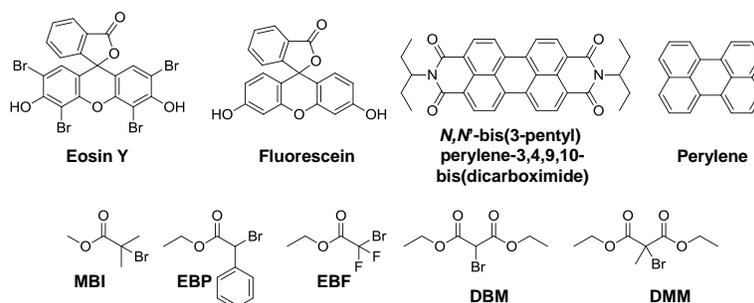


## Perylene as an Organic Photocatalyst for the Radical Polymerization of Functionalized Vinyl Monomers through Oxidative Quenching with Alkyl Bromides and Visible Light

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**Figure SI 1.** Structures of dyes and initiators examined in this study.

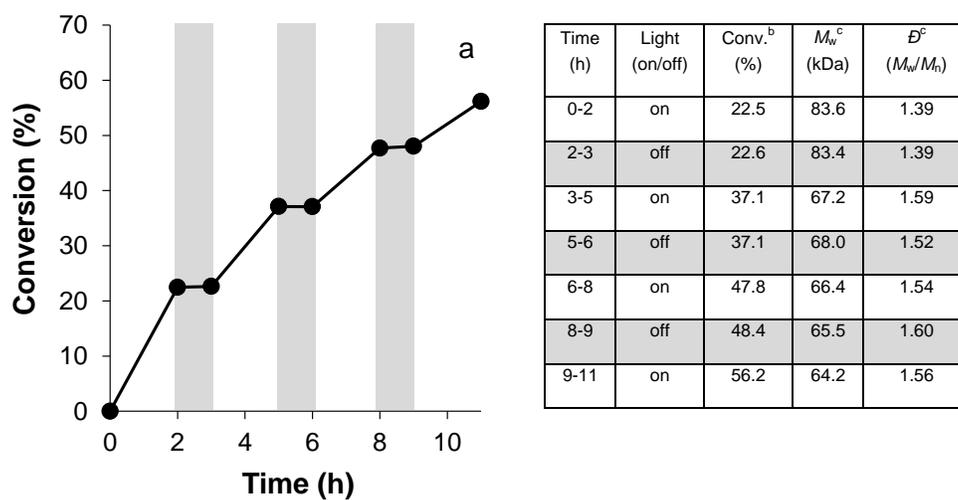
**Table SI 1.** Results of the Polymerization of Methyl Methacrylate.<sup>[a]</sup>

Run No	[MMA]:[I]:[Dye]	Dye	I	Yield (%) <sup>[b]</sup>	$M_w$ (kDa) <sup>[c]</sup>	$M_n$ (kDa) <sup>[c]</sup>	$\mathcal{D}$ ( $M_w/M_n$ ) <sup>[c]</sup>	Theo. $M_n$ (kDa) <sup>[d]</sup>	$I^*$ (EBP) (%) <sup>[e]</sup>	$I^*$ (I) (%) <sup>[f]</sup>
S1	875:9:1	Eosin Y	MBI	Trace	--	--	--	--	--	--
S2	875:9:1	Fluorescein	MBI	0	--	--	--	--	--	--
S3	875:9:1	<i>N,N</i> -bis(3-Pentyl) Perylene-3,4,9,10-bis(dicarboximide)	MBI	12.9	163	125	1.38	1.26 (11.3)	1.0	9.0
S4	875:9:1	Perylene	MBI	43.8	78.1	61.5	1.27	4.26 (38.4)	6.9	62
S5	875:9:1	Perylene	EBP	47.9	50.1	35.0	1.43	4.66 (41.9)	13	120
S6	875:9:1	Perylene	EBF	48.1	67.7	48.7	1.39	4.68 (42.1)	9.6	87
S7	875:9:1	Perylene	DBM	51.8	135	78.0	1.73	5.04 (45.4)	6.5	58
S8	875:9:1	Perylene	DMM	41.9	51.4	34.9	1.47	4.08 (36.7)	12	105

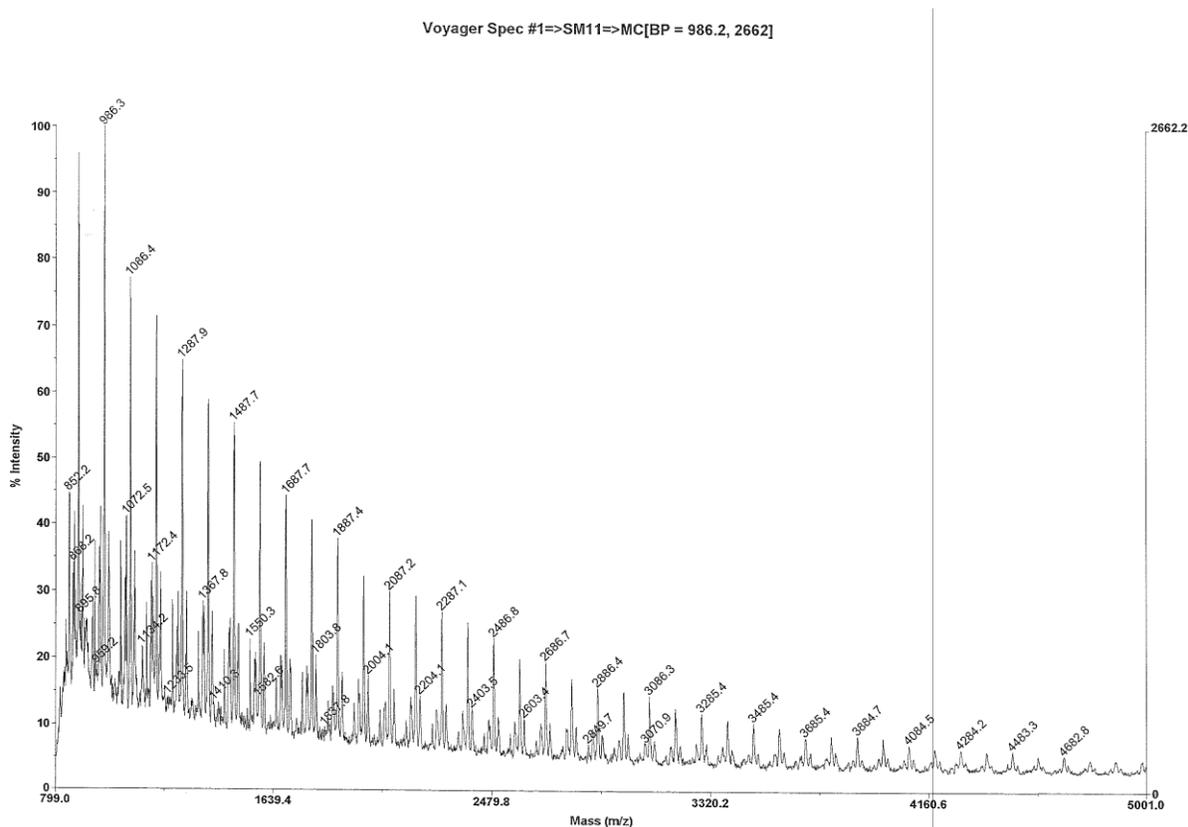
<sup>[a]</sup>Performed in 4.00 mL of DMF and with 1.00 mL (9.35 mmol, 875 equiv) of MMA, 2.7 mg (10.7  $\mu\text{mol}$ , 1 equiv) and 96.3  $\mu\text{mol}$  of the initiator specified in Table SI 1. Samples were irradiated by a white LED for 24 hours before work-up. Initiators (I) used were ethyl  $\alpha$ -bromophenylacetate (EBP), methyl  $\alpha$ -bromoisobutyrate (MBI), ethyl bromodifluoroacetate (EBF), diethyl bromomalonate (DBM), and diethyl 2-bromo-2-methylmalonate (DMM). <sup>[b]</sup>Isolated yield. <sup>[c]</sup>Determined by light-scattering. <sup>[d]</sup>Theoretical  $M_n$  calculated by  $[\text{MMA}]/[\text{I}]$  or  $[\text{MMA}]/[\text{dye}]$  (in parenthesis) \* polymer yield. Initiator efficiency ( $I^*$ ) = theoretical  $M_n$  / experimental  $M_n$  \* 100 calculated using the theoretical  $M_n$  based on  $[\text{MMA}]/[\text{I}]$ <sup>[e]</sup> or  $[\text{MMA}]/[\text{dye}]$ <sup>[f]</sup>.



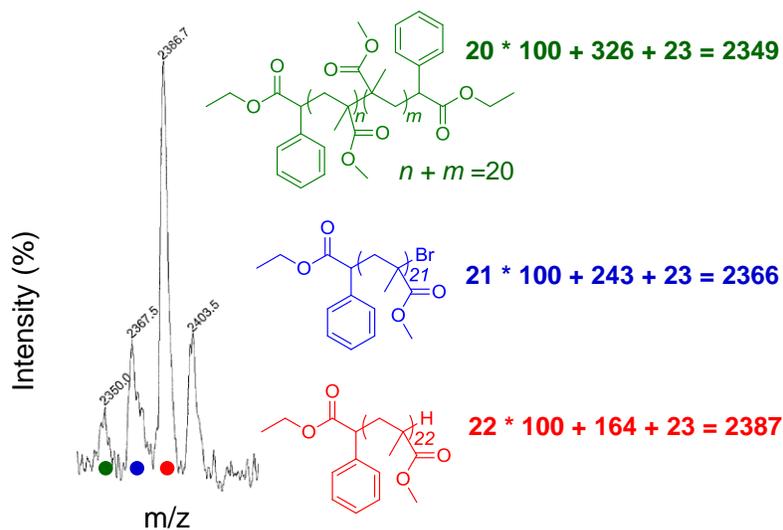
**Figure SI 2.** Photograph of experimental setup for polymerizations conducted using LED irradiation.



**Figure SI 3.** A plot of monomer conversion vs time (left) for the polymerization of MMA using a pulsed light sequence. A table (right) of the molecular weight properties of the polymer at each time point. Performed in 1.00 mL of DMF and 1.00 mL (0.935 mmol) MMA. [MMA]:[EBP]:[**1**] = 875:9:1.



**Figure SI 4.** Spectrum from MALDI-TOF analysis of a poly(MMA) oligomer.



**Figure SI 5.** A portion of the MALDI-TOF spectrum with the assignment of the peaks to an oligomer with the specified number of MMA repeat units, the identified chain-end groups, and sodium (ionizing agent).

**Table SI 2.** Polymerization Results of the Chain-Extension Polymerization from a Poly(MMA) Macroinitiator.<sup>[a]</sup>

Run No	Co-Monomer	Yield (%) <sup>[b]</sup>	$M_w$ (kDa) <sup>[c]</sup>	$M_n$ (kDa) <sup>[c]</sup>	$\bar{D}$ ( $M_w/M_n$ ) <sup>[c]</sup>
S9	MMA	35.5	343	237	1.45
S10	BMA	23.1	523	205	2.55
S11	BA	18.1	219	130	1.68
S12	S	9.2	165	119	1.39

<sup>[a]</sup>Performed using the conditions described in the Experimental Section. <sup>[b]</sup>Isolated yield.

<sup>[c]</sup>Determined by light-scattering.

### Styrene Polymerization

The polymerization used the general conditions described in the Experimental Section. A 20 mL was loaded with a stir bar, 2.7 (10.7  $\mu\text{mol}$ , 1 equivalent) mg of perylene, 1.00 mL DMF, and 1.07 mL (9.31 mmol, 870 equivalents) of styrene. 16.4  $\mu\text{L}$  (93.7  $\mu\text{mol}$ , 9 equivalents) EPB was added by syringe. The polymerization was irradiated by a white LED for 23 hours before the reaction was terminated and 167 mg (17.2 %) of polystyrene was isolated as mentioned above.  $M_w = 84.5$  kDa,  $\bar{D} = 1.39$ .