Electronic Supplementary Information (ESI)

Reverse Iodine Transfer Polymerization (RITP) of Chloroprene

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Synthesis and Characterization of a Macrotransfer Agent PCP-I with $M_{n,targeted}$ = 2900 g mol^{-1} ([CP]/[ABVN]/[I_2] = 60/1.7/1). CP (10 g, 1.13×10^{-1} mol), ABVN (0.7948 g, 3.20×10^{-3} mol), iodine (0.4781 g, 1.88×10^{-3} mol), and benzene (15 mL) were introduced in a 50 mL round bottomed flask equipped with a magnetic bar. The reaction medium was purged with argon for 10 min at 0 °C to remove oxygen. Five freeze-thaw-pump cycles were completed and the flask was placed in an oil bath at 50 °C. The polymerization was conducted in the dark, with magnetic stirring and under argon atmosphere. The reaction was stopped when the monomer conversion reached 100% for 18 h.

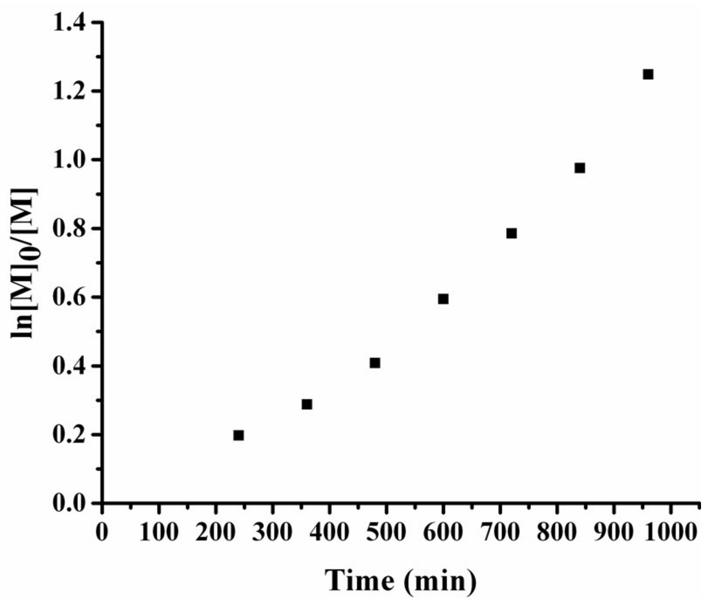


Figure S1. Kinetic plots of ln([M_0]/[M]) vs. time, performed during the synthesis of PCP by RITP of CP initiated with ABVN in benzene at 50 °C: [CP]$_0$: [ABVN]$_0$: [I_2]$_0$ = 60: 1.7: 1, $M_{n,targeted}$ = 2900 g mol^{-1}.

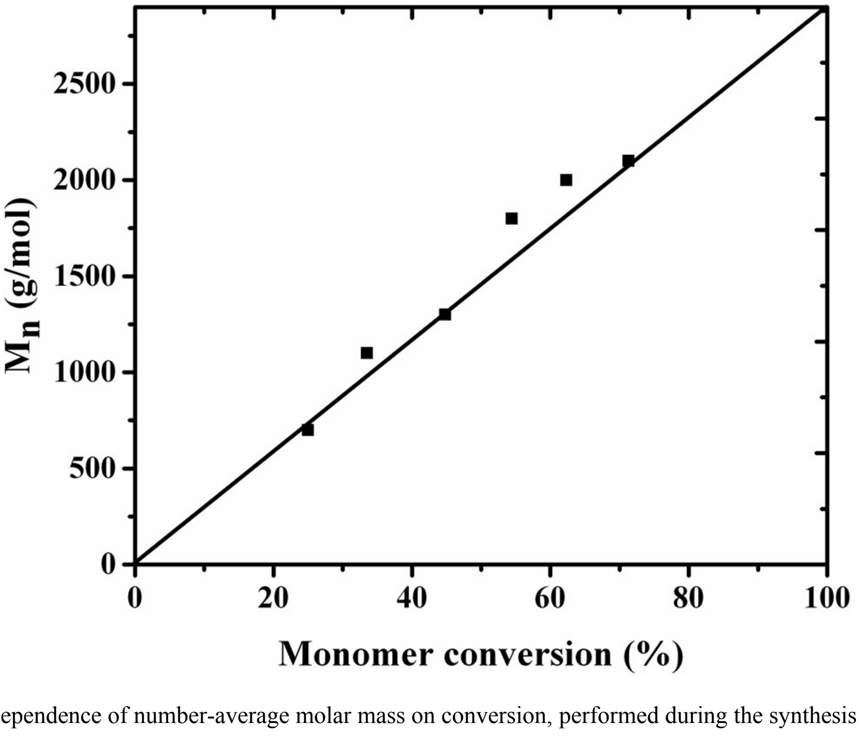


Figure S2. Dependence of number-average molar mass on conversion, performed during the synthesis of PCP by

RITP of CP initiated with ABVN in benzene at 50 ºC: $[CP]_0$: $[ABVN]_0$: $[I_2]_0$ = 60: 1.7: 1, $M_{n,targeted}$ = 2900 g mol^{-1}.

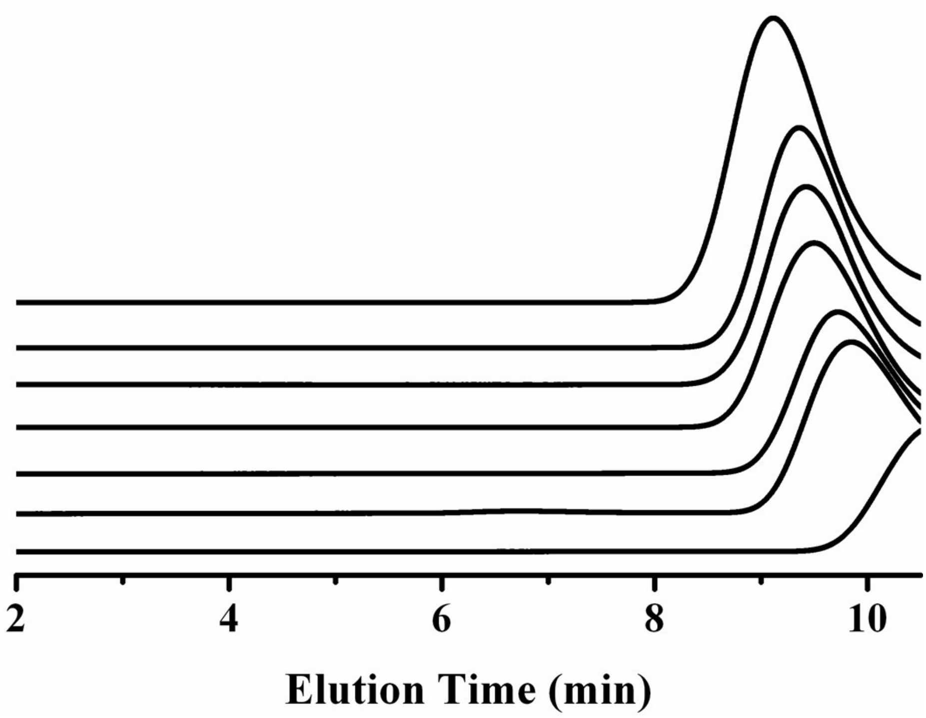
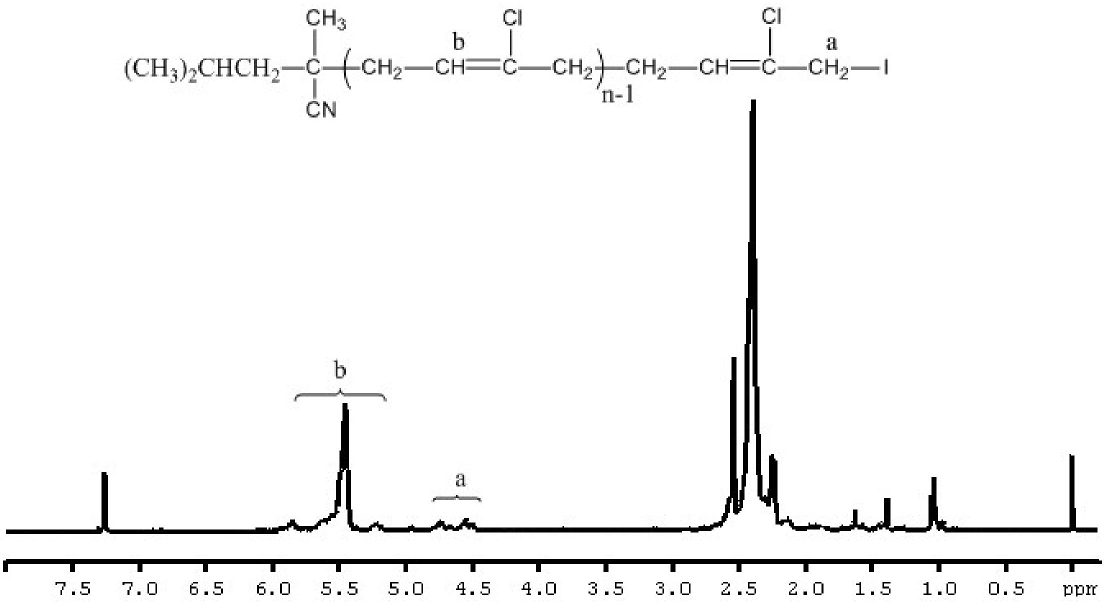


Figure S3. SEC traces from the synthesis of PCP by RITP of CP initiated with ABVN in benzene at 50 ºC: $[CP]_0$: $[ABVN]_0$: $[I_2]_0$ = 60: 1.7: 1, $M_{n,targeted}$ = 2900 g mol^{-1}.



$$(CH_3)_2CHCH_2-\underset{CN}{\overset{CH_3}{C}}\left(-CH_2-\overset{b}{CH}=\overset{Cl}{C}-CH_2-\right)_{n-1}CH_2-CH=\overset{Cl}{C}-\overset{a}{CH_2}-I$$

Figure S4. ^{1}H NMR spectrum in $CDCl_3$ of a PCP sample synthesized by RITP process in benzene and precipitated in cold petroleum ether (CP (10 g, 1.13 × 10^{-1} mol), ABVN (0.7948 g, 3.20 × 10^{-3} mol), iodine (0.4781 g, 1.88 × 10^{-3} mol), and benzene (15 mL), 50 ºC, 18 h, monomer conversion 100%, $M_{n,th} = [(m_{CP} \times \text{conversion})/(2 \times n_{I2}) + M_{chain\ ends}]$ = 2900 g mol^{-1} with $M_{chain\ ends}$ = 237 g mol^{-1}, $M_{n,SEC}$ = 2800 g mol^{-1}, $M_{n,NMR} = [(2 \times I_b/I_a) \times M_{CP} + M_{chain\ ends}]$ = 2700 g mol^{-1}).

PCP-PSt/MMA copolymer

The GPEC method was attempted to separate the PCP-PSt/PMMA copolymer. Agilent 1260 high-performance liquid chromatography (HPLC) system, with ELSD (Agilent 1290 infinity II ELSD) was used. Unfortunately, the retention time of PSt/PMMA and PCP are almost same, it may be caused by the similar solubility or the polarity of the PSt/PMMA and PCP. For example, the GPEC method was attempted to separate the PCP-PSt copolymer, using acetonitrile+THF, hexane+THF, and hexane+cyclohexane as eluent, respectively. Figure S5. shows the retention times of PCP and PSt homopolymers under the selected conditions.

Table S1. Solvent composition timetable[a]

Time (min)	Hexane (%)	THF (%)
0	100	0
5	100	0
15	0	100

[a] SB-CN, 4.6*150mm, Hexane-THF, 35C

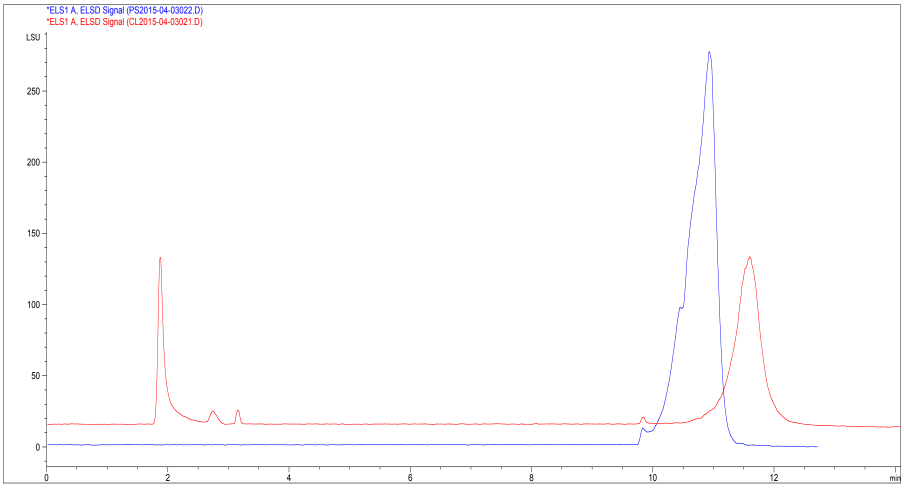


Figure S5. HPLC elution chromatogram of PSt (left, $M_n = 10000$) and PCP (right, $M_n = 3000$).

Acetone could dissolve homopolymers of PSt with low M_n and PMMA, and couldn't dissolve homopolymers of PCP. PCP-based block copolymers are generally insoluble in acetone. Small amount of PSt/PMMA homopolymers were found. The reserved copolymers were precipitated from acetone and dried under vacuum for SEC analysis. In contrast to the previous SEC traces, similar SEC traces were observed. In other words, most of the polychloroprene chains were controlled and took part in the formation of the desired block copolymer.