

Supporting Information

Preparation and Thermal Cross-linking Mechanism of Copolyester Fiber with Flame Retardancy and Anti-dripping by in-situ Polymerization

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1. Structure and properties of flame retardant

Fig.S1 shows the ¹H-NMR spectra of flame retardant DDP-EG and **Table.S1** shows the chemical shift of groups in the molecular structure. There is no proton signal for carboxylic group -COOH. Peak f (2.7ppm) is attributed to the proton signals of hydroxyl group -OH. Peak p (7.0-8.1 ppm) corresponds to the aromatic protons of the terephthalate units. The ratio of peak area between hydroxyl group and benzene is about 1:4. These results indicate that the esterification reaction is occurred between DDP and EG-terminated.

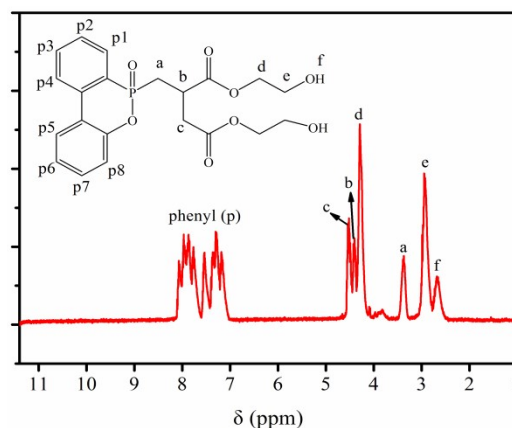


Fig. S1The ¹H-NMR of DDP-EG

Table. S1 The ¹H-NMR data of DDP-EG

Chemical shift	Integral area	Atomic ratio	Groups
7.0-8.1ppm	4.41	4	Phenyl (p)
4.5 ppm	1.08	2	c
4.4 ppm	0.64	1	b
4.3 ppm	2.43	4	d
3.4 ppm	1.07	2	a
2.9 ppm	2.35	4	e
2.7 ppm	1.00	2	f

The thermal properties of DDP-EG were measured by TGA. **Fig.S2** shows the thermal gravimetric curves of DDP and DDP-EG at nitrogen atmosphere. The analysis data is presented in **Table.S2**. $T_{5\%}$, T_{dmax} and DTG represent the initial decomposition temperature, the temperature at maximum weight loss rate and the maximum weight loss rate separately. It can be seen $T_{5\%}$, T_{dmax1} , and T_{dmax2} of DDP-EG are higher than that of flame retardant DDP, indicating DDP-EG with higher thermal properties after esterification reaction. The reason why DDP-EG has good thermal performance is that DDP-EG has the EG-terminated structure. The excellent thermal properties of DDP-EG make it more beneficial to the copolymerization of PET.

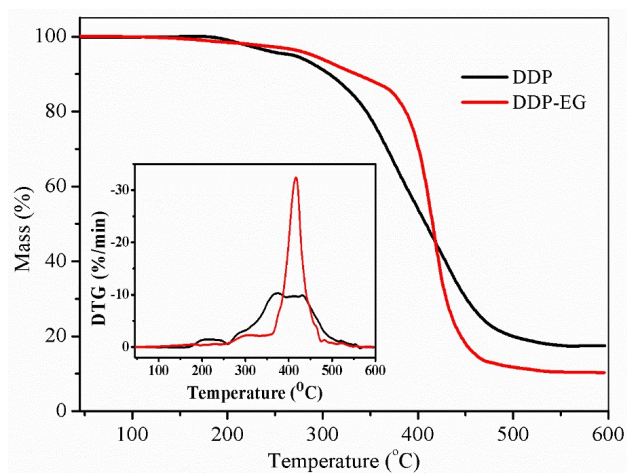
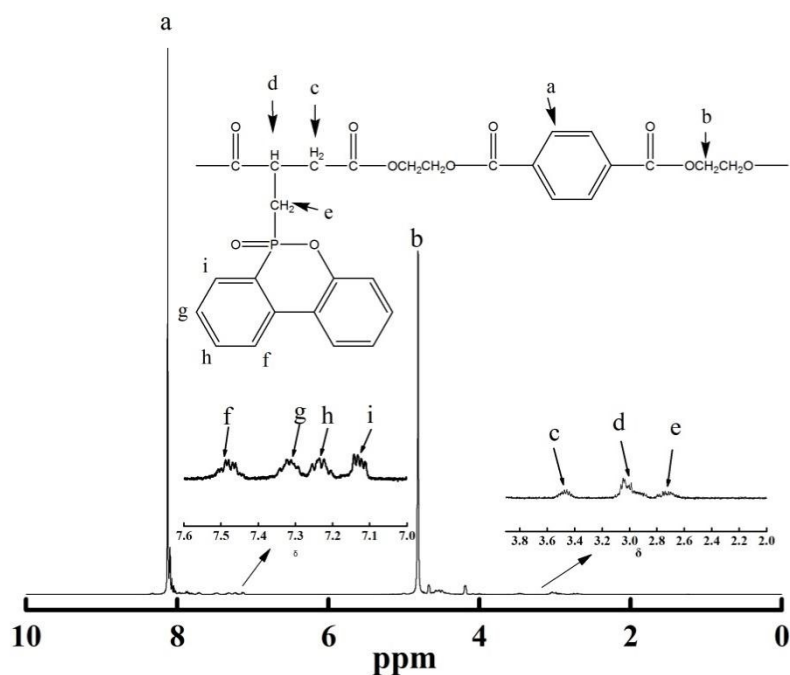
**Fig. S2 The TGA and DTG of DDP and DDP-EG (at nitrogen atmosphere)**

Table. S2 The TGA and DTG data of DDP and DDP-EG

Smamples	$T_{5\%}$ (°C)	$T_{dmax 1}$ (°C)	DTG d_1 (%/min)	$T_{dmax 2}$ (°C)	DTG d_2 (%/min)	$T_{dmax 3}$ (°C)	Residual (wt %)
DDP	269	225.1	-1.4	374.8	-10.3	431.3	17.5
DDP-EG	290	310.2	-1.7	417.2	-32.4	-	10.3

2. Structure and properties of flame retardant

The $^1\text{H-NMR}$ spectra of modified PET polyesters (PETP is taken as an example) is shown in **Fig. S3**. Peak a (8.20ppm) is attributed to the proton signals of aromatic protons of the terephthalate units. Peaks of multiple splitting i, h, g, f (7.1-7.5 ppm) corresponds to the proton signals of benzene ring on DDP-EG structure. Chemical shifts at 2.6 to 3.6 ppm correspond to the proton signals of methylene on ethylene glycol. The peaks of chemical shifts at 4.25 to 4.70 ppm attributed to the proton signals of diethylene glycol formed during polymerization process. The $^1\text{H-NMR}$ spectra of PETP suggests that the introduction of flame retardant DDP-EG is incorporated into polyester chain segments by copolymerization. The prepared samples are the target products.

**Fig. S3 The $^1\text{H-NMR}$ spectra of PETP**

3. Melting and crystallization behavior of copolyesters

To investigate the melting and crystallization behavior of these polyesters, DSC

analysis for cooling and heating was carried out (curves shown in **Fig. S4**, analysis results presented in **Table.S3**. The parameters of crystallization temperature, crystallization enthalpy, melting enthalpy and melting temperature are lower than those of pure PET due to the introduction of DDP with large steric hindrance into PET chain, leading the decrease of molecular chain regularity. With the increase of nano-SiO₂ silica sol content, the parameters of T_g of modified PET copolyesters show a decreasing trend caused by the nano-SiO₂ leading the free volume V_m between molecular chains increase and PET chain easier to move. The crystallization temperature T_c of modified PET copolyesters increases with the increase of the nano-SiO₂ content, indicating improvement of the nucleation rate. The faster the nucleation rate is, the better the crystallization property is. It is due to nano-SiO₂ silica sol as the function of crystallization nucleating agent in PETP matrix.

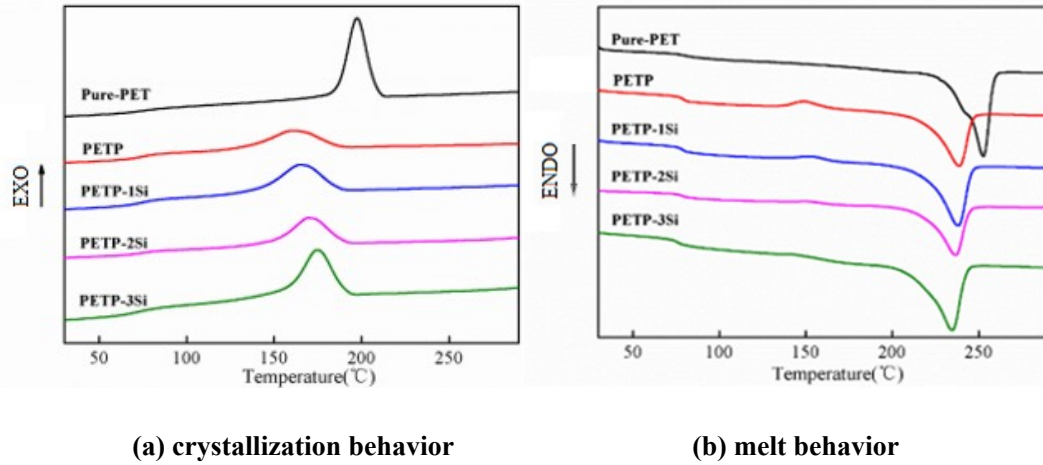


Fig. S4 The DSC of copolyesters

Table. S3The DSC of copolyesters

Samples	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	ΔT_c (°C)	D (°C)
Pure-PET	82.1	252.7	41.8	197.3	43.9	55.4	10.7
PETP	78.7	239.2	32.2	160.2	26.4	79.0	26.8
PETP-1Si	77.8	238.5	33.6	164.9	28.9	73.6	21.9
PETP-2Si	76.3	237.2	34.7	169.3	32.6	67.8	20.2
PETP-3Si	75.2	235.1	32.5	174.0	34.1	62.0	16.4

4. Characteristic viscosity of copolymers

Table.S4 shows the effect of acidic SiO₂ sol on polymerization process and intrinsic viscosity. The acidic SiO₂ sol does not catalyze the degradation of polyester, but the network structure of acid SiO₂ sol can improve that the entanglement effect of macromolecular chain and increase the characteristic viscosity of silicon - phosphorus copolymer ester. However, the structure of entangled macromolecules affects the transesterification reaction, which leads to the decrease of molecular weight and intrinsic viscosity. Using inert inorganic acid silica sol as anti-fuse modifier can not only guarantee good molecular weight, but also guarantee the flame retardancy of silicon-phosphorus co-polyester. Using the cross-linking characteristics of acidic reticulated silica sol, the network structure of silica sol was transformed into cross-linked structure, and the anti-melting modification of silicon-phosphorus copolyester was achieved.

Table. S4 The intrinsic viscosity of copolyester

Samples	DDP (mol%)	Nano-SiO ₂ (wt%)	Intrinsic viscosity (dL·g ⁻¹)
Pure PET	0	0	0.660
PETP	5	0	0.728
PETP-1Si ^d	5	1	0.631
PETP-2Si	5	2	0.530
PETP-3Si	5	3	0.525