Supplementary Information

Straightforward synthesis of functionalized cyclic polymers in high yield via RAFT and thiolactone/disulfide chemistry

*Milan M. Stamenović, Pieter Espeel, Eisuke Baba, Takuya Yamamoto, Yasuyuki Tezuka and Filip E. Du Prez**

[1]Polymer Chemistry Research Group, Ghent University, Department of Organic Chemistry,
Krijgslaan 281 (S4-bis), 9000 Ghent, Belgium

[22]Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo, 152-8552, Japan

email: filip.duprez@ugent.be

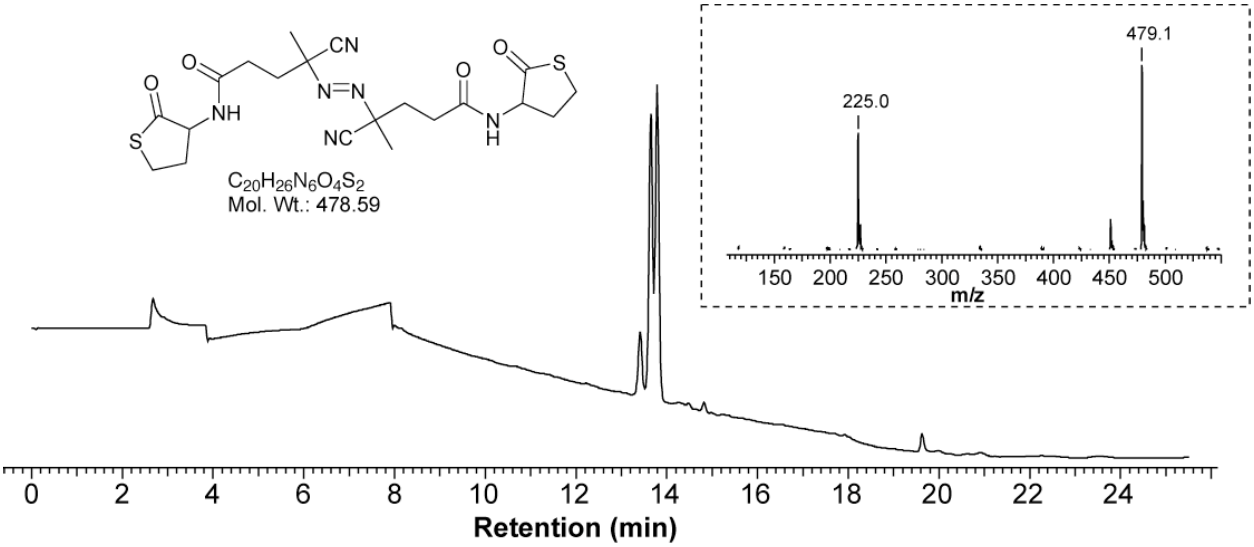

Figure S1. LC-MS analysis of purified azo-compound **3** (Scheme 1). Insert: ESI-MS spectrum (positive mode) of the main peaks.

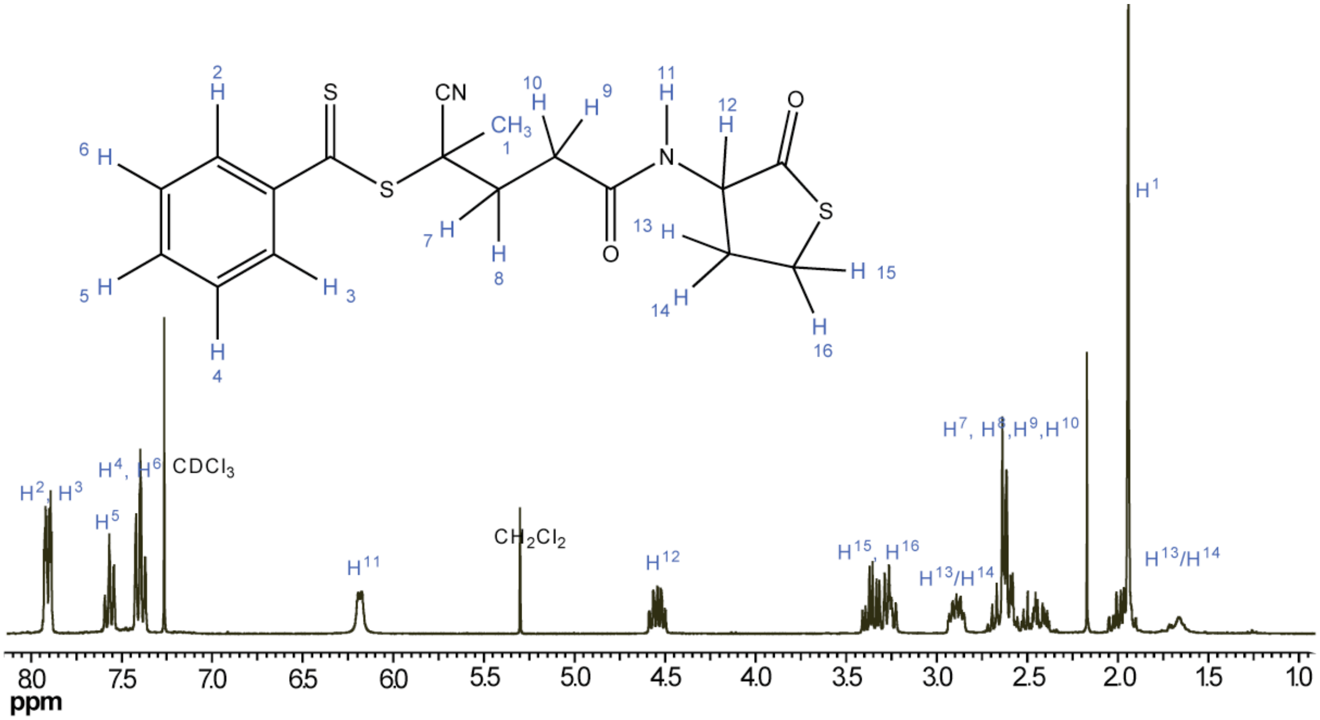

Figure S2. ^{1}H-NMR (300 MHz, $CDCl_3$) analysis of purified **TLa-CTA** (Scheme 1, **5**) with corresponding signal assignment.

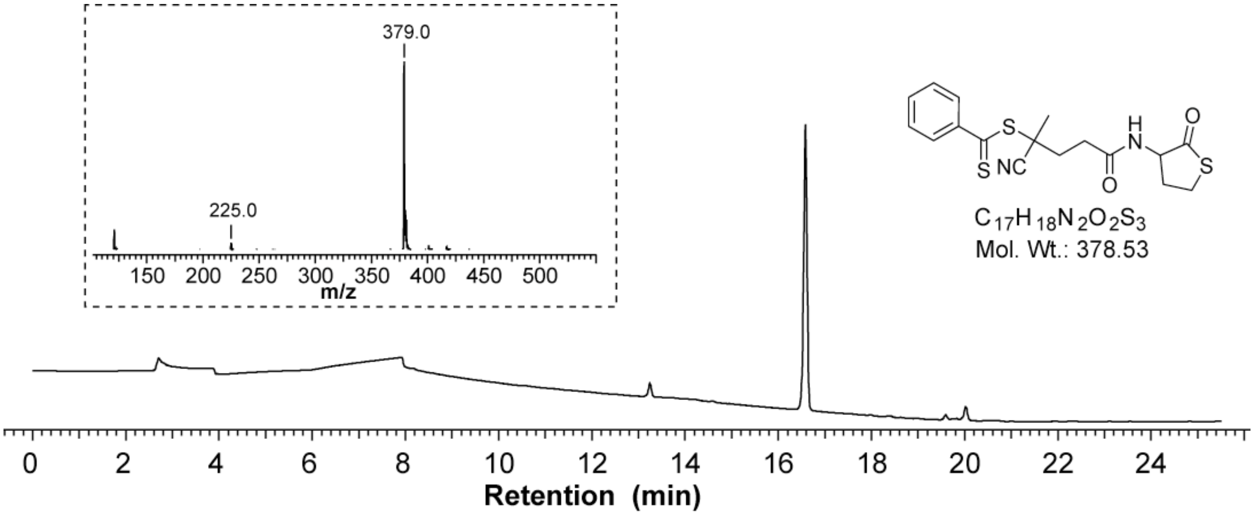

Figure S3. LC-MS analysis of **TLa-CTA** (Scheme 1, **5**). Insert: ESI-MS spectrum (positive mode) of the main peak.

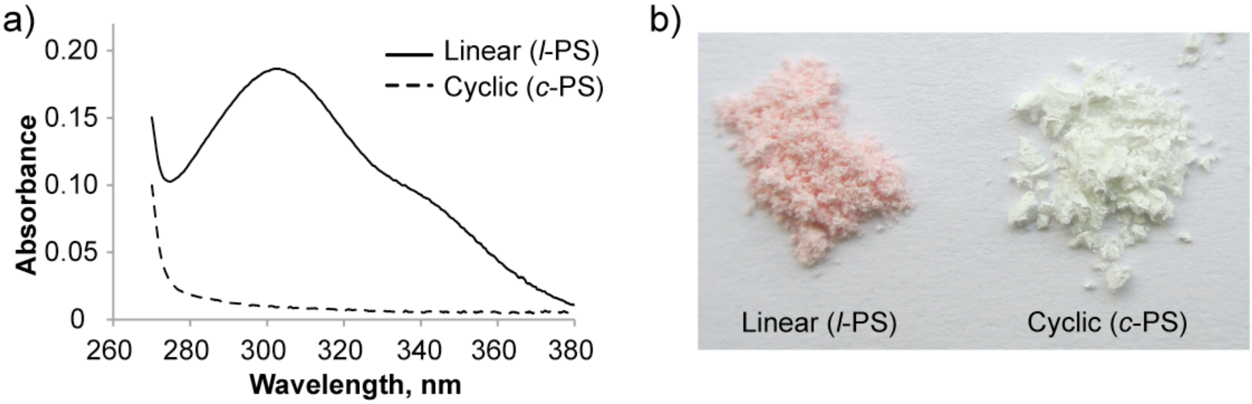

Figure S4. a) UV-vis spectrum of *l*-PS showing absorbance at ca. 303 nm (presence of dithiobenzoate group) and *c*-PS (no absorbance after removing dithiobenzoate group); b) visual inspection of *l*-PS (light-pink) and *c*-PS (white) indicating successful removal of dithiobenzoate group evidenced in a clear color change.

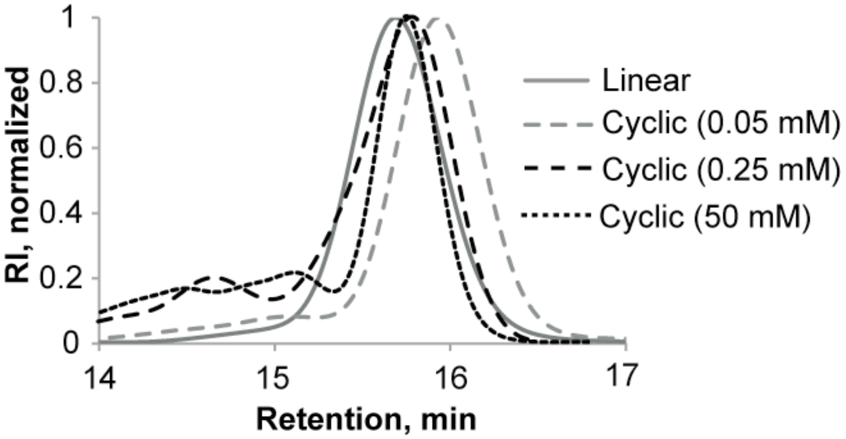

Figure S5. SEC profiles of: *l*-PS (**6**), *c*-PS (**7a**) prepared at 0.05 mM concentration and cyclization attempts at higher polymer concentrations (0.25 mM and 50 mM) with high MW tailing (lower retention), indicating intermolecular disulfide formation.

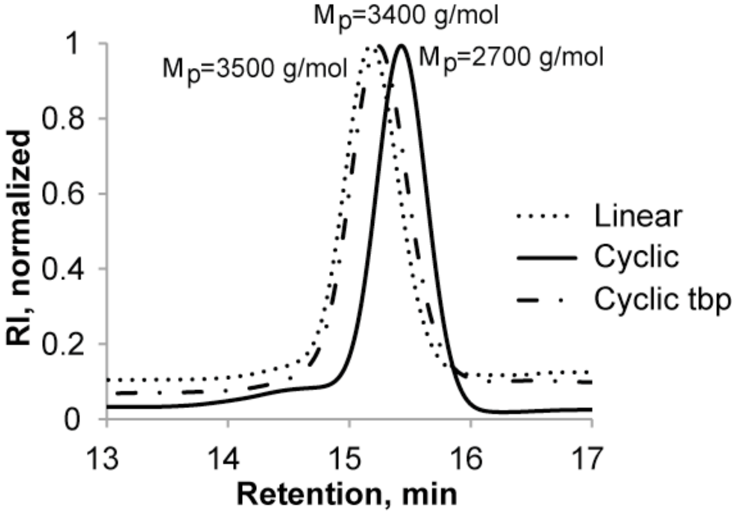

Figure S6. SEC profiles of *l*-PS (**6**), *c*-PS (**7a**) and *c*-PS after the reaction with tri-*n*-butylphosphine.

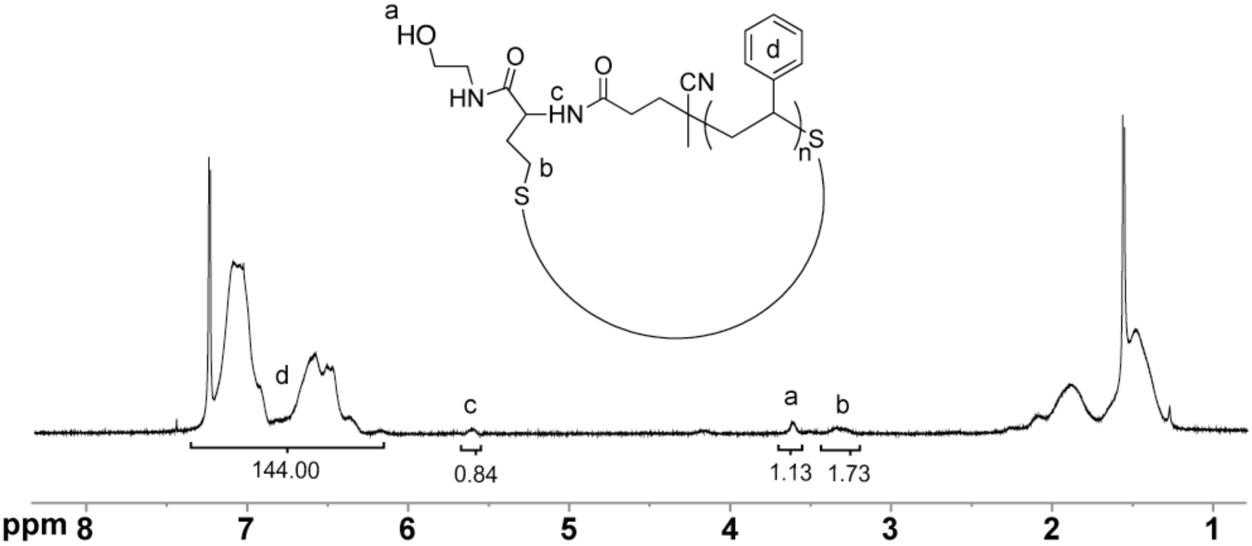

Figure S7. ^{1}H-NMR (500 MHz, $CDCl_3$) spectra of cyclic PS (*c*-PS, **7b**) with corresponding signal assignment.