

Supporting Information

Photo-Induced Ligation of Acrylonitrile-Butadiene Rubber: Selective Tetrazole-Ene Coupling of Chain-End Functionalized Copolymers of 1,3-Butadiene

Christoph J. Dürr,¹ Paul Lederhose,¹ Lebohang Hlalele,¹ Doris Abt,¹ Andreas Kaiser,²

*Sven Brandau² and Christopher Barner-Kowollik^{*1}*

¹Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe and Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz Platz1, 76344 Eggenstein-Leopoldshafen, Germany.

²Lanxess Emulsion Rubber, BP 7 – Z.I. Rue du Ried, 67610 La Wantzenau, France.

Experimental Procedures

Synthesis of ethyl 2-(((dodecylthio)carbonothioyl)thio)propanoate (**8**)

DoPAT (2.000 g, 5.7 mmol), DMAP (0.014 g, 0.1 mmol) and ethanol (0.616 g, 13.4 mmol) were dissolved in 10 mL THF. After the solution was cooled to 0 °C, DCC (1.290 g, 6.3 mmol) was added. The reaction mixture was stirred at ambient temperature for 16 h. THF was removed in vacuum. The obtained solid was dissolved in Et₂O, extracted with 1 M hydrochloric acid (4×100 mL) and washed with saturated NaHCO₃ solution (100 mL). The organic layer was dried over MgSO₄ and Et₂O was removed under reduced pressure. The crude product was purified via column chromatography on silica gel using hexane/ethyl acetate (3:1, v/v, *R_f* 0.61) as the eluent. After drying under high vacuum compound **10** was obtained as yellow oil (1.430 g, 66%). ¹H and ¹³C NMR characterization are provided in Fig. S19 and Fig. S20, respectively.

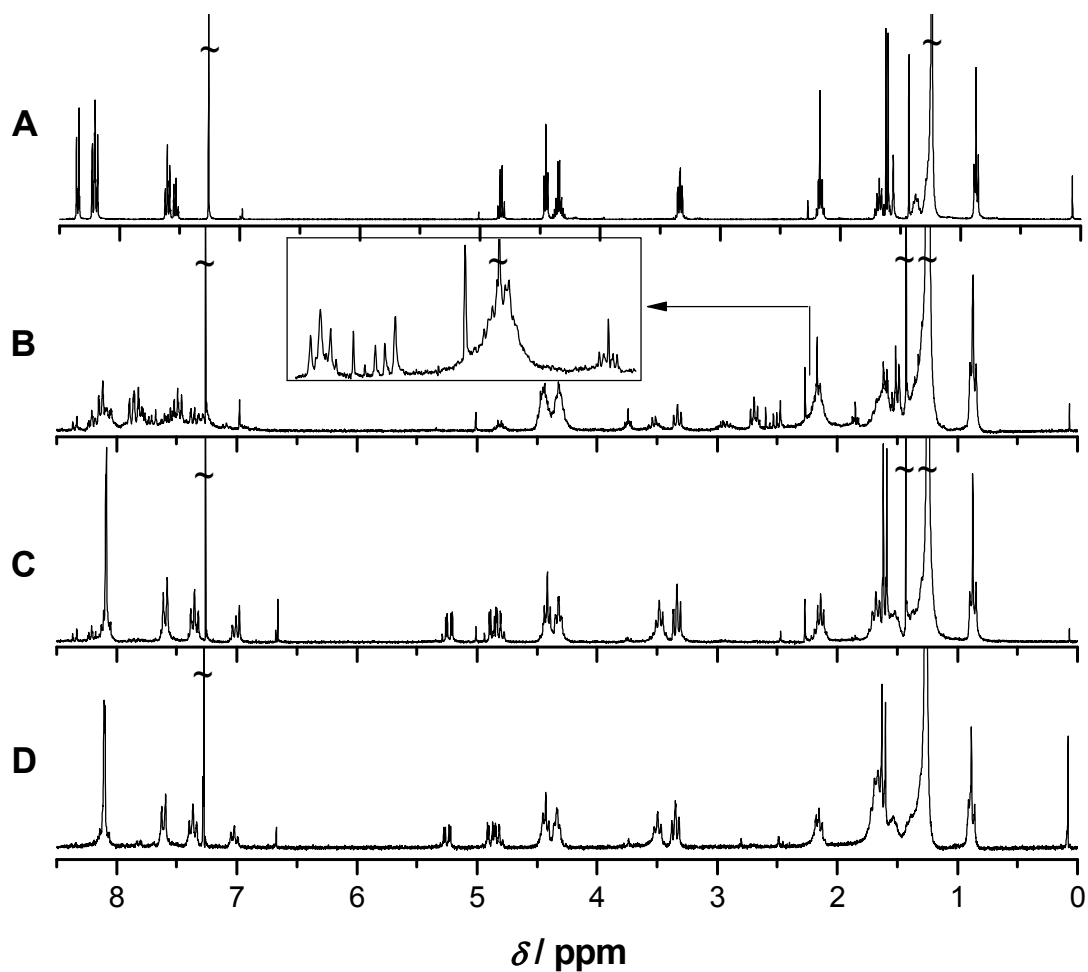


Figure S1. ¹H NMR spectra (CDCl₃) of A) the diaryl tetrazole-functional RAFT agent **3** and B-D) the reaction mixtures obtained after irradiation with UV light of 254 nm at ambient temperature in acetonitrile in the presence of olefins: B) reactants: **3**, *trans*-3-octene (ratio 1:1), 3 h; C) reactants: **3**, *trans*-3-octene, linker **5** (1:1:0.5), 3 h; D) reactants: **3**, linker **5**, (ratio 1:1) 15 min. Acetonitrile was removed under reduced pressure prior to analysis.

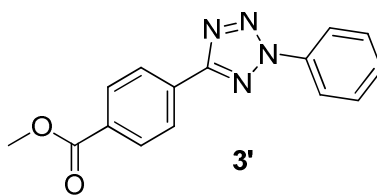


Figure S2. Chemical structure of the diaryl tetrazole precursor **3'** of the nitrile imine intermediate employed in the DFT calculation of the HOMO energy level of the 1,3-dipole for the discussion of the selectivity of the cycloadditions towards various olefins.

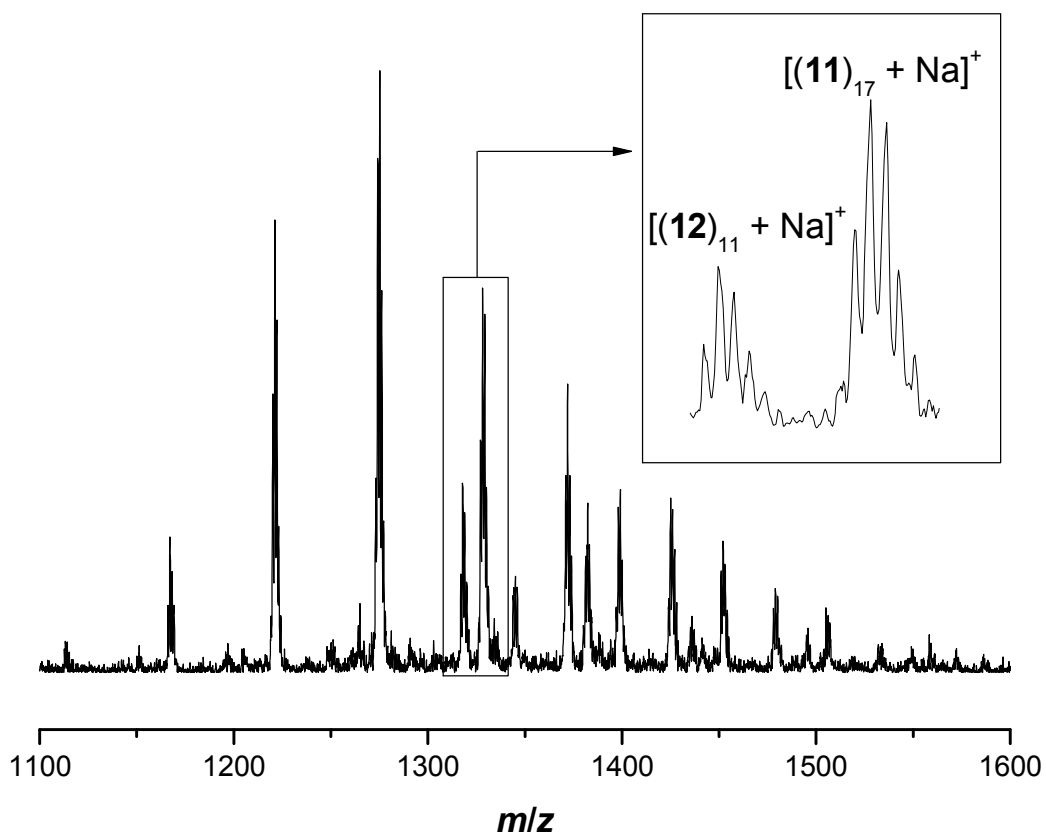


Figure S3. Magnified view into the region of 1100-1600 Da of the SEC-ESI mass spectrum of a polymer sample obtained after irradiation of a plain solution of tetrazole-functional NBR **4a** in acetonitrile with UV light of 254 nm for 3 h. For simplification of the SEC-ESI-MS analysis, the UV labile trithiocarbonate chain-end was removed with 1,1'-azobis(cyclohexane-1-carbonitrile) (0.34 mmol per gram of **4a**) in the presence of 1-ethylpiperidine hypophosphite (7.2 mmol per gram of **4a**) in toluene (35 mL per gram of **4a**) at 100 °C for 8 h prior to the irradiation, in analogy to a procedure described previously.⁵ For signal assignments of structures **11** and **12** refer to Fig. S4.

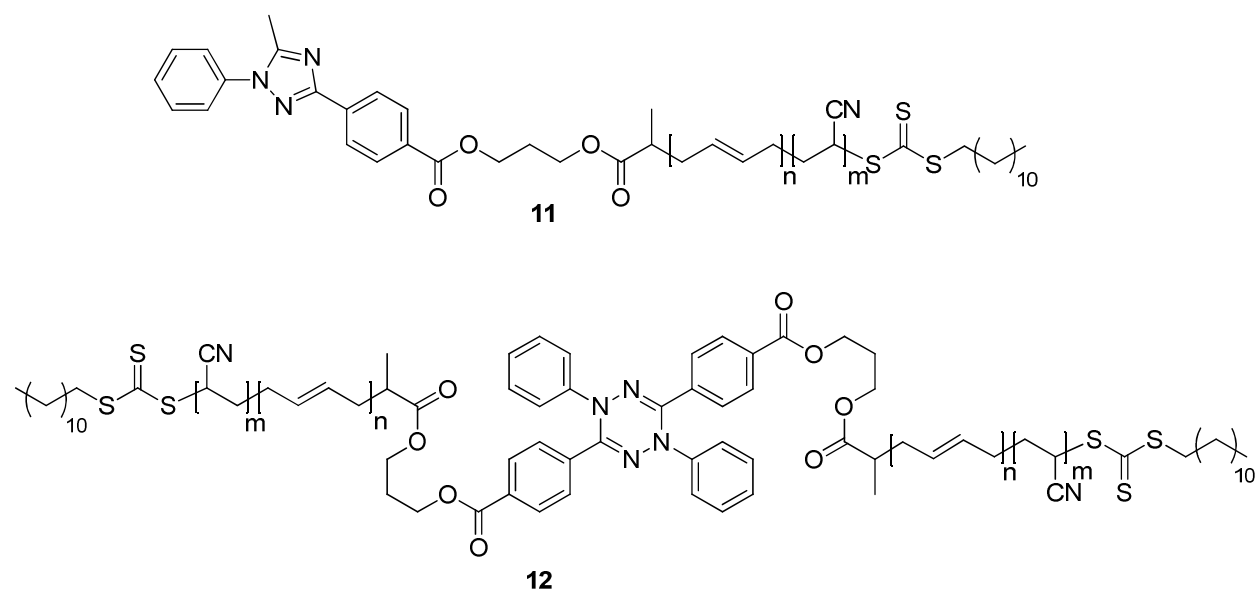


Figure S4. Structures of the side products formed during irradiation of a plain solution of tetrazole-functional NBR **4a** with UV light of 254 nm for 3 h in acetonitrile. The side products were observed in ESI-MS after removal of the UV labile trithiocarbonate prior to irradiation. For simplification, the side products are depicted with the trithiocarbonate chain-end structures. The cycloadduct **11** is formed via the reaction of the nitrile moiety of acetonitrile with the nitrile imine of the NBR formed via UV irradiation. The cycloadduct **12** is formed via the reaction of the nitrile imine moieties (formed *in-situ* from the tetrazole-functional NBRs) of two polymer chains.

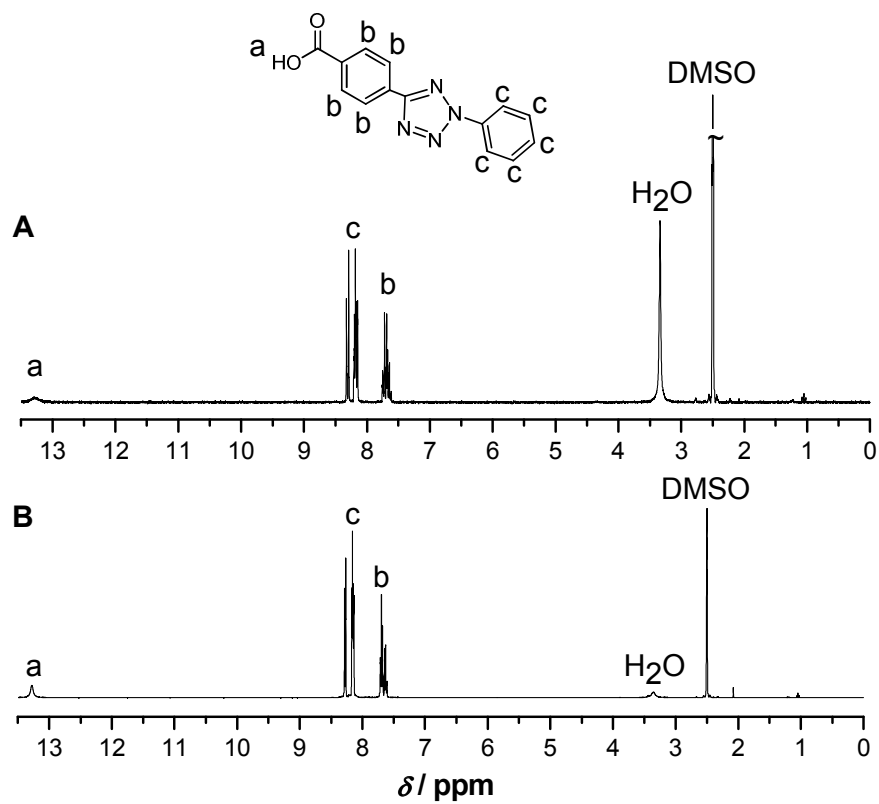


Figure S5. Investigation of the temperature stability of tetrazole **1**: ^1H NMR spectra in DMSO-d_6 A) before and B) after heating **1** to 100 °C for a period of 8 h.

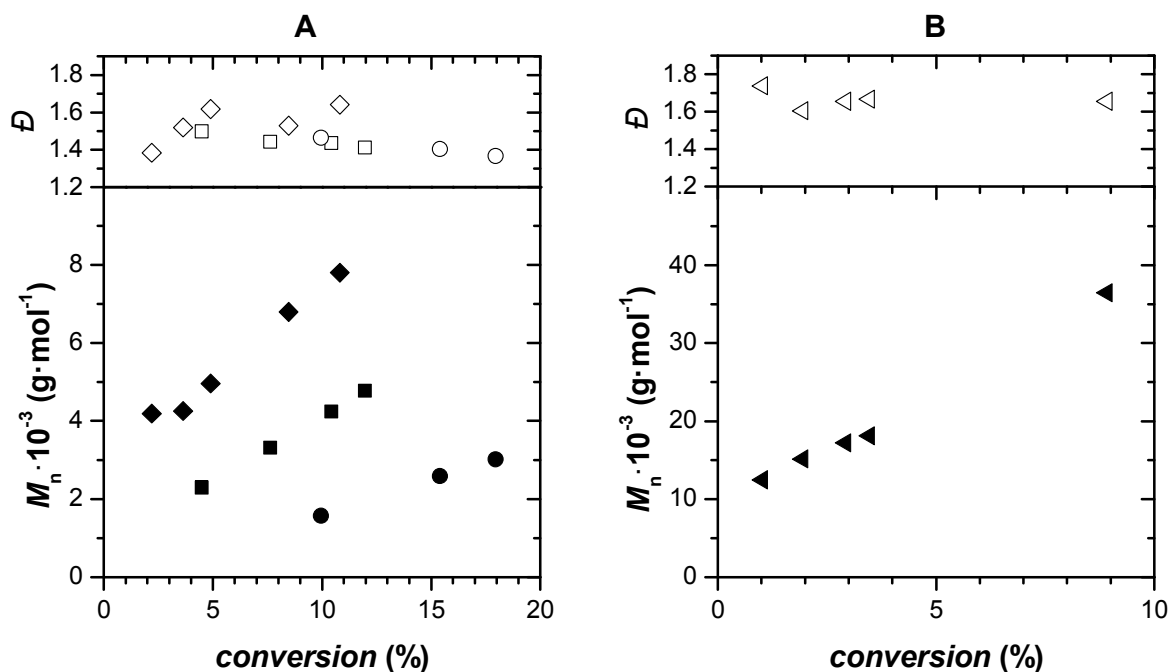


Figure S6. Evolution of molar mass and dispersity with conversion for a selection of RAFT mediated copolymerizations of AN and BD in their azeotropic ratio of 38/62 ($[M]_0$ 9.5 M). Polymerizations were performed in chlorobenzene at 100 °C, employing the tetrazole-functional controlling agent **3** and 1,1'-azobis(cyclohexane-1-carbonitrile) as the initiator. Conditions: A) rhombs: $[3]_0$ 3.5 mM, $[Ini]_0$ 0.3 mM (Table 2, entry 5), boxes: $[3]_0$ 8.4 mM, $[Ini]_0$ 1.0 mM (Table 2, entry 4), circles: $[3]_0$ 21.0 mM, $[Ini]_0$ 2.6 mM (Table 2, entry 3); B) triangles: $[3]_0$ 0.8 mM, $[Ini]_0$ 0.2 mM (Table 2, entry 6).

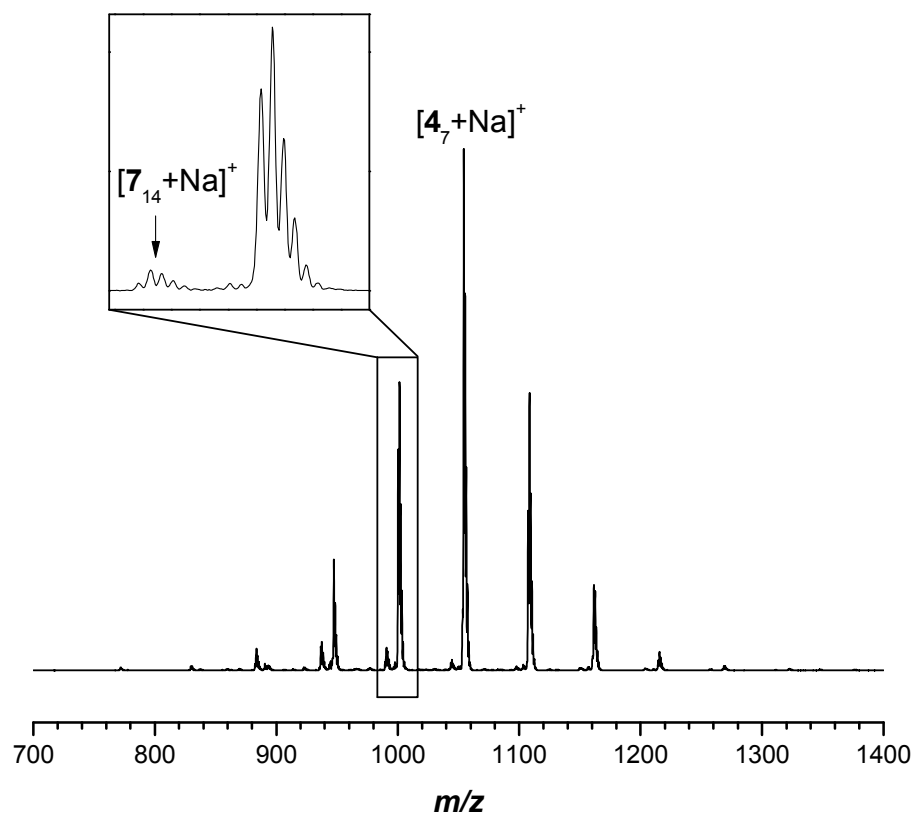


Figure S7. Magnified view into the region of 700 to 1400 Da of a SEC-ESI mass spectrum of the tetrazole-functionalized NBR **4a**. Polymer **7** is formed by recombination of two growing copolymer chains that were both initiated by the azo initiator fragment and is an inevitable side product of the RAFT process.

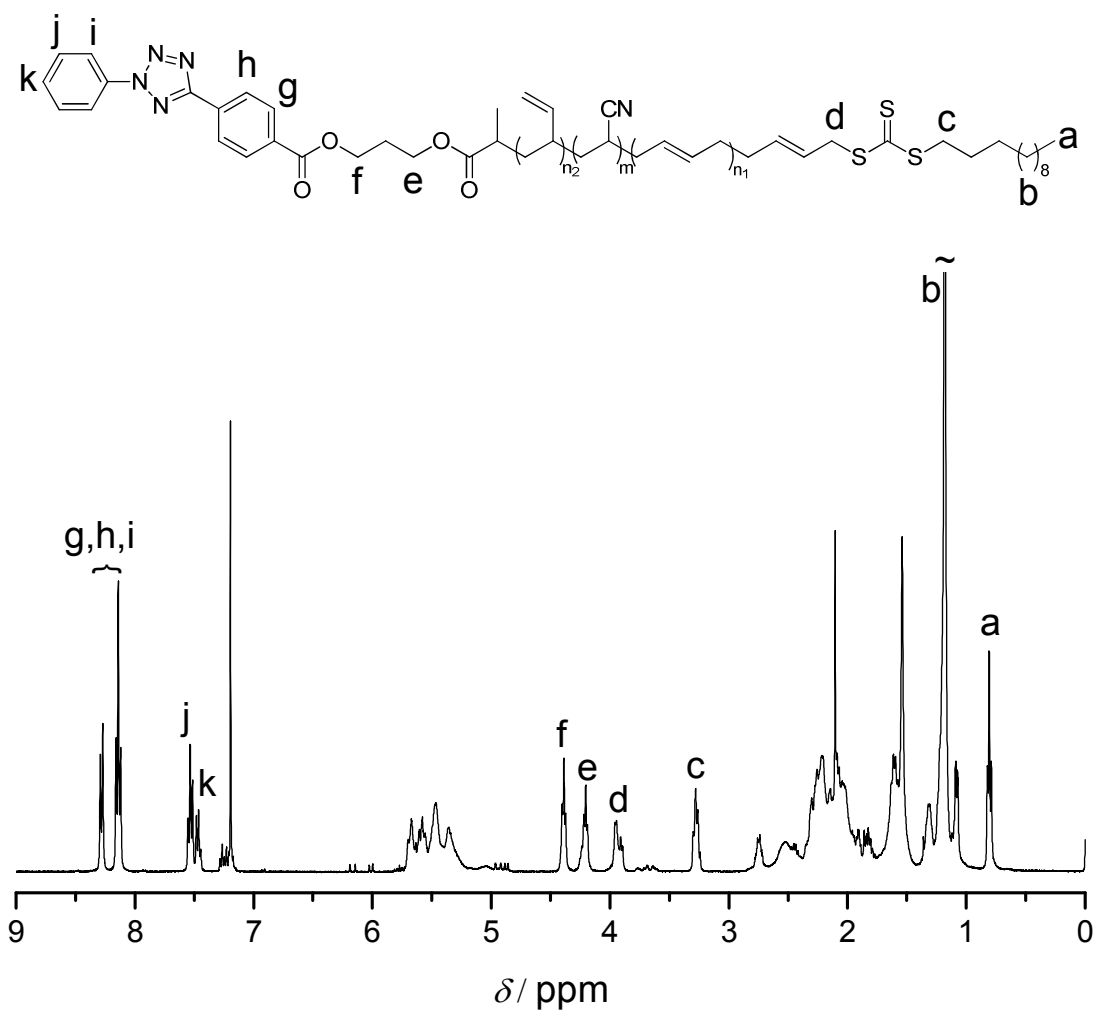


Figure S8. ^1H NMR characterization of the chain-end proton resonances of the tetrazole-functionalized NBR **4a**.

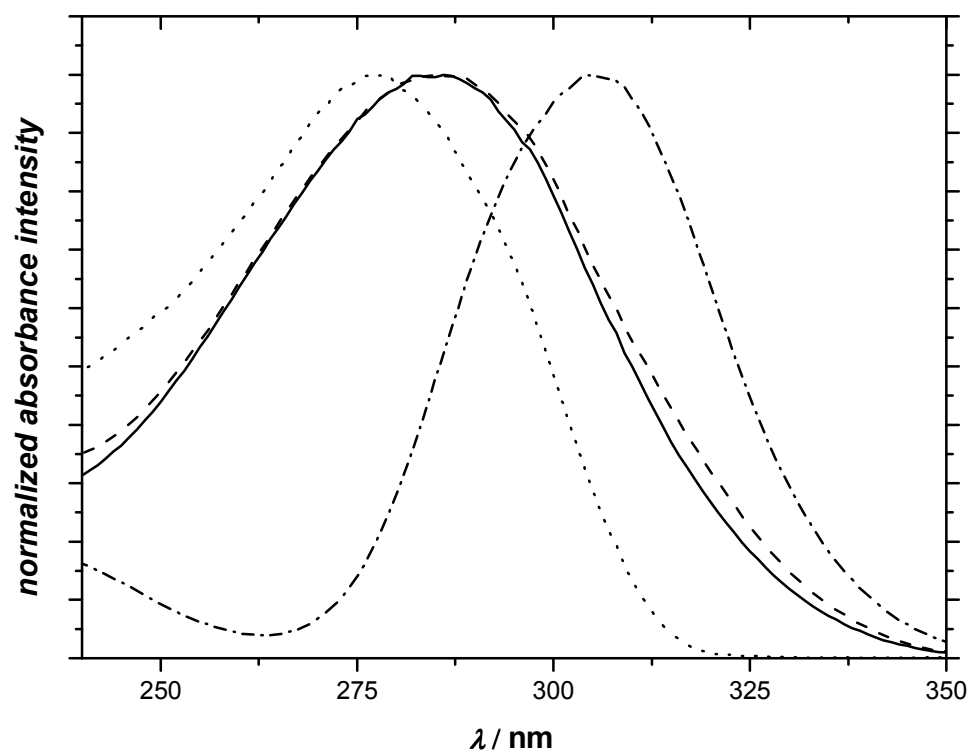


Figure S9. UV absorption spectra of tetrazole-functional controlling agent **3** (solid line), tetrazole-functional RAFT NBR **4a** (dashed line), trithiocarbonate **8** (dash-dotted line) and tetrazole **9** (dotted line).

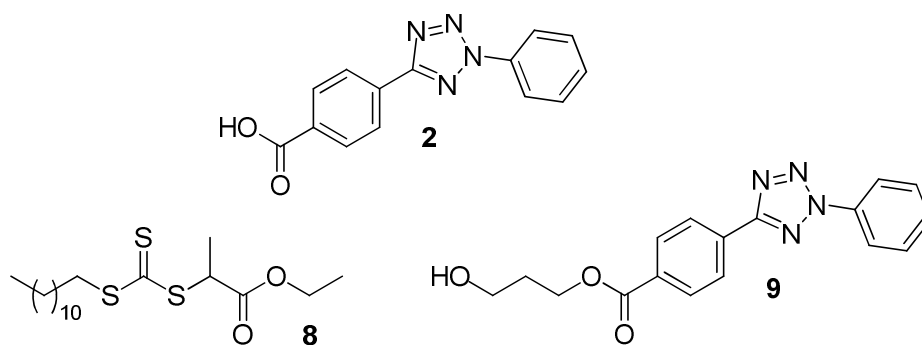


Figure S10. Chemical structures of compounds discussed in the manuscript.

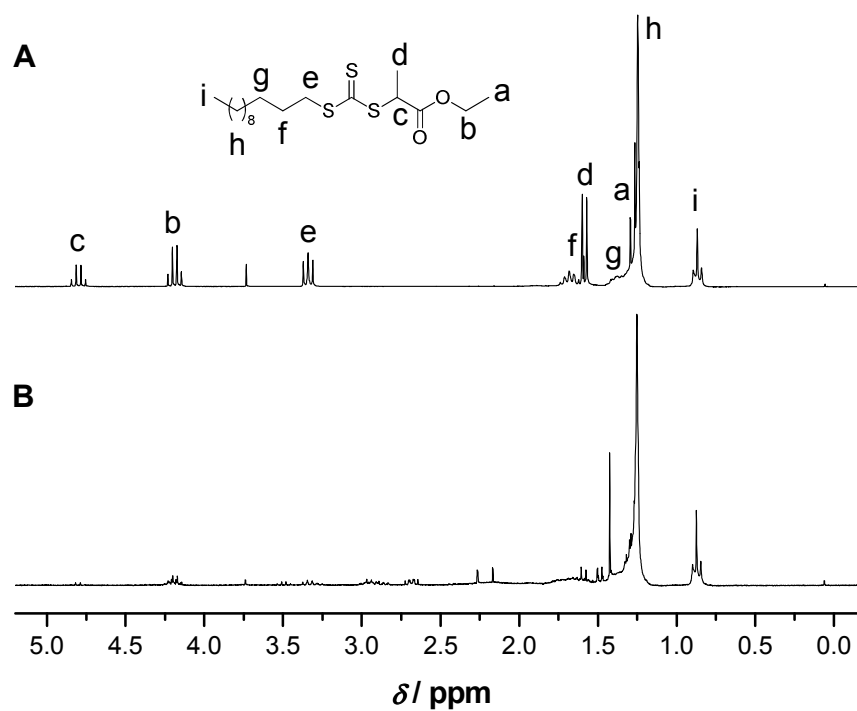


Figure S11. ^1H NMR spectra (CDCl_3) of alkyl-functional RAFT agent **8** A) before and B) after irradiation with UV light of 254 nm for 3 h, evidencing the decomposition of the trithiocarbonate under UV irradiation.

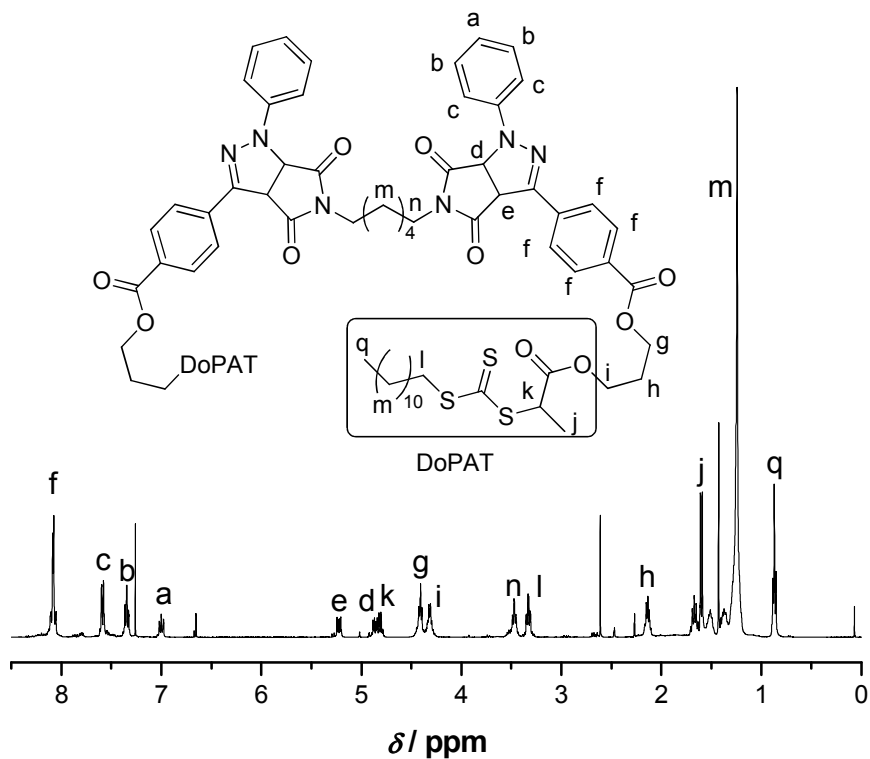


Figure S12. ^1H NMR characterization (ambient temperature, CDCl_3) of compound **10** obtained in the NITEC reaction of tetrazole-functional controlling agent **3** with 0.5 equivalents of bis(maleimido)hexane **5** upon irradiation with UV light of 254 nm for 15 min.

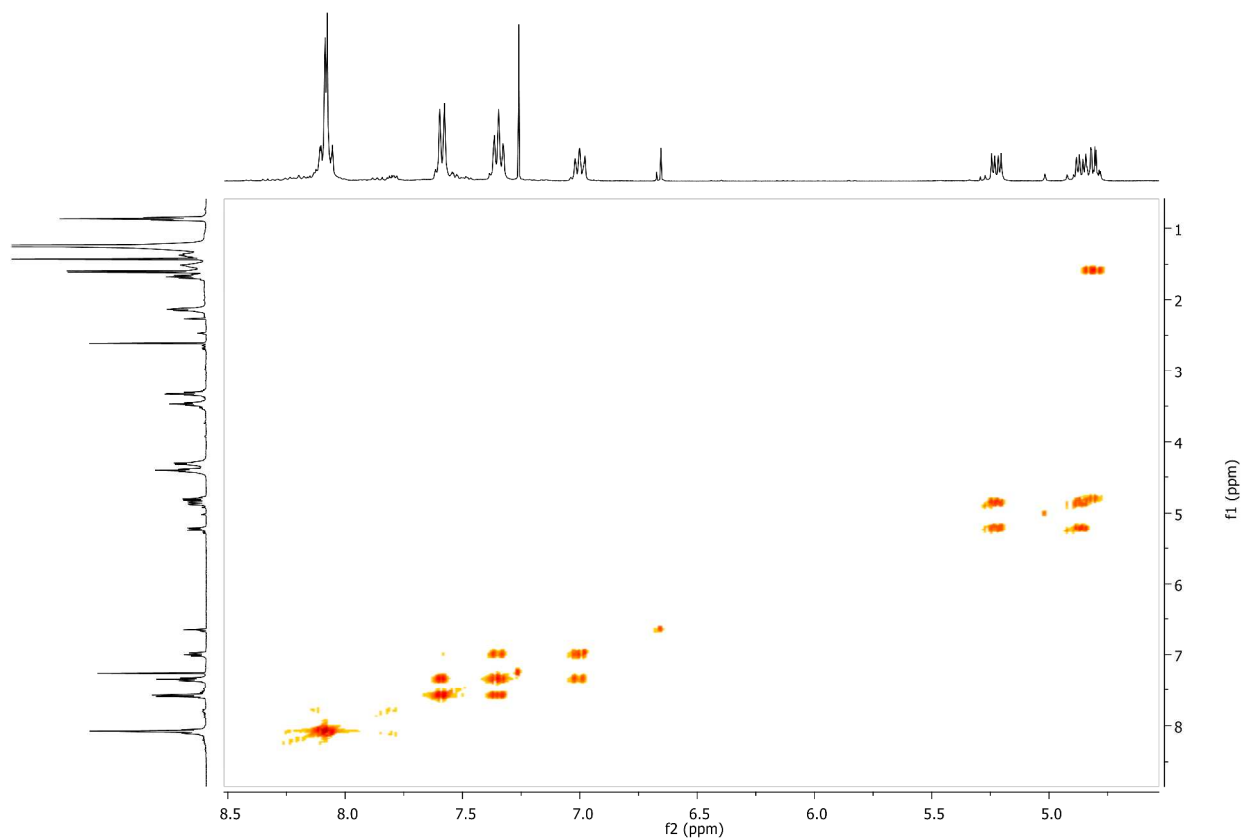


Figure S13. ^1H - ^1H COSY NMR spectrum (ambient temperature, CDCl_3) of compound **10** obtained in the NITEC reaction of tetrazole-functional controlling agent **3** with 0.5 equivalents of **5** after irradiation with UV light of 254 nm for 15 min. The provided zoom allows signal assignments of the aromatic protons (a, b, c and f, see Fig. S12) and the methine protons (d, e and k, see Fig. S12).

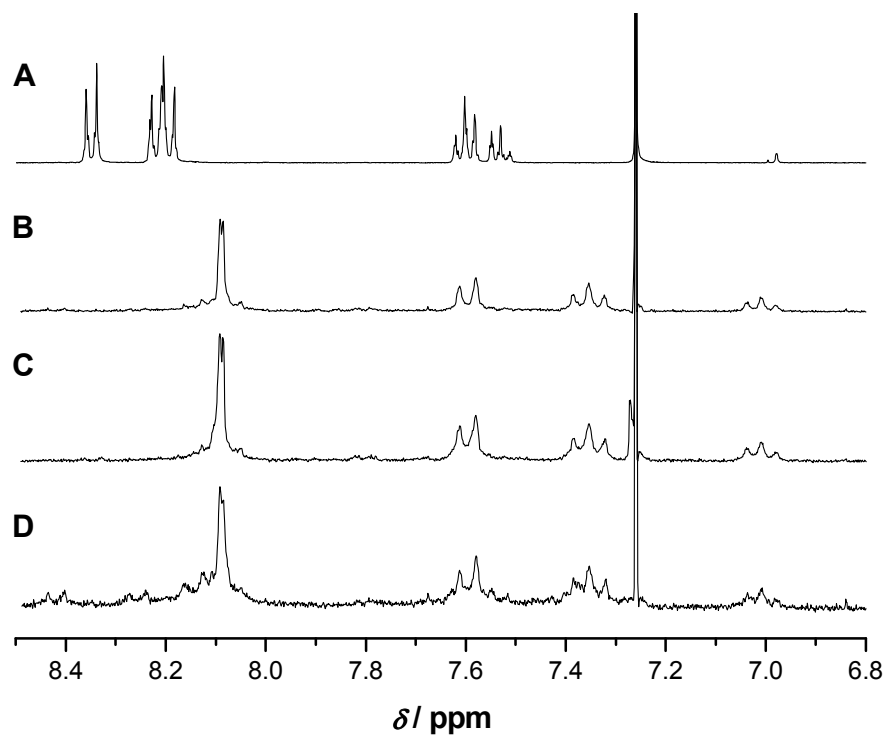


Figure S14. Magnified view into the region of 8.5-6.8 ppm of the ¹H NMR spectra following the NITEC reaction of tetrazole-functional RAFT agent **3** with 0.5 equivalents of linker **5**: A) before and B) after 15 min, C) after 60 min and D) after 180 min of irradiation with UV light of 254 nm.

Table S1. Experimental details for the light-induced coupling of NBR building blocks **4** in the presence of 0.5 equivalents of **5**.^a

entry	coupling of	m(4) (mg)	V_{total} (ml) ^b
1	4b	40	6
2	4e	40	6
3	4f	120	6

^a Conditions: Irradiation with UV-light of 254 nm for 3 h in acetonitrile. ^b V_{total} is the total reaction volume of the coupling experiments.

Table S2. SEC data of the light-induced coupling of NBR building blocks **4** in the presence of 0.5 equivalents of **5**.^a

entry	tetrazole-functional NBR 4			coupling product 6		
		M_n (g·mol ⁻¹) ^b	\bar{D}^b		M_n (g·mol ⁻¹) ^b	\bar{D}^b
1	4b	1800	1.2	6b	3200	1.3
2	4e	9400	1.5	6e	17 000	1.5
3	4f	38 000	1.6	6g	48 000	1.7

^a Conditions: Irradiation with UV-light of 254 nm for 3 h in acetonitrile. ^b Obtained from SEC via universal calibration employing the MHKS parameters of NBR.³

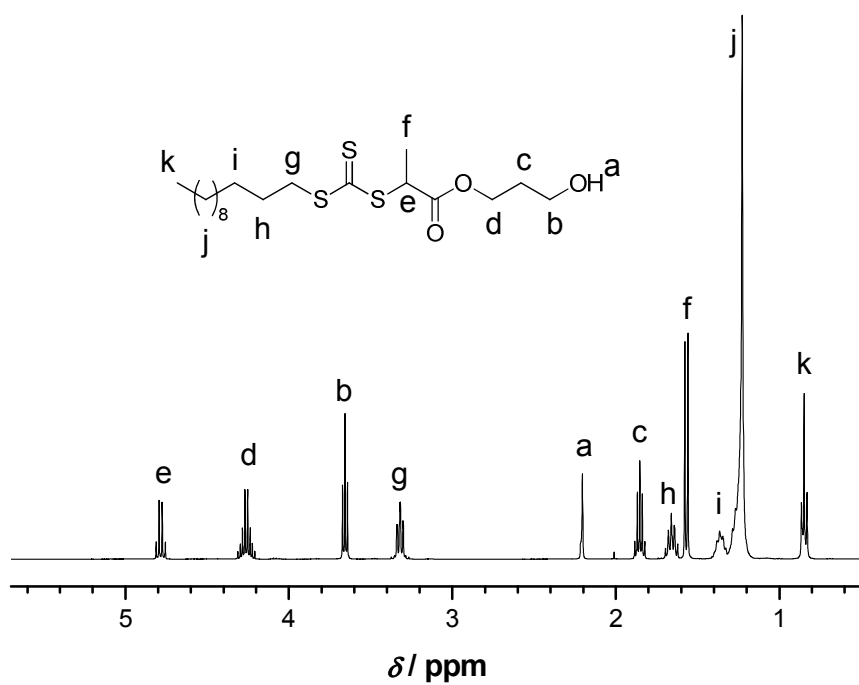


Figure S15. ^1H NMR characterization of trithiocarbonate **2** in CDCl_3 .

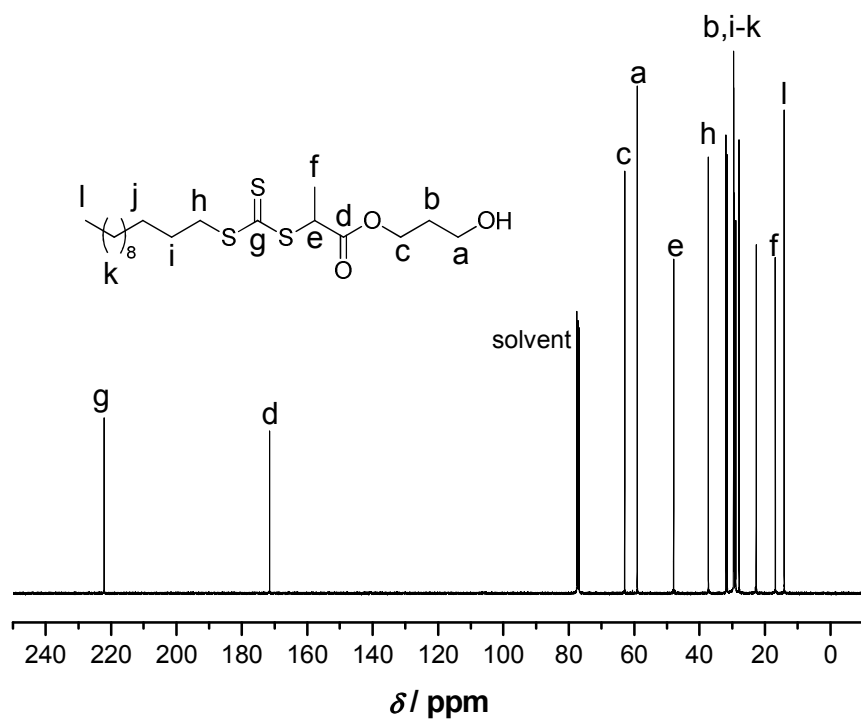


Figure S16. ^{13}C NMR characterization of trithiocarbonate **2** in CDCl_3 .

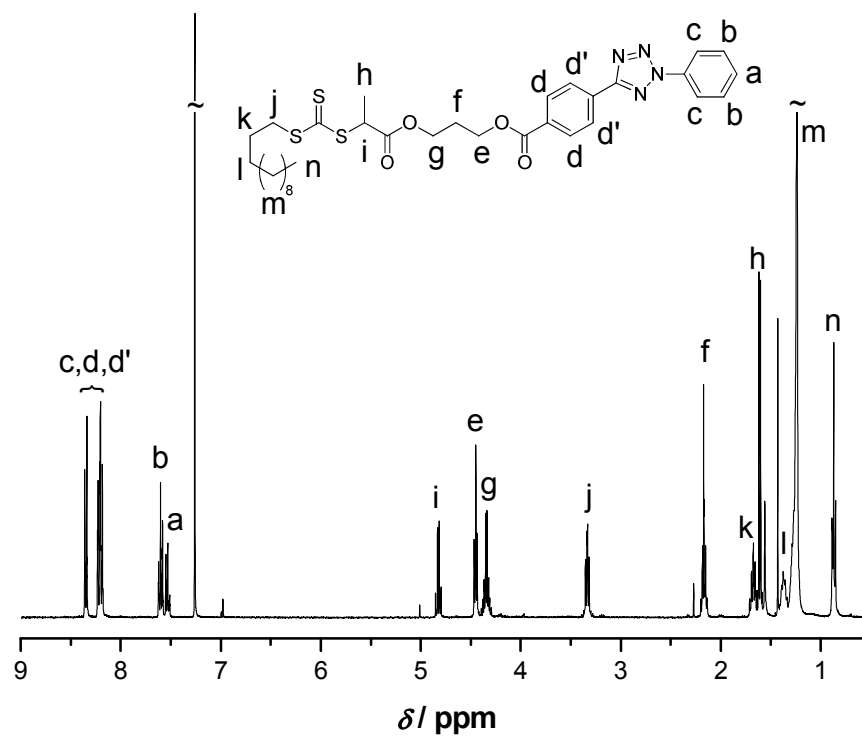


Figure S17. ^1H NMR characterization of diaryl tetrazole-functional controlling agent **3** in CDCl_3 obtained via esterification of hydroxyl-functional RAFT agent **2** and diaryl tetrazole **1**.

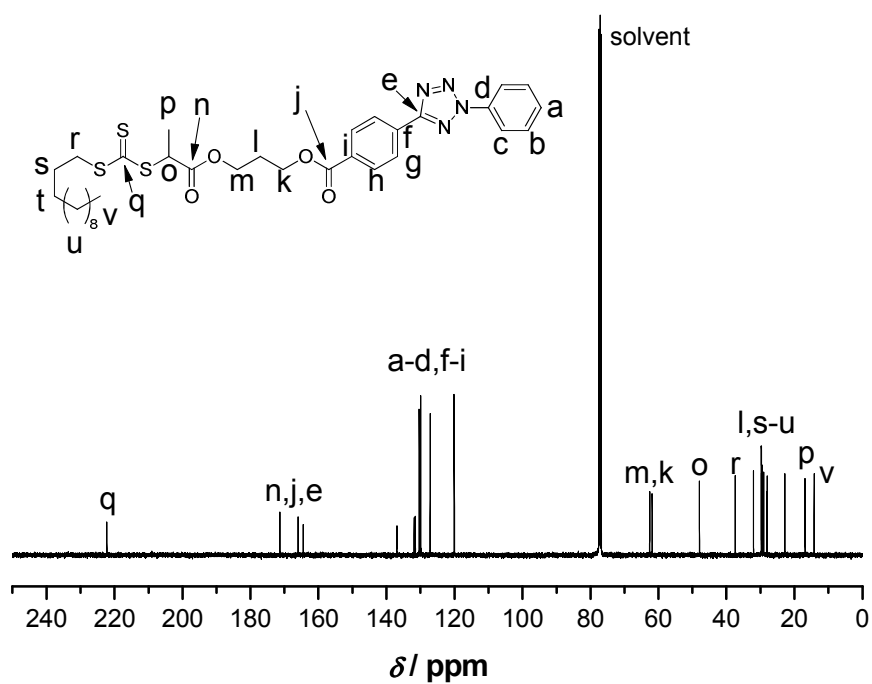


Figure S18. ^{13}C NMR characterization of diaryl tetrazole-functional controlling agent **3** in CDCl_3 obtained via esterification of hydroxyl-functional RAFT agent **2** and diaryl tetrazole **1**.

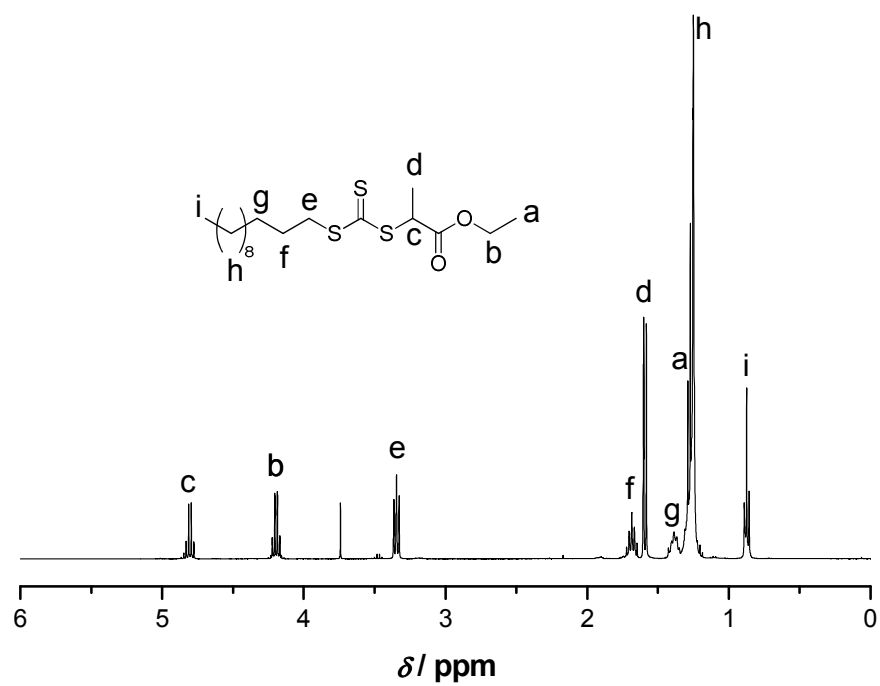


Figure S19. Ambient temperature ^1H NMR characterization of controlling agent **8** in CDCl_3 obtained via esterification of DoPAT with ethanol.

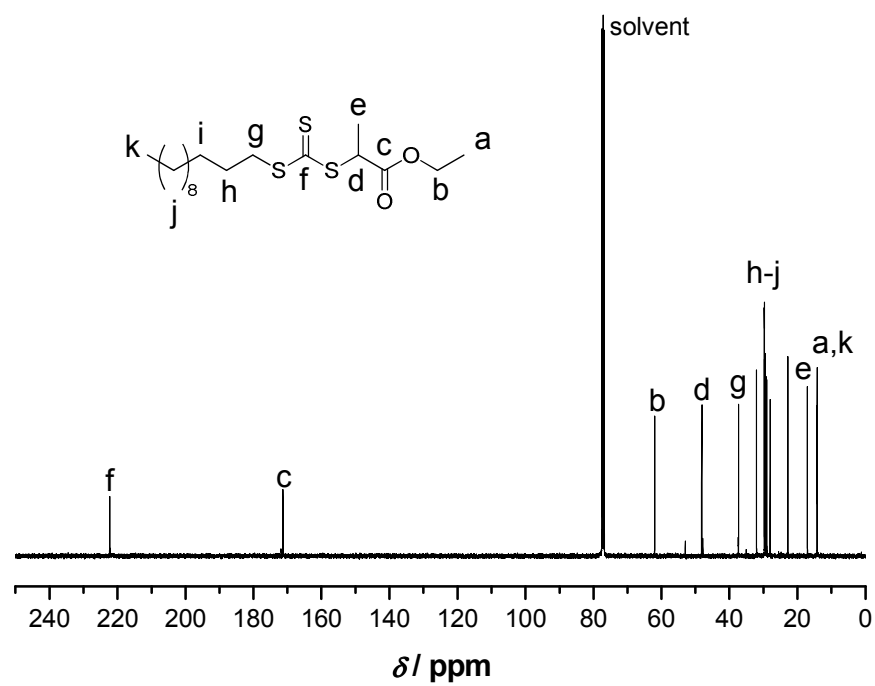


Figure S20. Ambient temperature ^{13}C NMR characterization of controlling agent **8** in CDCl_3 obtained via esterification of DoPAT with ethanol.

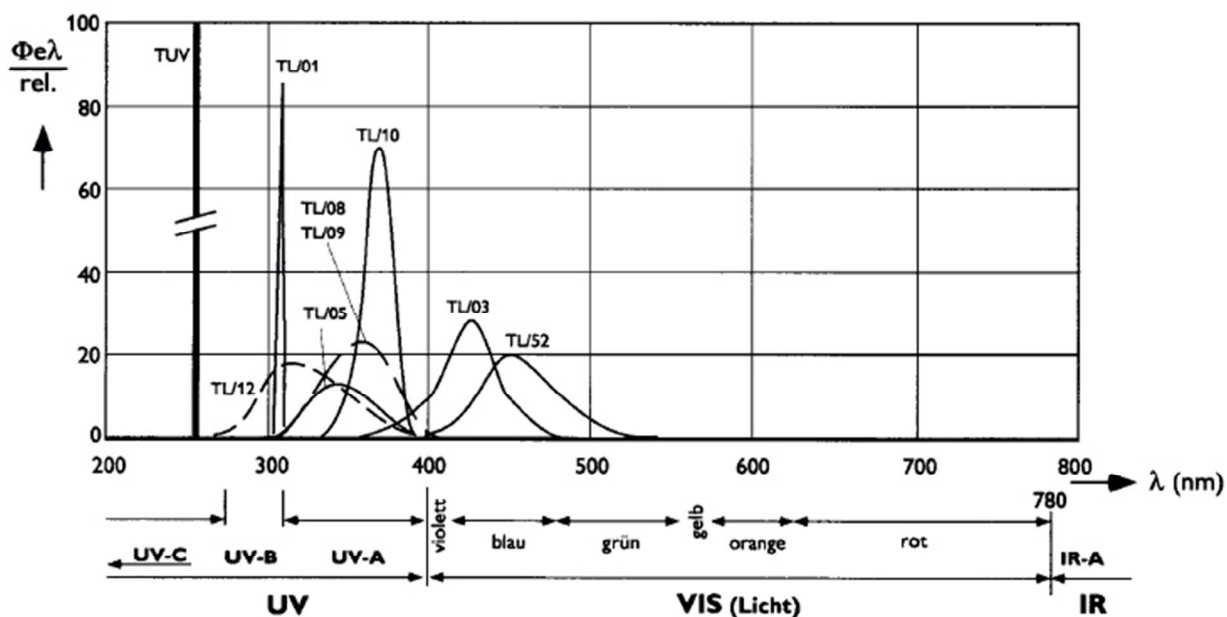


Figure S21. Emission spectrum of the UV lamp (TUV) as provided by Philips Lighting Professional.

References

1. Song, W.; Wang, Y.; Qu, J.; Madden, M. M.; Lin, Q., *Angew. Chem. Int. Ed.* **2008**, 47 (15), 2832-2835.
2. Kaiser, A.; Brandau, S.; Klimpel, M.; Barner-Kowollik, C., *Macromol. Rapid Commun.* **2010**, 31 (18), 1616-1621.
3. Dürr, C. J.; Hlalele, L.; Schneider-Baumann, M.; Kaiser, A.; Brandau, S.; Barner-Kowollik, C., *Polym. Chem.* **2013**, DOI: 10.1039/C3PY00580A.
4. Dietrich, M.; Glassner, M.; Gruendling, T.; Schmid, C.; Falkenhagen, J.; Barner-Kowollik, C., *Polym. Chem.* **2010**, 1 (5), 634-644.
5. Vogt, A. P.; Sumerlin, B. S., *Macromolecules* **2008**, 41 (20), 7368-7373.