

Electronic Supplementary Information (ESI)
**Reversible-Deactivation Radical Polymerization of
Chloroprene and the Synthesis of Novel Polychloroprene-
Based Block Copolymers by the RAFT Approach**

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Radical Polymerization of Chloroprene in the Presence of DBTTC

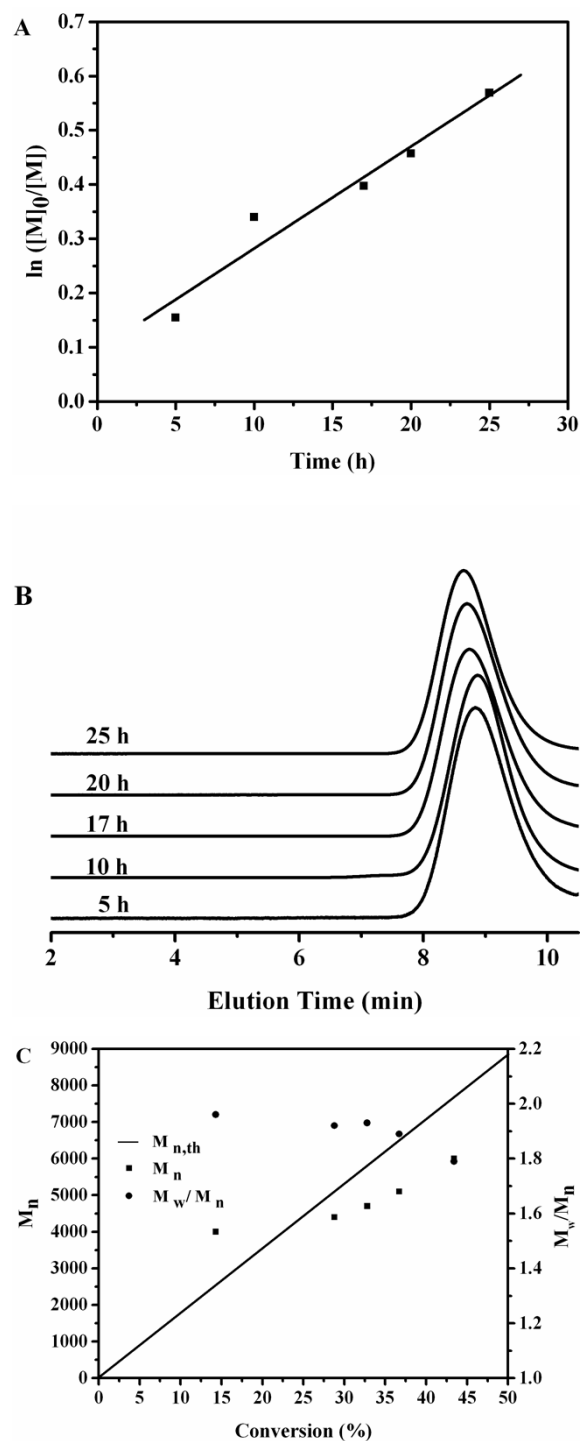


Figure S1. (A) Relationships of $\ln([M]_0/[M])$ with polymerization time, (B) SEC traces, and (C) Plots of M_n and M_w/M_n vs conversion in the RAFT polymerization of CP using DBTTC as RAFT agent in benzene at 60 °C (entry 1 in Table 3).

PCP-PMMA copolymer

PCP macro-RAFT agent was synthesized as described in Experimental Section employing CPDB as RAFT agent (Page 2 Line 86-89). Then 2 g of PCP-macro RAFT agent ($M_n = 1800 \text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.21$), 22.25 g of MMA (222 mmol), 0.0456 g of AIBN (0.28 mmol) were dissolved in 33.4 g of benzene and purged with argon for 10 min. After five freeze-thaw-pump cycles, the flask was filled with argon and immersed in a preheated oil bath at 75 °C.

Figure S2. displays the ^1H NMR of PCP prepared via RAFT polymerization mediated by CPDB. The resonances at $\delta = 5.2\text{-}5.9$ (b) are attributed to the methyldyne protons of PCP backbone. The resonances at $\delta = 7.8\text{-}8.0$ (a) are due to the aromatic protons of RAFT end group.

Provided that each PCP macromolecule contains only one CPDB group, the number averaged molecular weights based on ^1H NMR spectrum ($M_{n, \text{NMR}}$) can be calculated according to Equation (1):

$$M_{n, \text{NMR}} = \left[\frac{I_b/1}{I_a/2} \right] \times M_{\text{CP}} + M_{\text{CPDB}} \quad (1)$$

Where I_b and I_a are the integral values of the peaks b and a, respectively.

The calculated $M_{n, \text{NMR}}$ was 2000, which was close to the theoretical value (1900) and $M_{n, \text{SEC}}$ (1800). These indicate that each PCP macromolecule contains one dithioester group. In other words, PCP capped with dithioester group as the macro-RAFT agent was high purity and narrow dispersity end-functional polymer.

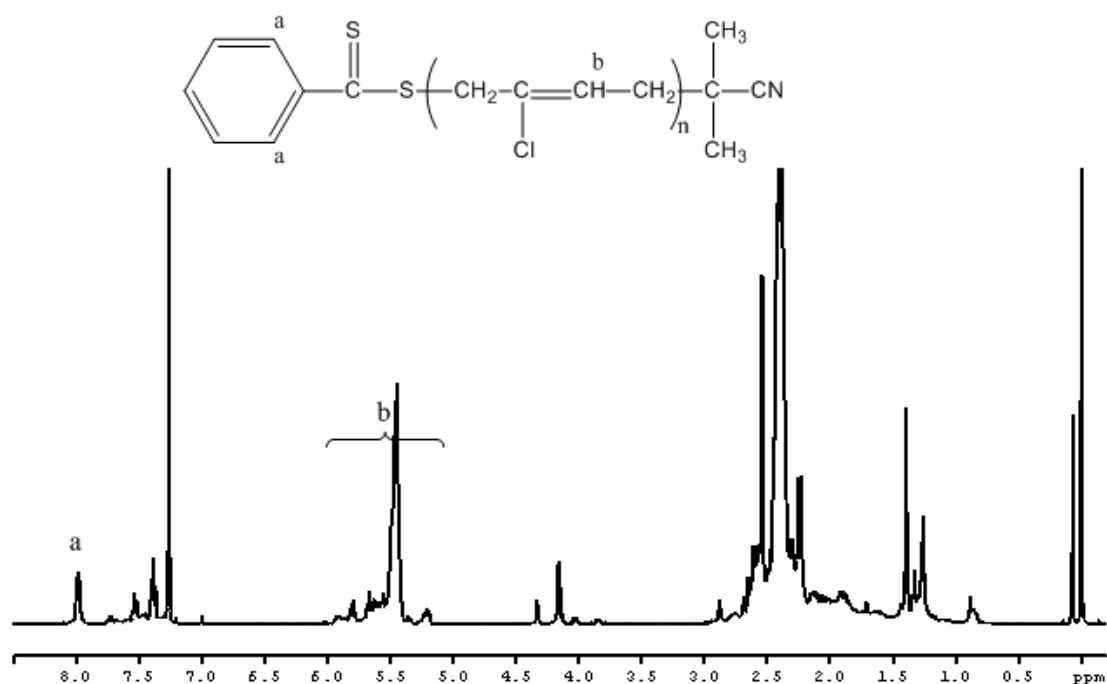


Figure S2. ^1H NMR spectrum of PCP with CPDB as the CTA in benzene at 60 °C ($[\text{CP}] = 5.64 \text{ M}$, $[\text{CP}]_0/[\text{CPDB}]_0/[\text{AIBN}]_0 = 200:1:0.25$).

Table S1. Experimental results for the PCP-PMMA copolymer with PCP as macro-RAFT agent

Sample Name	M_n	M_w	\bar{D}
PCP macro-RAFT agent	1800	2200	1.21
15h	10900/1700	14400/2200	1.34/1.25
30h	16700/1700	28000/2100	1.68/1.23

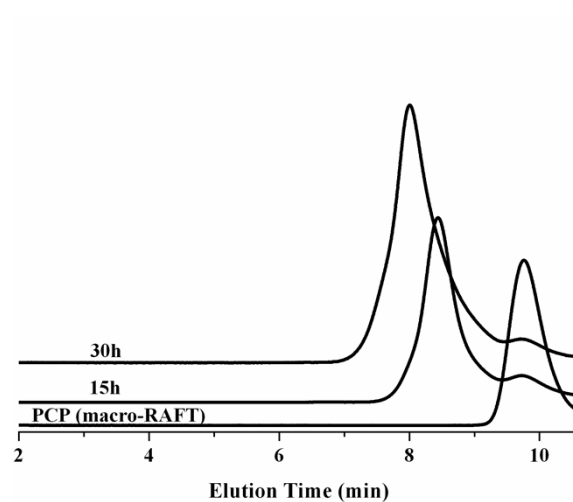


Figure S3. SEC traces of the attempted RAFT polymerization using MMA as monomer and PCP ($M_n = 1800 \text{ g} \cdot \text{mol}^{-1}$, $M_w/M_n = 1.21$) as macro-chain-transfer agent.

PCP-PSt copolymer

PCP macro-RAFT agent was synthesized as described in Experimental Section employing EPDTB as RAFT agent (Page 2 Line 86-89). Then 2 g of PCP-macro RAFT agent ($M_n = 3000$ g·mol⁻¹, $M_w/M_n = 1.23$), 13.89 g of St (133 mmol), 0.0274 g of AIBN (0.17 mmol) were dissolved in 20.8 g of benzene and purged with argon for 10 min. After five freeze-thaw-pump cycles, the flask was filled with argon and immersed in a preheated oil bath at 60 °C.

Figure S4. displays the ¹H NMR of PCP prepared via RAFT polymerization mediated by EPDTB. All the characteristic protons signals of the RAFT terminals and chloroprene units are clearly observed. The peaks at $\delta=7.92$ ppm, originating from RAFT agent-EPDTB, appeared in the obtained polymers. The signals d (4.15) are attributed to the methylene protons of -COO-CH₂-CH₃. The signals b and c (1.20) are attributed to the methyl protons of -C(CH₃)₂-COO-CH₂-CH₃. The signals e (5.2-5.9) are attributed to the methyldiene protons of PCP.

Provided that each PCP macromolecule contains only one EPDTB group, the number averaged molecular weights based on ¹H NMR spectrum ($M_{n, NMR}$) can be calculated according to Equation (2):

$$M_{n, NMR} = \left[\frac{I_e/1}{I_a/2} \right] \times M_{CP} + M_{EPDTB} \quad (2)$$

Where I_e and I_a are the integral values of the peaks e and a, respectively. The calculated $M_{n, NMR}$ was 3100, which was close to the theoretical value (3000) and $M_{n, SEC}$ (3000). These indicate that each PCP macromolecule contains one dithioester group. These demonstrate that PCP capped with dithioester group as the macro-RAFT agent was high purity and narrow dispersity end-functional polymer.

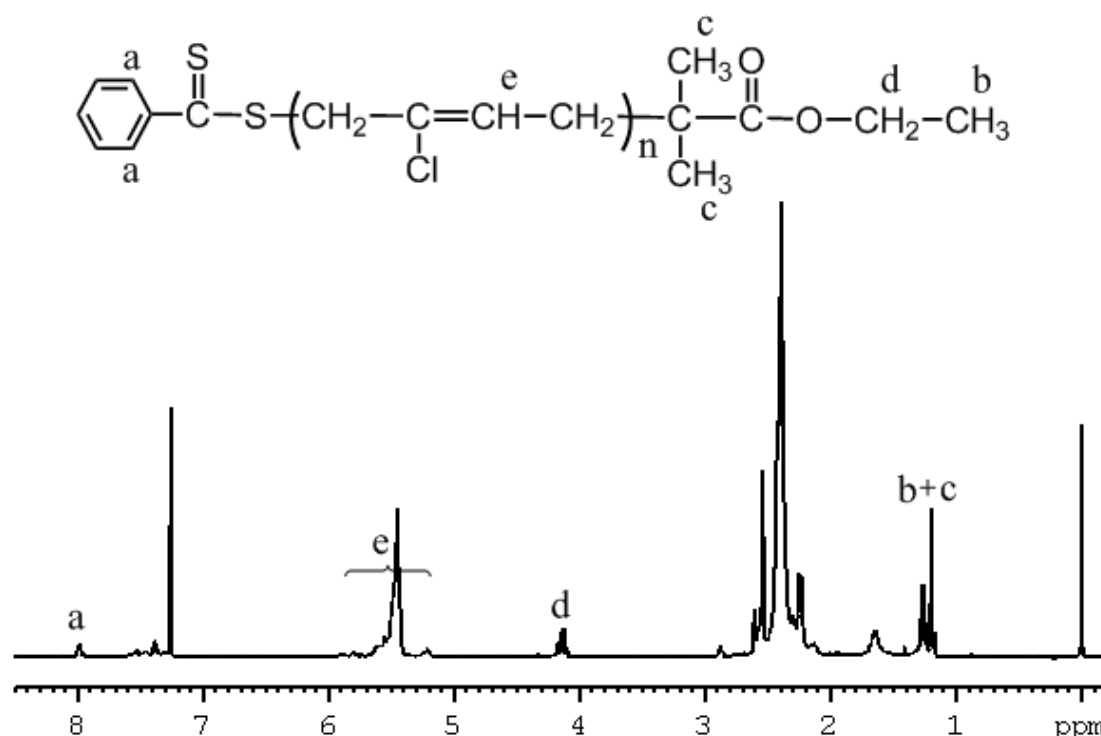


Figure S4. ¹H NMR spectrum of PCP with EPDTB as the CTA in benzene at 60 °C ([CP] = 5.64 M, [CP]₀/[EPDTB]₀/[AIBN]₀ = 200:1:0.25).

Table S2. Experimental results for the PCP-PSt copolymer with PCP as macro-RAFT agent

Sample Name	M_n	M_w	\bar{D}
PCP macro-RAFT agent	3000	3700	1.23
24h	8600/3000	9300/3600	1.08/1.20
36h	10200/3100	10900/4200	1.07/1.35

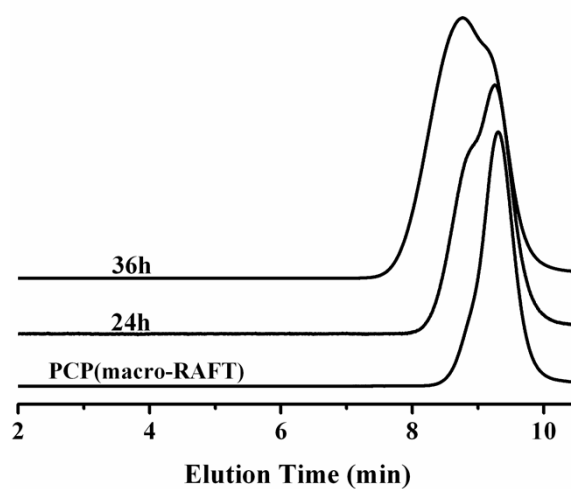


Figure S5. SEC traces of the attempted RAFT polymerization using St as monomer and PCP ($M_n = 3000 \text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.23$) as macro-chain-transfer agent.