Supporting Information

Phosphorus-, nitrogen- and carbon- containing polyelectrolyte complex: preparation, characterization and its flame retardant performance on polypropylene

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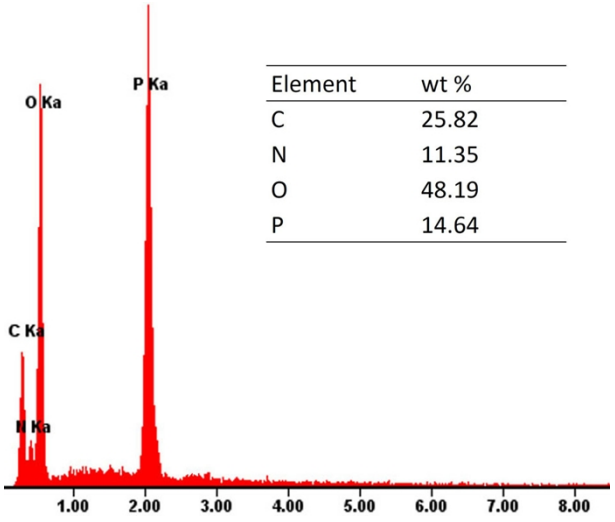
EDX spectrum of PEC



Element	wt %
C	25.82
N	11.35
O	48.19
P	14.64

Fig. S1 EDX spectrum of PEC. The inset shows the elemental composition of C, N, O and P.

Observation of PEC in N,N-dimethylformamide, chloroform, deionized water and dilute NaOH solution

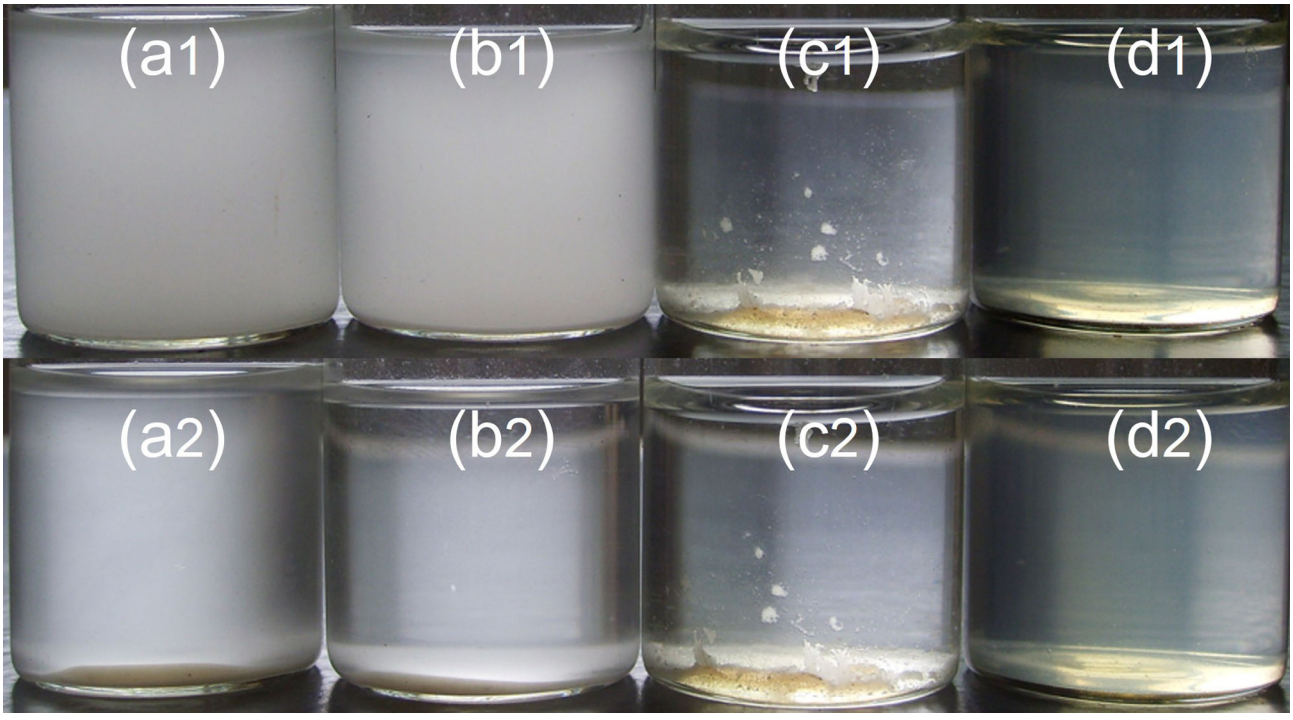


Fig. S2 Observation of 100 mg PEC in 10 mL N,N-dimethylformamide (first column), chloroform (second column), deionized water (third column) and dilute NaOH solution (fourth column, NaOH: 0.05 mol/L) (first row: after stirring at room temperature for 1 h, second row: after standing at room temperature for 0.5 h).

As can be seen, the PEC can disperse in N,N-dimethylformamide under vigorous stirring. However, this suspension is not stable, which precipitates easily at the bottom of vials (see Fig. S2 (a1, a2)). In the case of PEC in chloroform, the same phenomenon is observed (see Fig. S2 (b1, b2)). After stirring at room temperature for 1 h in deionized water, the PEC changes from solid powder to gelatinous mass (see Fig. S2 (c1, c2)). These results demonstrate the nonsoluble property of PEC in common organic solvents and water.[1,2]

However, after adding some dilute NaOH solution, the PEC can dissolve slowly (see Fig. S2 (d1, d2)), which shows similar phenomenon to that of poly(diallyldimethylammonium chloride) (PDDA)/sodium carboxymethyl cellulose (CMCNa) PEC[3].

Comparison of intumescent effect for PEI, PA and PEC after burning in air

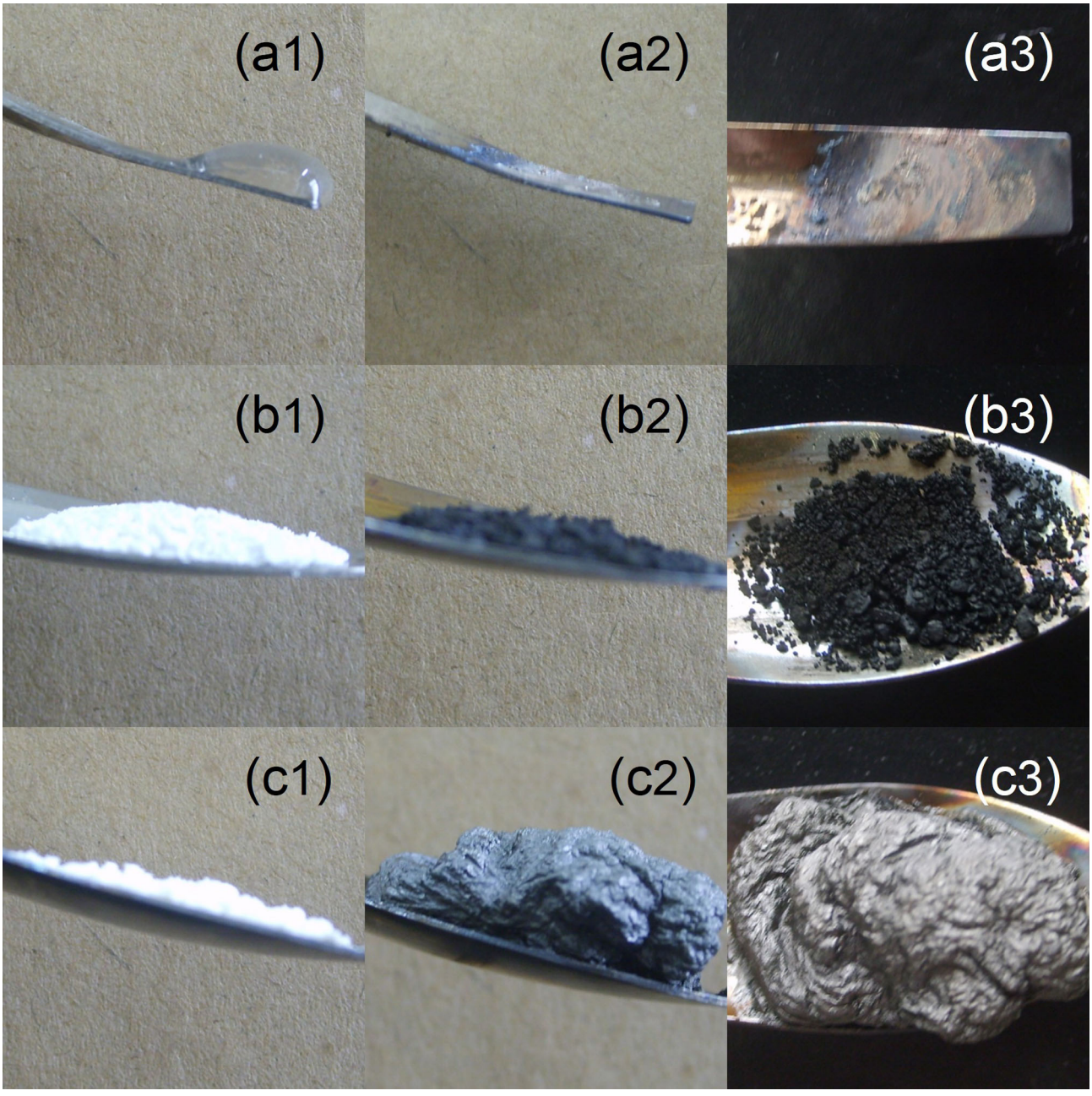


Fig. S3 Images of PEI (first row), PA (second row) and PEC (third row) before (first column, 100 mg) and after (second column) burning in air. The third column is top view of the second column.

Fig. S3 shows the images of PEI, PA and PEC before and after burning in air. Clearly,

the PEI is almost burned out, and leaves a very thin layer of char residue (see Fig. S3 (a1-a3)). As for PA, the char residue is very loose and without obvious intumescence (see Fig. S3 (b1-b3)). However, the char residue of PEC is very compact, which demonstrates excellent intumescent effect (see Fig. S3 (c1-c3)).

Thermal properties of PEI, PA and PEC under nitrogen atmosphere

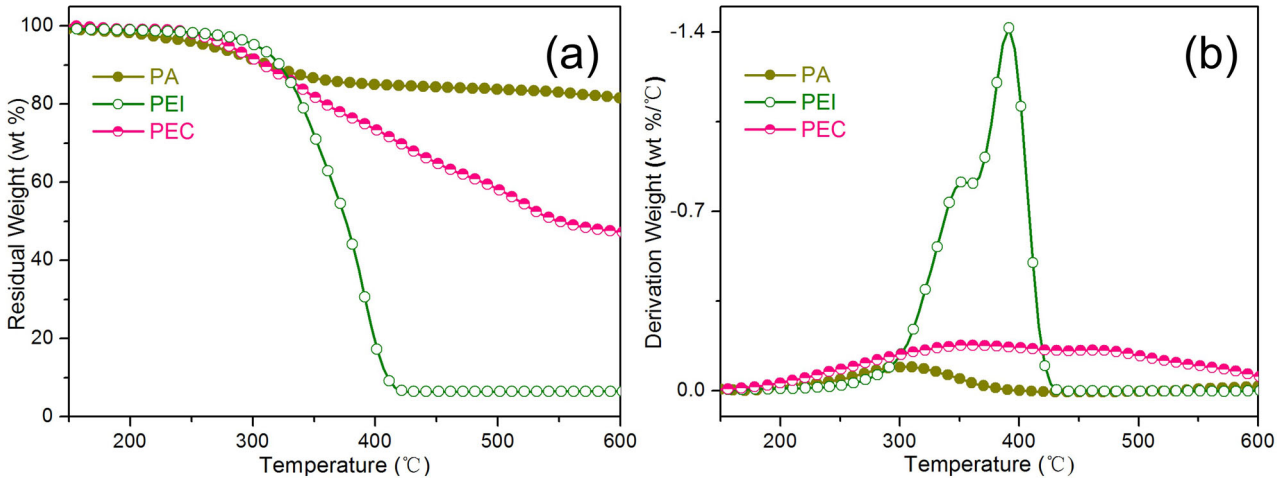


Fig. S4 TGA (a) and DTG (b) curves of PEI, PA and PEC under nitrogen atmosphere.

Table S1 Thermal properties of PEI, PA and PEC under nitrogen condition

Sample	$T_{5\%}$ (°C)	T_{max} (°C)	Char (wt %)
PEI	301	391	7
PA	264	307	82
PEC	276	356	47

Note: $T_{5\%}$: 5 wt % weight loss temperature; T_{max}: maximum weight loss temperature; Char: char residues at 600 °C.

Fig. S4 presents the TGA and DTG curves of PEI, PA and PEC under nitrogen atmosphere, and the detailed data are listed in Table S1. As can be seen, the 5 wt % weight loss temperature ($T_{5\%}$) and maximum weight loss temperature (T_{max}) of PEC are between those of PA and PEI. This result is most likely due to the performance of PA, which can produce pyrophosphate and polyphosphate at an earlier stage and catalyze the decomposition of PEI.[4] On the other hand, this catalytic process is also beneficial, which can trigger the char formation.[5] As shown in Fig. S4 (b), PA displays a weak and broad mass loss peak from 200 to 400 °C. As for the PEI, a shoulder peak and then a sharp peak

can be clearly seen, which partially overlap with that of PA. In this case, PEI also plays an important role, which can provide rich carbon and nitrogen elements.[6] Consequently, PEC exhibits a weak and broad peak, and leaves a char residue of 47 wt % at 600 ^{o}C.

Thermal properties of PP, PP/5PEC, PP/10PEC and PP/20PEC under nitrogen atmosphere

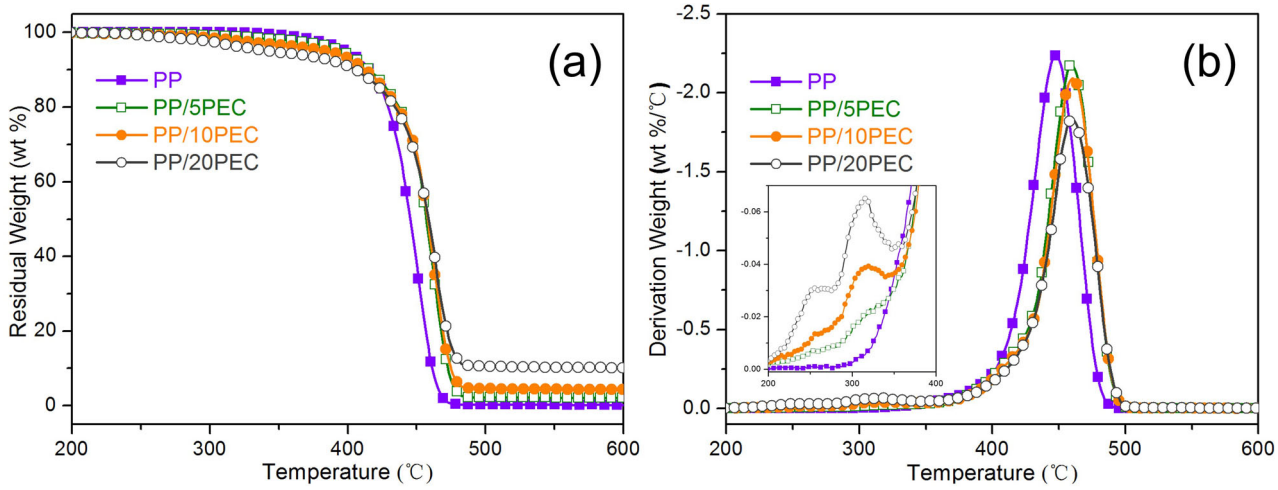


Fig. S5 TGA (a) and DTG (b, the insert shows the magnified curves over the range of 200-400 °C) curves of PP, PP/5PEC, PP/10PEC and PP/20PEC under nitrogen atmosphere.

Table S2 Thermal properties of PP, PP/5PEC, PP/10PEC and PP/20PEC under nitrogen condition

Sample	$T_{5\%}$ (°C)	T_{max} (°C)	Char (wt %)
PP	398	447	0
PP/5PEC	396	459	2
PP/10PEC	384	460	4
PP/20PEC	342	460	10

Fig. S5 presents the TGA and DTG curves of PP, PP/5PEC, PP/10PEC and PP/20PEC under nitrogen atmosphere, and the detailed data are listed in Table S2. Compared to the pristine PP, a reduction in $T_{5\%}$ is observed with the addition of PEC, which is mostly due to the earlier degradation of PEC over the range of 200-400 °C.[7] However, it is worth noting that the T_{max} especially the char residues from 500 to 600 °C for the PP/PEC systems are significantly higher than those of the pristine PP, indicative of the enhancement of thermal

stability and char formation at high temperature provided by PEC.[8] Furthermore, the peak value of DTG curve also decreases gradually as the content of PEC increases, signifying the lower mass loss rate during decomposition.[9,10] It is also found that the TGA and DTG curves are similar in shape over the range of 350-550 ^{o}C before and after adding PEC. Similar results were observed in PP/poly(4,4-diaminodiphenylmethane-*O*-bicyclic pentaerythritol phosphate phosphate) (PDBPP) system, which is mostly due to the uniformly dispersed fillers in PP matrix.[7]

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