

Supporting Information

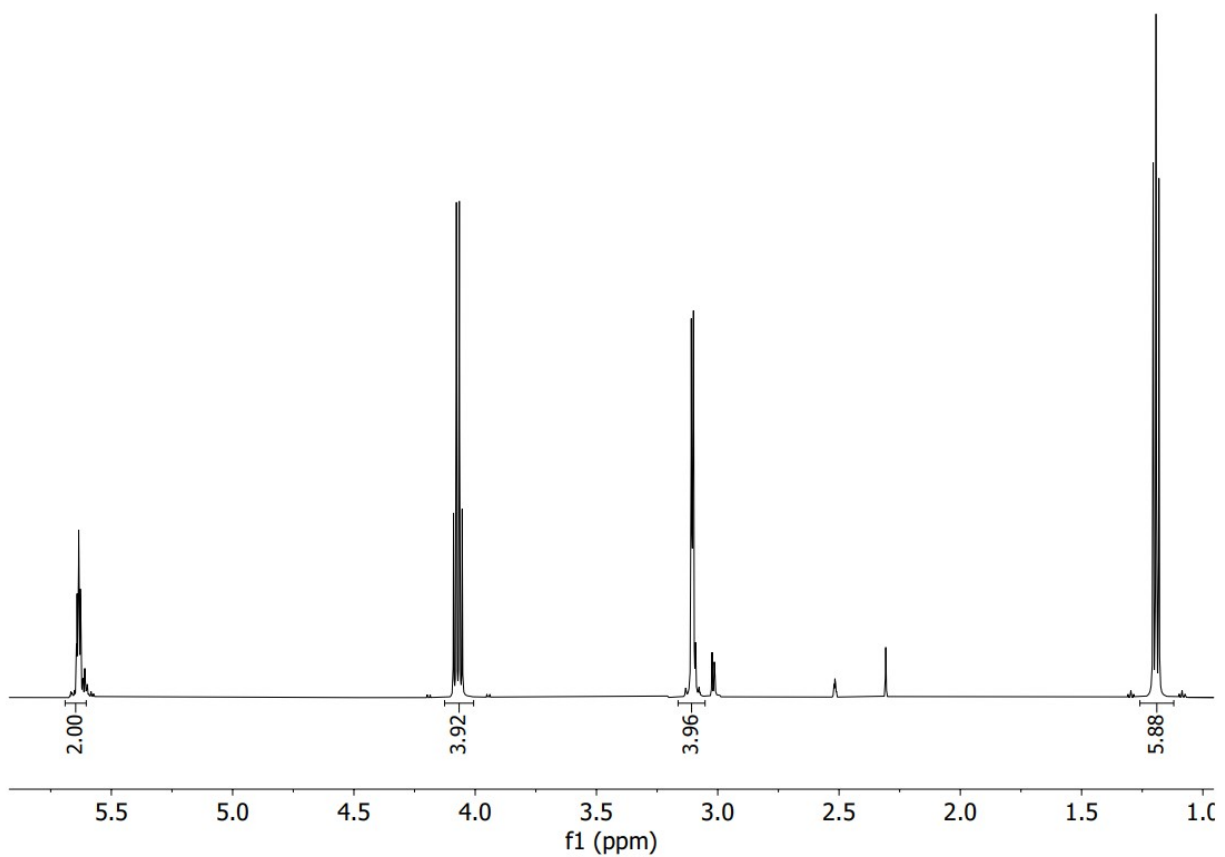


Figure S1: NMR of the HDA showing the isomerization from 3-HDA to 2-HDA.

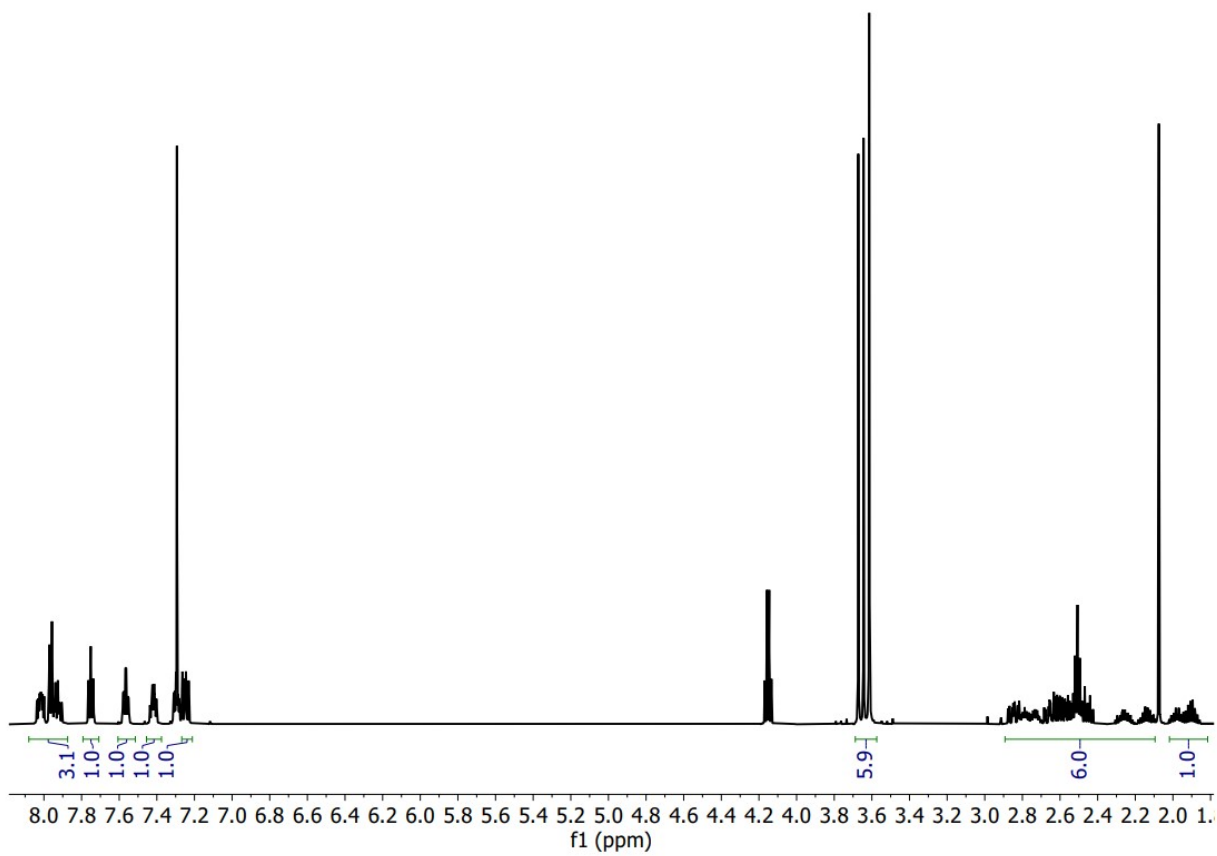


Figure S2: The full NMR of the DOPO-functionalized HDA. The peak at 4.2 is the hydrogen α to the carbonyl. The lack of a peak in the rest of the 4-5 range demonstrates the DOPO molecule added to the β position.

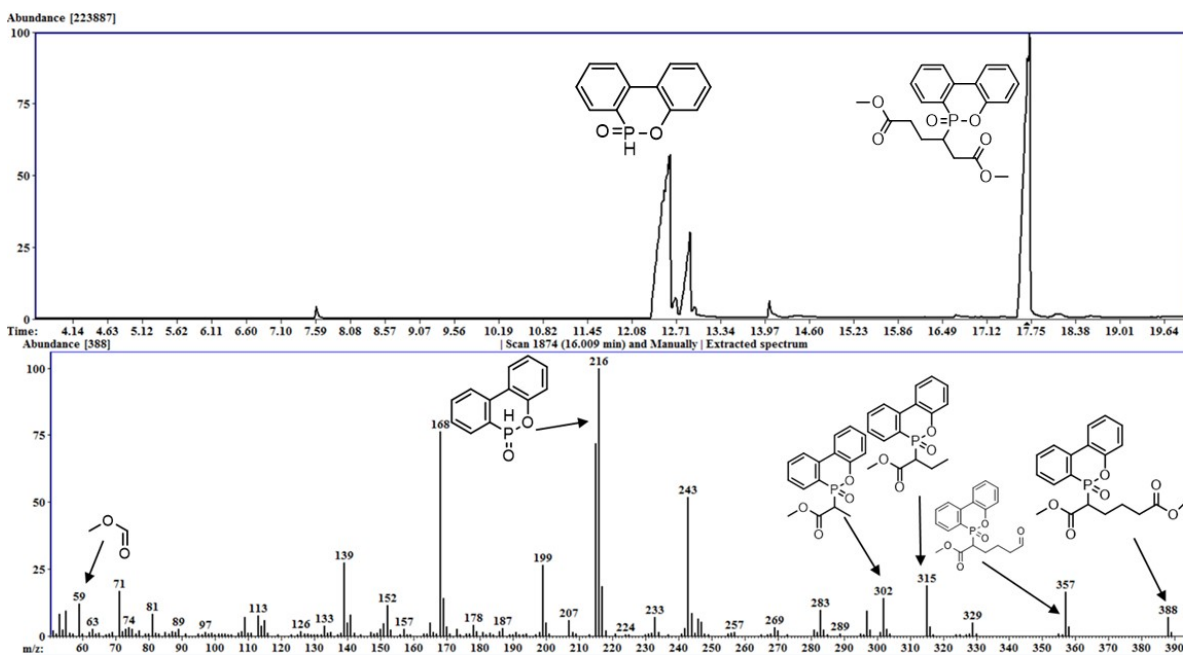


Figure S3. GC-MS for the one-pot isomerization and Michael-addition product after 96 hours of reaction time.

PCS175-5.1.fid
DOPO:HMDA salt in D2O

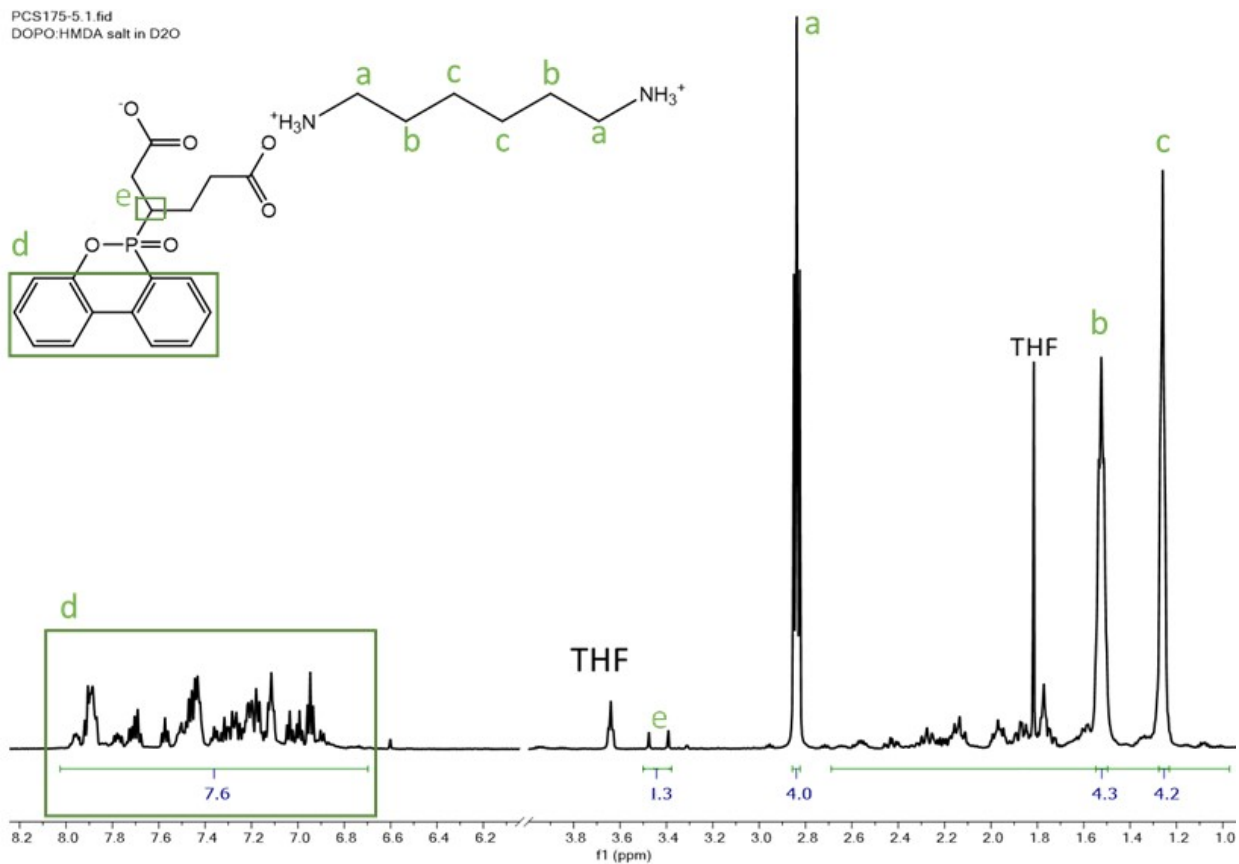


Figure S4. ¹H NMR of salt in D₂O. The salt was prepared by precipitating the functionalized diacid with HMDA in THF.

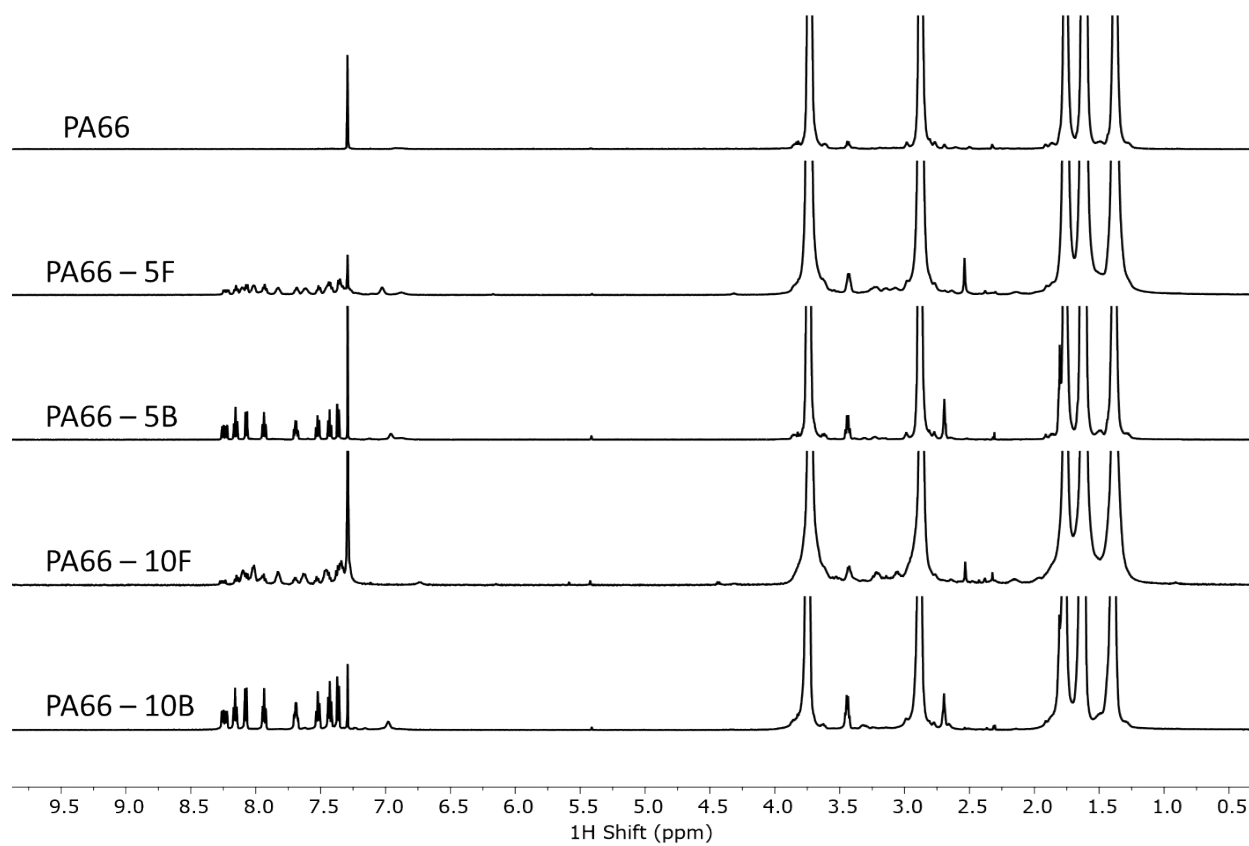


Figure S5. ¹H NMR of polymers shown in this study. Percent incorporation of DOPO was calculated through the integration of the aromatic region with respect to the HMDA peak at 3.7 ppm.

PA66-10B



PA66-10F



135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
31P Shift (ppm)

Figure S6. ^{31}P -NMR of polymers with 10 wt% DOPO incorporation.

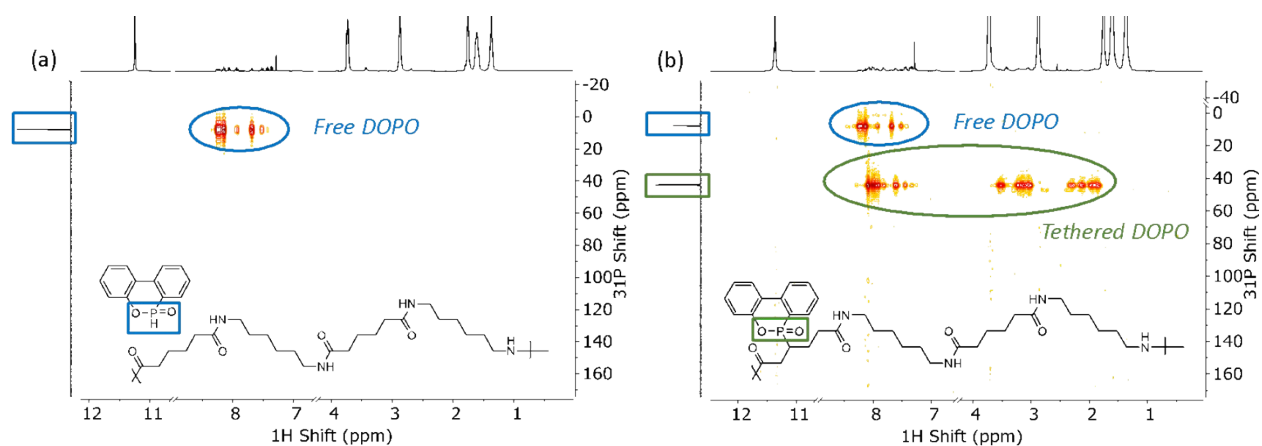


Figure S7. HMBC spectra of ^{31}P versus ^1H for (a) PA66-10B and (b) PA66-10F in CDCl_3 . The appearance of cross peaks highlighted in green in (b) shows the majority (75%) of DOPO remains grafted onto the polymer backbone during polymerization.

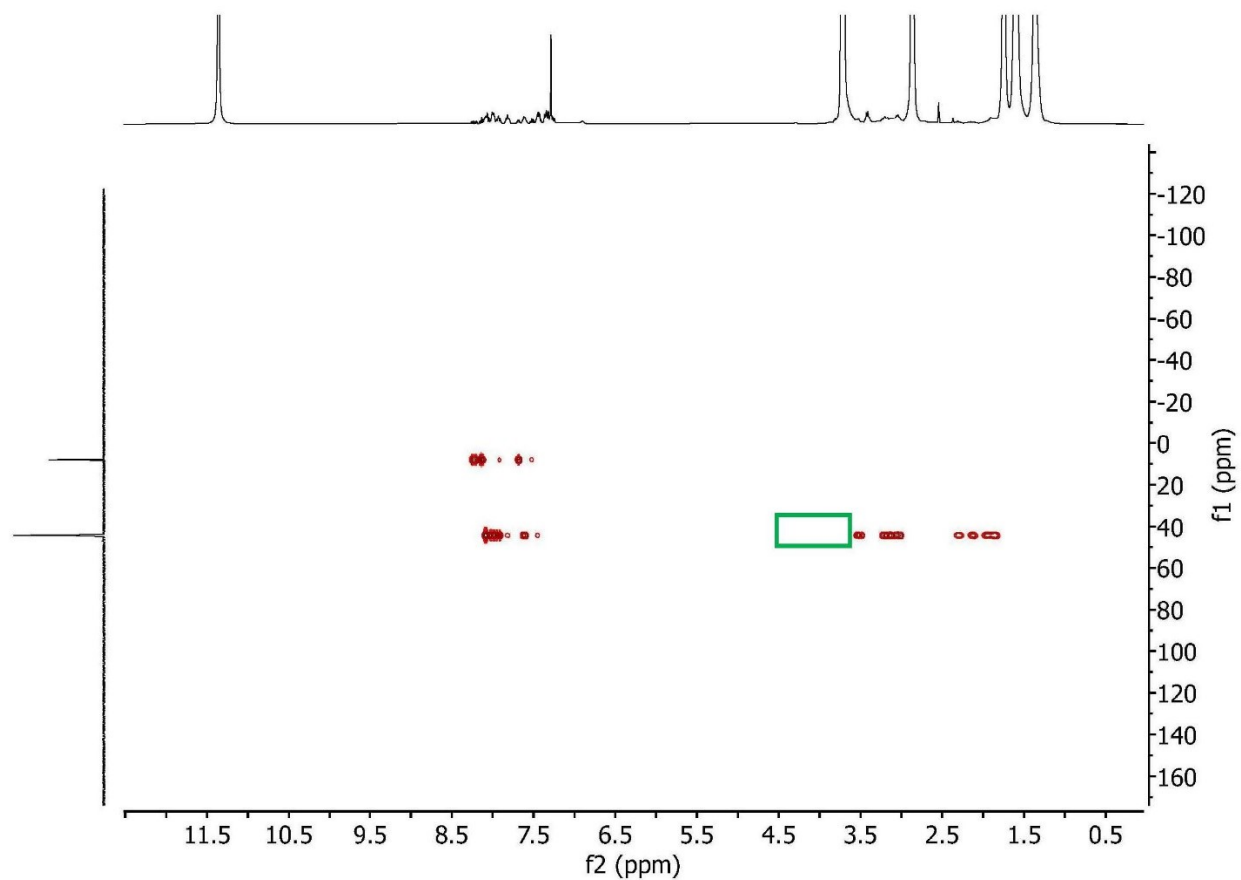


Figure S8: Full HMBC spectra of ^{31}P versus ^1H for PA66-10F in CDCl_3 . The box shows where correlations where 2-addition would be anticipated to appear. The lack of any cross peaks demonstrates the DOPO molecule adds to the beta position.

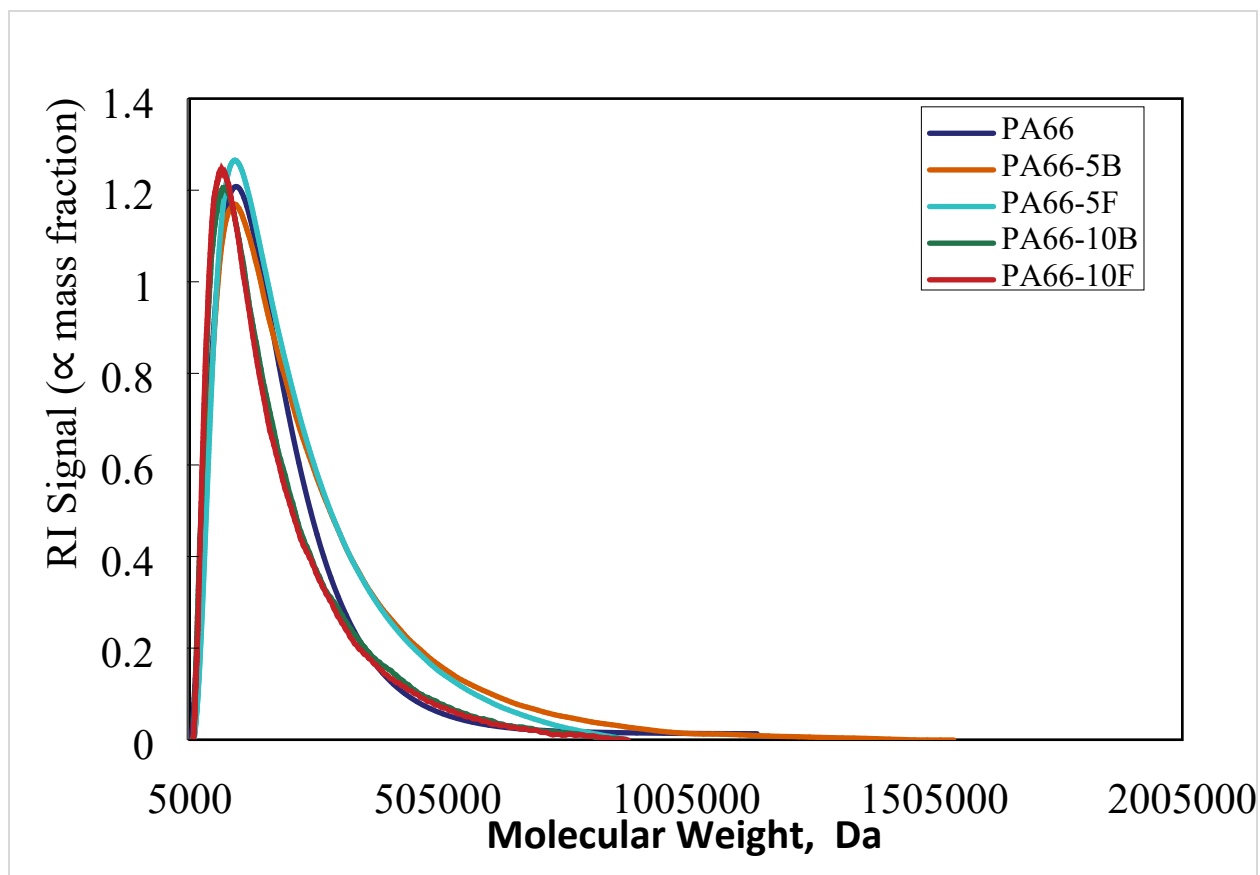


Figure S9: GPC chromatograms for the polyamide series, normalized to unit area.

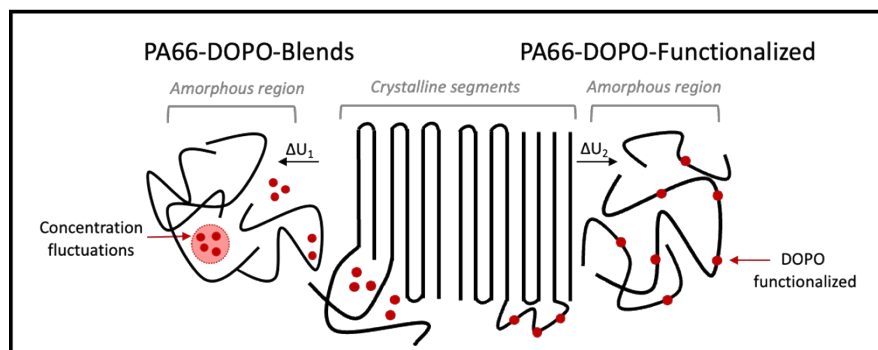


Figure S10: Crystal formation in the presence of free and tethered DOPO. Functionalized DOPO attached to the polymer backbone shows higher crystallinity than its blended counterpart.

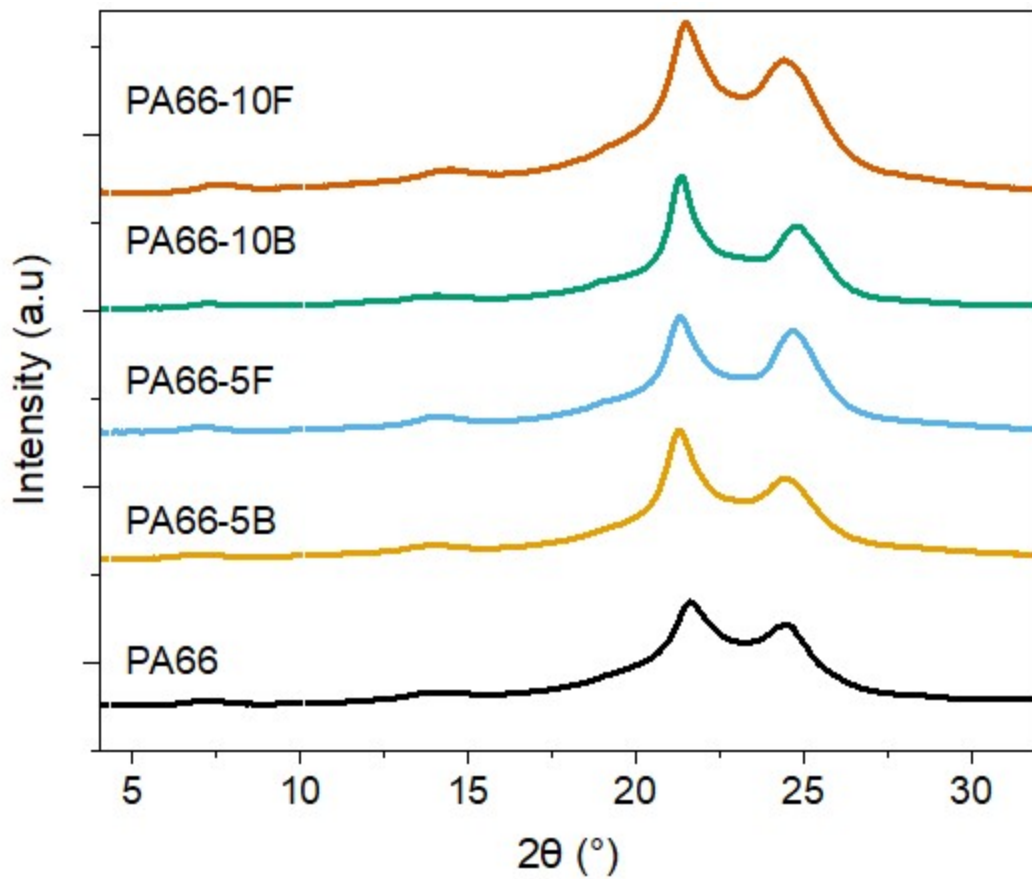


Figure S11: WAXS for the flame-retardant polyamide series with respect to PA66 showing room temperature wide-angle X-ray scattering.

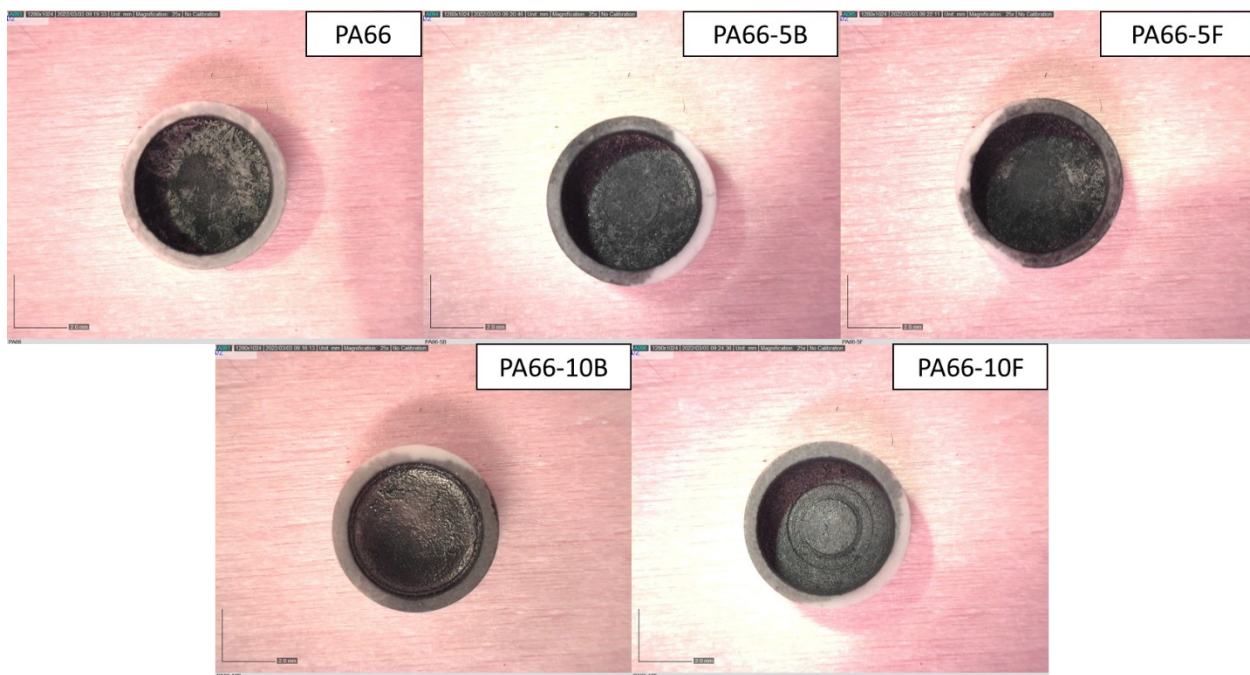


Figure S12. Char residues of the samples that underwent MCC. Images suggest that samples flowed before charring and flowed up to the edges of crucibles prior to being fully pyrolyzed.

Table S1. Heat release rate (HRR) and other MCC data for polyamides.

Samples	Char Yield (wt%)	FGC (J/g-k)	HRR Peak (s) (W/g)	HRR Max Temp (°C)	Total HR (kJ/g)
PA66	1.45	487	560	478	28.0
	1.40	485	560	482	28.2
	1.28	487	566	480	28.3
PA66	1.10	515			29.4
	1.19	521			29.2
	1.29	515			29.1
PA66-5B	1.74	333	374, 237	423, 487	28.0
	1.77	333	383, 243	422, 486	28.0
	1.67	326	388, 250	424, 490	27.8
PA66-5F	1.63	323	329, 228	430, 486	27.4
	1.70	329	338, 243	430, 488	28.0
	2.02	323	327, 230	427, 485	27.5
PA66-10B	1.55	335	315, 220	423, 487	27.7
	1.65	327	325, 217	424, 489	27.6
	1.55	324	384, 220	419, 490	27.6
	1.50	324	371, 223	421, 489	27.9

^aAn additional replicate was run for PA66-10B sample due to the scatter in heat release data

