

# Supporting Information for

## Bottom-up design of model network elastomers and hydrogels from precise star polymers

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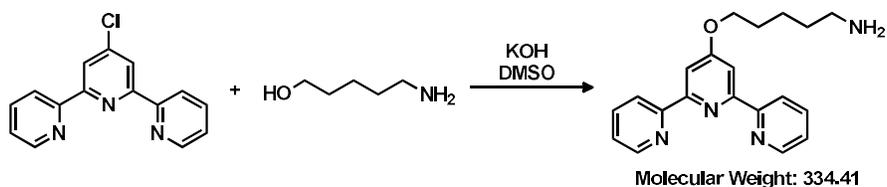
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## 1. Instrumentation

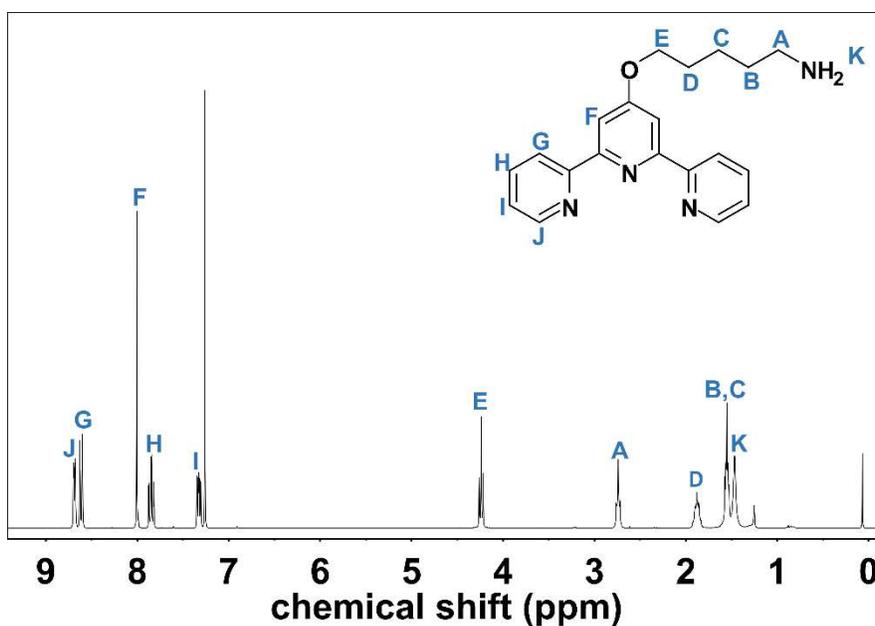


**Figure S1.** Photograph of the UV polymerization setup, consisting of 4 x 9 365 nm UV lamps and a custom made reflective cooling plate.

## 2. Synthesis

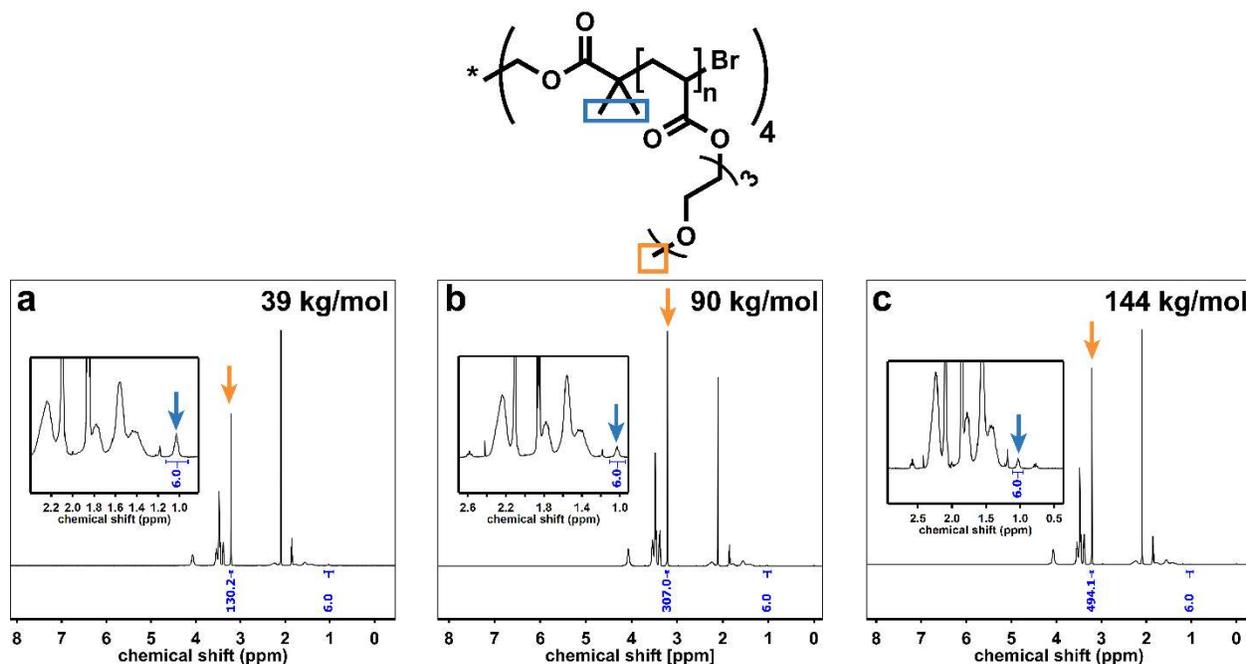


**Figure S2.** Reaction scheme for the synthesis of 5-aminopentyl 4'-(2,2':6',2''-terpyridinyl) ether.

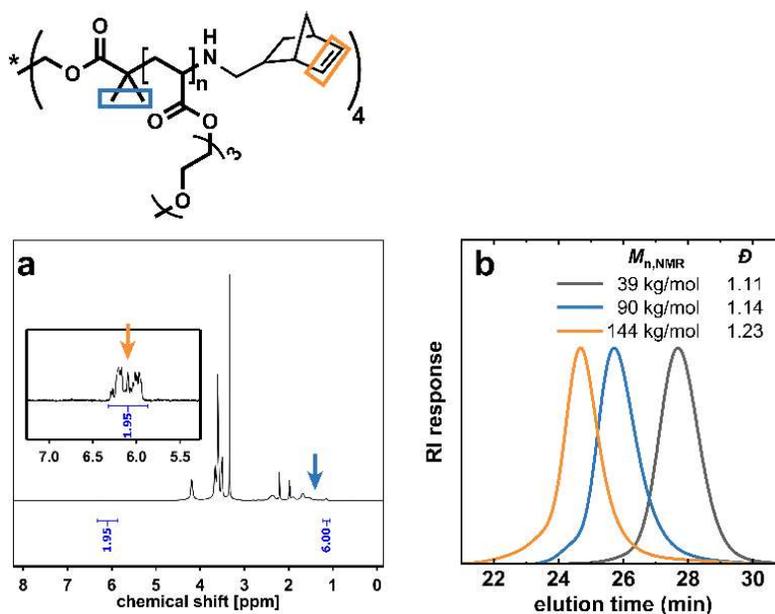


**Figure S3.** <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz) of ter5-aminopentyl 4'-(2,2':6',2''-terpyridinyl) ether.

### 3. Additional characterization by $^1\text{H-NMR}$ , SEC, DSC



**Figure S4.** Analysis of  $M_{n,NMR}$  of 4-arm p(mTEGA) after purification by  $^1\text{H-NMR}$  ( $\text{CD}_3\text{CN}$ , 300 MHz) via comparison of the initiator isobutryl 6H to the mTEGA methoxy 3H for three different molecular weight star polymers.



**Figure S5.** (a)  $^1\text{H-NMR}$  ( $\text{CD}_3\text{CN}$ , 300 MHz) analysis showing full norbornene-methylamine functionalization by comparing initiator 6H and norbornene 2H for 4-arm p(mTEGA) with  $M_{n,NMR} = 39$  kg/mol. (b) SEC traces for norbornene-methylamine functionalized 4-arm p(mTEGA) after purification with different molecular weights.

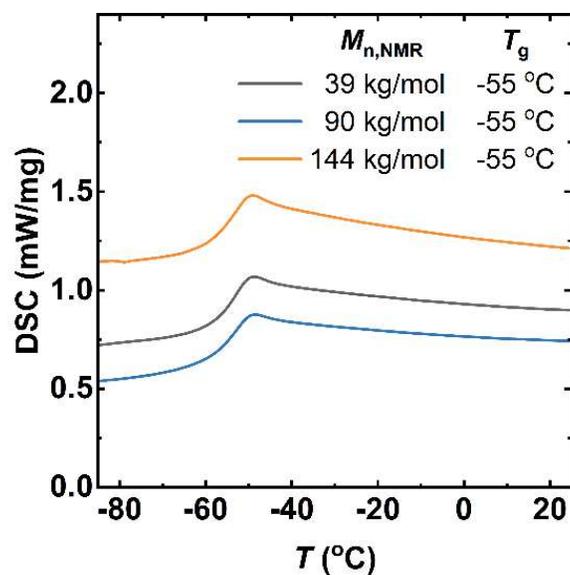


Figure S6. DSC measurements for purified and dried 4-arm p(mTEGA) of different molecular weights.

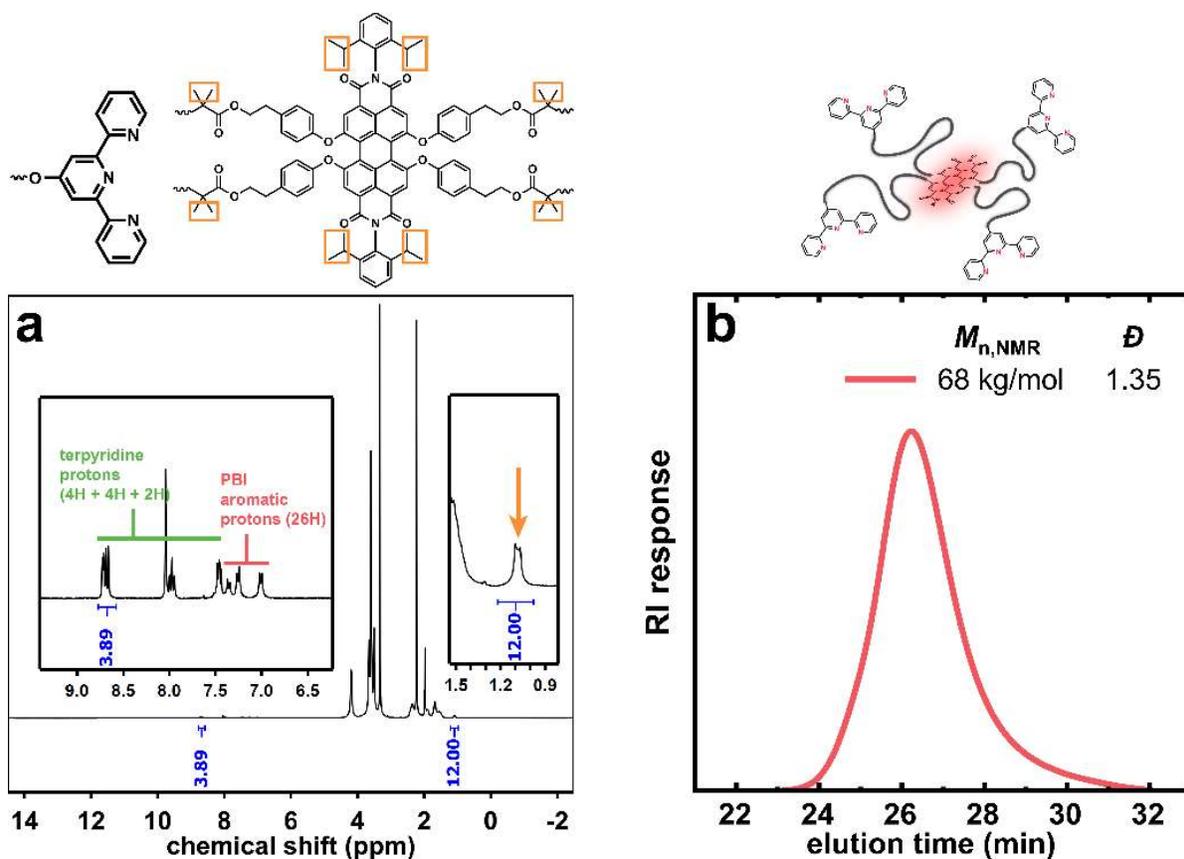
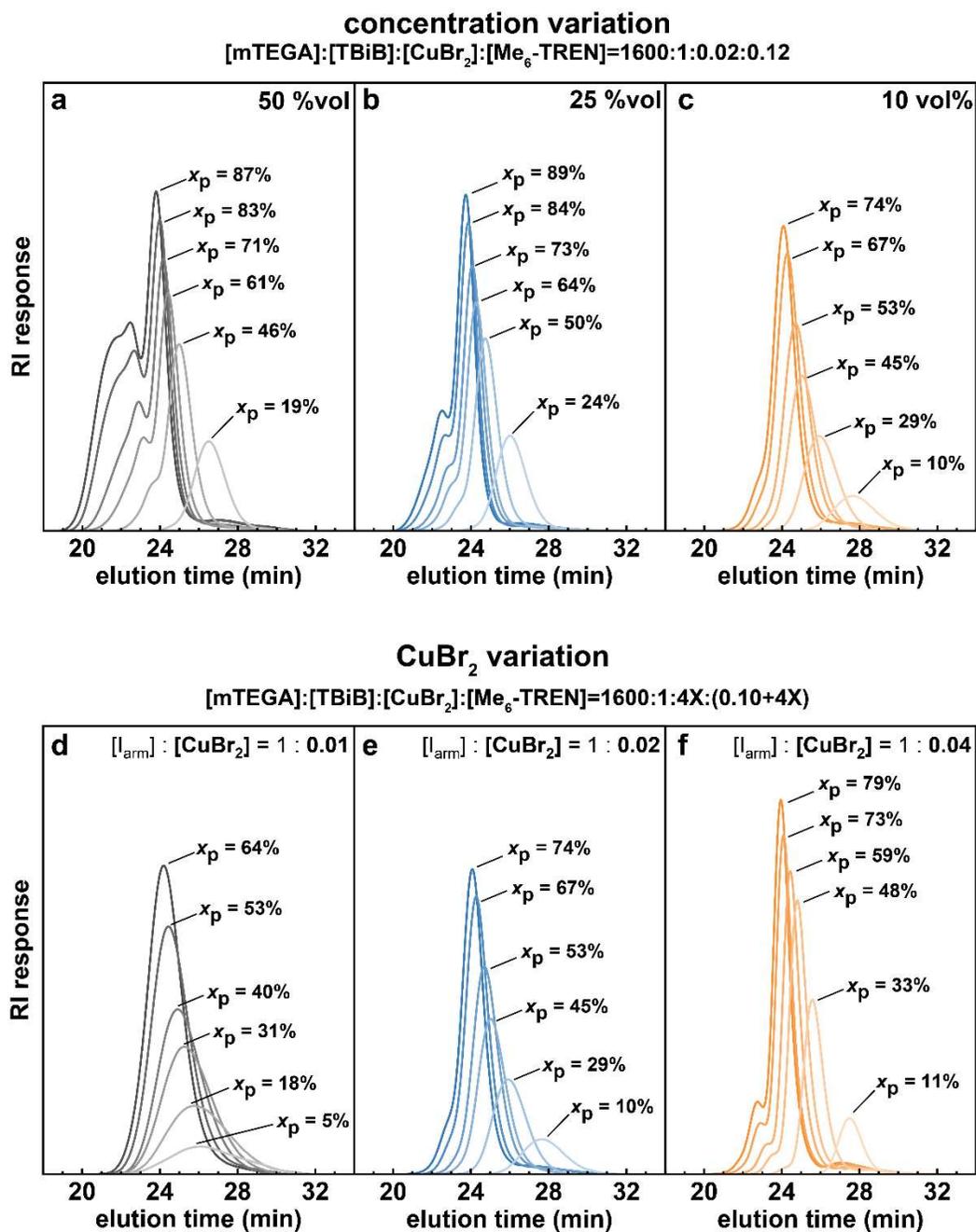


Figure S7. (a)  $^1\text{H-NMR}$  ( $\text{CD}_3\text{CN}$ , 300 MHz) analysis showing full conjugation of a fluorescent PBI-core 4-arm p(mTEGA) with terpyridine-amine. (b) SEC trace for the PBI-core p(mTEGA)-terpyridine star polymer after purification.

## 4. Full SEC traces of polymerization experiments



**Figure S8.** All SEC traces measured for during the UV-induced Cu-RDRP experiments of 4-arm star p(mTEGA) with  $[m\text{TEGA}]:[\text{TBiB}]=1600:1$  in DMSO for (a-c) the variation of the monomer concentration and (d-f) the variation of the  $[\text{l}_{\text{arm}}]:[\text{CuBr}_2]$  ratio X.