Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

3D printable robust shape memory PET copolyesters with fire safety via π-stacking and synergistic crosslinking

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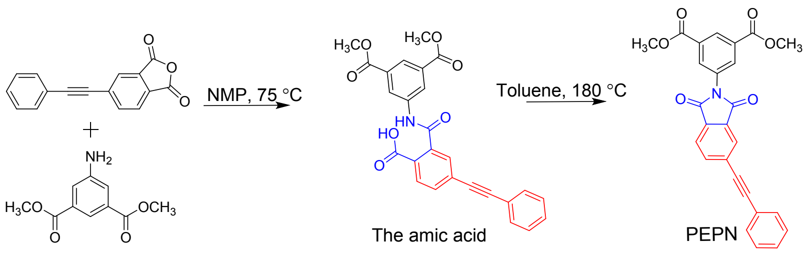
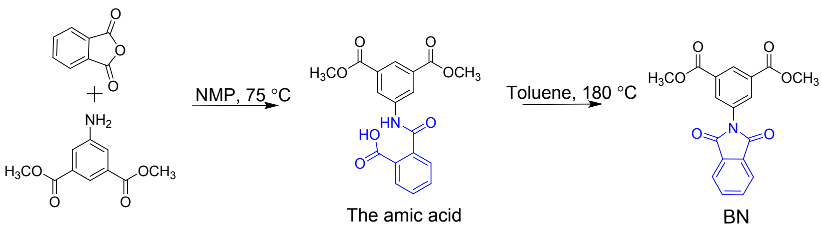
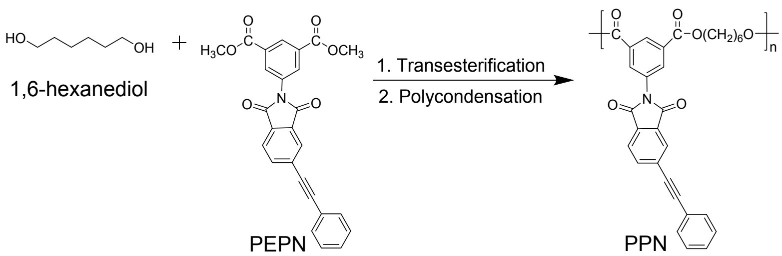


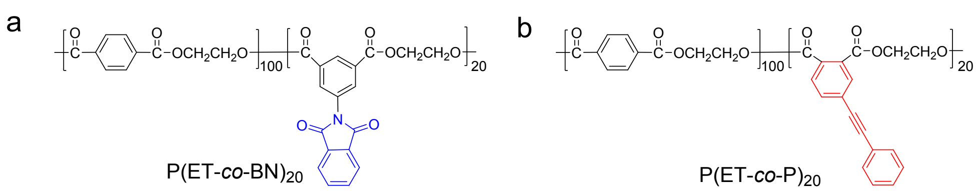
Scheme S1 Synthesis process of phenylacetylene-phenylimide containing PEPN monomer.



Scheme S2 Synthesis process of phenylimide containing BN monomer.



Scheme S3 Synthesis process for model polymer PPN.



Scheme S4 Chemical structure of phenylimide-containing copolyester P(ET-*co*-BN)$_{20}$ (a) and phenylacetylene-containing copolyester P(ET-*co*-P)$_{20}$ (b).

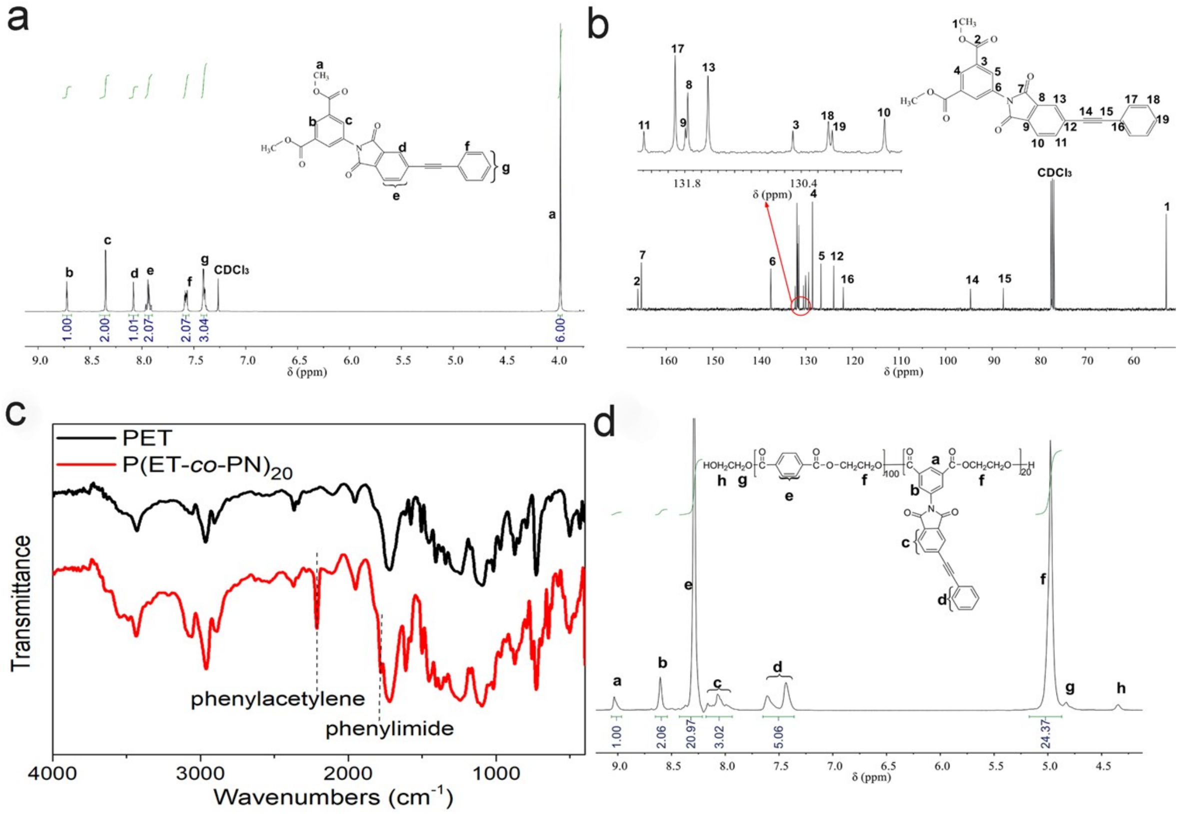


Fig. S1 Structural characterization. (a) ^{1}H NMR spectrum of monomer PEPN. (b) ^{13}C NMR spectrum of monomer PEPN. (c) FT-IR spectra of PET and P(ET-*co*-PN)$_{20}$; (d) ^{1}H NMR spectrum of P(ET-*co*-PN)$_{20}$.

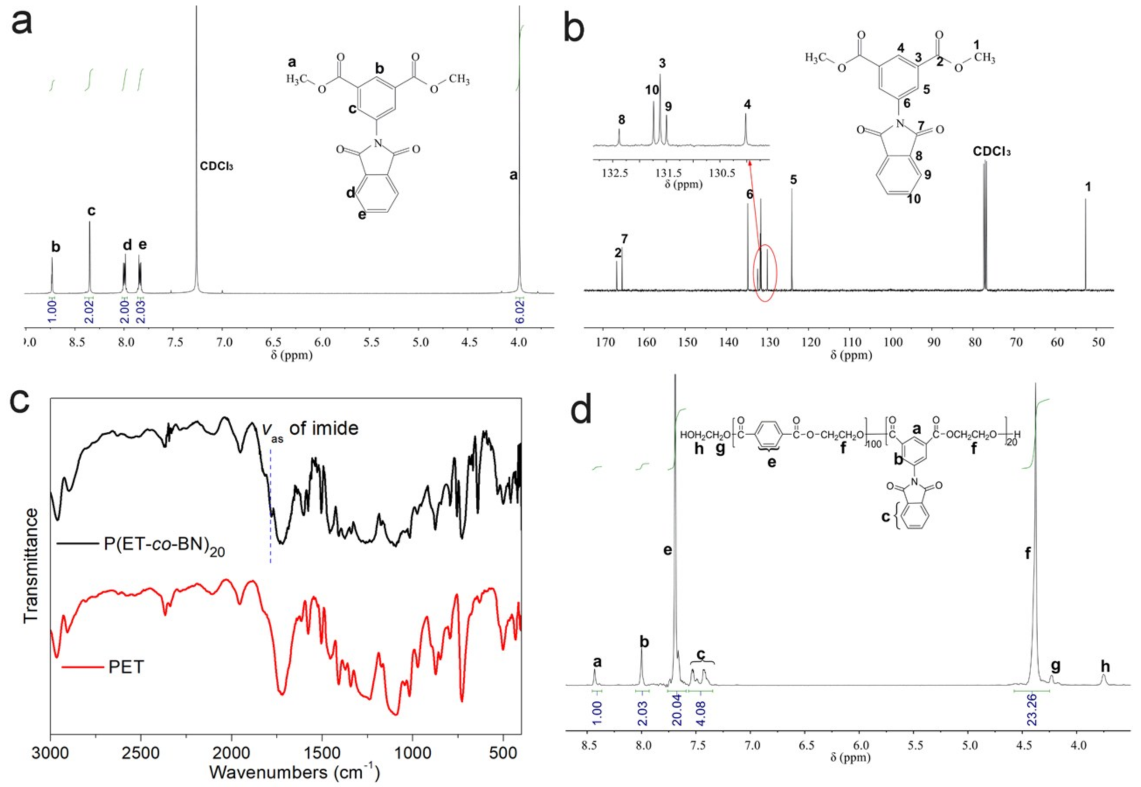


Fig. S2 Structural characterization. (a) ^{1}H NMR spectrum of monomer BN. (b) ^{13}C NMR spectrum of monomer BN. (c) FT-IR spectra of PET and P(ET-*co*-BN)$_{20}$; (d) ^{1}H NMR spectrum of P(ET-*co*-BN)$_{20}$.

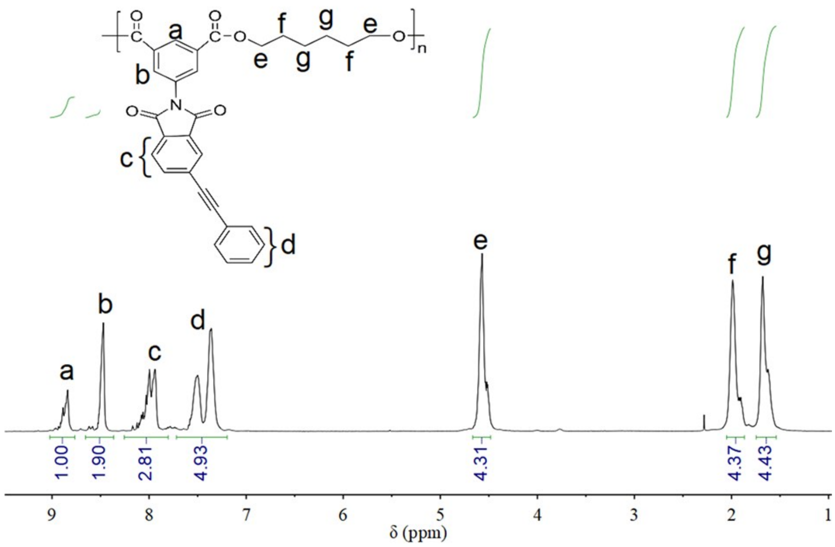


Fig. S3 ^{1}H NMR spectrum of model polymer PPN

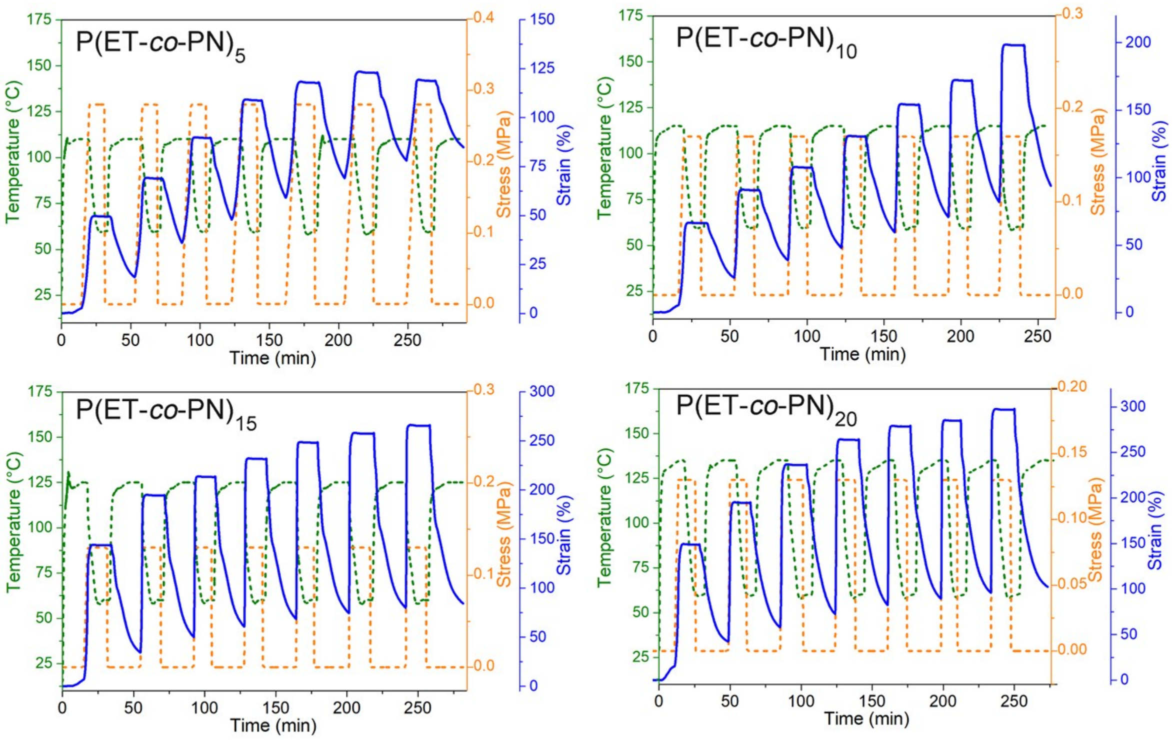


Fig. S4 DMA curves of shape memory effect for copolyesters P(ET-*co*-PN)$_n$

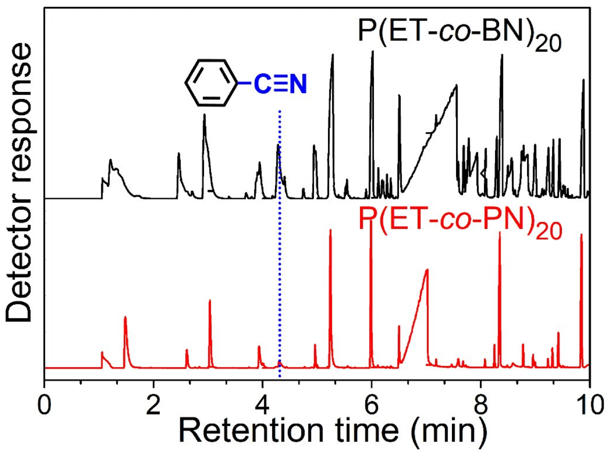


Fig. S5 Total ion chromatogram of P(ET-*co*-BN)$_{20}$ and P(ET-*co*-PN)$_{20}$ in the pyrolysis gas chromatography-mass spectrometry test.

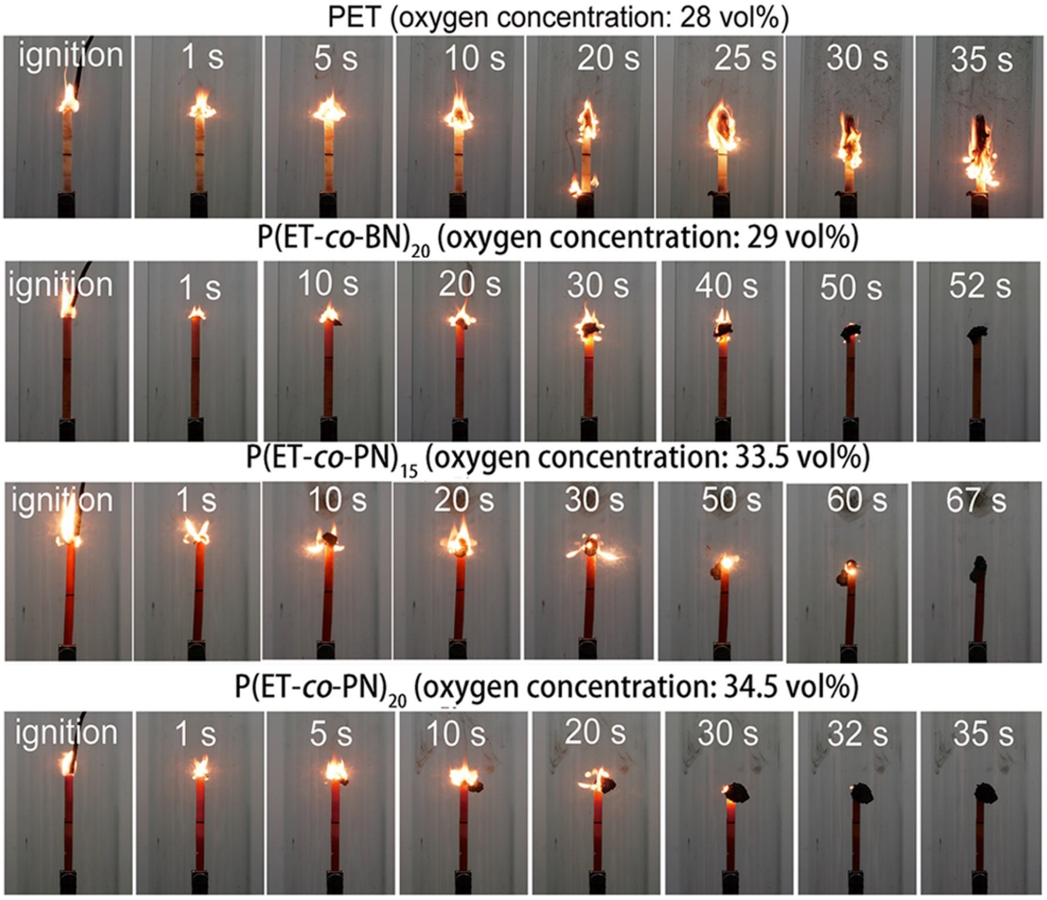


Fig. S6 Combustion processes of PET, P(ET-*co*-BN)$_{20}$, P(ET-co-PN)$_{15}$ and P(ET-co-PN)$_{20}$ during LOI testing at different time.

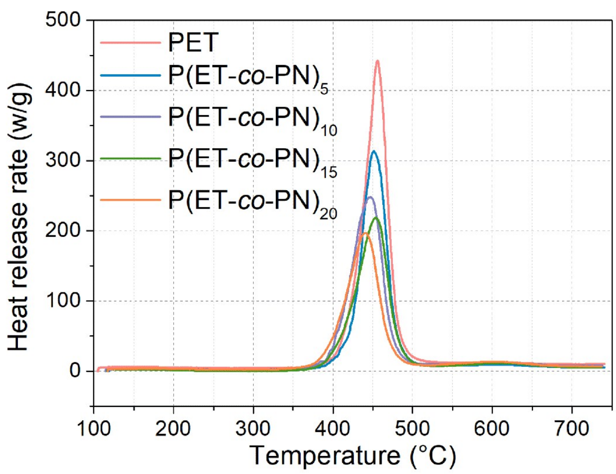


Fig. S7 Heat release rate curves of PET and copolyesters P(ET-*co*-PN)$_n$ in microcalorimetry test

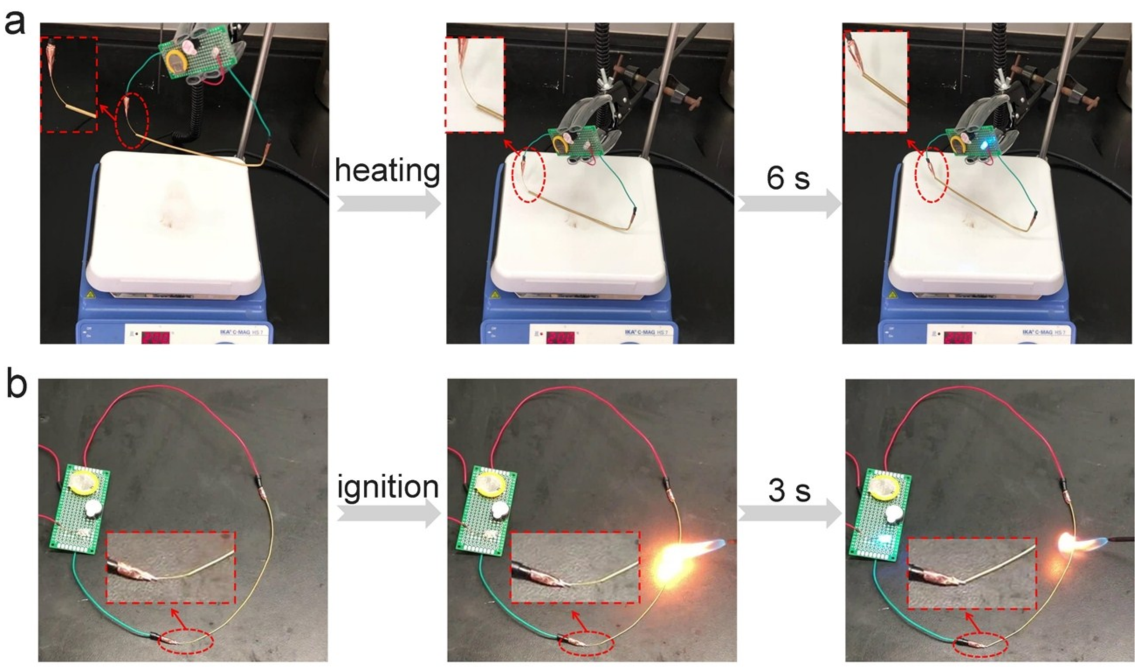


Fig. S8 (a) High temperature early warning of the sensor in precombustion using a copper tube with a diameter of 2 mm and a thickness of 0.2 mm. (b) Realtime monitoring for the changes of the sensor using a copper tube with a diameter of 1 mm and a thickness of 0.2 mm

Table S1 Basic parameters of PET and P(ET-*co*-PN)$_n$

Sample	PEPN content [mol%]		[η] [dL g^{-1}]	N_t [%][b]	N_a [%][c]	ΔH_m [J/g]	T_g [°C]	T_m [°C]	δ (MPa)[d]	ε [%][e]
	theoretical	actual[a]								
PET	-	-	0.62	-	-	48.6	73	254	61.8 ± 2.4	362 ± 110
P(ET-*co*-PN)$_5$	4.8	5.0	0.78	0.33	0.41	32.9	88	240	79.6 ± 2.4	311 ± 33
P(ET-*co*-PN)$_{10}$	9.1	9.5	0.73	0.59	0.58	17.2	92	229	82.5 ± 0.7	244 ± 35
P(ET-*co*-PN)$_{15}$	13.0	13.6	0.72	0.82	0.88	12.4	96	213	86.8 ± 2.1	172 ± 37
P(ET-*co*-PN)$_{20}$	16.7	17.1	0.65	1.00	1.04	-	101	-	89.6 ± 3.1	41 ± 33

[a] molar percentage of PEPN calculated by the integral area ratio of “a” peak and “e” peak in ^{1}H NMR
[b] theoretical nitrogen content of the copolyesters
[c] actual nitrogen content of the copolyesters determined by elemental analysis
[d] Tensile strength
[e] Elongation at break

Table S2 Corresponding microcalorimetry testing data of PET and copolyesters P(ET-*co*-PN)$_n$

Sample	HRC (J g^{-1} k^{-1})	p-HRR (w g^{-1})	THR (kJ g^{-1})
PET	465	436	17.9
P(ET-*co*-PN)$_5$	329	310	13.3
P(ET-*co*-PN)$_{10}$	261	244	12.7
P(ET-*co*-PN)$_{15}$	231	216	11.6
P(ET-*co*-PN)$_{20}$	210	193	11.0