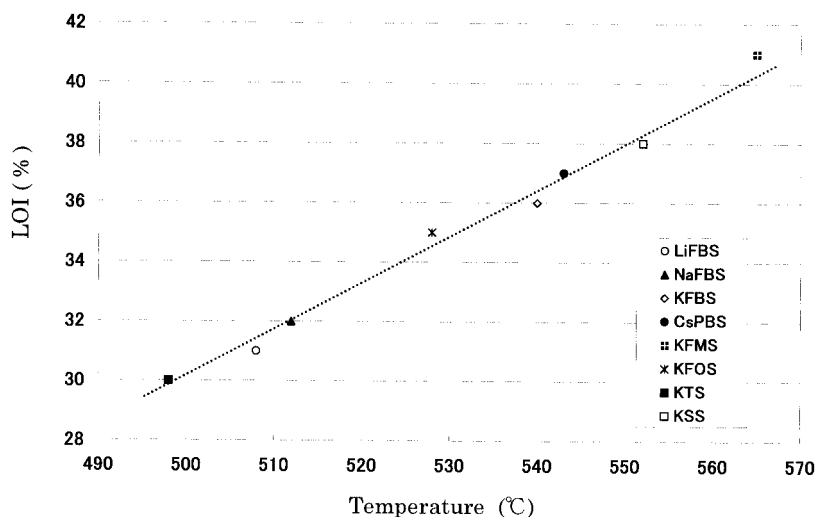| Additive organic salt	LiFBS	NaFBS	KFBS	CsPBS	KFMS	KFOS	KTS	KSS	None
Salt									
5 wt % loss temp. (°C)	354	418	468	460	533	440	345	505	—
Final loss temp. (°C)	508	512	540	542	565	528	498	552	—
Resin									
5 wt % loss temp. (°C)	480	484	514	525	534	510	485	527	534
Max rate temp. (°C)	510	515	538	542	567	535	508	553	574
Max LOI (%)	31	32	36	37	41	35	30	38	27

Figure 12   Relationship between LOIs and final loss temperatures of the organic metal salt in this study.

TABLE III
Amount of Gases from Pure Polycarbonate and Polycarbonate Containing 4.5×10^{-3} mol/kg Salt by Pyrolysis GC-MS

	PC %	PC with LiFBS %	PC with KFBS %	PC with CsFBS %
Bisphenol A	71.0	84.6	84.9	85.2
Isopropenyl phenol	12.1	5.2	5.1	5.0
Isopropyl phenol	1.6	1.8	1.8	1.8
Vinyl phenol	3.7	2.2	2.2	2.1
Ethyl phenol	3.4	1.4	1.3	1.3
Cresol	5.7	3.0	3.0	3.0
Phenol	2.4	1.7	1.7	1.6

difference of loss rate is thought to depend on the reaction temperature and the catalyst efficiency.

CONCLUSION

The organic metal salt in polycarbonate decomposing during combustion promotes intermolecular-exchange and isomerization reactions of polycarbonate as a catalyst. Decomposition products from the organic salt, e.g., alkaline substances, would exhibit activity to the reactions. These reactions raise the decomposition rate of polycarbonate and quickly cause the formation of a char layer on the surface that inhibits the supply of flammable gas and heat transfer. The flame retardancy is related to the final decomposition temperature of organic metal salt and is highest when the temperature is close to the maximum decomposition temperature of pure polycarbonate. This is because the initial ignition and the spread of flame are inhibited at lower temperature. The flame-retardant technology of polycarbonate by the organic metal salt is thought to be the flame-retardant system that controls the decomposition and activation of the salt and could be effective for extinguishing the small initial flame.

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