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Study of fire-retardant polymers using temperature jump/Fourier transform infrared spectroscopy[1]

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Abstract

In this study we applied temperature jump/Fourier transform infrared spectroscopy, once called fast thermolysis/FT-IR spectroscopy, to quantify the thermal decomposition gases from two kinds of fire-retardant polymers. In the case of nylon-6, the addition of melamine-cyanurate accelerated the reduction of molecular weight, which caused the function of molten polymer drip away from the ignited flame. In the case of a fire-retardant PBT, the evolution of a large amount of carbon dioxide (incombustible gas) dominated in the extinguishing stage.

Keywords: Pyrolysis; FT-IR; Time-resolve; Fire-retardant polymer; Evolved gas

1. Introduction

Thermogravimetric analysis (TGA) is widely known as a technique for characterizing the degradation mechanism of fire-retardant engineering plastics [1]. These techniques will not permit real time in situ analysis of thermal decomposition gases that exist during ignition, combustion and explosion of a bulk material. Temperature jump/Fourier transform infrared spectroscopy (T-jump/FT-IR spectroscopy), which was once named fast thermolysis/FT-IR, has enabled material to be pyrolyzed at a heating rate exceeding 10°C s^{-1} and measurement of the gas spectra in real time [2]. In previous work, we found that the decomposition products depended strongly on the heating rate [3]. We carried out experiments at a rather fast heating rate of 10°C s^{-1}, which was determined from temperature profiles of the burning polymer surface reported by Ballistreri et al. [4].

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Melamine-cyanurate is widely used as a fire retardant for polyamide resign especially nylon-6 and nylon-66 [5,6]. Recently the mechanism of thermal degradation of melamine salts was studied using TGA by Costa et al. [7]. They postulated that polymeric melamine condensed on the surface of polymer materials during burning reduced the flammability of the base polymer. On the other hand, in the study of the mechanisms of various fire-retardant systems, the function of molten polymer drip away from the ignited area must be considered [8]. To understand the role of melamine-cyanurate in the fire-retardant system, we measured the decomposition gas from a fire-retardant nylon-6.

Halogenated polymers containing antimony oxide are presently available commercially. Although Lewin proposed a reaction scheme for antimony oxide and a chlorinated polymer in which evolution of gaseous antimony trichloride is a flame extinguishing factor [9], the mechanism of flame extinguishing of antimony oxide and brominated additives is not satisfactorily understood. We also studied the decomposed gases from a fire-retardant poly(butylene terephthalate) (PBT), which was prepared by combining PBT mechanically with brominated polycarbonate and antimony oxide.

2. Experimental

All materials and reagents were purchased from Hayashi Kasei Co., Ltd. The fire-retardant nylon resin was prepared by combining nylon-6 mechanically with melamine-cyanurate (ca. 10 wt%). The fire-retardant PBT was prepared by combining PBT with brominated-polycarbonate resin (15 wt%) and Sb_2O_3 (5 wt%). These resin samples were reduced to fine powder by Spex 6700 Freezer/Mill under liquid nitrogen.

We used Nicolet Magna-550 FT-IR, CDS Analytical Pyroprobe-2000 and Brill's IR cell [2] for this study. The heating conditions for the T-jump/FT-IR measurement were 10°C s^{-1} heating rate from room temperature to 600°C under a nitrogen atmosphere. We loaded the sample, weighing 200 μg, onto a quartz boat, then inserted the boat straight into the platinum coil filament of a pyroprobe. The spectrometer was set at a spectral resolution of 4 cm^{-1} with time resolution of 1.47 s. We placed the filament a few millimeters below the path of the infrared beam so that the volatile products diffused into the beam could be detected immediately. In order to prevent the pyrolyzed materials from condensing on the windows, the Brill's IR cell was kept at 230°C with a nitrogen purge gas flow of 40 ml min^{-1}. The components of decomposed gas were identified using the Nicolet high resolution vapor phase library.

3. Results and discussion

Fig. 1 shows the T-jump/FT-IR spectra of nylon-6 and the spectra search result of a linked trace at 1.157 min. Each spectrum in the figure was averaged at each data point in a time region of 5 s. The library searching result identified the decomposition product of nylon-6 as ε-caprolactam, which was a typical pyrolyzate from nylon-6 obtained by pyrolysis-GC/MS [10]. Fig. 2 shows the T-jump/FT-IR spectra of the fire-retardant nylon-6 with the spectra search result. The three characteristic peaks appearing at 1787, 1599 and

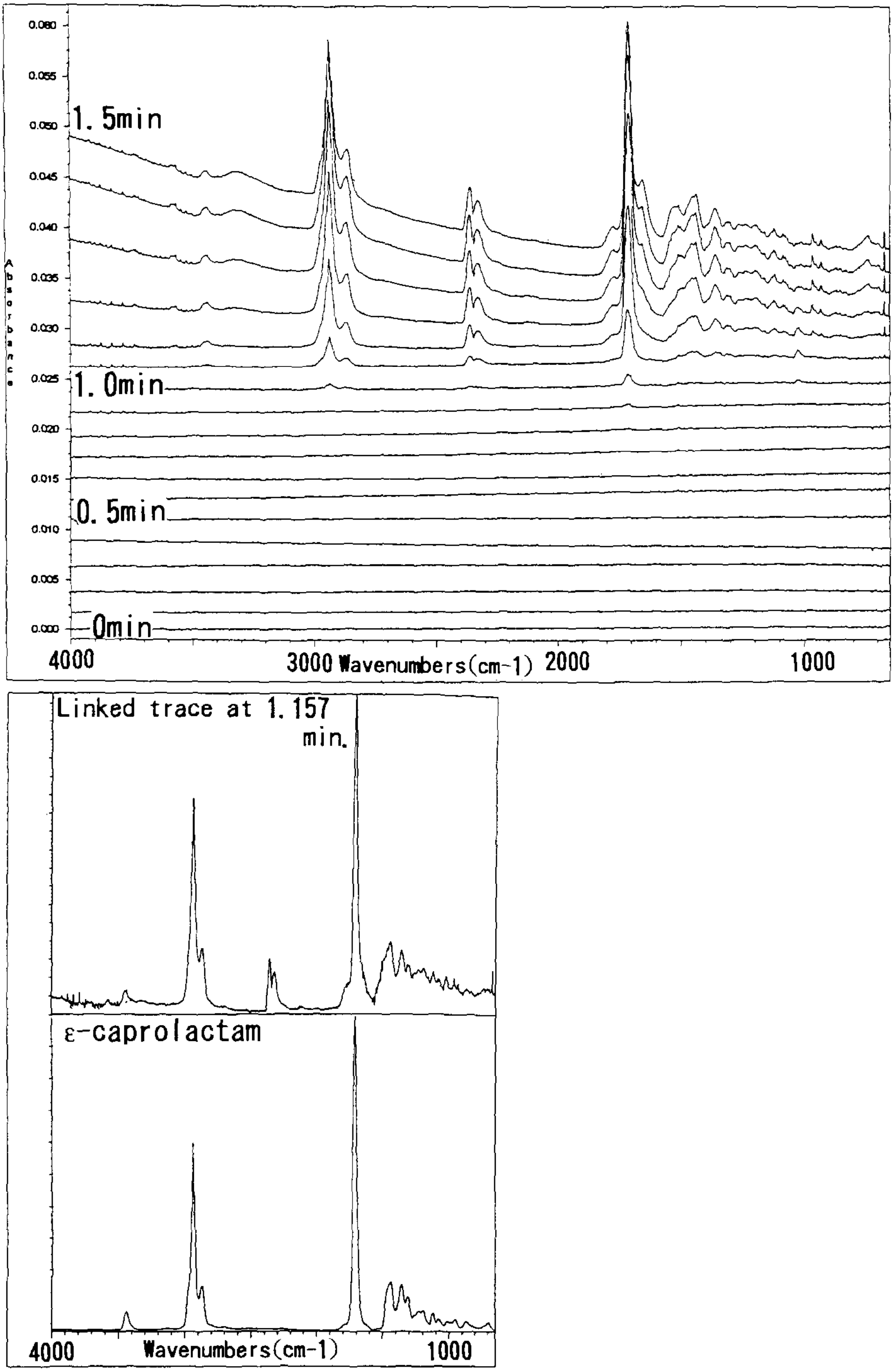

Fig. 1. T-jump/FT-IR spectra of nylon-6 and the spectra search result of a linked trace at 1.157 min.

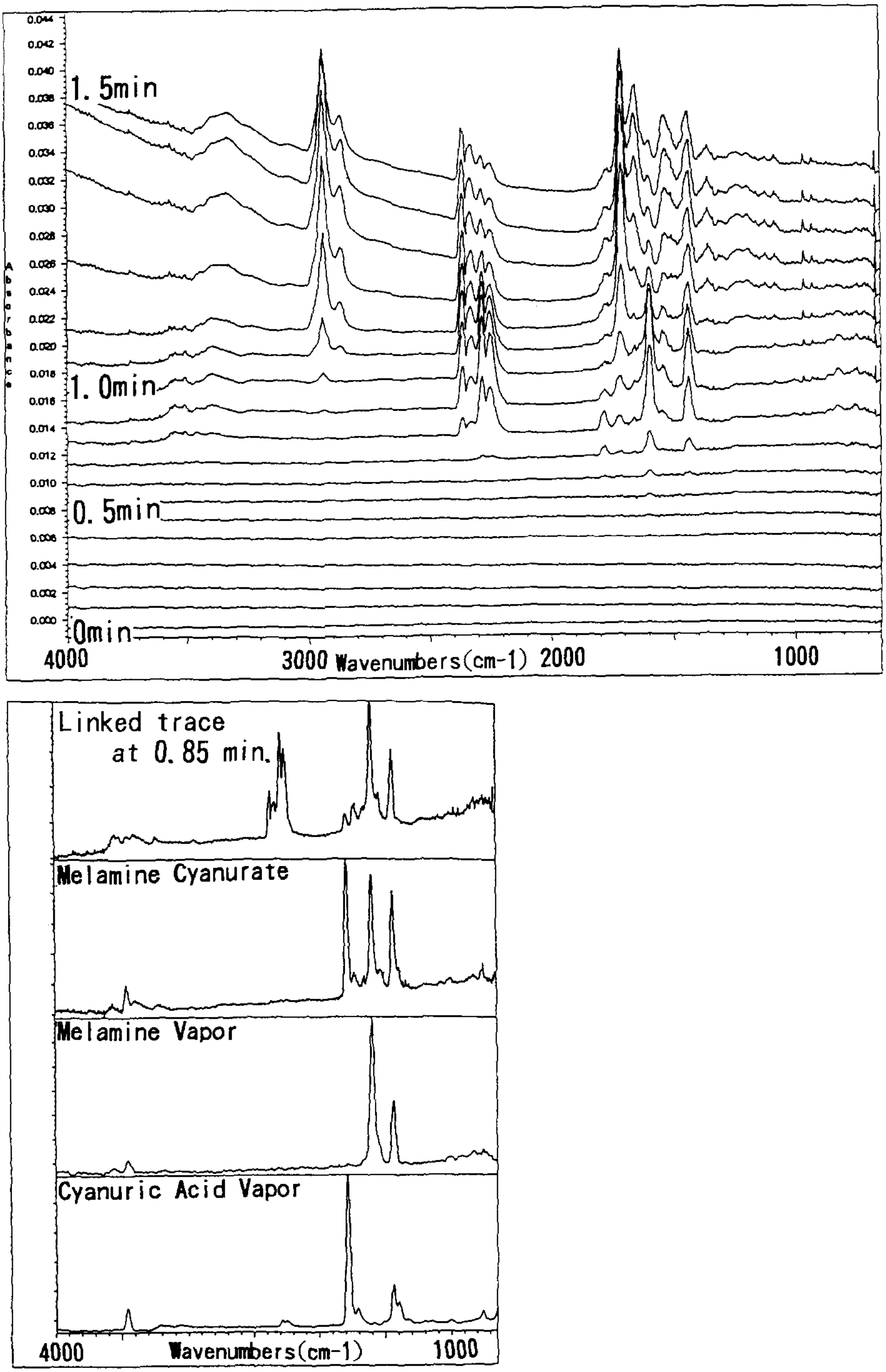

Fig. 2. T-jump/FT-IR spectra of fire-retardant nylon-6 and the spectra search result of a linked trace at 0.85 min.

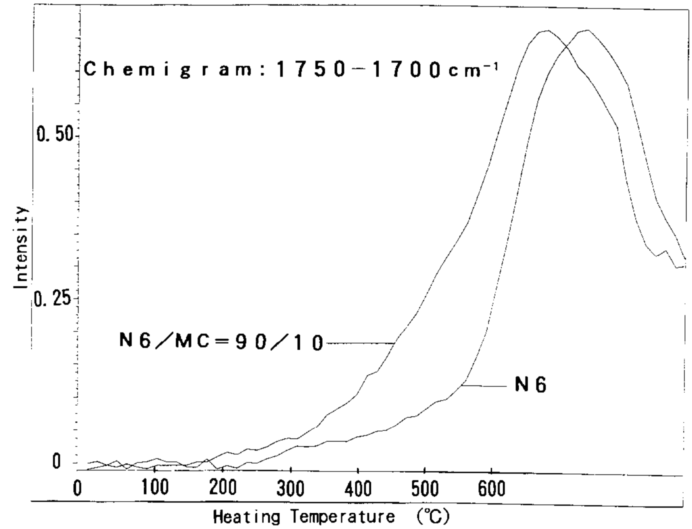

Fig. 3. Chemigrams of nylon-6 and fire-retardant nylon-6 reconstructed from an infrared response over 1750–1700 cm^{-1}.

1438 cm^{-1} were assigned to cyanurate, melamine and an overlapping band of melamine and cyanurate, respectively. Besides the melamine and cyanuric acid bands in the region between 1400 cm^{-1} and 1800 cm^{-1}, an intense band due to the CN stretching mode of cyanic acid appeared at 2284 cm^{-1} and 2251 cm^{-1}. These results suggest that the thermal dissociation of melamine-cyanurate to melamine and cyanuric acid occurs under the conditions at a heating rate of 10°C s^{-1}. Moreover, we have found that a large amount of cyanuric acid decomposes to volatile cyanic acid under these heating conditions.

Fig. 3 shows chemigrams reconstructed from the infrared response over a spectral region of amide I band (1750–1700cm^{-1}) versus the heating temperature. The difference in two profiles in Fig. 4 indicates clearly that the degradation of nylon-6 to ε-caprolactam is accelerated by the addition of melamine-cyanurate.

The T-jump/FT-IR spectra of PBT and the spectra search result are shown in Fig. 4. The spectrum linked at 1.03 min, which evaluated by library spectral search, was assigned to the alkyl terephthalate. As the peak position of OH stretching vibration at 3682.1 cm^{-1} was in good agreement with that of terephthalic acid, the entire spectrum is a superposition of dibutyl or diallyl terephthalate and terephthalic acid.

Although the T-jump/FT-IR spectra of fire-retardant PBT in Fig. 5 resemble that of PBT, the intense carbon dioxide band appearing at 2360 cm^{-1} is conspicuous. The chemigrams reconstructed from the infrared response over 2250 cm^{-1} to 2400 cm^{-1} emphasizes that the combustion of brominated-polycarbonate containing Sb_2O_3 produces sizable amounts of carbon dioxide gas (Fig. 6).

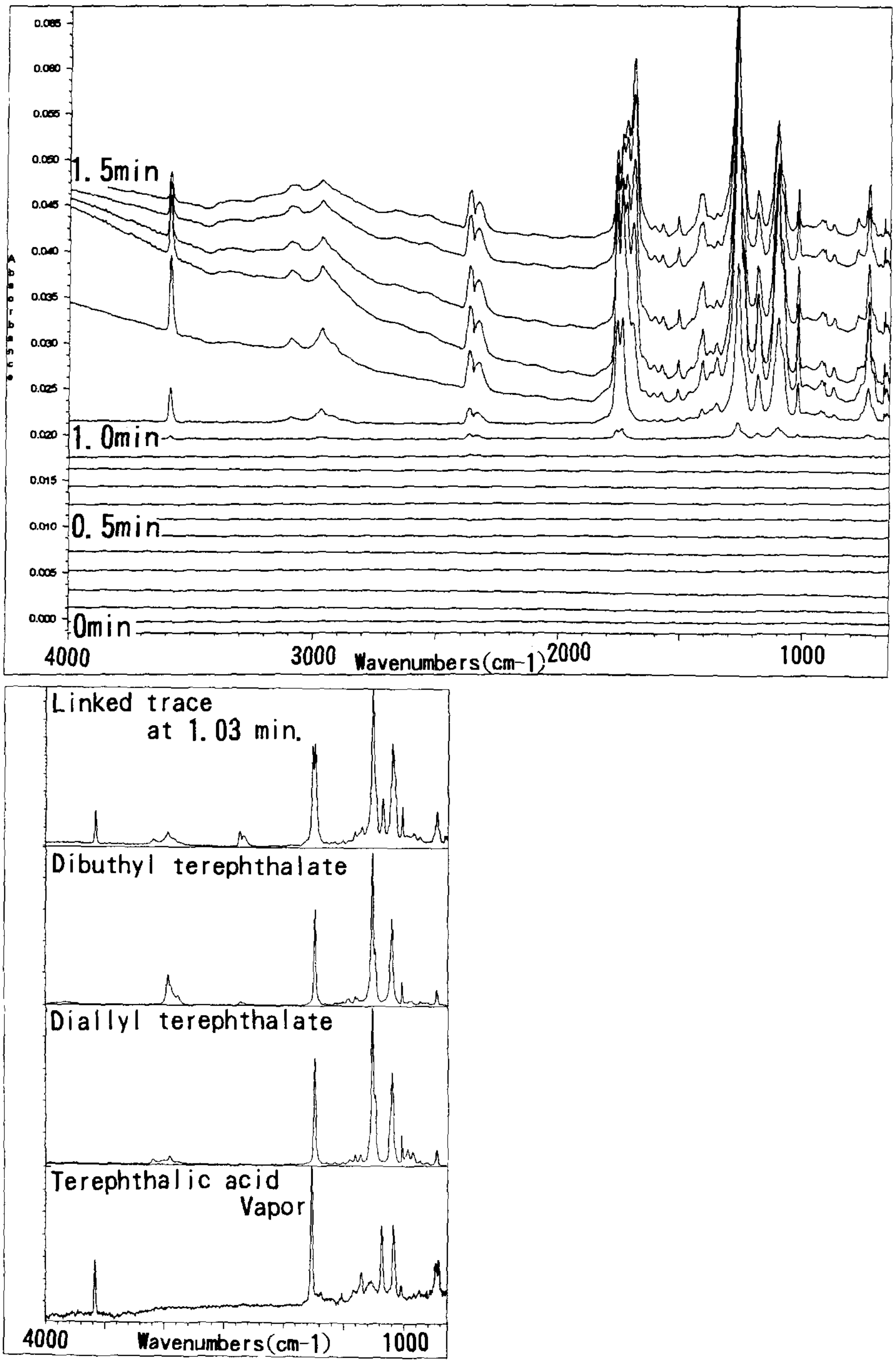

Fig. 4. T-jump/FT-IR spectra of PBT and the spectra-search result of linked trace at 1.03 min.

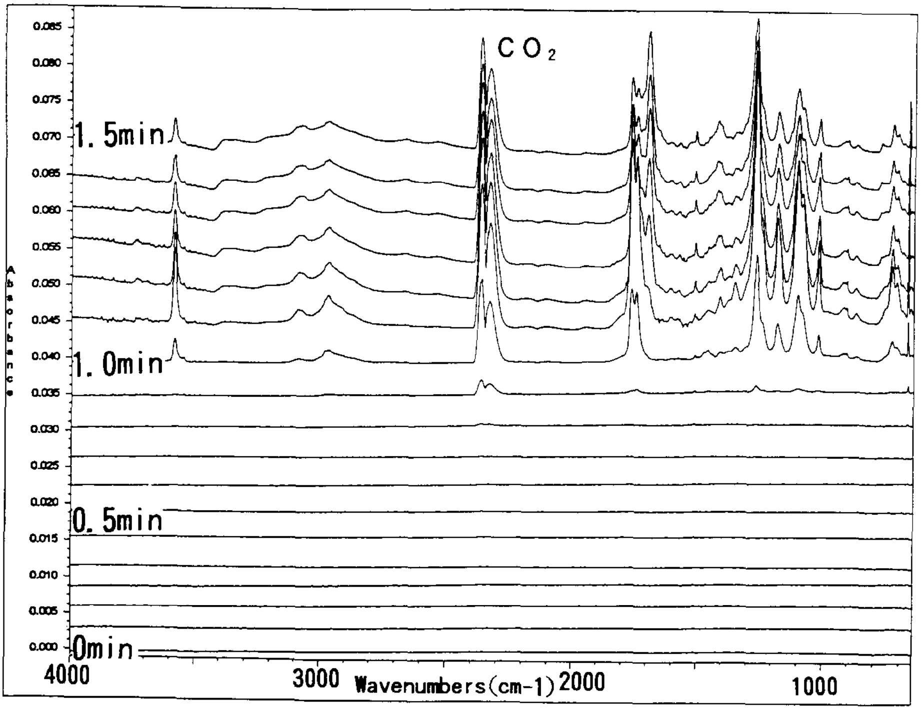

Fig. 5. T-jump/FT-IR spectra of fire-retardant PBT.

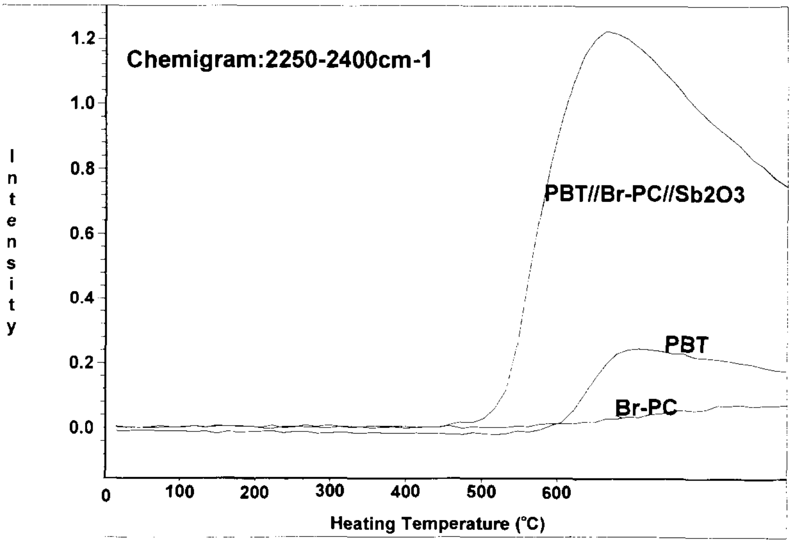

Fig. 6. Chemigrams of PBT, brominated-polycarbonate and fire-retardant PBT reconstructed from an infrared response over 2250–2400 cm^{-1}.

4. Conclusions

We have found that the thermal dissociation of melamine-cyanurate to melamine, cyanuric acid and cyanic acid becomes efficient at a fast heating rate (10°C min^{-1}). Although Costa et al. pointed out that the condensation of melamine to polymeric product formed thermal stable char [7], the results of nylon-6 suggested that melamine pyrolyzing at a relatively fast heating rate probably had no role to play in the formation of the polymeric product. In the study of the mechanisms of various fire-retardant systems, the function of molten polymer drip away from the ignited area must be considered [8]. Considerable differences in the chemigrams between the nylon-6 and the one containing melamine-cyanurate has provided evidence that this additive accelerated the thermal degradation of nylon-6. This factor might cause a reduction of molecular weight and degrade the polymer to low viscosity. The flow of a molten polymer away from the burning site contributed to the self-extinguishing mechanism (dripping).

A gaseous antimony tribromide was not observed in the case of PBT containing brominated polycarbonate and Sb_2O_3. The evolution of a large amount of carbon dioxide (incombustible gas), which might be a decomposition product of polycarbonate, dominated in the extinguishing stage.

As the fast heating rate is controlled easily, T-jump/FT-IR is an excellent tool for studying fire-retardant polymers. This advantage may supply reliable information for understanding extinguishing mechanisms.

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