Electronic Supplementary Material (ESI) for Polymer Chemistry

Reversible Addition-Fragmentation Chain Transfer Polymerization of 2-Chloro-1,3-Butadiene

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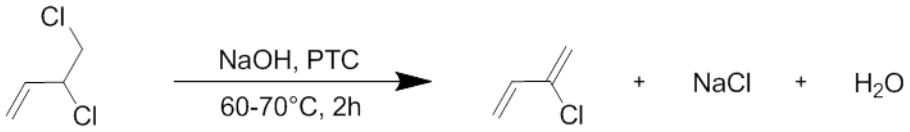
Scheme S1. Synthesis of CB.



The following figures (Figures S1 to S8) show the GPC traces of the RAFT polymerization of 2-chloro-1,3-butadiene (CB) using AIBN at 60 °C in two different solvents (xylene and THF) with the four different chain transfer agents (CTAs); cyanomethyl methyl(phenyl)carbamodithioate (CMPCD), cyano-2-propylbenzodithioate (CPD), *S*-1-dodecyl-*S*′-(α,α′-dimethyl- α′′-acetic acid)trithiocarbonate (DDMAT), *S*-(thiobenzoyl)thioglycolic acid (TBTA).

CMPCD-xylene

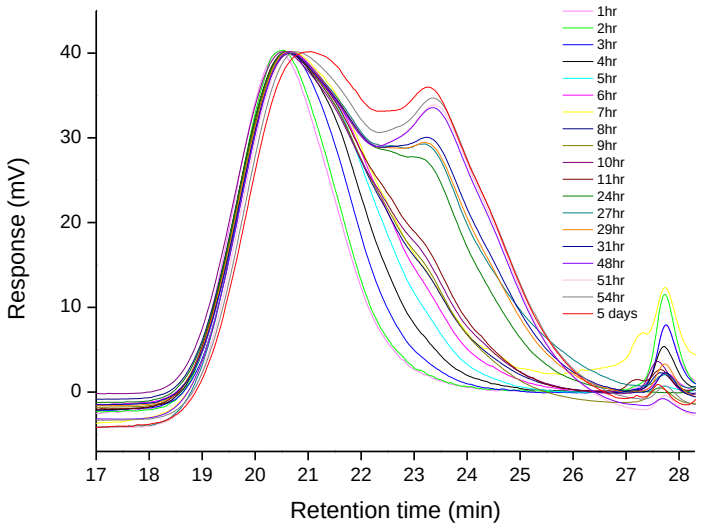


Figure S1. GPC traces during the RAFT polymerization of CB using CMPCD in xylene.

CPD-xylene

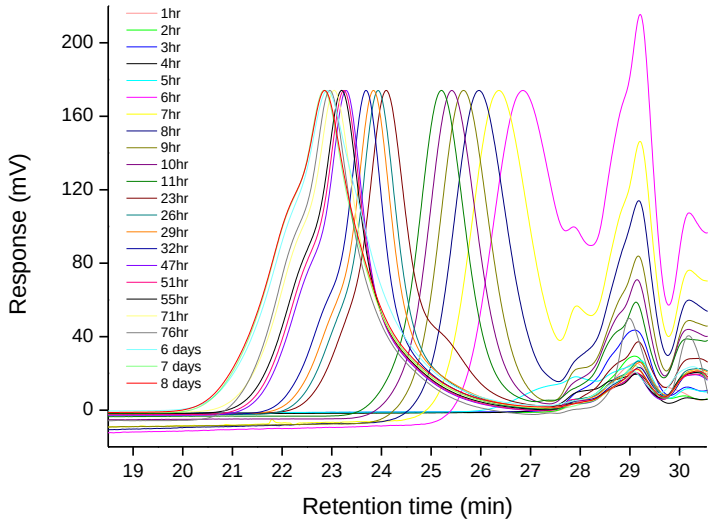


Figure S2. GPC traces during the RAFT polymerization of CB using CPD in xylene.

DDMAT-xylene

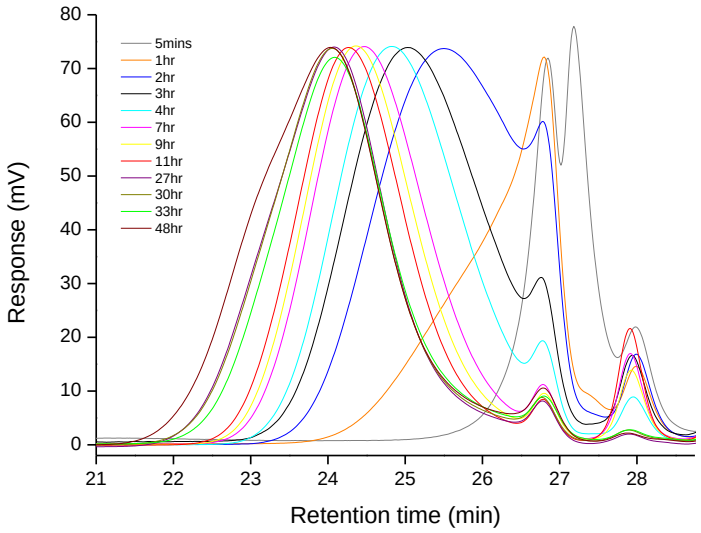


Figure S3. GPC traces during the RAFT polymerization of CB using DDMAT in xylene.

BTA-xylene

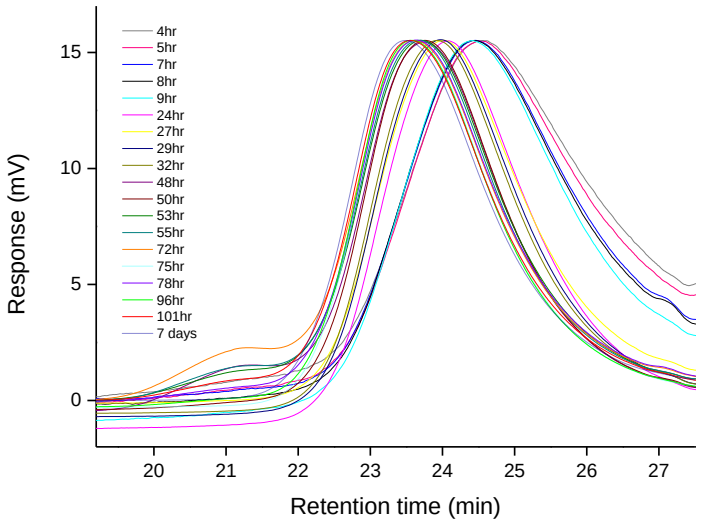


Figure S4. GPC traces during the RAFT polymerization of CB using TBTA in xylene.

CMPCD-THF

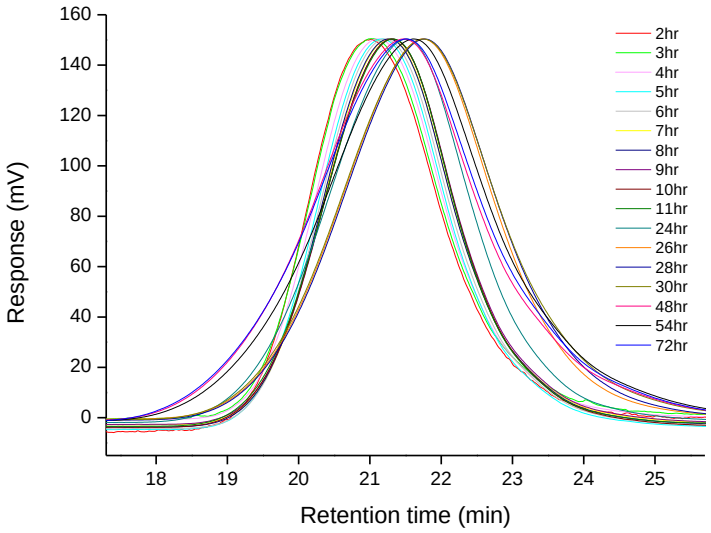


Figure S5. GPC traces during the RAFT polymerization of CB using CMPCD in THF.

CPD-THF

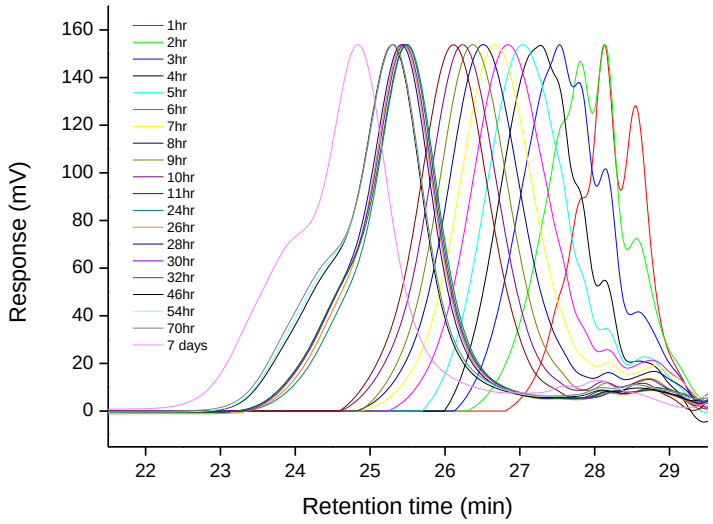


Figure S6. GPC traces during the RAFT polymerization of CB using CPD in THF.

DDMAT-THF

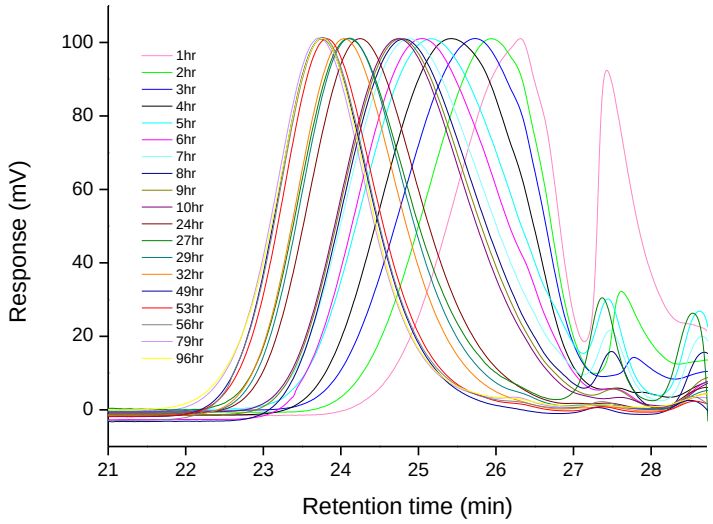


Figure S7. GPC traces during the RAFT polymerization of CB using DDMAT in THF.

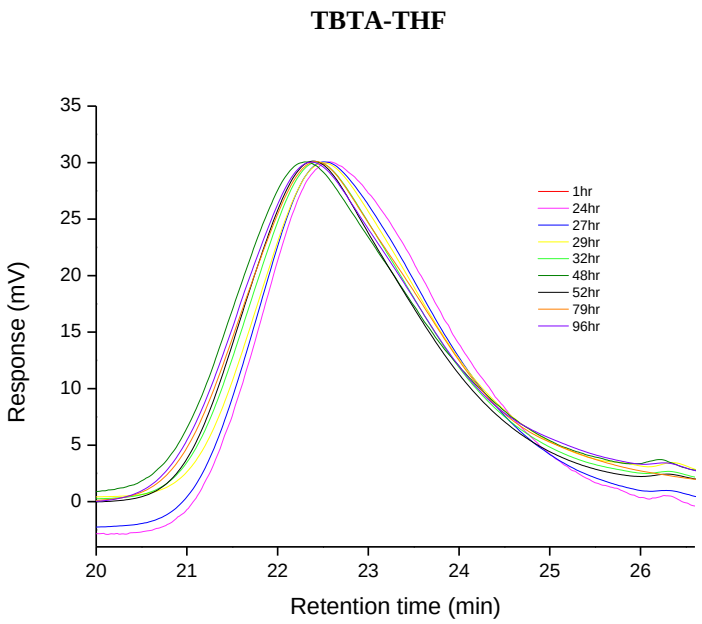


Figure S8. GPC traces during the RAFT polymerization of CB using TBTA in THF.

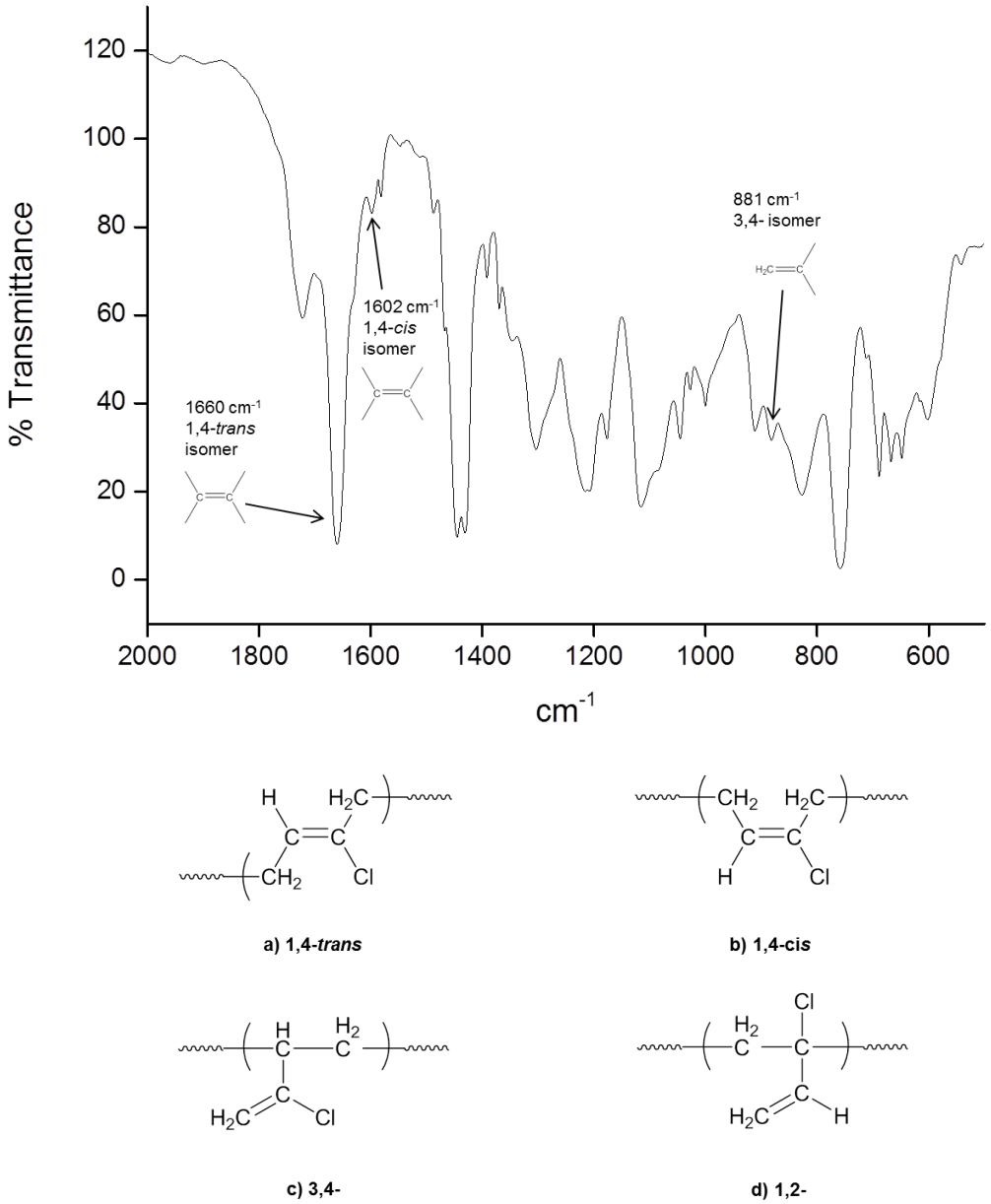


Figure S9. FTIR spectrum (top) of PCB synthesized using CPD illustrating the main peaks pertaining to three of the four PCB isomers shown below the spectrum (those responsible to the 1,2- isomer are masked in the fingerprint region at 925 cm^{-1}). The IR spectrum is in agreement with that of commercial gumstock resin and proves that PCB synthesized by this route is also predominantly the 1,4-*trans* isomer. The following analytical data correspond to the main 1,4-*trans* isomer, with remaining peaks arising from the minor isomers and CTA chain-ends, (NaCl thin film, cm^{-1}): 2918, 2857 (s, CH_2), 1660 (s, C=C), 1444, 1430 (d, CH_2), 1303 (w, CH_2), 1215, 1115 (s, C-C), 827, 759 (r, CH_2), 667 (s, C-Cl).

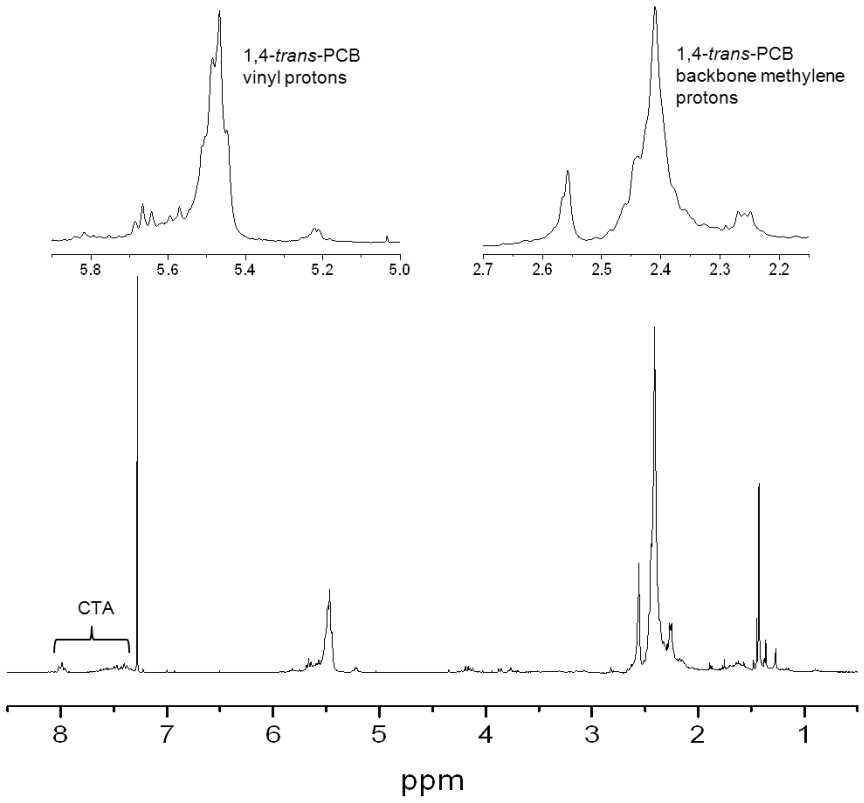


Figure S10. ^{1}H NMR spectrum of PCB synthesized using CPD. The following analytical data correspond to the main 1,4-*trans* isomer, with remaining peaks arising from the minor isomers and CTA chain-ends, (300 MHz, $CDCl_3$, δ ppm): reference $CDCl_3$ = 7.28 ppm, δ = 5.90-5.03 (br, —CH_2C(Cl)C(**H**)CH_2—), 2.56 (br, —C**H**$_2$C(Cl)C(H)CH_2—), 2.55-2.35 (br, —CH_2C(Cl)C(H)C**H**$_2$—).

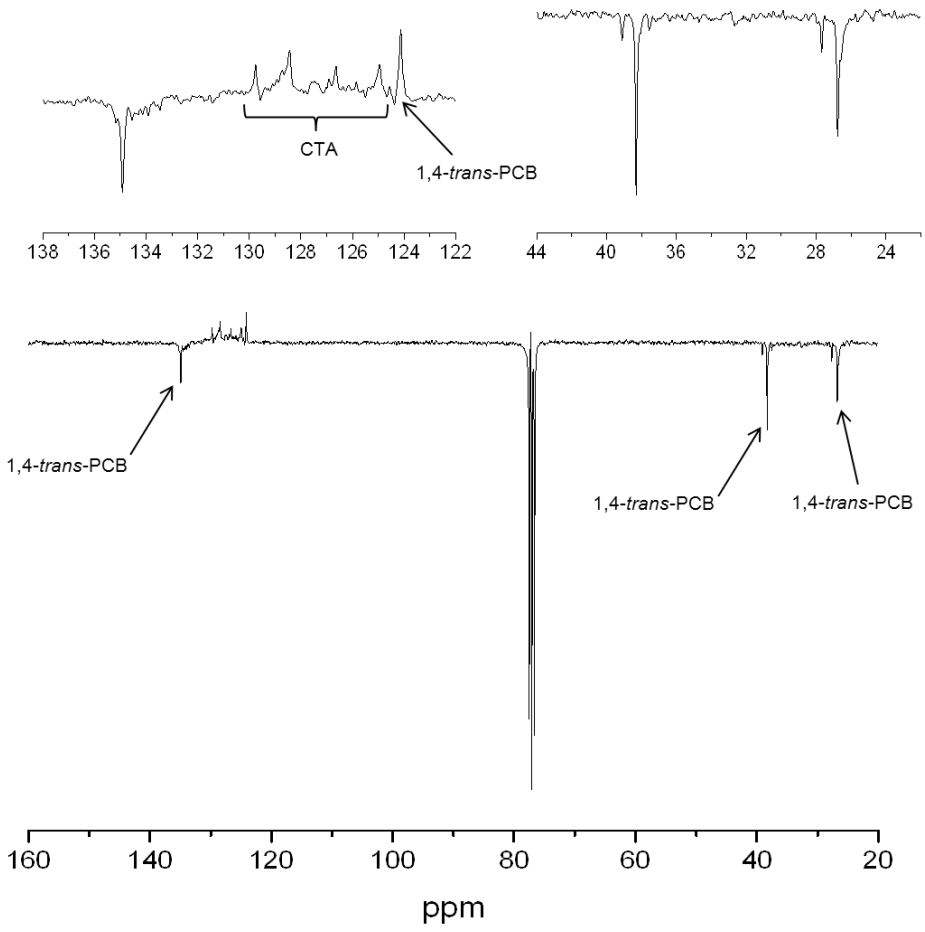


Figure S11. PENDANT ^{13}C NMR spectrum of PCB synthesized using CPD. The following analytical data correspond to the main 1,4-*trans* isomer, with remaining peaks arising from the minor isomers and CTA chain-ends, (75 MHz, $CDCl_3$, δ ppm): reference $CDCl_3$ = 77.17 ppm, δ = 134.86 (—CH_2**C**(Cl)C(H)CH_2—), 124.08(—$CH_2C(Cl)$**C**$(H)CH_2$—), 38.29 (—**C**$H_2C(Cl)C(H)CH_2$—), 26.75 (—$CH_2C(Cl)C(H)$**C**H_2—).