

SUPPORTING INFORMATION:

Size exclusion chromatography experiments:

The number average molecular weights (M_n) and polydispersity index ($PDI=M_w/M_n$) were determined by size exclusion chromatography SEC using a Waters 515 HPLC pump equipped with 2 columns (PSS SDV LINEAR M 5 μ m), and two detectors: UV/visible (Waters 486) and DRI (Waters 2414). Measurements were performed in tetrahydrofuran THF at room temperature, with a flow rate of 1 mL.min⁻¹. Toluene was used as a flow rate marker. Calibration was based on polystyrene standards (kit EasyCal from Polymer Laboratories M_n between 580 - 377,400 g.mol⁻¹) and Mark-Houwink parameters (PS $K = 11.4 \times 10^{-3}$ mL.g⁻¹, $\alpha = 0.716$; PBA $K = 12.2 \times 10^{-3}$ mL.g⁻¹, $\alpha = 0.70$).[1]

For the **CH_1**/MDEA/R-Br photoinitiating system upon halogen lamp exposure in lauryl acrylate, a polymer characterized by M_n of 34,000 g.mol⁻¹ and a PDI of 3.3 has been observed.

[1] Beuermann, S.; Paquet, D. A.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1996**, 29, 4206-4215.

Figure S1. (A) Cyclic voltammogram of **CH_1** in acetonitrile. (B) (a) Absorption and (b) fluorescence spectra of **CH_2** in acetonitrile.

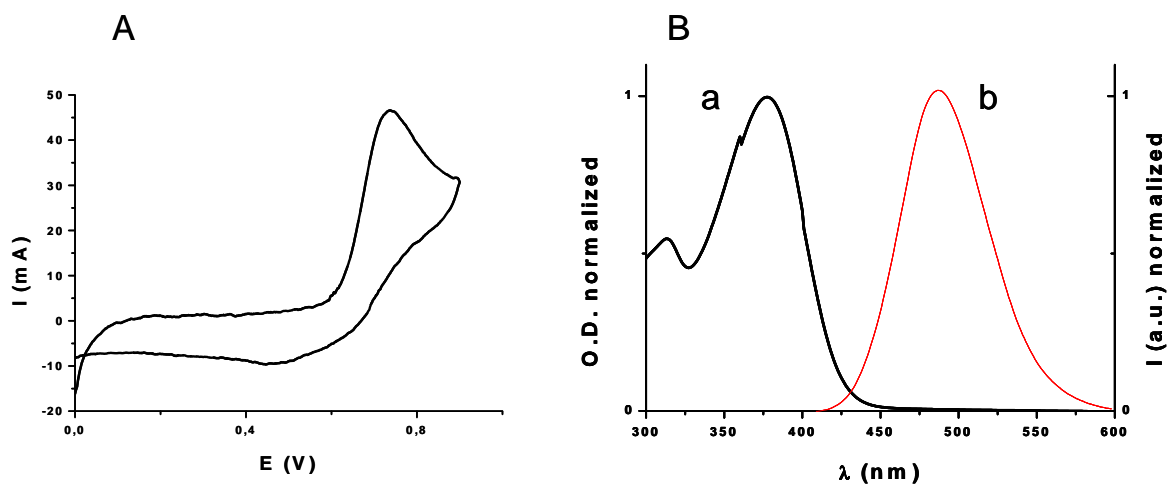


Figure S2. fluorescence spectra of **CH_1** in TMPTA and EPOX.

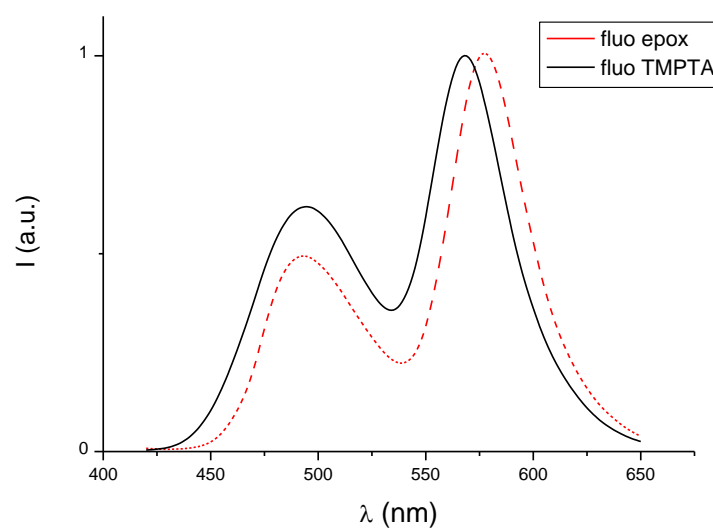


Figure S3. Fluorescence spectra (normalized to 1.0 for T*) in the course of the polymerization of a TMPTA/EPOX blend; initiating system **CH₁**/Iod/NVK (see text).

