

Supplementary Materials: Halogen-Free Flame-Retardant Compounds. Thermal Decomposition and Flammability Behavior for Alternative Polyethylene Grades

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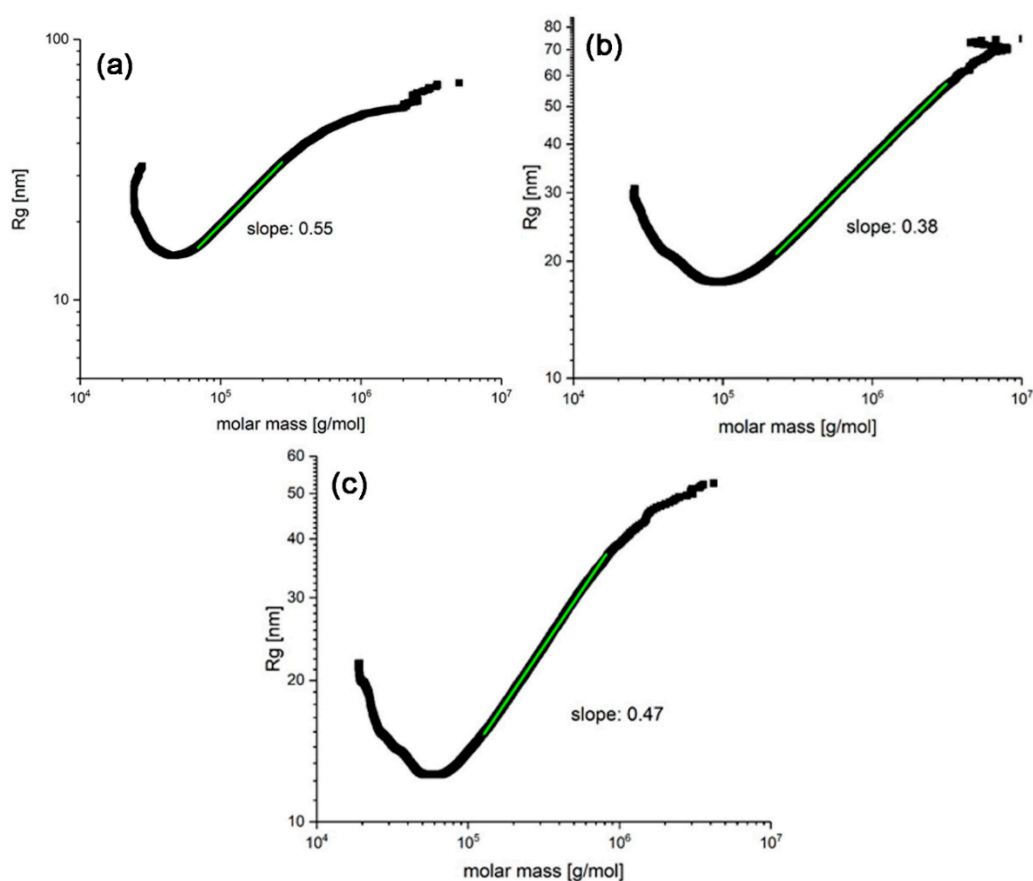
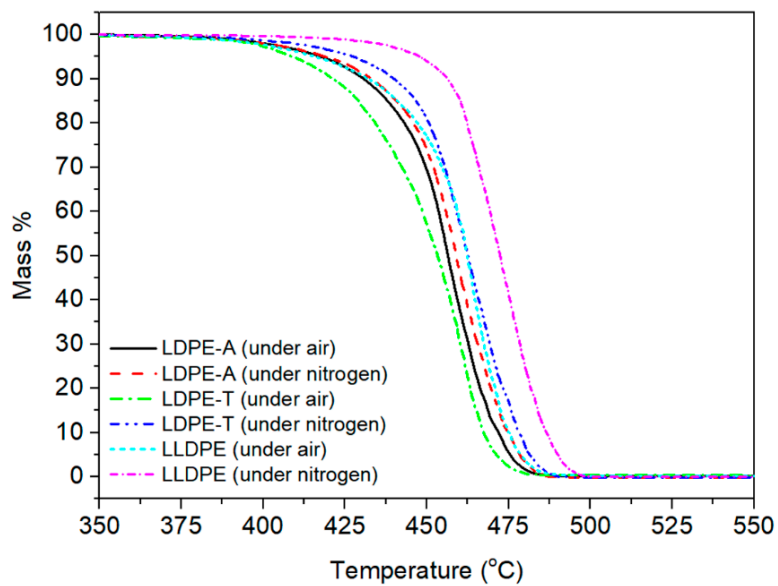
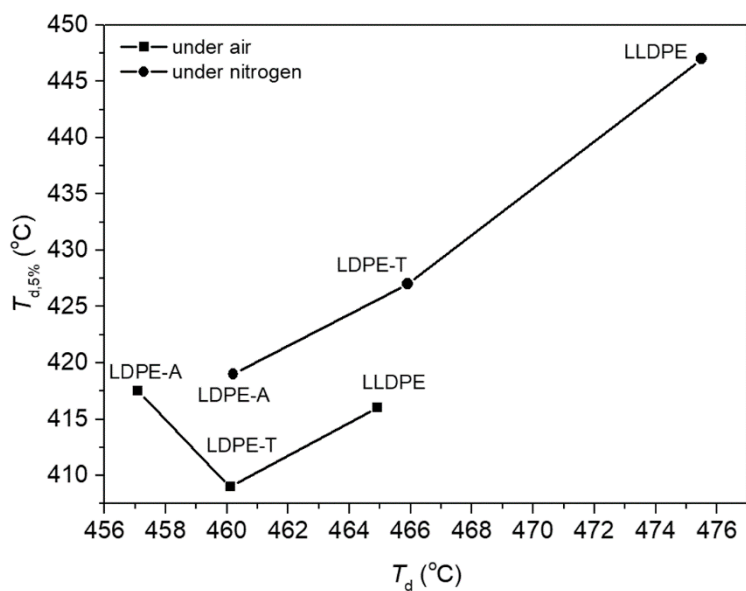


Figure S1. Conformation plot for (a) LLDPE, (b) LDPE-A, and (c) LDPE-T. The green line is a linear fit of the data.



(a)



(b)

Figure S2. (a) TGA curves of the pure polymers (LDPE-A, LDPE-T, LLDPE) under air and nitrogen atmosphere, (b) Correlation between the onset of thermal degradation ($T_{d,5\%}$) and the temperature at the maximum rate of weight loss (T_d) for the pure polymers under air and nitrogen atmosphere.

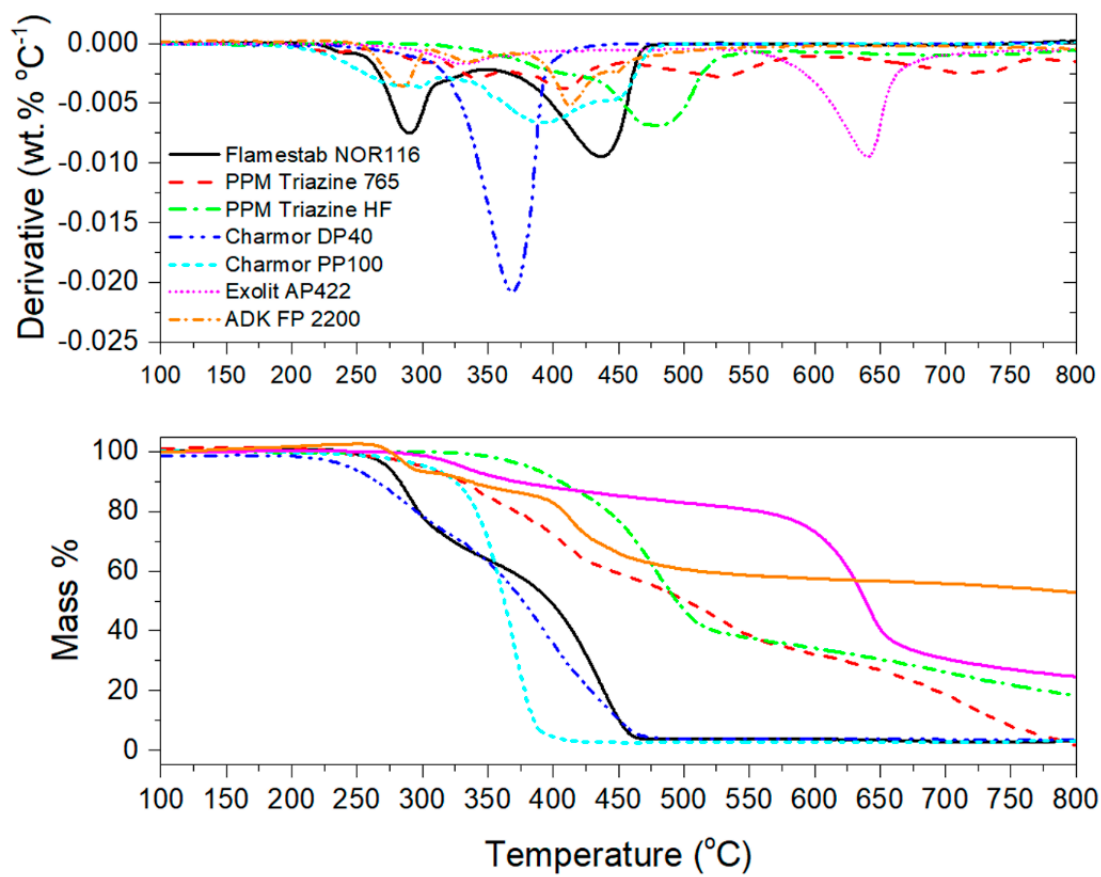


Figure S3. TGA curves of pure FR additives under nitrogen atmosphere.

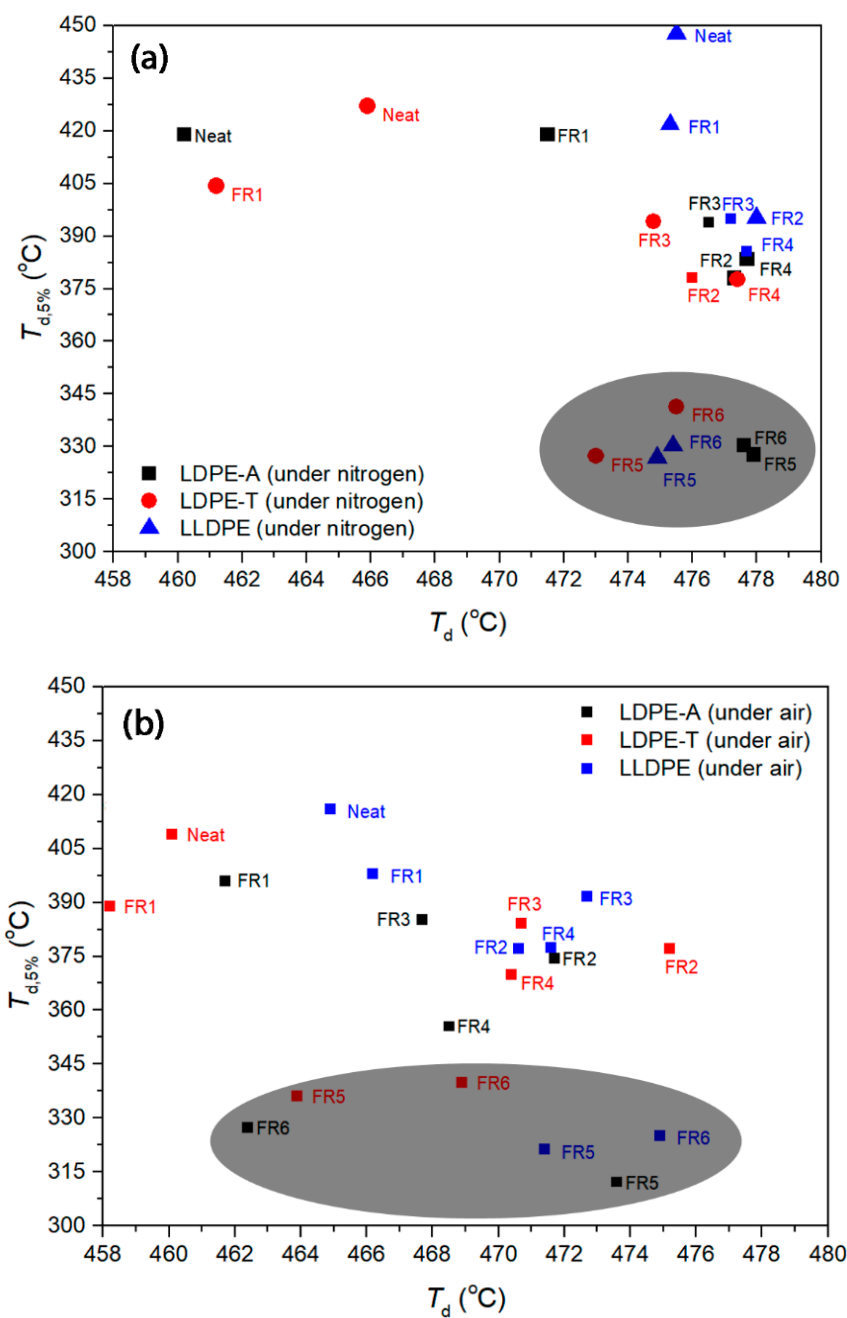


Figure S4. Correlation between the onset of thermal degradation ($T_{d,5\%}$) vs. the temperature at the maximum rate of weight loss (T_d) for the FR-containing compounds under (a) nitrogen and (b) air atmosphere TGA.

Table S1. Characteristics of the examined halogen-free flame retardants (FRs).

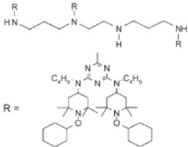
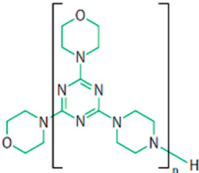
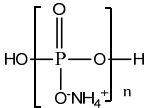
FR Product (Company)	Composition	MW (g mol ⁻¹)	Melting (°C)	TGA weight loss (%)
Flamestab NOR 116 (BASF)	Monomeric N-alkoxy hindered amine (triazine derivative)	2261	108-123	1% (260 °C) 10 % (285 °C)
				
MCA® PPM Triazine 765	Ammonium polyphosphate (APP) + poly-[2, 4-(piperazine-1, 4-yl)-6- (morpholine-4-yl)-1, 3, 5- triazine]/Piperazin (MCA® PPM triazine HF)	>2500	Infusible (>290°C)	<2 % up to 300 °C
MCA® PPM Triazine HF (MCA Technologies GmbH)	poly-[2, 4-(piperazine-1, 4-yl)-6- (morpholine-4-yl)-1, 3, 5- triazine]/Piperazin			
				
Exolit AP422 (Clariant)	Ammonium polyphosphate (APP) [NH ₄ PO ₃] _n	n>1000		5 % (350 °C) 10 % (450 °C) 20 % (550 °C)
				
ADK Stab FP-2200 (Adeka)	Nitrogen-phosphorus FR (blend)		Not observed (< 270 °C)	1% (260 °C) 5% (285 °C)
Charmor DP40	Pentaerythritol derivative, dimer		222 °C	Onset 330 °C
Charmor PP100 (Perstorp)	Pentaerythritol derivative, polymer		160-180 °C	240 °C

Table S2. Activation energies (E_a) and correlation coefficients (R^2) of thermo-oxidative degradation (TGA under air) of FR polyolefin systems according to the Kissinger model.

	E_a (kJ mol ⁻¹)	R^2
LDPE-A	303	0.9823
LDPE-A/FR1	353	0.9714
LDPE-A/FR2	211	0.9167
LDPE-A/FR3	346	0.9874
LDPE-A/FR4	498	0.6825
LDPE-A/FR5	292	0.8607
LDPE-A/FR6	391	0.7822
LDPE-T	319	0.9894
LDPE-T/FR1	432	0.9977
LDPE-T/FR2	397	0.7877
LDPE-T/FR3	262	0.8391
LDPE-T/FR4	388	0.9923
LDPE-T/FR5	282	0.6190
LDPE-T/FR6	461	0.7612
LLDPE	287	0.9945
LLDPE/FR1	324	0.9538
LLDPE/FR2	274	0.9739
LLDPE/FR3	348	0.9728
LLDPE/FR4	308	0.9890
LLDPE/FR5	328	0.9139
LLDPE/FR6	274	0.9873

Table S3. The kinetic parameters (reaction order (n), activation energy (E_a), pre-exponential factor (A)) of FR polyolefin systems using the Coats-Redfern method (TGA under nitrogen).

	n	E_a (kJ mol ⁻¹)	A	R^2
LDPE-A	1.1	363	5.135×10^{22}	0.9968
LDPE-A/FR1	0.9	328	5.713×10^{19}	0.9944
LDPE-A/FR2	0.4	214	3.070×10^{11}	0.9953
LDPE-A/FR3	0.7	218	6.244×10^{11}	0.9974
LDPE-A/FR4	0.2	185	2.488×10^9	0.9991
LDPE-A/FR5	1.0	249	1.076×10^{14}	0.9969
LDPE-A/FR6	0.9	245	5.766×10^{13}	0.9966
LDPE-T	1.2	408	6.266×10^{25}	0.9991
LDPE-T/FR1	1.0	340	1.071×10^{21}	0.9956
LDPE-T/FR2	0.3	159	3.297×10^7	0.9940
LDPE-T/FR3	0.4	157	2.429×10^7	0.9937
LDPE-T/FR4	0.1	148	4.703×10^6	0.9943
LDPE-T/FR5	0.4	156	2.187×10^7	0.9946
LDPE-T/FR6	0.6	205	8.135×10^{10}	0.9981
LLDPE	1.5	537	4.240×10^{34}	0.9989
LLDPE/FR1	0.9	327	4.600×10^{19}	0.9996
LLDPE/FR2	0.6	229	3.826×10^{12}	0.9984
LLDPE/FR3	0.5	184	2.083×10^9	0.9953
LLDPE/FR4	0.2	168	1.452×10^8	0.9953
LLDPE/FR5	0.5	188	4.279×10^9	0.9971
LLDPE/FR6	0.6	209	1.373×10^{11}	0.9951

Table S4. The kinetic parameters (reaction order (n), activation energy (E_a), pre-exponential factor (A)) of the FR polyolefin systems using the Coats-Redfern method (TGA under air).

	n	E_a (kJ mol ⁻¹)	A	R^2
LDPE-A	1.3	413	2.782×10^{26}	0.9972
LDPE-A/FR1	1.3	337	5.291×10^{20}	0.9979
LDPE-A/FR2	0.4	128	2.521×10^5	0.9935
LDPE-A/FR3	0.5	120	6.542×10^4	0.9982
LDPE-A/FR4	0.3	127	2.099×10^5	0.9965
LDPE-A/FR5	0.9	158	4.091×10^7	0.9982
LDPE-A/FR6	0.4	170	1.947×10^8	0.9978
LDPE-T	0.4	218	1.358×10^{12}	0.9973
LDPE-T/FR1	0.4	207	2.107×10^{11}	0.9968
LDPE-T/FR2	0.4	97	1.245×10^3	0.9978
LDPE-T/FR3	0.1	89	2.814×10^2	0.9985
LDPE-T/FR4	0.5	135	9.051×10^5	0.9980
LDPE-T/FR5	1.1	277	9.417×10^{15}	0.9945
LDPE-T/FR6	0.2	167	9.916×10^7	0.9930
LLDPE	0.8	347	2.281×10^{21}	0.9913
LLDPE/FR1	1.1	298	9.826×10^{17}	0.9977
LLDPE/FR2	0.3	101	2.527×10^3	0.9908
LLDPE/FR3	0.1	109	8.588×10^3	0.9896
LLDPE/FR4	0.1	135	7.127×10^5	0.9964
LLDPE/FR5	0.5	185	2.951×10^9	0.9972
LLDPE/FR6	0.5	189	5.176×10^9	0.9959

Table S5. Composition of the new FR formulations in wt% for the polyethylene grades.

	PPM Triazine HF	Exolit AP422	ADK Stab FP2200	Total FR (% wt)	CFA:APP
LDPE-A/FR3_n	8.75	26.25		35	1:3
LDPE-A/FR4_n			35	35	
LDPE-T/FR3_n	14	21		35	2:3
LDPE-T/FR4_n			30	30	
LLDPE/FR3_n	8.75	26.25		35	1:3
LLDPE/FR4_n			40	40	