

# Mild Halogenation of Polyolefins Using an *N*-Haloamide Reagent

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## Materials

Polyethylene ( $M_n = 3.60 \text{ kg mol}^{-1}$ , PDI = 3.82) was kindly supplied by the Institute of Chemistry, The Chinese Academy of Sciences. Isotactic polypropylene ( $M_n = 13.53 \text{ kg mol}^{-1}$ , PDI = 2.04) was purchased from Sigma-Aldrich. Acetic acid (99.8%, Aladdin), sodium hypochlorite (1.5 M, Aladdin), *tertiary*-butanol (99.5%, Aladdin), 3,5-bis(trifluoromethyl)benzoic acid (98%, Energy Chemical) and oxalyl chloride (98%, Energy Chemical) were all used as received. 1,1,2,2-tetrachloroethane (99%, Energy Chemical) was stored over 4 Å molecular sieves and degassed by purging with N<sub>2</sub> for 1 hour prior to use. *Tertiary*-butylamine (98%, Aladdin) was stored over KOH pellets. Tetrahydrofuran was dried and distilled from sodium/benzophenone ketal. Dimethyl formamide and dichloromethane were purified with a Solvent Purification System (MF-300) before use. Ethyl acetate, diethylether, toluene and methanol were analytical grade from Guangzhou Chemical Reagent Factory and were used directly. Visible light irradiation was performed using 2 x Teanre Lighting SL-440 lamps (max: 40W) using standard 25W compact fluorescent bulbs.

## Characterization

**Nuclear Magnetic Resonance (NMR) Spectroscopy:** <sup>1</sup>H NMR spectra were recorded using a Bruker Ascend 400 using CDCl<sub>3</sub> as a solvent or using a Bruker

AVANCE III 400 at 100 °C using  $o\text{-C}_6\text{D}_4\text{Cl}_2$  as a solvent. The spectra were collected with 16 scans for small molecules or 64 scans for polymer samples.

**Size Exclusion Chromatography (SEC):** Molecular weights and molecular weight distributions of polymers were examined on a Polymer Laboratories GPC-220 liquid chromatograph equipped with three Polymer Laboratories gel 10  $\mu\text{m}$  Mixed-B columns, a refractive index detector, a Viscotek 220R viscosity detector and a binary angles ( $15^\circ$ ,  $90^\circ$ ) ( $\lambda = 658 \text{ nm}$ ) light scattering detector. Analysis was carried out at 150 °C in 1,2,4-trichlorobenzene with a flow rate of 1.0 mL/min. Polystyrene standards were used for calibration.

**Thermogravimetric Analysis (TGA):** Thermal decomposition behaviors of the polymers were recorded using a PerkinElmer Pyris TG 2000 from 30–800 °C with a heating rate of 10 °C/min under a nitrogen atmosphere (40 mL/min).

**X-ray Photoelectron Spectroscopy (XPS):** Data was obtained with an ESCALab220i-XL electron spectrometer (VG Scientific) using 300 W Al  $K\alpha$  radiation. The binding energies were referenced to the C1s line at 284.6 eV.

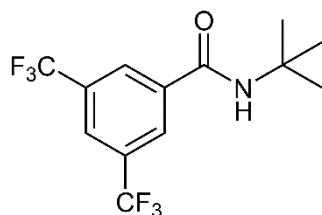
**Differential Scanning Calorimetry (DSC):** The melting and crystallization behaviors of polymers were measured using a NETZSCH DSC 214 Polyma instrument from 30 to 160 °C at 10 °C/min under a nitrogen atmosphere (40–60 mL  $\text{min}^{-1}$ ). The melting temperature ( $T_m$ ) was based on the second heating scan.

**Fourier-Transform Infrared Spectroscopy (FT-IR):** Infrared spectra were obtained on a Thermo Scientific Nicolet iS10 FT-IR spectrometer. The spectra were collected with 32 scans in transmission mode with background deduction and atmospheric suppression.

**Elemental Analysis:** Elemental analysis was performed on a vario EL cube (CHN mode).

## Experimental Procedures

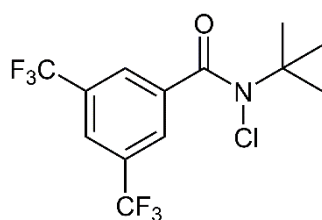
### Synthesis of *N*-(*tert*-butyl)-3,5-bis(trifluoromethyl)benzamide<sup>1,2</sup>



To a 0 °C solution of 3,5-bis(trifluoromethyl)benzoic acid (4.69 g, 18.16 mmol) in DCM (75 mL) and DMF (50  $\mu\text{L}$ ) was added oxalyl chloride (3.25 mL, 37.85 mmol). The solution was stirred at 0 °C for fifteen minutes, followed by at room temperature for 1.5 h. The solution was then evaporated to almost dryness, dissolved in THF (40 mL) and cooled to 0 °C. *Tertiary*-butylamine (5.05 mL) was added dropwise and the solution allowed to warm and stir overnight at RT. The reaction mixture was

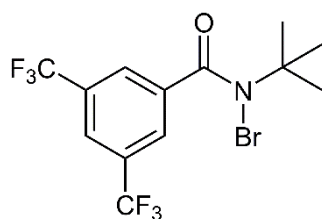
then diluted with Et<sub>2</sub>O, washed with 2.5 M (2 x 40 mL) and 1 M HCl (2 x 40 mL). The reaction mixture was dried (MgSO<sub>4</sub>) and concentrated under reduced pressure to give *N*-(*tert*-butyl)-3,5-bis(trifluoromethyl)benzamide (5.03 g, 88%) as a white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.15 (s, 2H), 7.98 (s, 1H), 5.98 (s, 1H), 1.50 (s, 9H).

### Synthesis of *N*-chloroamide Compound (***N*-CA**) from *N*-(*tert*-butyl)-3,5-bis(trifluoromethyl)benzamide<sup>1</sup>



To a solution of *N*-(*tert*-butyl)-3,5-bis(trifluoromethyl)benzamide (2.9 g, 9.26 mmol) in *tert*-butanol (5.75 mL) and ethyl acetate (150 mL) was added dropwise a solution of sodium hypochlorite (105 mL, 1.5 M) in acetic acid (42 mL). After a period of three hours, a second addition of sodium hypochlorite (105 mL, 1.5M) in acetic acid (42 mL) was performed and the reaction allowed to stir for a further 3 h. The reaction was then transferred to a separatory funnel and the aqueous layer discarded. The organic layer was washed with a saturated solution of NaHCO<sub>3</sub> (3 x 100 mL), dried (MgSO<sub>4</sub>) and concentrated under reduced pressure to give the *N*-chloroamide (***N*-CA**) (3.05 g, 95%) as a green oil. **NOTE:** Reaction has the potential to generate chlorine gas, Cl<sub>2</sub>. Reactions should thus be performed using adequate safety equipment inside a fume hood. Note: Stable if stored under darkness in a freezer. Reagent can be weighed on bench top without decomposition. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.06 (s, 2H), 7.93 (s, 1H), 1.57 (s, 9H).

### Synthesis of *N*-bromoamide Compound (***N*-BA**) from *N*-(*tert*-butyl)-3,5-bis(trifluoromethyl)benzamide<sup>2,3</sup>



To a foil-wrapped flask of freshly distilled carbon tetrachloride (100 mL) was added silver acetate (3.34 g, 20 mmol). The suspension was cooled to 0°C before bromine (1.03 mL, 40 mmol) was added dropwise. The reaction was stirred in the dark for 15 m at 0°C before being rapidly filtered into a dry, foil-wrapped flask. The residual solid was washed with carbon tetrachloride (3 mL). To the filtered solution was added *N*-(*tert*-butyl)-3,5-bis(trifluoromethyl)benzamide (2.28 g, 7.28 mmol) and the reaction stirred at room temperature for 2 h before being concentrated under reduced pressure. The residue was then recrystallized from acetone/cold water to provide the *N*-bromoamide (***N*-BA**) (1.87 g, 66%) as a yellow solid. Note: Stable if stored under darkness in a freezer. Reagent can be weighed on

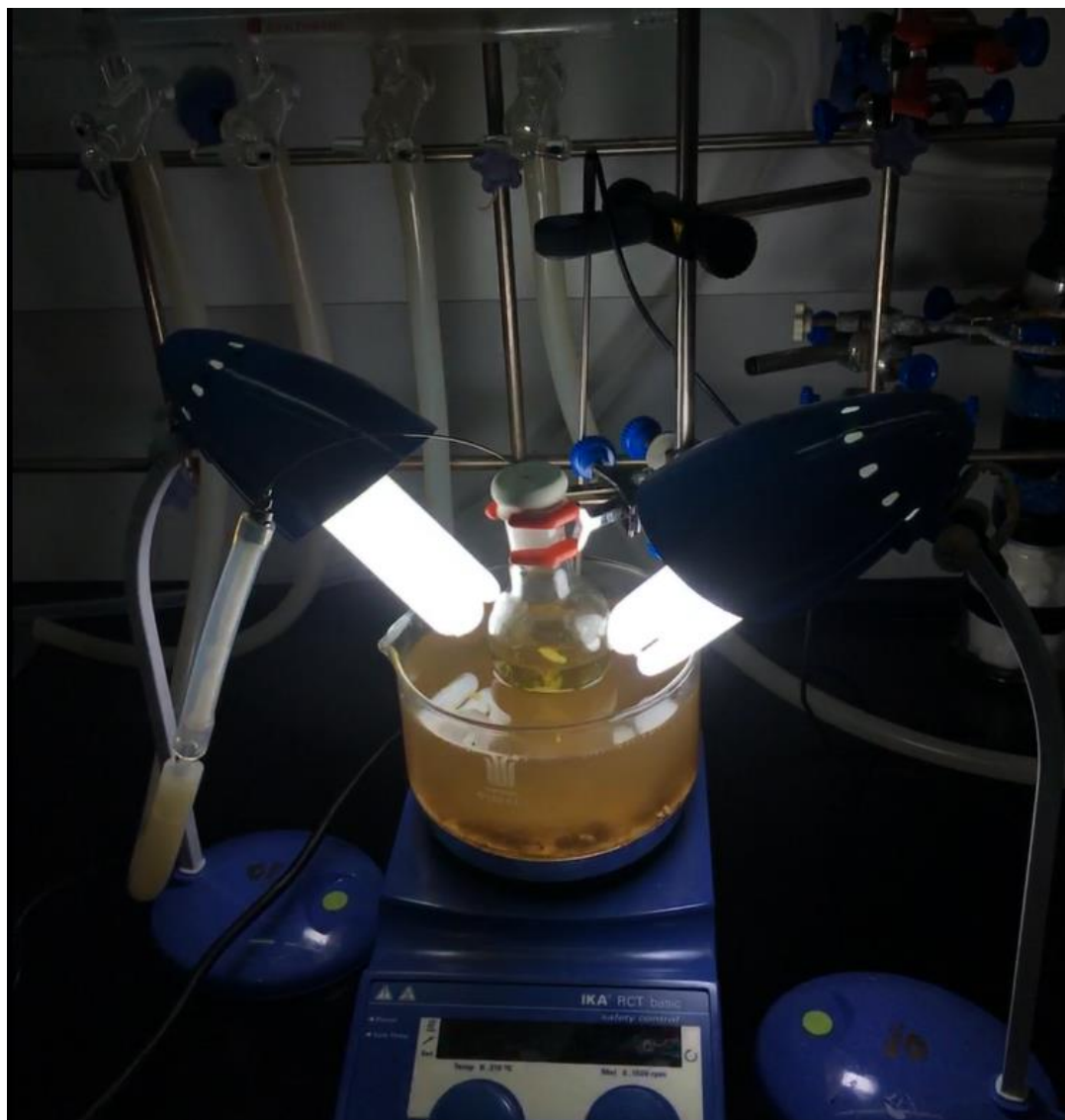
*bench top without decomposition.*  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.06 (s, 2H), 7.95 (s, 1H), 1.60 (s, 9H).

### **Standard Polyolefin Halogenation Methodology:**

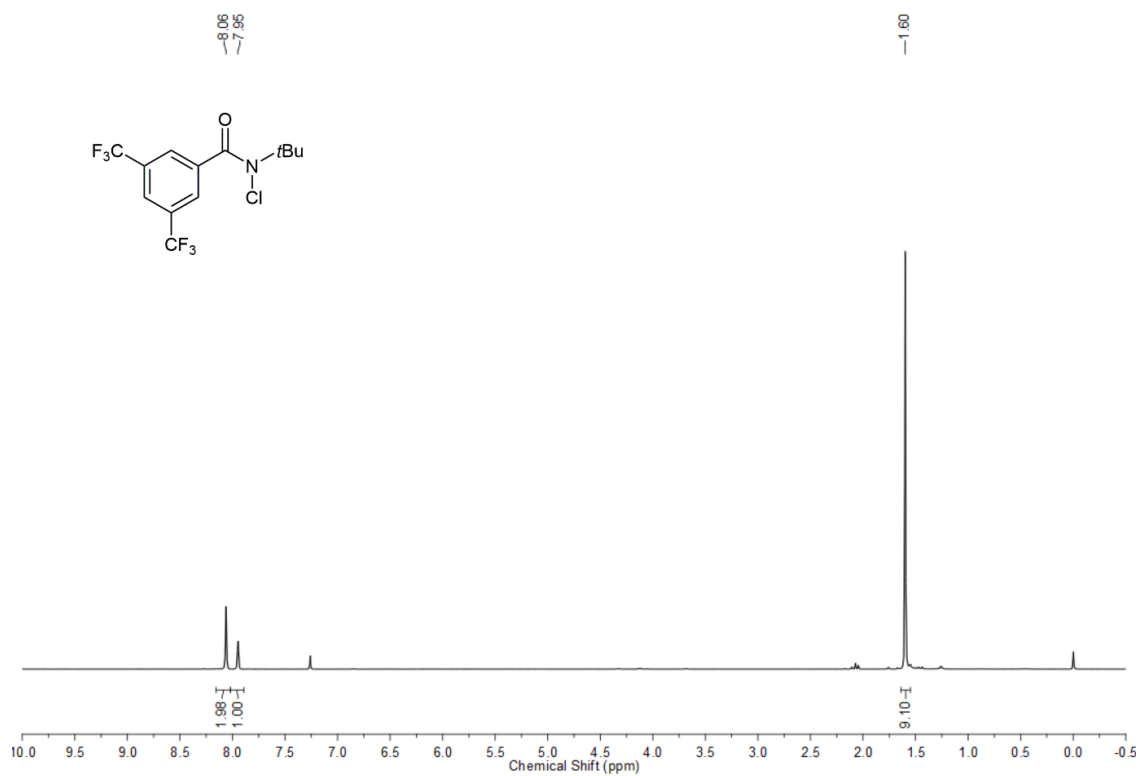
To a mixture of the polyolefin (3 mmol, based on repeating units of ethylene or propylene) and the *N*-haloamide compound (***N*-CA** or ***N*-BA**) (3 mmol) under a nitrogen atmosphere was added 1,1,2,2-tetrachloroethane (10 mL) and the reaction heated to 120°C for 3+ hours under visible light irradiation (2 x standard 25W compact fluorescent light bulb, see figure S1 for reaction setup). The reaction was then cooled to room temperature before being precipitated by its addition to MeOH (50 mL). The resulting suspension was centrifuged, the solvent decanted and the resulting solid dissolved in boiling toluene. The solution was then precipitated by its addition to MeOH (50 mL), followed by centrifugation. This procedure was repeated two times. The resulting solid was then dried under vacuum at 40 °C. ***NOTE: Reactions involving N-CA have the potential to generate chlorine gas,  $\text{Cl}_2$ . Reactions should thus be performed using adequate safety equipment inside a fume hood.***

### **Chlorination of Polyethylene Film:**

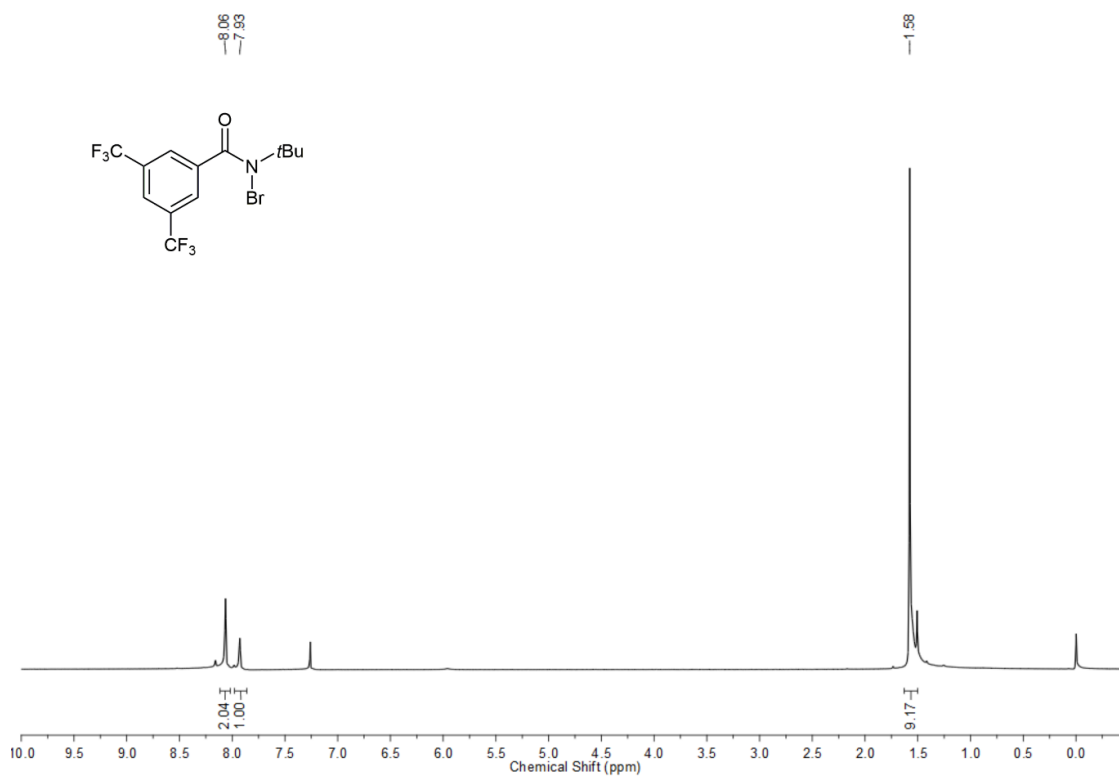
To a sample of HDPE film (14 mg, 0.5 mmol of ethylene repeating units) and ***N*-CA** (174 mg, 0.5 mmol) under a nitrogen atmosphere was added 1,1,2,2-tetrachloroethane (10 mL) and the reaction heated to 70°C for 15 hours under visible light irradiation (2 x standard 25W compact fluorescent light bulb, see Figure S1 for reaction setup). The reaction was then cooled to room temperature, decanted and the HDPE film washed with methanol followed by being suspended and stirred in acetone (2 x 100 mL). The sample was then dried under vacuum at 40 °C. ***NOTE: Reactions involving N-CA have the potential to generate chlorine gas,  $\text{Cl}_2$ . Reactions should thus be performed using adequate safety equipment inside a fume hood.***



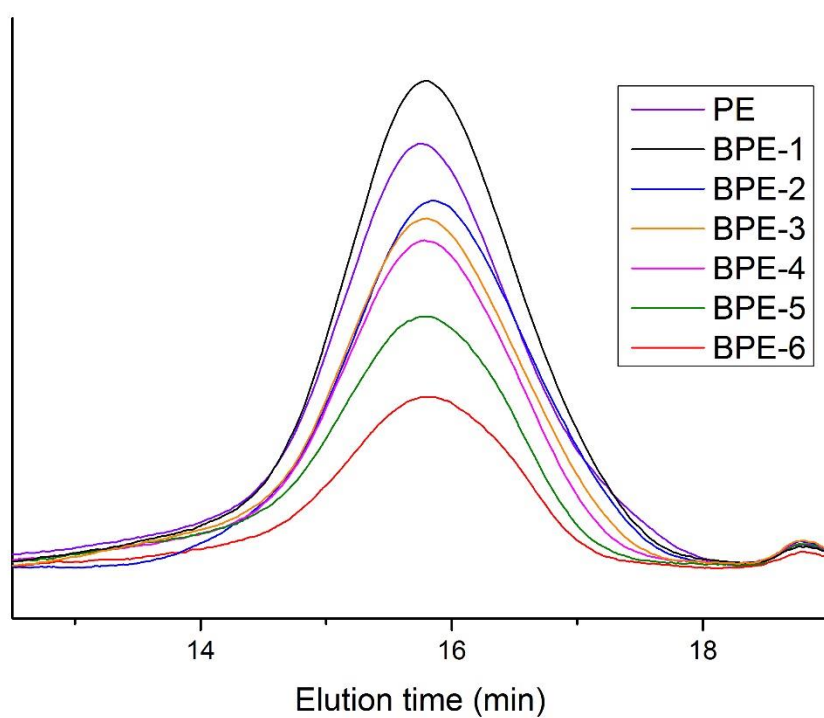
**Figure S1:** Photograph displaying typical reaction setup using 2 x Teanre Lighting SL-440 lamps (max: 40W) using standard 25W compact fluorescent bulbs. Temperature (120°C) and stirring speed (400 rpm) not shown.



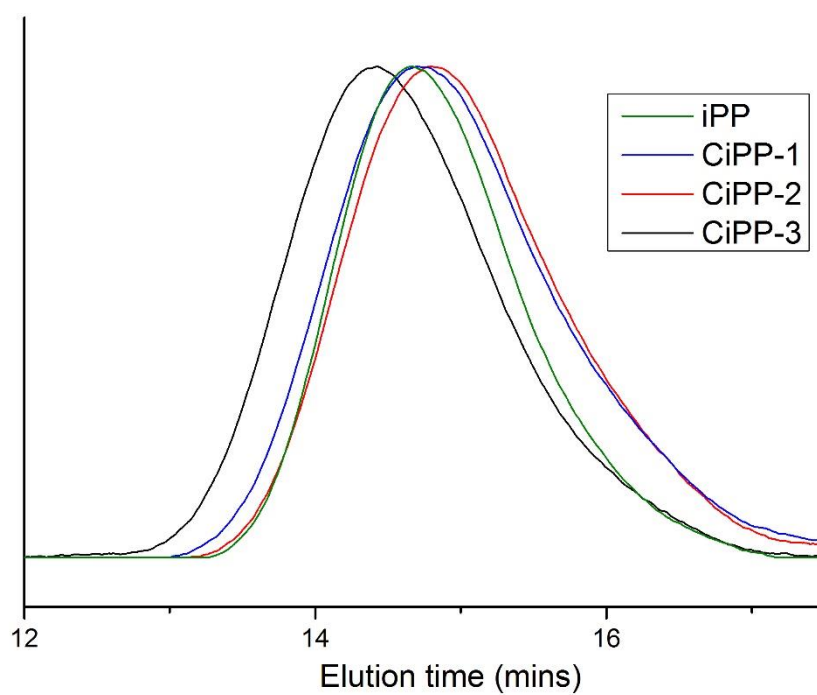
**Figure S2:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of **N-CA**.



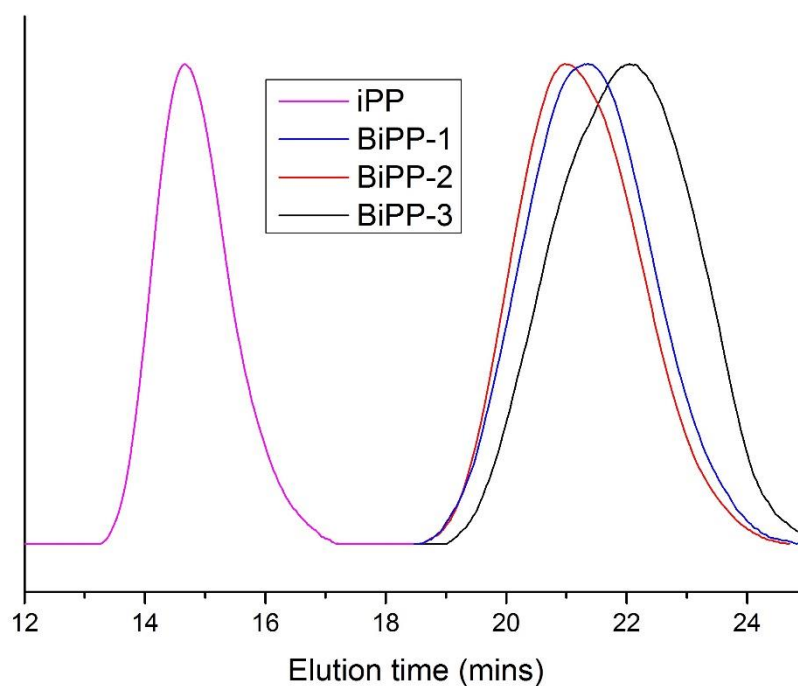
**Figure S3:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of **N-BA**.



**Figure S4:** High temperature SEC ( $\text{C}_6\text{H}_3\text{Cl}_3$ , 150 °C) of brominated polyethylene (BPE) samples.



**Figure S5:** High temperature SEC ( $\text{C}_6\text{H}_3\text{Cl}_3$ , 150 °C) of chlorinated polypropylene (CiPP) samples.



**Figure S6:** High temperature SEC ( $\text{C}_6\text{H}_3\text{Cl}_3$ , 150 °C) of brominated polypropylene (BiPP) samples.

## References

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