Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

for

Synthesis and Characterization of quaternary phosphonium-containing, trithiocarbonate RAFT agents

Longhe Zhang,[a] Qiang Tang,[b] R. A. Weiss, [a] Kevin A. Cavicchi*[a]

[a] Department of Polymer Engineering, The University of Akron, Akron, OH, 44325-0301, USA. Fax: +1 330 972 3406; Tel: +1 330 972 8368; E-mail: kac58@uakron.edu;

[b] School of Chemistry and Chemical Engineering, Hubei University of Technology, Wuhan 430068, China

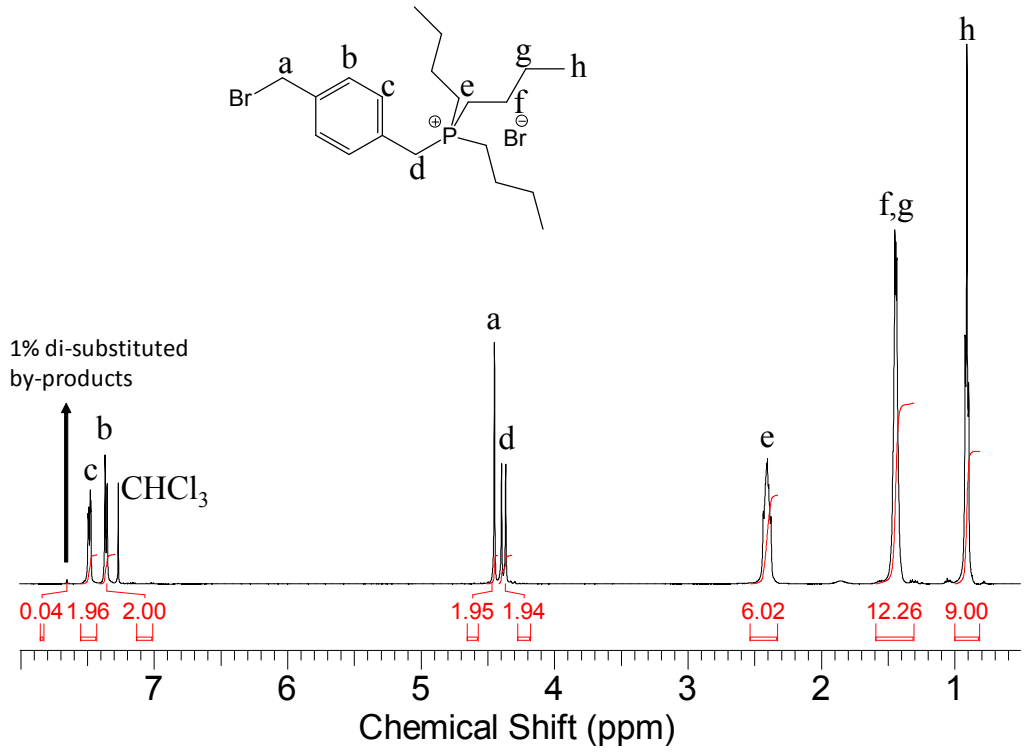


Fig. S1 ^{1}H NMR spectrum in $CDCl_3$ of Br-Ph-PBu_3.

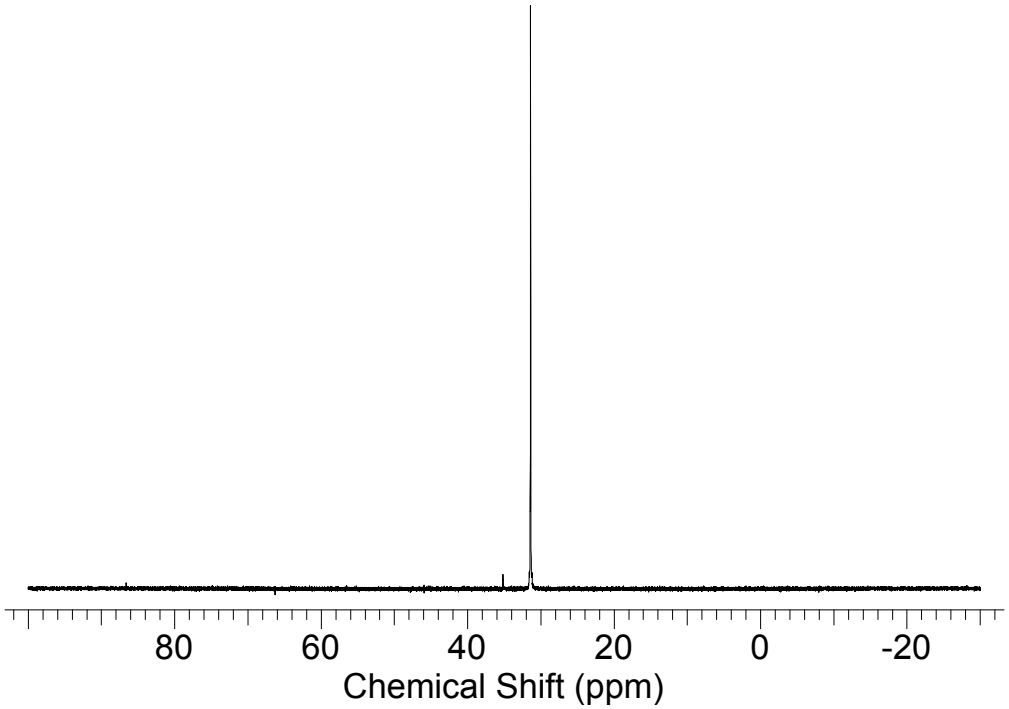


Fig. S2 ^{31}P NMR spectrum in $CDCl_3$ of Br-Ph-PBu_3.

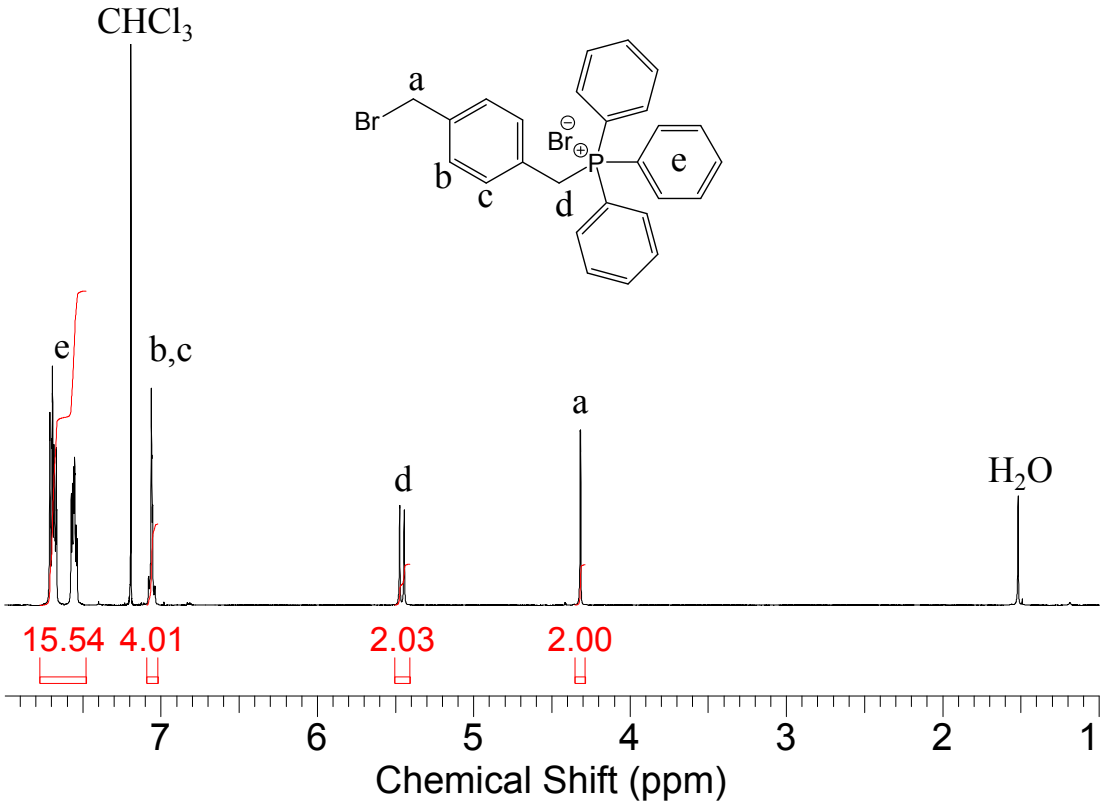


Fig. S3 ^{1}H NMR spectrum in $CDCl_3$ of Br-Ph-PPh_3.

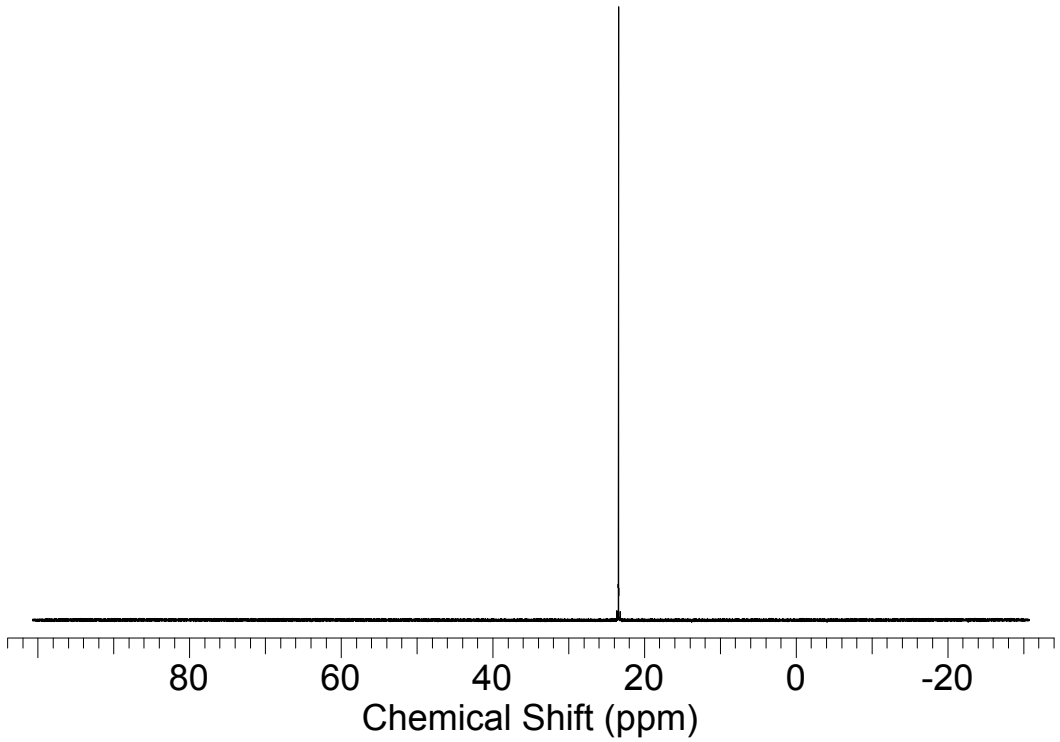


Fig. S4 ^{31}P NMR spectrum in $CDCl_3$ of Br-Ph-PPh_3.

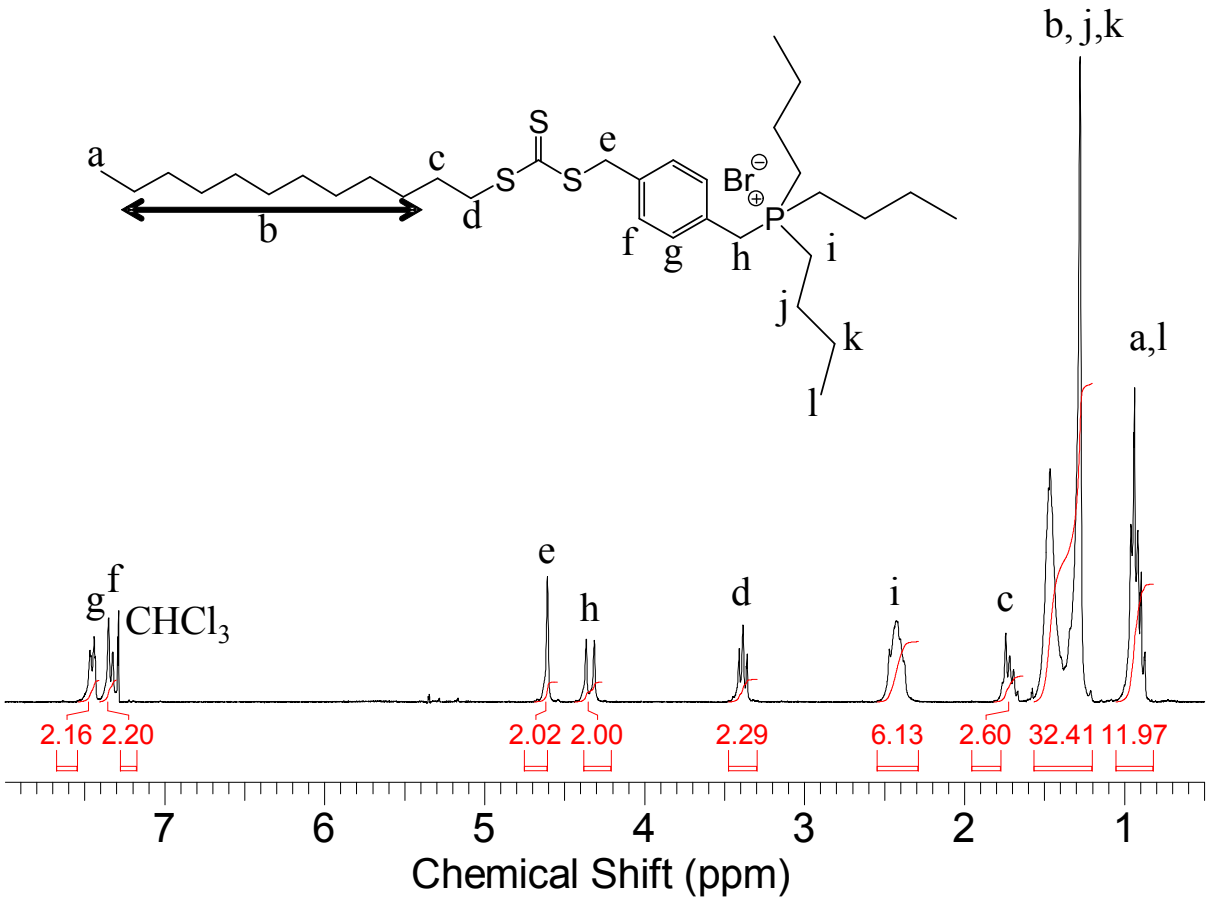


Fig. S5 ^{1}H NMR spectrum in $CDCl_3$ of RAFT-PBu_3.

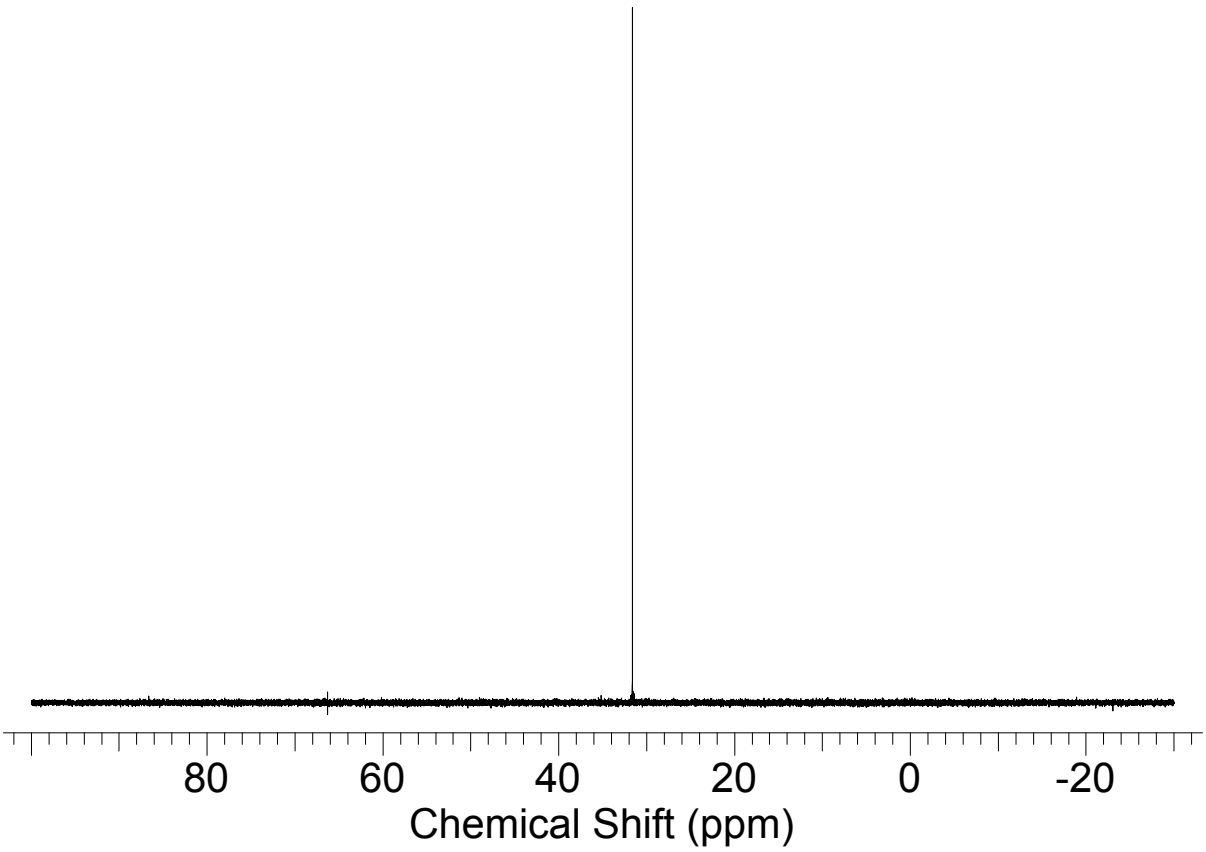


Fig. S6 ^{31}P NMR spectrum in $CDCl_3$ of RAFT-PBu_3.

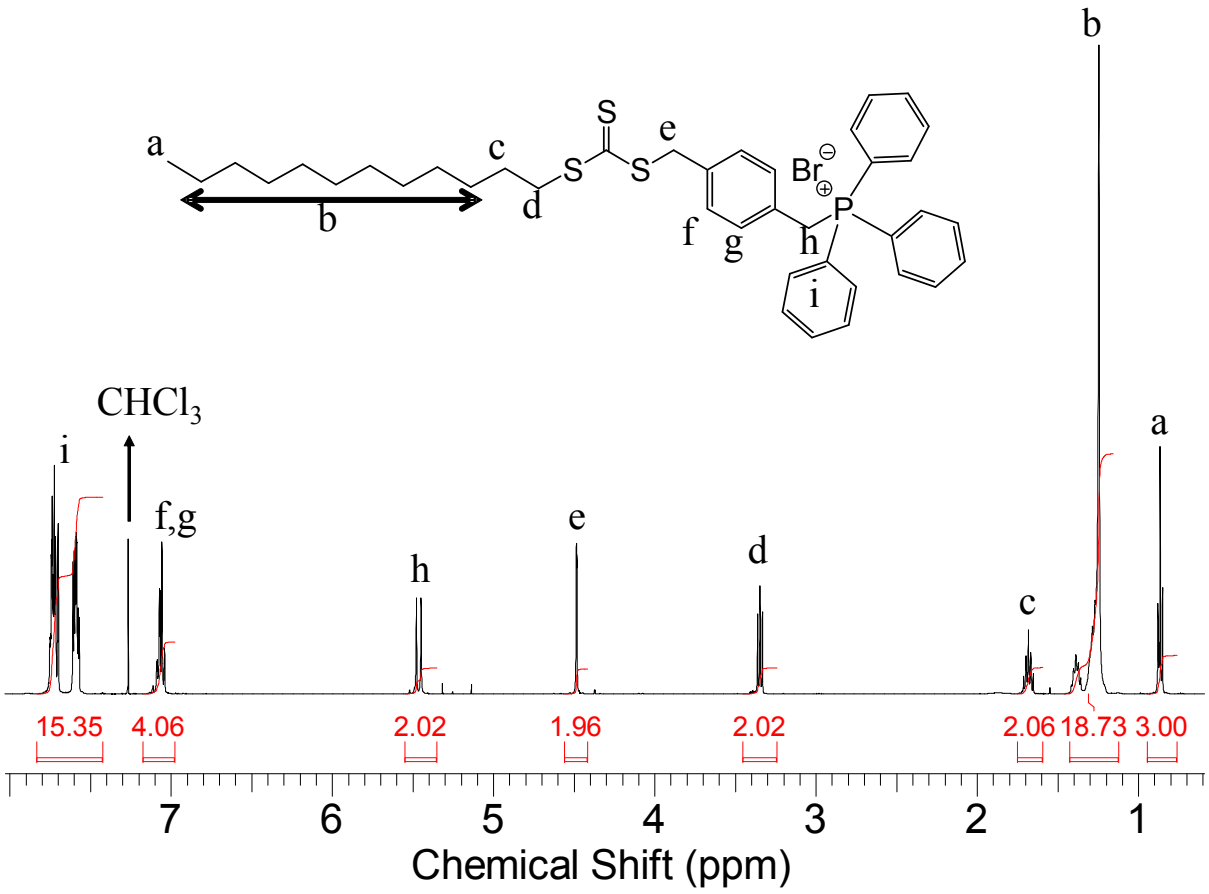


Fig. S7 ^{1}H NMR spectrum in $CDCl_3$ of RAFT-PPh_3.

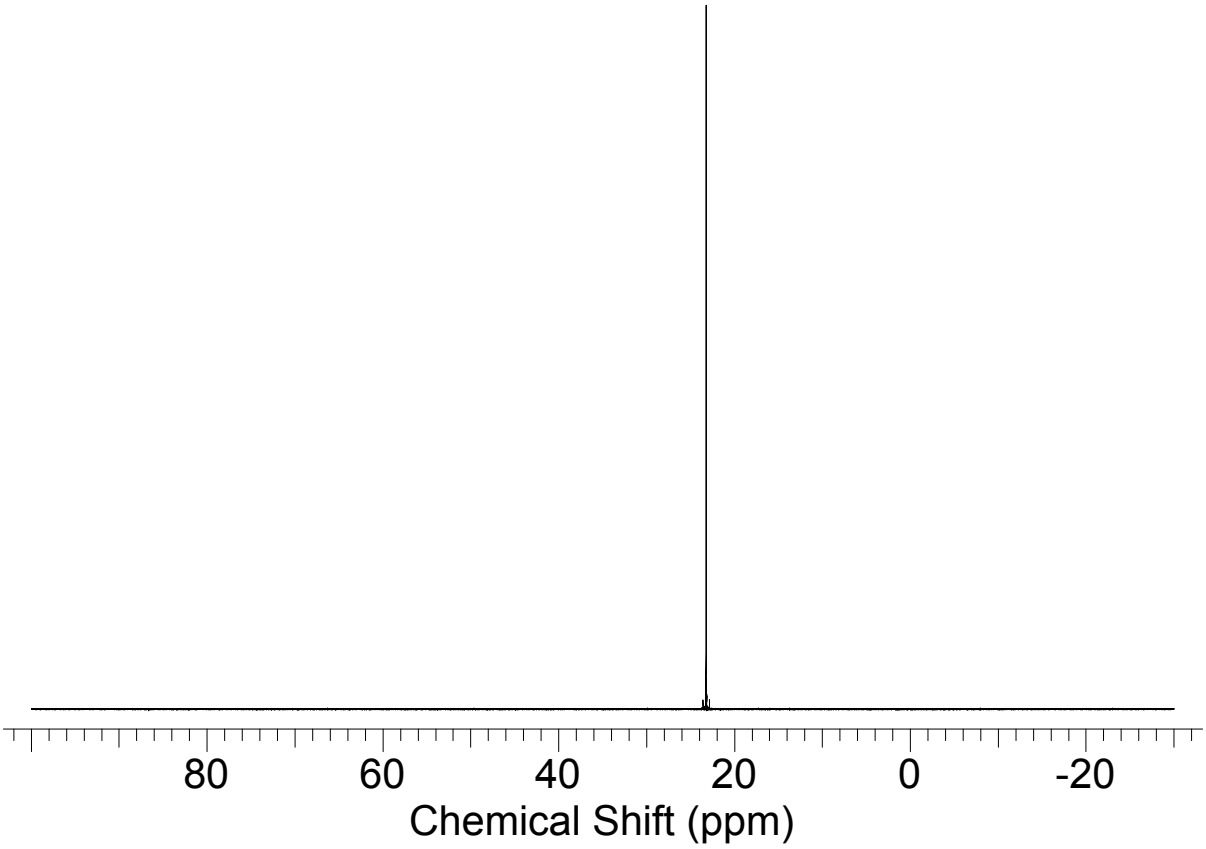


Fig. S8 ^{31}P NMR spectrum in $CDCl_3$ of RAFT-PPh_3.

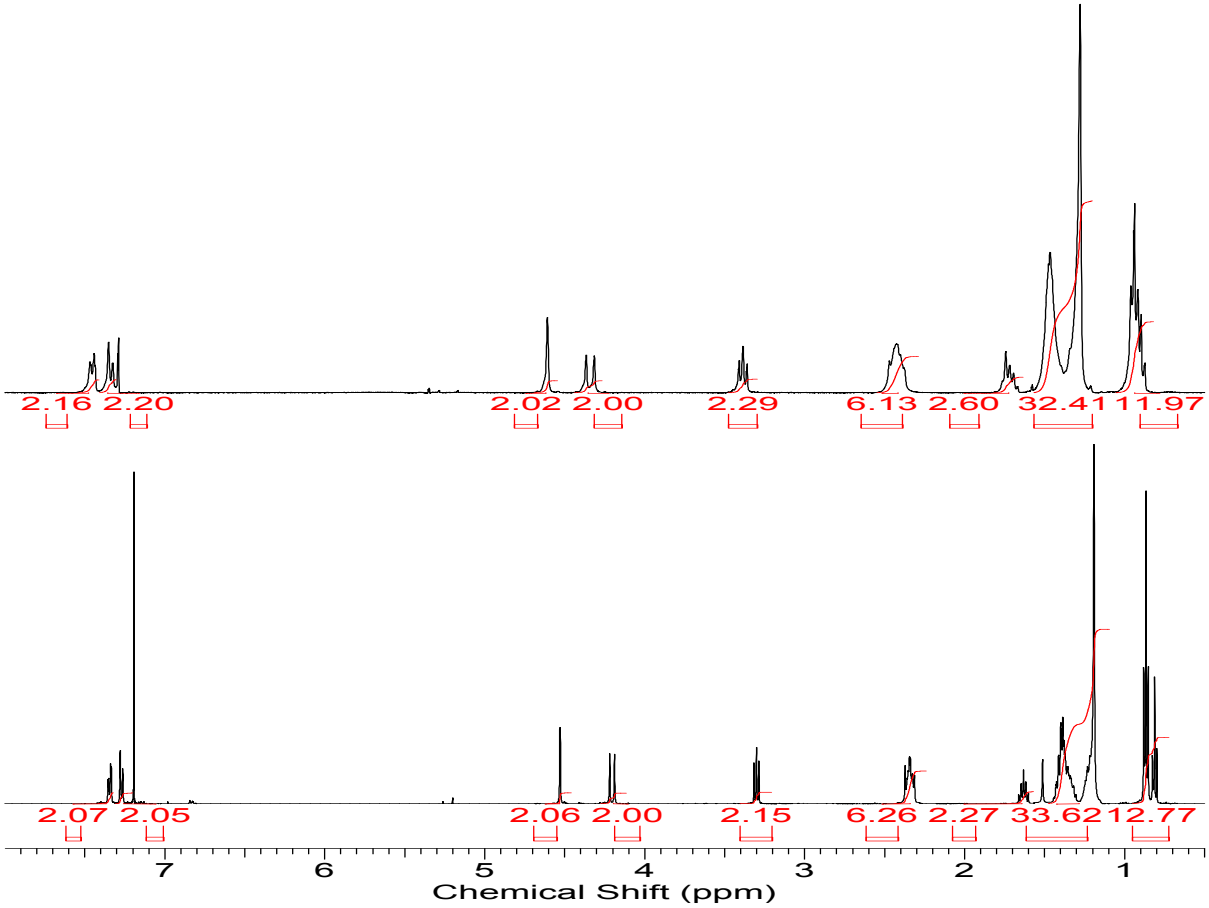


Fig. S9 ^{1}H NMR spectrum in $CDCl_3$ of RAFT-PBu_3 before (top) and after (bottom) the isothermal TGA test. The spectra before and after the TGA tests were collected by 300 MHz NMR and 500 MHz NMR, respectively.

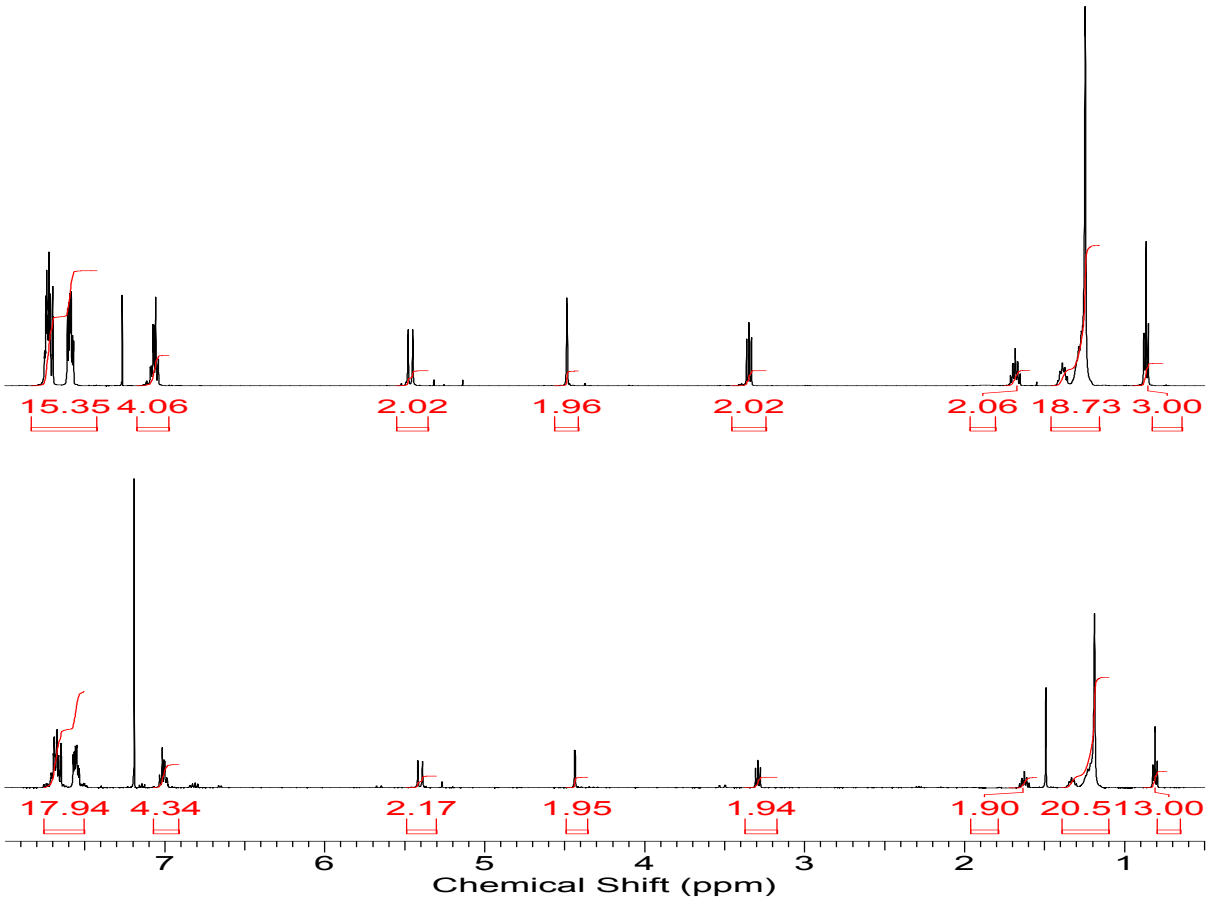


Fig. S10 ^{1}H NMR spectrum in $CDCl_3$ of RAFT-PPh_3 before (top) and after (bottom) the isothermal TGA test. The spectra before and after the TGA tests were collected by 300 MHz NMR and 500 MHz NMR, respectively.

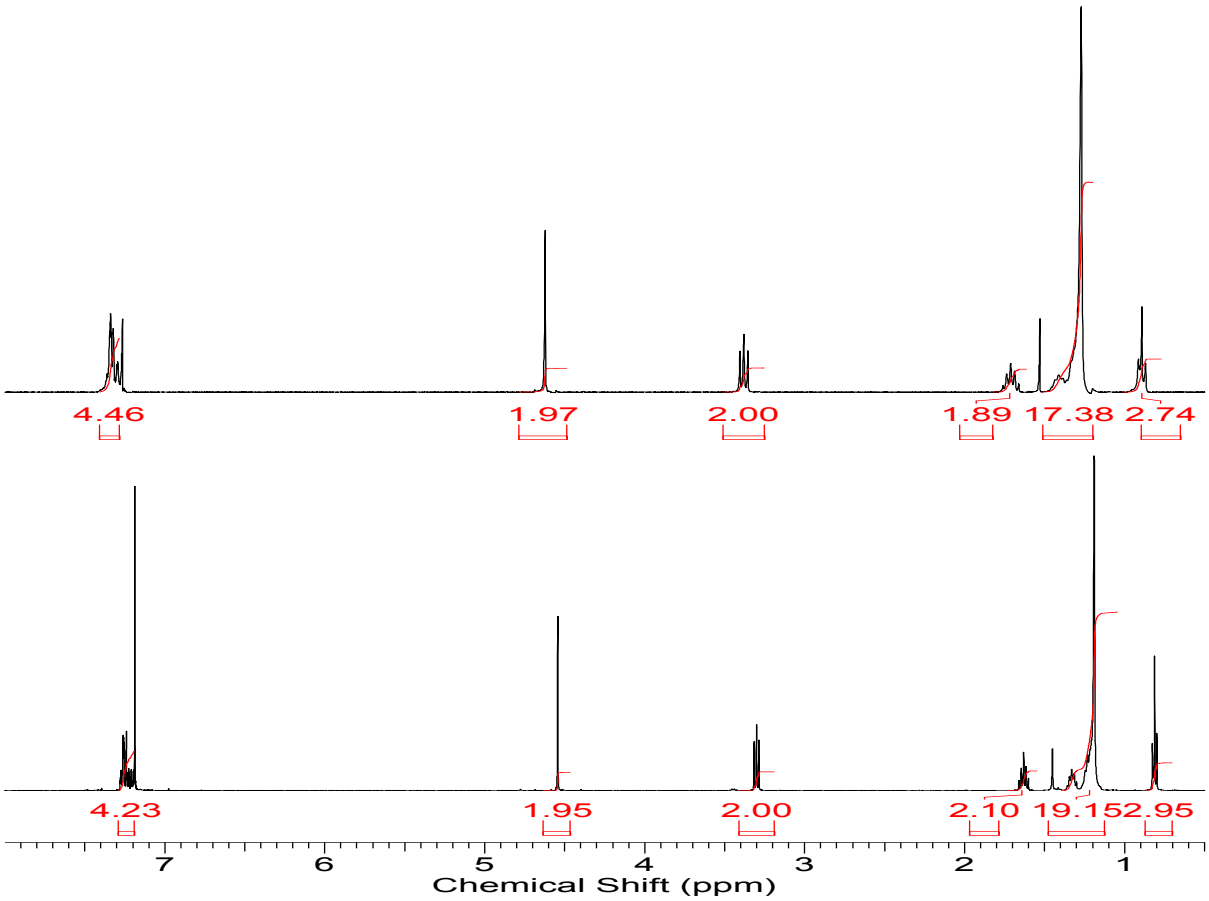


Fig. S11 ^{1}H NMR spectrum in $CDCl_3$ of BDTC before (top) and after (bottom) the isothermal TGA test. The spectra before and after the TGA tests were collected by 300 MHz NMR and 500 MHz NMR, respectively.

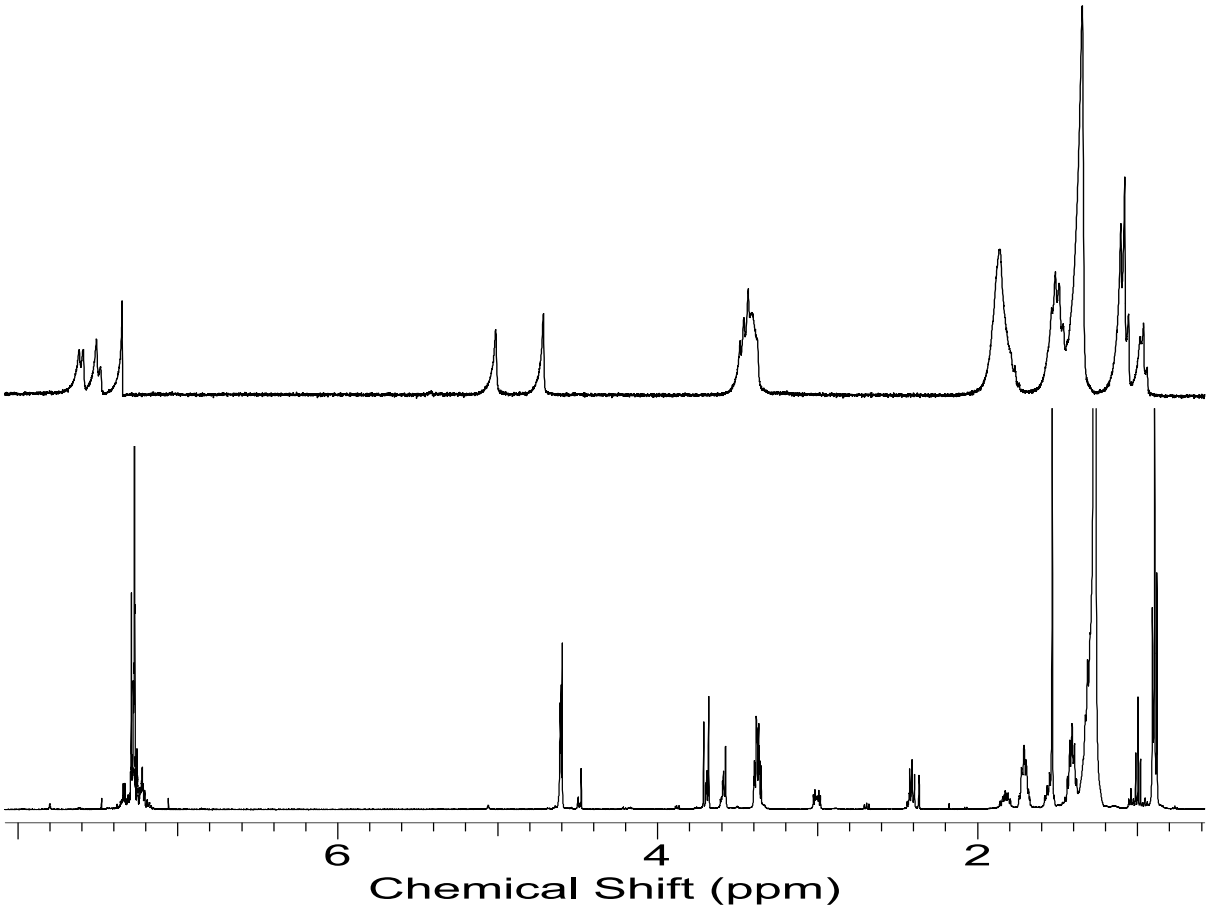


Fig. S12 ^{1}H NMR spectrum in $CDCl_3$ of RAFT-NBu_3 before (top) and after (bottom) the isothermal TGA test. The spectra before and after the TGA tests were collected by 300 MHz NMR and 500 MHz NMR, respectively.

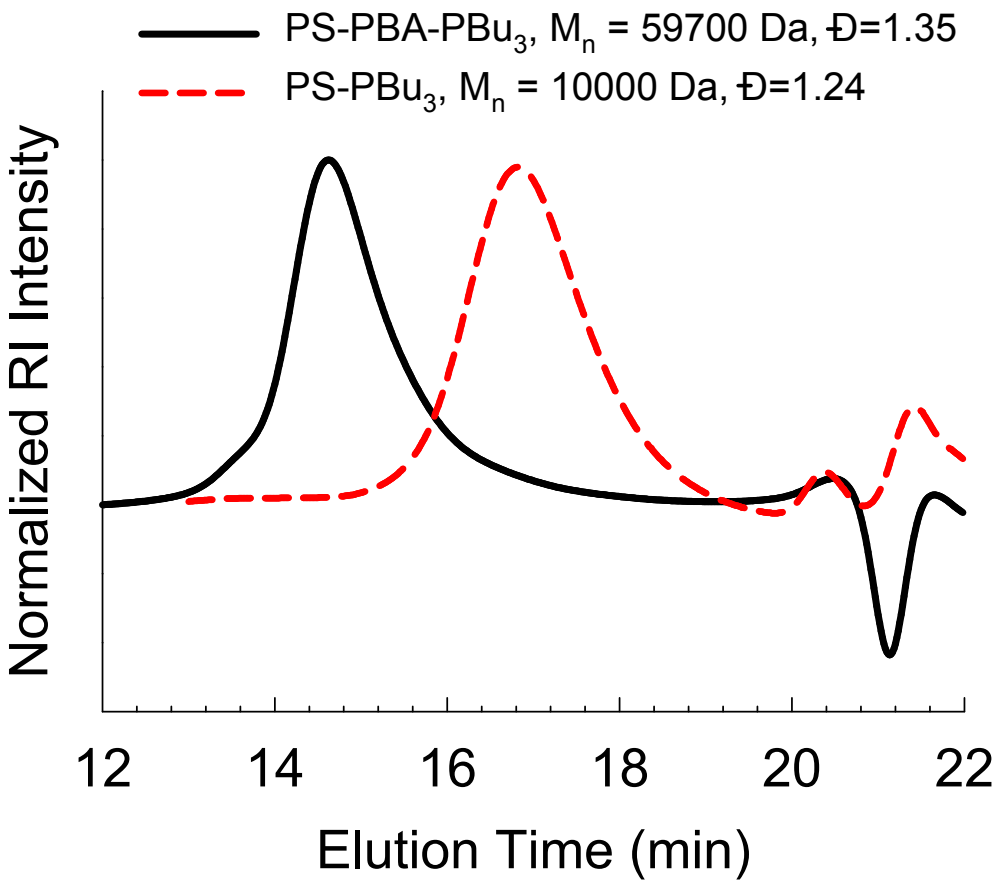


Fig. S13 SEC traces of PS-PBA-PBu_3 and the corresponding macro-RAFT agent, PS-PBu_3.

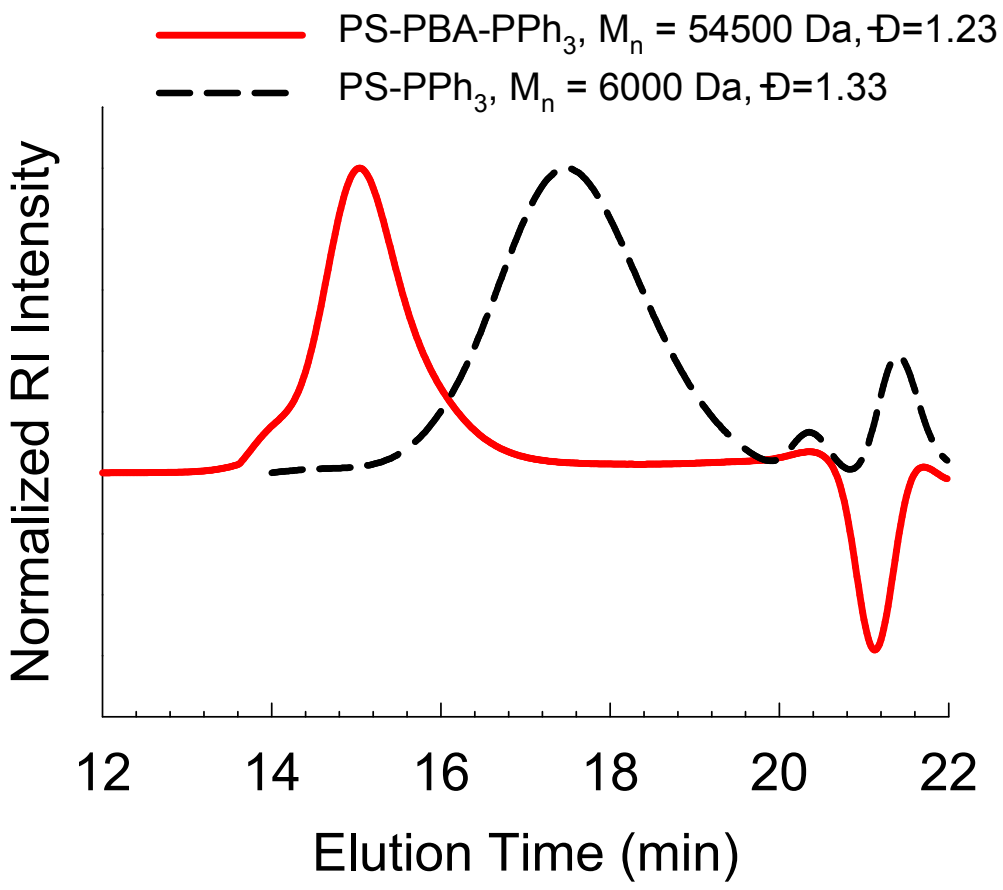
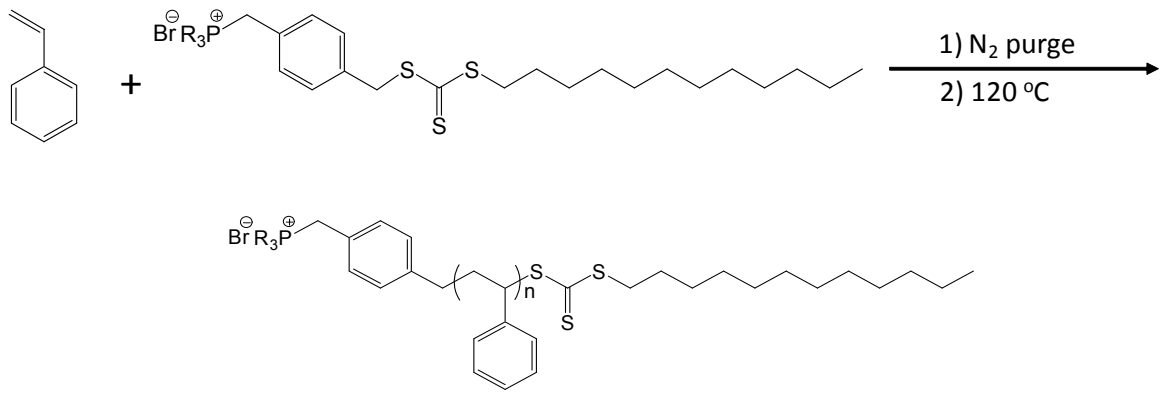


Fig. S14 SEC traces of PS-PBA-PPh_3 and the corresponding macro-RAFT agent, PS-PPh_3.

Table S1. Bulk styrene polymerization using RAFT-PR_3 with different target molecular weights



R	Target M_n (Da)	Time (h)	Conv. (%)	$M_{n,SEC}$ (Da)	$M_{n,\ theo}$ (Da)	Đ
PBu_3	15000	6	40.1	7100	6400	1.23
PBu_3	25000	6	38.4	10000	10000	1.24
PBu_3	40000	6	43.4	19500	17700	1.24
PPh_3	15000	8	32.5	4200	5400	1.35
PPh_3	25000	8	34.8	7200	9200	1.29
PPh_3	40000	8	45.0	19200	18400	1.30

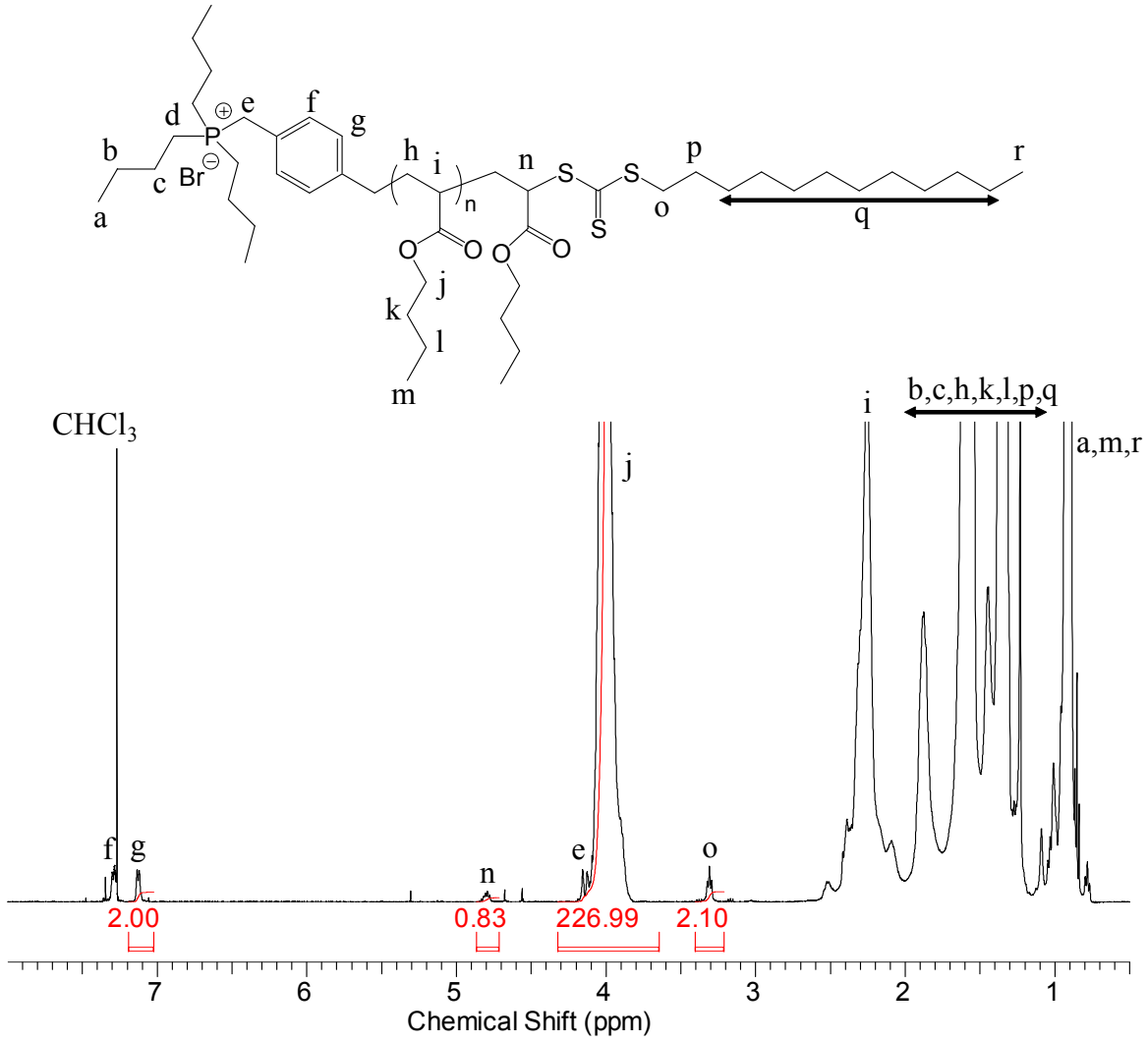


Fig. S15 ^{1}H NMR spectrum in $CDCl_3$ of PBA-PBu_3. The spectrum was collected by 500 MHz NMR.

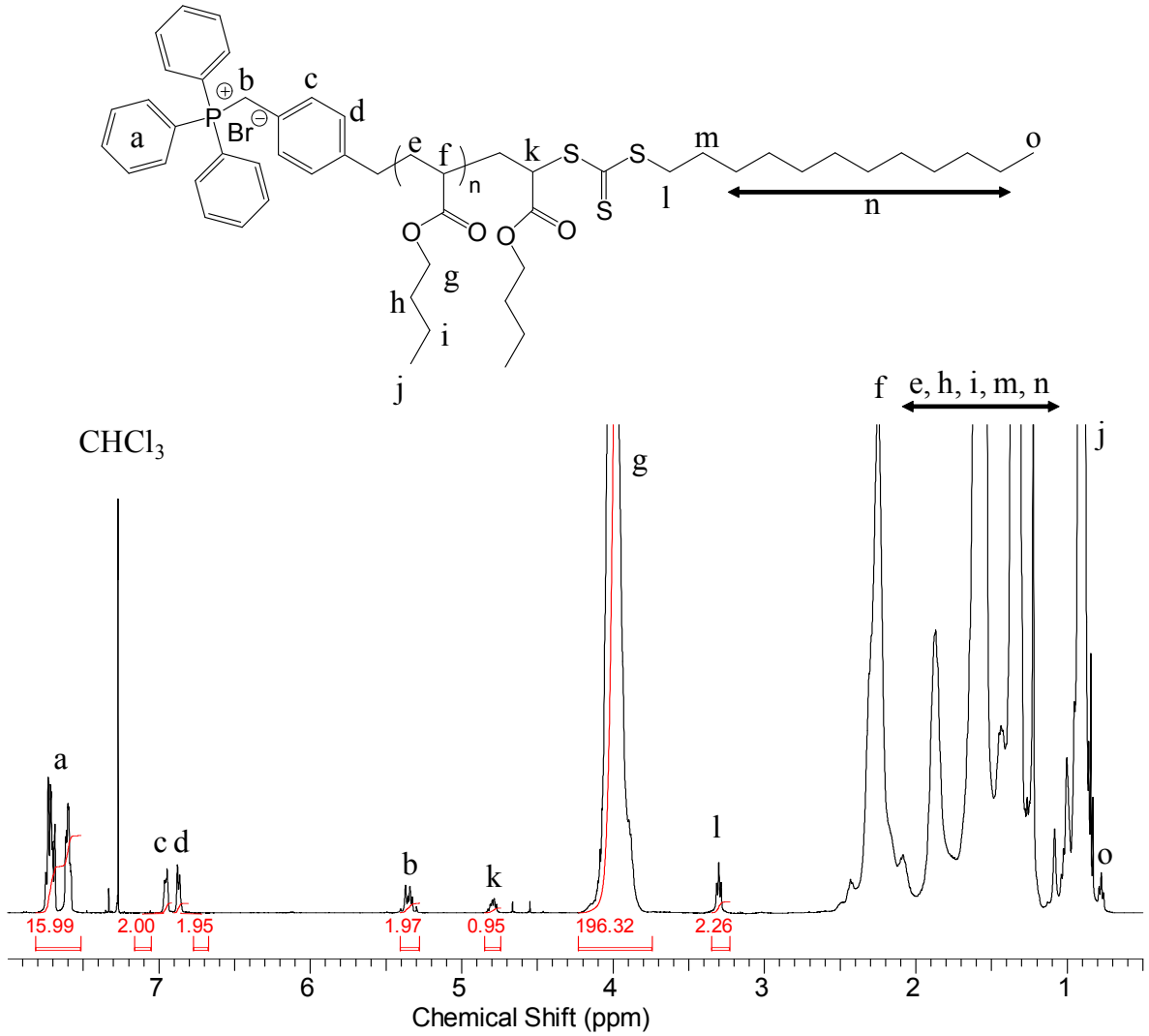


Fig. S16 ^{1}H NMR spectrum in $CDCl_3$ of PBA-PPh_3. The spectrum was collected by 500 MHz NMR.