

Supporting information

In situ phthalocyanine synthesis chemistry in flame towards molecular fireproof engineering

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1. Materials

Dimethyl terephthalate (DMT), zinc acetate and ethylene glycol antimony (EGA) were provided by Sinopharm Chemical Reagent Co. Ltd. Ethylene glycol (EG), acetic acid, *N,N*-dimethylacetamide, methanol, concentrated sulfuric acid, and potassium carbonate were all purchased from Kelong Chemical Industries Reagent Co. Ltd. Dimethyl 5-hydroxyisophthalate (DHP), phthalonitrile (PN), and 4-Nitrophthalonitrile were purchased from Shanghai Bidepharm Co. Ltd.

2. Experimental

2.1 Synthesis of MF molecules

The nucleophilic reaction of 4-nitrophthalonitrile and dimethyl 5-hydroxyisophthalate was maintaining at 50 °C for 24 h in DMF solvents. Then, the MF is obtained after filter and washing. MF: (white powder, 85.1% yield), m. p: 162 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.37 (t, *J*=1.5, 1H), 8.15 (d, *J*=8.7, 1H), 7.92 (dd, *J*=14.3, 2.0, 3H), 7.55 (dd, *J*=8.7, 2.6, 1H), 3.90 (s, 6H). FT-IR (cm⁻¹): 2231 ν(C≡N), 1711 ν(C=O), 1583 ν(C=C), 1502 ν(C=C) 1434 γ(C-H) 1302 asv(Ar-O-Ar), 1222 asv(C-O-C), 1166 ν(Ar-C), 1105 sv(Ar-O-Ar), 1004 sv(C-O-C), 849 γ(Ar-H), 764 γ(Ar-H), 688 γ(Ar-H), 652 γ(Ar-H). Its structure characterization is the same as reported in the literature.

2.2 Fire treatments experiment

The MF, PN and DHP powder, about 5 g, are spread evenly in an alumina crucible. Then we use the butane torch (over 1000 °C) burning the samples with 45° angles, and the combustion phenomenon is recorded by the Sony camera.

2.3 Synthesis of PET and P(ET-co-MF)₁₅

The P(ET-co-MF)₁₅ and PET were all fabricated by melt polycondensation. The synthesis

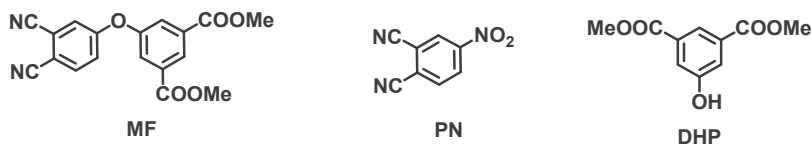
processes are shown in Scheme S1. The preparation of P(ET-co-MF)₁₅ is as follows. 25.4 g bis-hydroxyethyl terephthalate (0.1 mol bis(2-Hydroxyethyl) terephthalate, transesterified by 0.1 mol DMT and 0.22 mol EG), 5.40 g MF (0.015 mol), 0.05 g zinc acetate and 0.011 g ethylene glycol antimony as the catalysts were added to a two-necked polymerization bottle. The transesterification processes were carried out for about 2.5 h with mechanical stirring at 220 °C. Then the polycondensation, maintaining at 250 °C, was carried out at 250 °C under 40 Pa pressure. PET was also prepared by similar processes with a polycondensation at 275°C.

In order to eliminate the molecular weight influence on the polyester properties, the intrinsic viscosities [η] of P(ET-co-MF)₁₅ and PET are controlled. The [η] of PET, and P(ET-co-MF)₁₅ are 0.63, 0.62 dL/g.

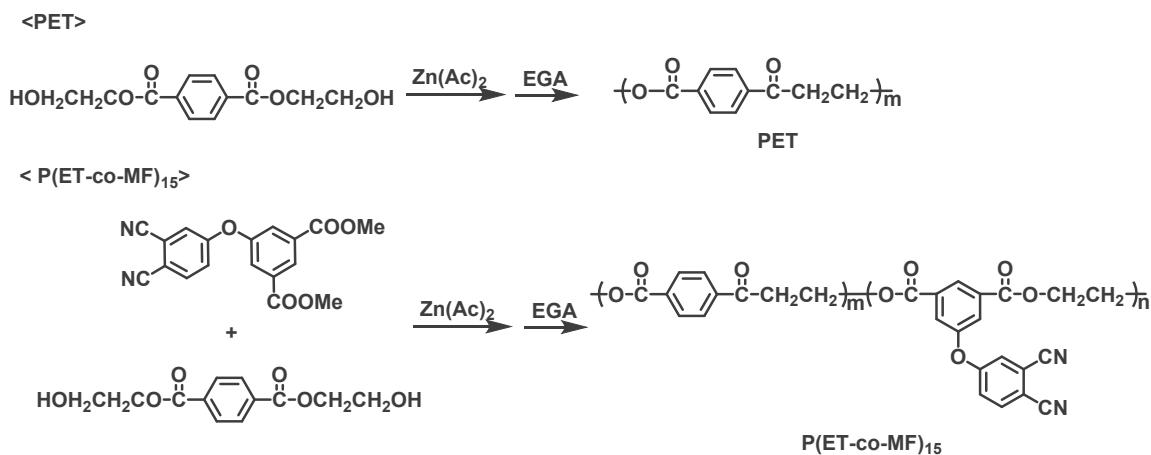
P(ET-co-MF)₁₅: FT-IR (cm⁻¹) 2964 asv(C-H), 2883 sv(C-H), 2229 v(C≡N), 1722 v(C=O), 1589 v(C=C), 1446 γ (C-H), 1259 asv(Ar-O-Ar), 1097 sv(Ar-O-Ar), 1014 sv(C-O-C), 725 cm⁻¹ γ (Ar-H). ¹H NMR (400 MHz, ppm, CF₃COOD): 8.31 (H in the terephthalic group), 8.93-8.79, 8.25-8.11, 8.10-7.96, 7.67-7.46 (H in MF structure), 5.12-4.82 (-CH₂-), 4.19 (H in the end group).

PET: FT-IR (cm⁻¹) 2964 asv(C-H), 2883 sv(C-H), 1722 v(C=O), 1589 v(C=C), 1446 γ (C-H), 1259 asv(Ar-O-Ar), 1097 sv(Ar-O-Ar), 1014 sv(C-O-C), 725 cm⁻¹ γ (Ar-H). ¹H NMR (400 MHz, ppm, CF₃COOD): 7.97-7.75 (H in the terephthalic group), 4.63-4.45 (-CH₂-), 3.92 (H in the end group).

Their FTIR spectra and ¹H NMR spectra are shown in Fig. S4.



Scheme S1. The chemical structure of MF, PN and DHP.



Scheme S2. The synthesis route of PET and P(ET-co-MF)₁₅.

3. Characterization

The chemical structure of MF, P(ET-co-MF)₁₅ and PET was characterized by NMR and FTIR analysis. NMR spectra are obtained at room temperature by Bruker AVANCE AV II-400 NMR instrument. The solvents are DMSO-d₆ for MF and CF₃COOD for the polymer. FTIR spectra were analyzed on Nicolet 6700 spectrometer.

Thermogravimetric analysis (TGA) and micro combustion calorimeter (MCC) analyzed fuel suppression effects. The thermal decomposition curves and the gaseous fuel releases are obtained from NETZSCH TG 209 F1 apparatus. The samples were heated from 40 °C up to 700 °C at a 10 °C/min heating rate at a nitrogen atmosphere. FTT 0001 MCC evaluated the heat release of the thermally-decomposed fuel. 8-10 mg samples in an alumina crucible are tested under a nitrogen/oxygen atmosphere (80/20, the total flow of 100 mL/min). The testing temperature is from 100 to 700 °C, with

a 1 °C/s heating rate.

The heat insulation property is analyzed by FTLR T420.

The magnetic circular dichroism (MCD) spectra were measured by (J-810, Jasco, Japan) with inserting the sample plate to the center of a permanent magnet (PM-491, 1.6 T, Jasco) in acetonitrile solvents.

The molecular fireproof processes driven by phthalocyanine chemistry are determined by UV-Vis with DMSO solvents, X-ray photoelectron spectroscopy (XPS) and pyrolysis–gas chromatography–mass spectrometry (PY-GC-MS). XPS spectra were recorded by a XSAM80 apparatus (Kratos Co., UK), using Al K α excitation radiation ($h\nu = 1486.6$ eV). The UV-Vis curves were obtained by Agilent Cary 50 at room temperature. The 0.02 g MF, MF₁₀, MF₂₀, and MF₃₀ are dissolved into 500 mL DMF before testing. PY-GC-MS tests were carried out with CDS5200 and DANI MASTER GC-TOF-MS. The pyrolysis temperature is 700 °C. The GC column was DN-1701 FAST 10 m 0.10 mm 0.10 mm. The pyrolysis products are analyzed by the NIST library.

The fire-safe properties of PET and P(ET-co-MF)₁₅ are evaluated by LOI, MCC and Cone tests. The limiting oxygen index (LOI) measurements were obtained according to ASTM D 2863-97 testing procedure. The samples were molded using HAAKE Mini Jet Pro (size 130 × 6.5 × 3.2 mm³) and tested by a CZF-2 instrument (Jiangning, China). The MCC tests are carried out by FTT 0001 MCC. The heat/smoke release of polymeric materials is by an FTT calorimeter (Cone tests) according to the ISO 5660-1 at a 50 kW m⁻² heat flux.

4. MCC

Table S1. The HRC and THR data

Samples	HRC ($\text{J g}^{-1} \text{K}^{-1}$)	THR (kJ g^{-1})
MF	317	26.4
MF ₁₀	124	16.8
MF ₂₀	112	15.2
MF ₃₀	97	10.7
DHP	873	33.9
PN	963	60.1

5. MCD spectra

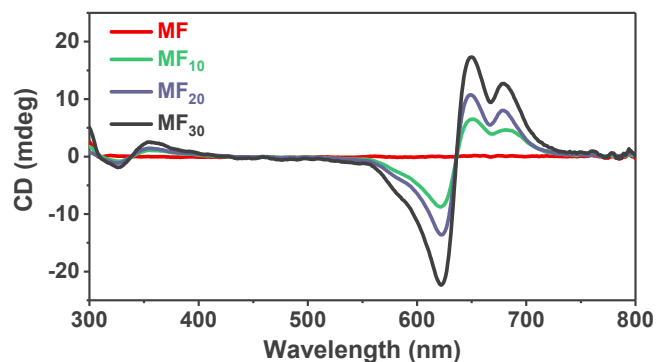


Fig. S1. The MCD spectra of MF, MF₁₀, MF₂₀ and MF₃₀

6. XPS results

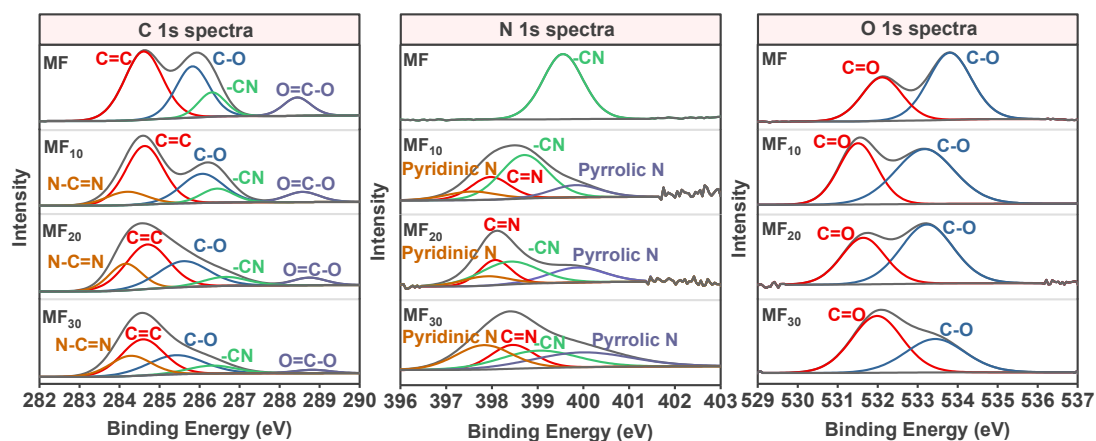


Fig. S2 The XPS spectra of C 1s, N 1s, and O1s spectra.

Table S2. The CN triple bonds and C=N bond contents in N 1s spectra.

Sample	MF	MF ₁₀	MF ₂₀	MF ₃₀
CN triple bonds contents (%)	100.0	52.2	39.1	20.0
C=N bonds contents (%)	0	22.1	23.6	26.0

7. PY-GC-MS

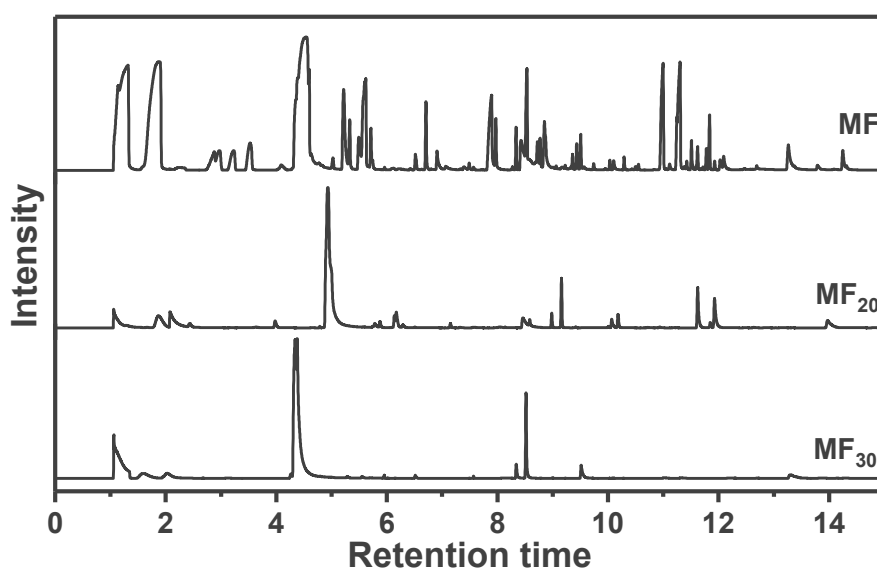
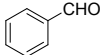


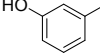

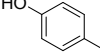

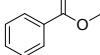
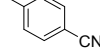

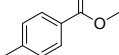
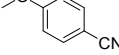

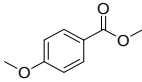
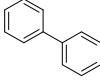
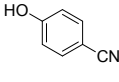
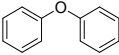
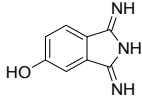
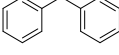
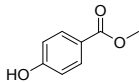
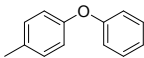
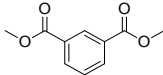
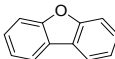
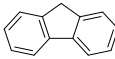
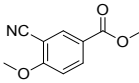
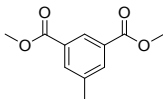
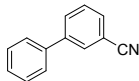
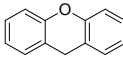
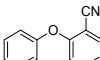
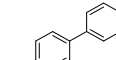
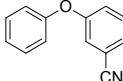
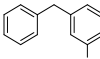
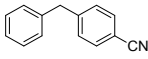
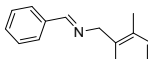
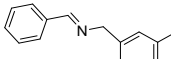
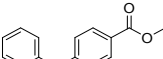
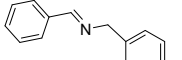


Fig. S3. The total ion chromatogram of MF, MF₂₀, and MF₃₀.

Table S3. The pyrolysis products of MF at 700 °C

Retention time (min)	M	Compounds	Major mass fragments
1.32	78	<chem>c1ccccc1</chem>	78, 77, 52, 51, 50
1.88	92	<chem>Cc1ccccc1</chem>	92, 91, 65, 63, 51
2.88	106	<chem>Cc1ccc(C)cc1</chem>	106, 91, 77
2.99	106	<chem>Cc1ccc(C)cc1</chem>	106, 91, 77
3.24	104	<chem>C=Cc1ccccc1</chem>	104, 103, 78, 77, 63, 51
3.52	108	<chem>COc1ccccc1</chem>	108, 93, 78, 65, 51

4.09	106		106, 105, 77, 51
4.32	103		103, 76, 50
5.03	116		116, 115, 89
5.22	108		108, 107, 90, 79, 77
5.33	117		117, 90, 89, 63
5.49	108		108, 107, 90, 79, 77
5.59	117		117, 90, 89, 63
5.61	136		136, 105, 77, 51
5.71	117		117, 90, 89, 63
6.51	128		128, 102, 51
6.71	150		150, 119, 91, 65
6.91	133		133, 118, 103, 90, 76, 63
7.90	128		128, 101, 75, 64, 50
7.97	166		166, 135, 128, 107, 92, 77, 62
8.33	154		154, 128, 76
8.42	119		119, 91, 64
8.54	170		170, 142, 141, 115, 77, 51
8.72	161		161, 132, 117, 104, 76, 66, 50
8.77	168		168, 167, 165, 153, 152, 115, 91, 65

8.85	152		152, 121, 115, 93, 65
9.36	184		184, 169, 156, 141, 115, 91, 77, 65, 51
9.43	194		194, 163, 135, 119, 103, 76
9.51	168		168, 139, 70, 51
10.03	166		166, 165, 164, 163, 162, 139, 83
10.10	191		191, 160, 132, 117, 102, 77
10.29	208		208, 177, 149, 134, 89
10.50	179		179, 152, 76
10.55	182		182, 181, 152, 76
10.99	195		195, 167, 140, 77, 51
11.11	179		179, 152, 76
11.30	195		195, 167, 140, 77, 51
11.42	193		193, 192, 191, 165, 91
11.51	193		193, 192, 164, 138, 83
11.62	209		209, 194, 180, 166, 116, 91, 77
11.78	209		209, 194, 180, 166, 116, 91, 77
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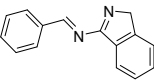
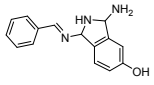
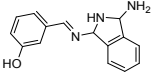








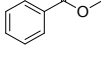
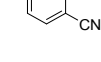


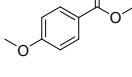
13.26	220		220, 192, 165, 143, 77, 51
13.78	253		253, 234, 222, 194, 166, 140
14.24	253		253, 222, 194, 166

Table S4. The pyrolysis products of MF₂₀ at 700 °C

Retention time (min)	M	Compounds	Major mass fragments
1.06	78		78, 77, 52, 51, 50
1.87	92		92, 91, 65, 63, 51
2.17	106		106, 91, 77, 65, 51
3.99	108		108, 91, 78, 65
4.93	103		103, 76, 50
5.78	108		108, 90, 79, 77
5.87	117		117, 116, 90, 89, 63
6.13	117		117, 116, 90, 89, 63
6.17	136		136, 105, 77, 51
6.29	117		117, 116, 90, 89, 63
7.15	128		128, 101, 75, 64, 50
8.46	128		128, 101, 75, 64, 50
8.58	166		166, 135, 128, 107, 92, 77, 64

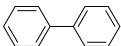
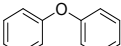
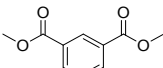
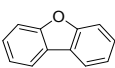
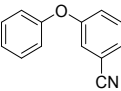
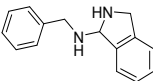
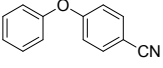
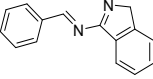
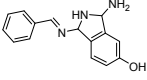
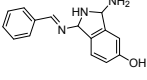
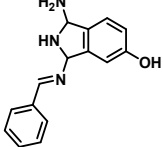













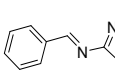
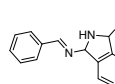
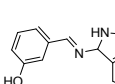
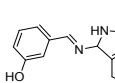
8.90	154		154, 128, 76
9.16	170	 oxydibenzene	170, 142, 141, 115, 77, 51
10.06	194		194, 163, 135, 120, 103, 76
10.18	168		168, 139, 70, 51
11.62	195		195, 167, 140, 77, 51
11.85	224		224, 193, 165, 150, 136, 119
11.92	195		195, 167, 140, 77, 51
13.97	220		220, 192, 165, 143, 77, 51
14.51	253		253, 234, 222, 194, 166, 140
14.81	253		253, 234, 222, 194, 166, 140
14.96	253		253, 234, 222, 194, 166, 140

Table S5. The pyrolysis products of MF₃₀ at 700 °C

Retention time (min)	M	Compounds	Major mass fragments
1.06	78		78, 77, 52, 51, 50
1.59	92		92, 91, 65, 63, 51
2.02	106		106, 91, 77, 65, 51
4.34	103		103, 76, 50
5.28	117		117, 116, 90, 89, 63
5.55	136		117, 116, 90, 89, 63
5.69	117		117, 116, 90, 89, 63
6.51	128		128, 102, 51
8.34	154		154, 128, 76
8.52	170		170, 142, 144, 115, 77, 51
9.51	168		168, 139, 70, 51
11.01	195		195, 167, 140, 77, 51
11.31	195		195, 167, 140, 77, 51
13.31	220		220, 192, 165, 143, 77, 51
13.83	253		253, 234, 222, 194, 166, 140
14.15	253		253, 222, 194, 166
14.27	253		253, 222, 194, 166

8. The structure characterization of PET and P(ET-co-MF)₁₅

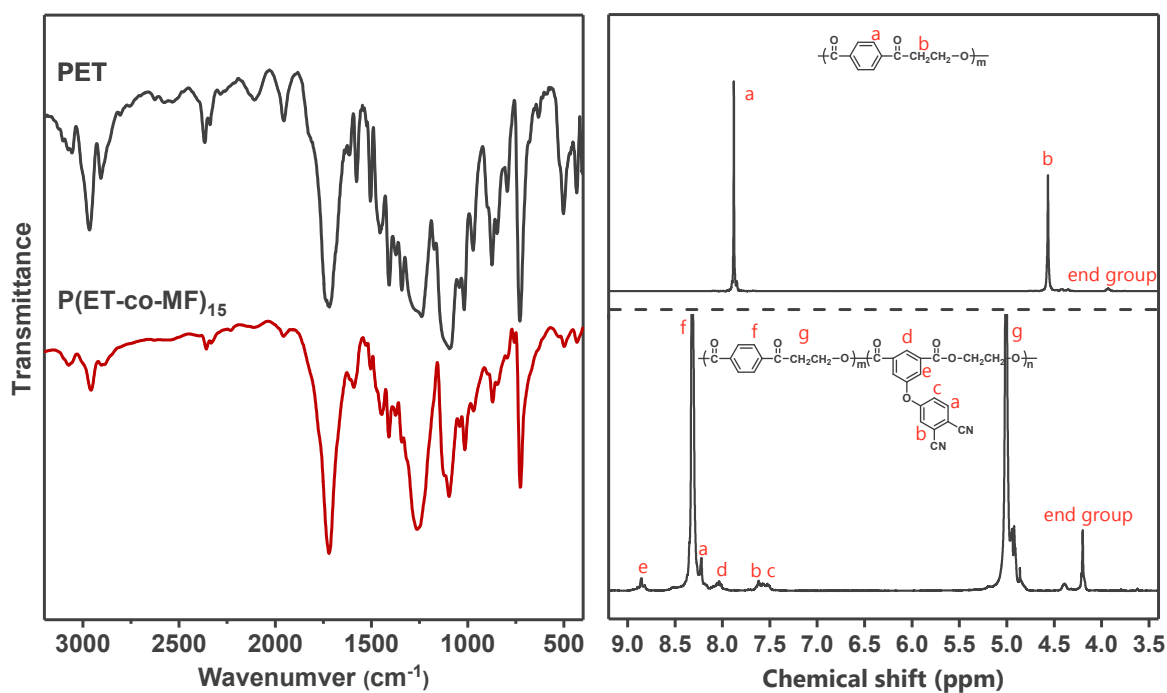


Fig. S4 FTIR spectra and ¹H NMR spectra of PET and P(ET-co-MF)₁₅.

9. Fire hazards and flame retardance data of PET and P(ET-co-MF)₁₅

Table S6 Fire hazards and flame retardance of P(ET-co-MF)₁₅ and FRM₂₀PET structure.

Sample	PET	P(ET-co-MF) ₁₅	FRM ₂₀ PET
Incorporation contents (mol%)*	0	13.0	20.0
LOI	22.0	30.0	32.0
HRC (J/ g K)	584	228	-
PHRR (kW m ⁻²)	734	301	405
THR (MJ m ⁻²)	71	65	64
TSR (m ² m ⁻²)	1703	1305	1230
UL-94	No rating	V-0	V-2
Dripping	Seriously	No	Slightly

* Contents represent the molar ratio of modified structure (MF or FRM) and terephthalate structure