

Photo-Induced Conjugation of Dithioester- and  
Trithiocarbonate-Functional RAFT Polymers with  
Alkenes

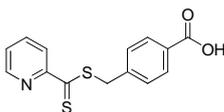
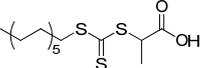
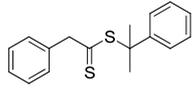
**Supporting Information**

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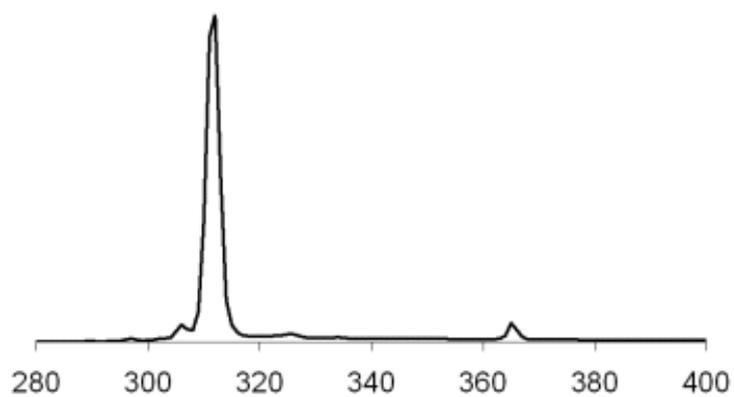
## Extinction coefficients of RAFT reagents used in the current study

4.0 mg of RAFT agent was dissolved in 50mL of MeOH. From this a concentration series was made by taking 0.250 mL, 0.500mL and 1.000mL of stock solution and diluting to 10 mL. These samples were then measured by UV-Vis spectroscopy and the molar absorption coefficient calculated using the Beer-Lambert law.

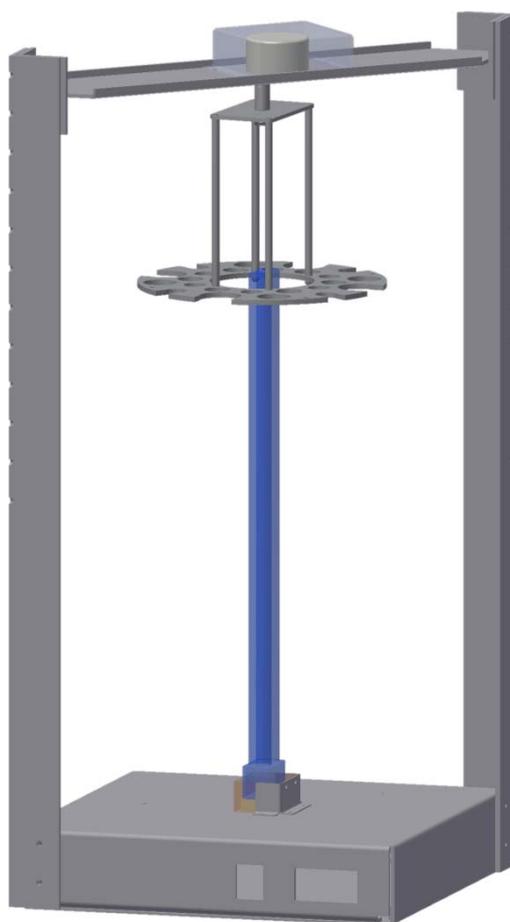
**Table S 1.** Maximum absorption wavelength and molar extinction coefficients of the  $\pi \rightarrow \pi^*$  transition for three typical RAFT-reagents, of which DoPAT and CPDA were employed in the current study.

RAFT agent	$\epsilon(\pi \rightarrow \pi^*)$	$\lambda_{\max}$
 PyrCOOH	10 240 L·mol <sup>-1</sup>	300 nm
 DoPAT	15 800 L·mol <sup>-1</sup>	309 nm
 CPDA	11 400 L·mol <sup>-1</sup>	311 nm

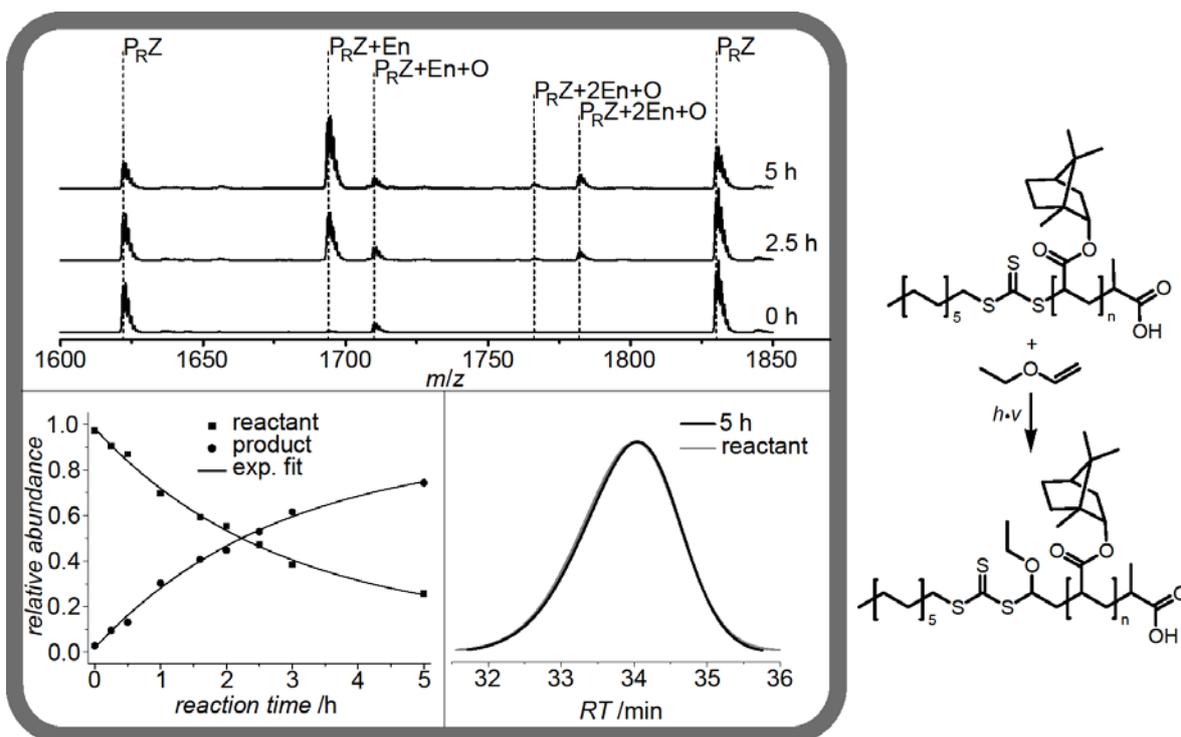
## Supporting Figures



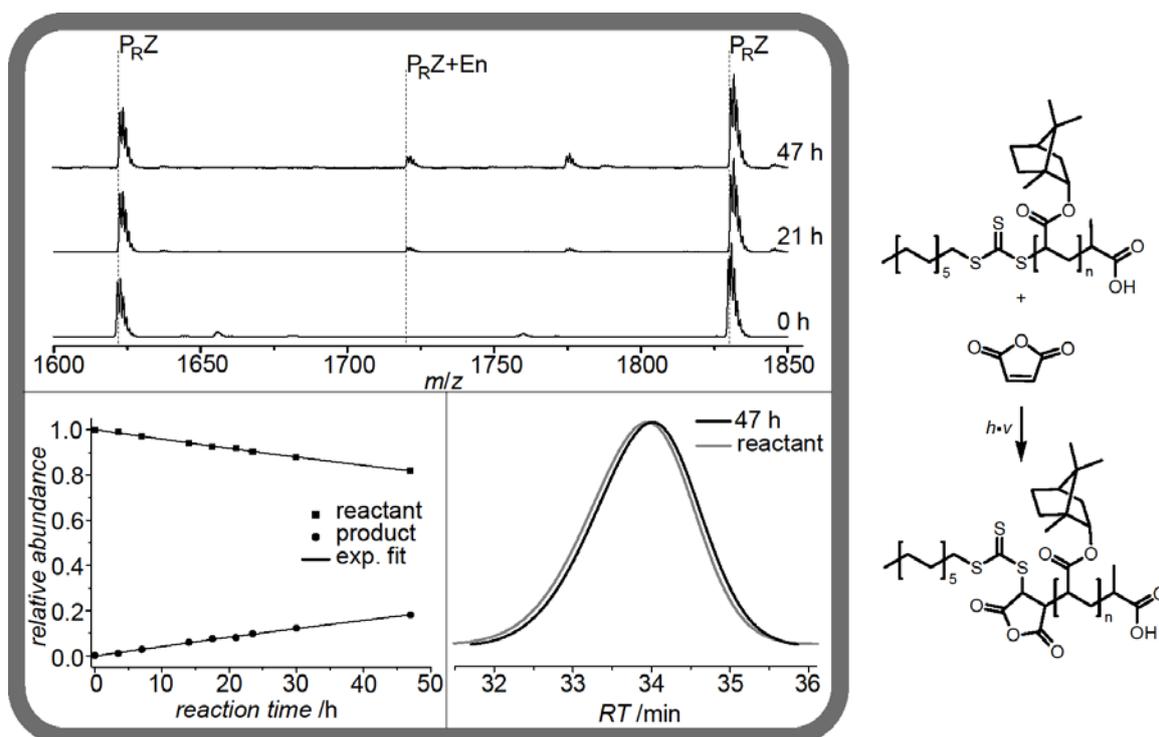
**Figure S 1.** Irradiance spectrum of the Philips Medical Therapy UV-B Narrow Band/01 compact fluorescent lamp (source: Philips data sheet).



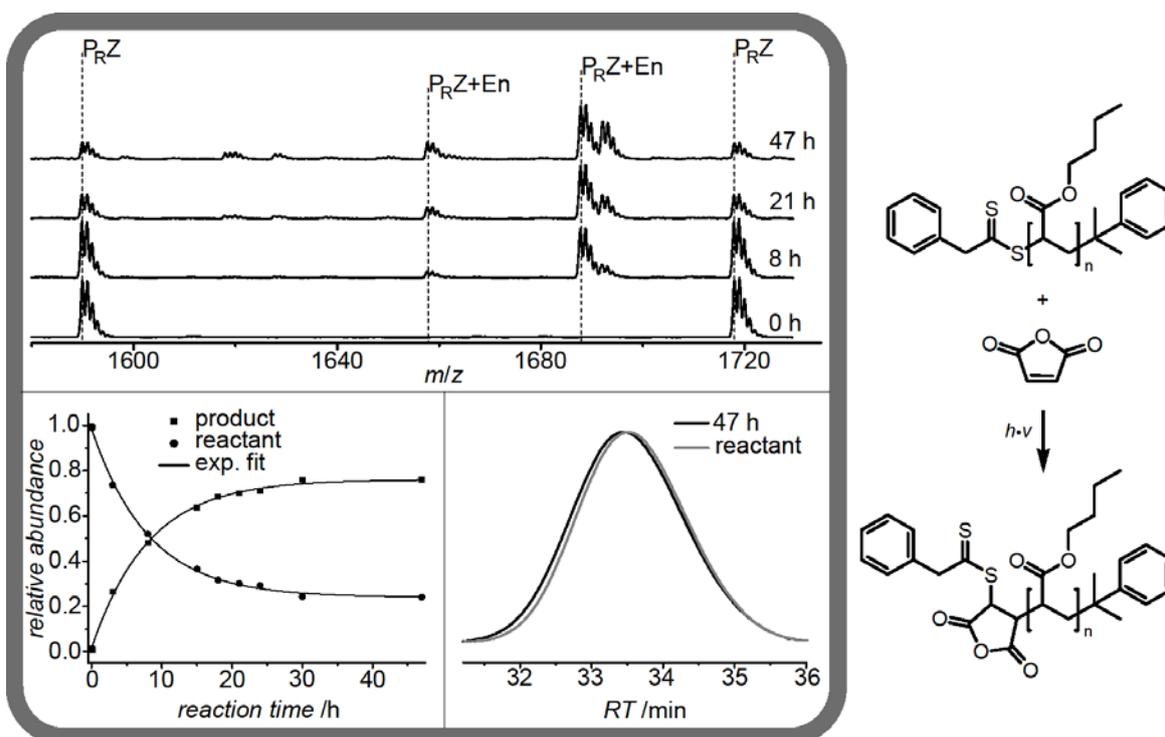
**Figure S 2.** Drawing of the custom-built photoreactor used in the current study.



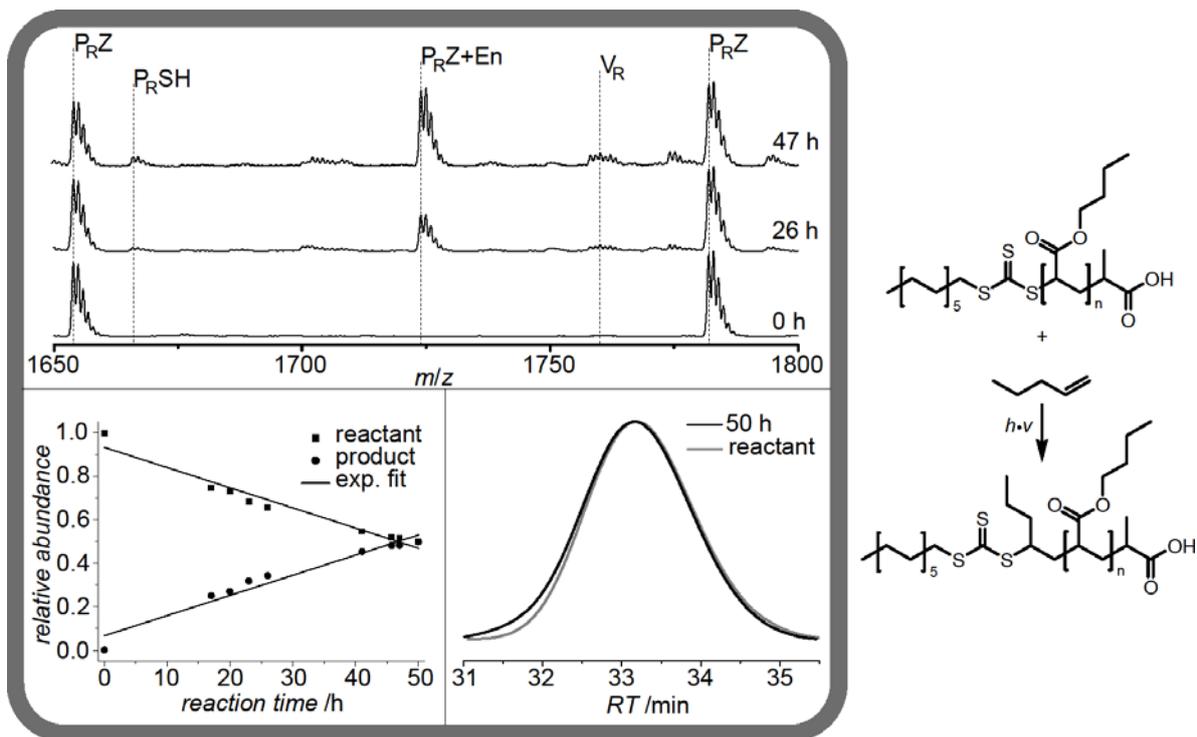
**Figure S 3.** SEC/ESI-MS investigation of the species formed during the conjugation reaction between ethyl vinyl ether and poly(isobornyl acrylate) carrying a trithiocarbonate endgroup from DoPAT-mediated polymerization at 315 nm. The development of the relative abundances of the major components during the reaction and the SEC-traces before and after the conjugation are shown in the lower left and lower right graphs of each inset respectively. Please refer to **Fehler! Verweisquelle konnte nicht gefunden werden.** for structural formulas corresponding to the shorthand assignments in the spectra.



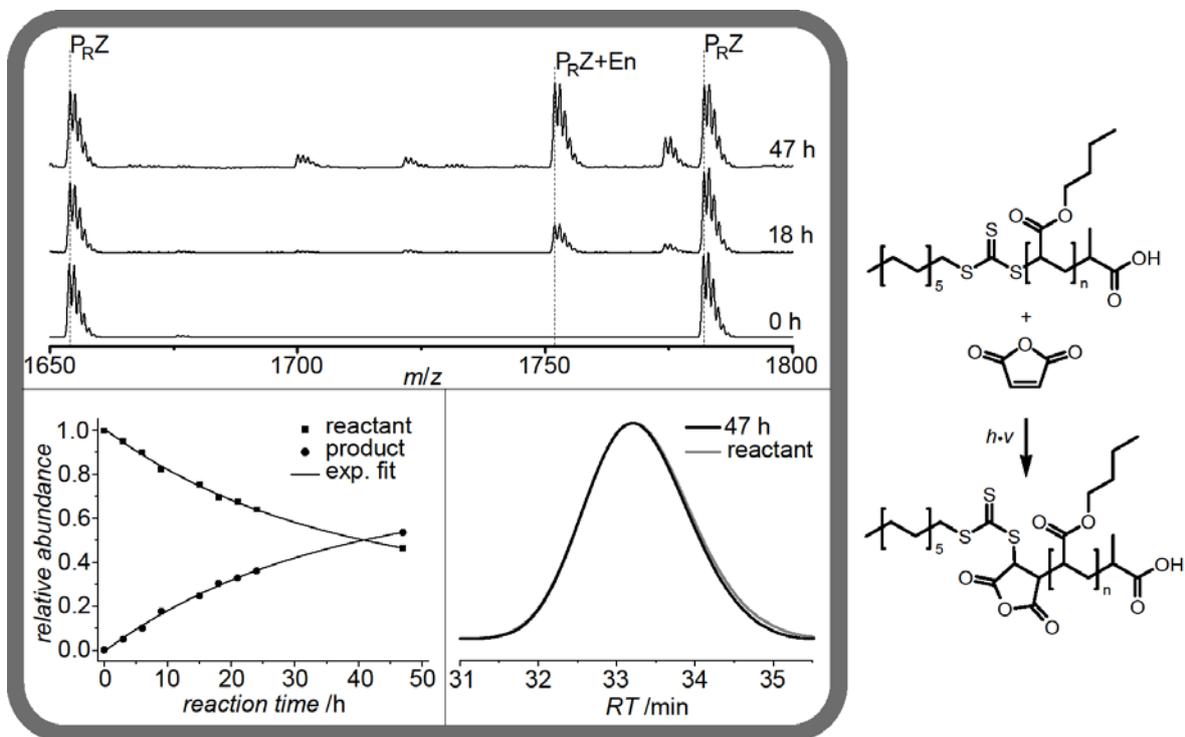
**Figure S 4.** SEC/ESI-MS investigation of the species formed during the conjugation reaction between maleic anhydride and poly(isobornyl acrylate) carrying a trithiocarbonate endgroup from DoPAT-mediated polymerization at 315 nm. The development of the relative abundances of the major components during the reaction and the SEC-traces before and after the conjugation are shown in the lower left and lower right graphs of each inset respectively. Please refer to **Fehler! Verweisquelle konnte nicht gefunden werden.** for structural formulas corresponding to the shorthand assignments in the spectra.



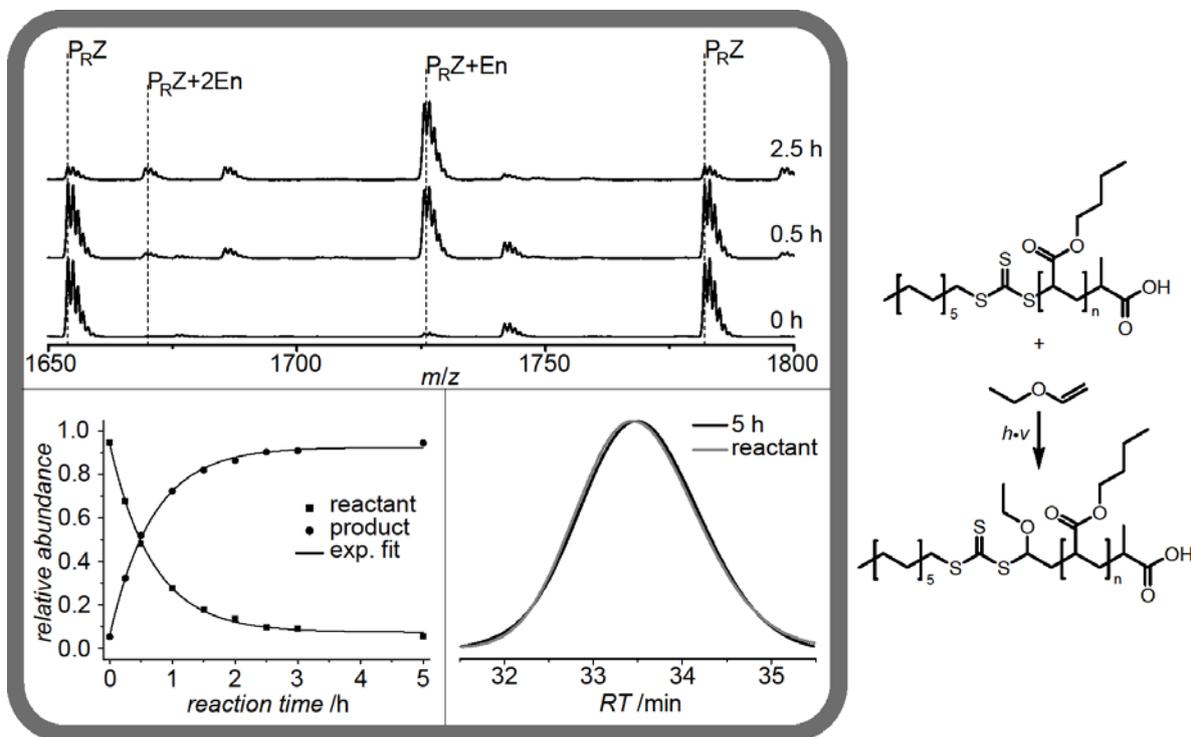
**Figure S 5.** SEC/ESI-MS investigation of the species formed during the conjugation reaction between maleic anhydride and poly(butyl acrylate) carrying a dithioester endgroup from CPDA-mediated polymerization at 315 nm. The development of the relative abundances of the major components during the reaction and the SEC-traces before and after the conjugation are shown in the lower left and lower right graphs of each inset respectively. Please refer to **Fehler! Verweisquelle konnte nicht gefunden werden.** for structural formulas corresponding to the shorthand assignments in the spectra.



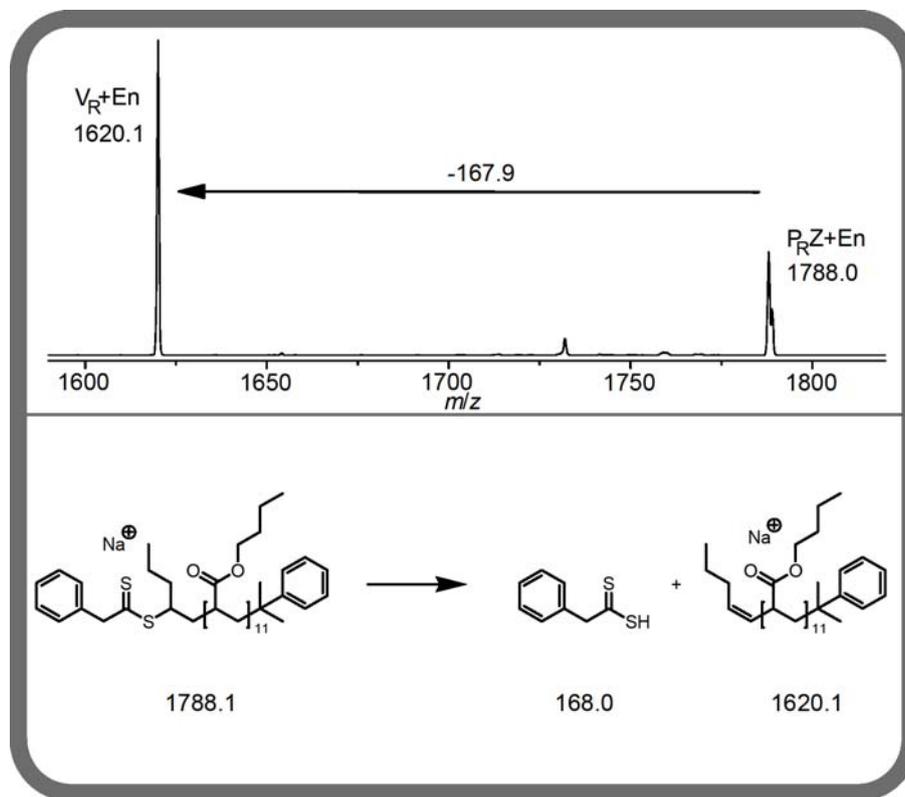
**Figure S 6.** SEC/ESI-MS investigation of the species formed during the conjugation reaction between 100 fold excess of 1-pentene and poly(butyl acrylate) carrying a trithiocarbonate endgroup from DoPAT-mediated polymerization at 315 nm. The development of the relative abundances of the major components during the reaction and the SEC-traces before and after the conjugation are shown in the lower left and lower right graphs of each inset respectively. Please refer to **Fehler! Verweisquelle konnte nicht gefunden werden.** for structural formulas corresponding to the shorthand assignments in the spectra.



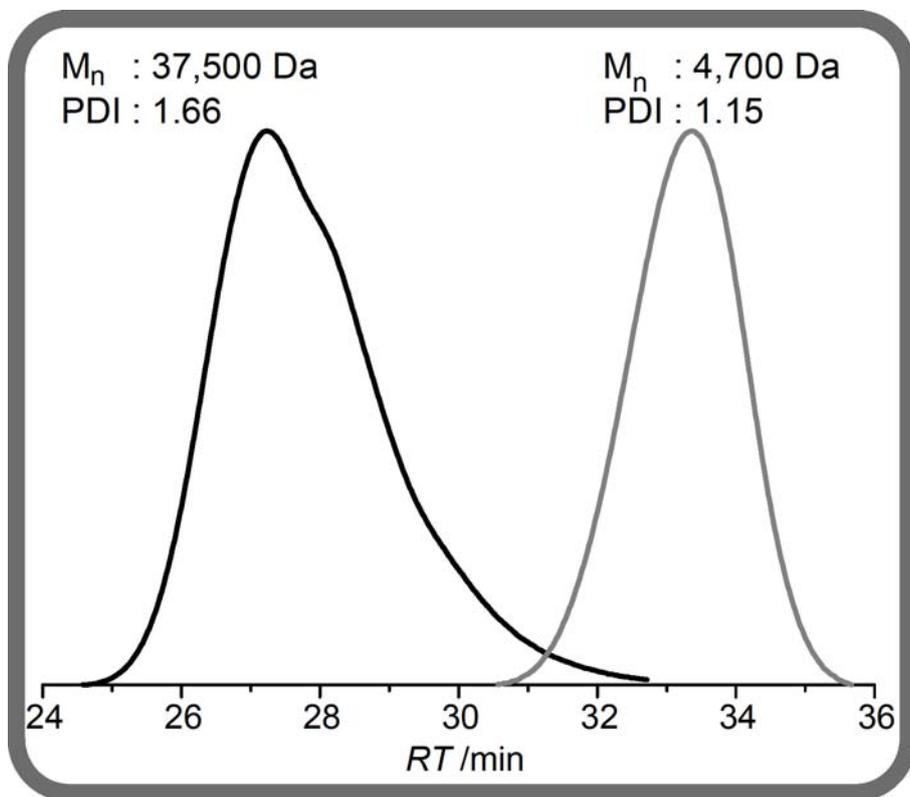
**Figure S 7.** SEC/ESI-MS investigation of the species formed during the conjugation reaction between maleic anhydride and poly(butyl acrylate) carrying a trithiocarbonate endgroup from DoPAT-mediated polymerization at 315 nm. The development of the relative abundances of the major components during the reaction and the SEC-traces before and after the conjugation are shown in the lower left and lower right graphs of each inset respectively. Please refer to **Fehler! Verweisquelle konnte nicht gefunden werden.** for structural formulas corresponding to the shorthand assignments in the spectra.



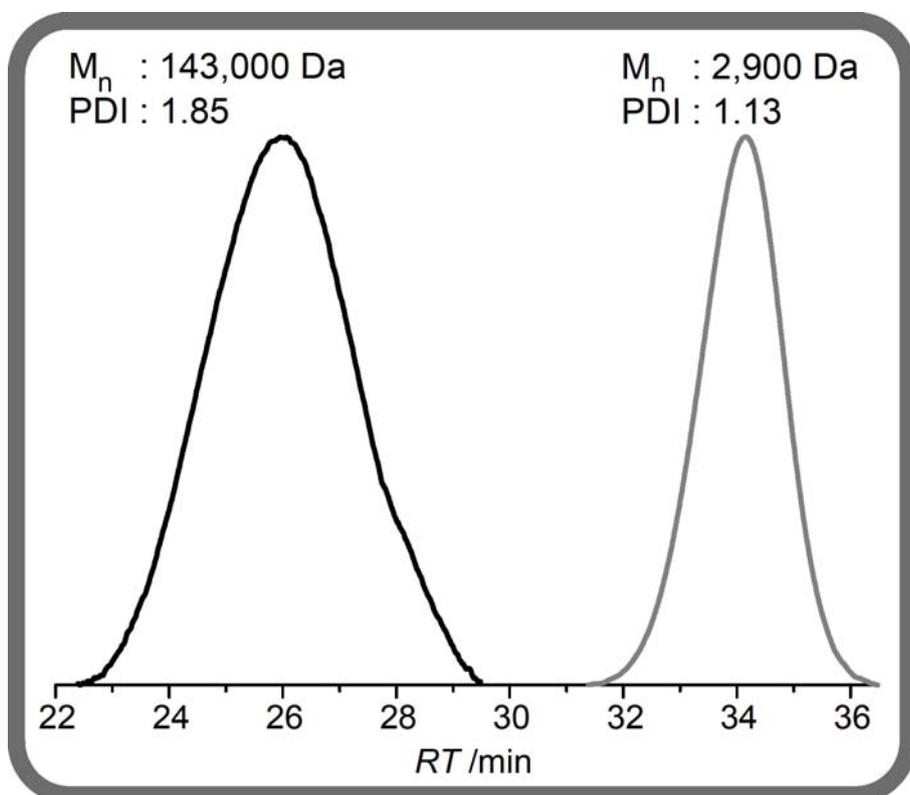
**Figure S 8.** SEC/ESI-MS investigation of the species formed during the conjugation reaction between ethyl vinyl ether and poly(butyl acrylate) carrying a trithiocarbonate endgroup from DoPAT-mediated polymerization at 315 nm. The development of the relative abundances of the major components during the reaction and the SEC-traces before and after the conjugation are shown in the lower left and lower right graphs of each inset respectively. Please refer to **Fehler! Verweisquelle konnte nicht gefunden werden.** for structural formulas corresponding to the shorthand assignments in the spectra.



**Figure S 9.** Tandem electrospray ionization mass spectrometric analysis of the main functional polymer species ( $\mathbf{P_RZ+En}$ ,  $m/z = 1788.0$  Th) formed by the photoreaction between 1-pentene and poly(butyl acrylate) carrying a dithioester endgroup from CPDA-mediated polymerization at 315 nm. Loss of a species with mass-to-charge ratio of 167.9 Th indicates that the phenyl dithioacetic acid is lost during CID.



**Figure S 10.** SEC -traces of the reactant DoPAT-functional poly(isobornyl acrylate) (grey curve) and of the reaction product from the photo-conjugation with styrene (black curve).



**Figure S 11.** SEC -traces of the reactant DoPAT-functional poly(isobornyl acrylate) (grey curve) and of the reaction product from the photo-conjugation with vinyl acetate (black curve).