

## Supporting Information

### Continuous production of hyperbranched polyhydrocarbons by electrochemical polymerization of chlorinated methanes

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## General Conditions

### Chemicals and Characterization

Lithium hexafluorophosphate ( $\text{LiPF}_6$ ) (battery grade,  $\geq 99.99\%$  trace metals basis; Sigma Aldrich) was used as received. Dichloromethane ( $\geq 99.5\%$ ; Daejung) and carbon tetrachloride ( $\geq 99.5\%$ , anhydrous; Sigma-Aldrich) were used as received. Chloroform ( $\geq 99\%$ , contains amylenes as a stabilizer; Sigma-Aldrich) and anhydrous  $\text{CH}_3\text{CN}$  (99.8%; Sigma-Aldrich) were purified by a solvent purifier from Vacuum Atmospheres Company before use. Hydrochloric acid (HCl) (37%, Sigma-Aldrich) was used for the purification process. Stainless steel sheets (SS304, SS316, and SS430; KwangEun), platinum electrode (99.98%; Nilaco), iron plate (99.85%; Good fellow), and brass plate (Jisung) were washed with acetone, isopropyl alcohol, and deionized (DI) water and dried at  $80\text{ }^\circ\text{C}$  in an air oven for 24 hours before use. Silica gel 60 (0.040-0.063mm; Merck) was used for column chromatography.

Cyclic voltammetry and chronoamperometry results were measured with a Gamry Reference 600+. The potential range from 0.0 V to -6.0 V was applied to the solution with a 10 mV/s scan rate using an Ag/AgNO<sub>3</sub> reference electrode and SS316 working and counter electrodes.  $^1\text{H}$ -NMR spectra were recorded on a Bruker Ascend 400 (400 MHz) and quantitative  $^{13}\text{C}$ -NMR, DEPT  $^{13}\text{C}$ -NMR, and  $^1\text{H}$ - $^{13}\text{C}$  HSQC combined with DEPT spectra were recorded using an Agilent VNMRS 600 (600 MHz) located in the UNIST Central Research Facilities (UCRF). Chloroform-d ( $\text{CDCl}_3$ ) was used as the NMR solvent for the  $^1\text{H}$  and  $^{13}\text{C}$  experiments. The  $^1\text{H}$ -NMR spectra were calibrated with residual non-deuterated solvent shift ( $\text{CHCl}_3 = 7.26\text{ ppm}$ ), and the  $^{13}\text{C}$ -NMR spectra were calibrated using a solvent chemical shift ( $\text{CHCl}_3 = 77.16\text{ ppm}$ ). FT-IR spectra were obtained using an Agilent 600 series spectrometer in the absorption mode. The ICP-MS spectra of the PHC were recorded using an ELAN DRC-II. The combustion analysis was done with a Thermo Flash 2000. Gel permeation chromatography (GPC) analyses were done using an Agilent 1200/miniDAWN TREOS system (Plgel MIXED-C column, 5 microns,  $7.5 \times 300\text{ mm}$  ( $\times 2$ ), Plgel MIXED-E column, 3 microns,  $7.5 \times 300\text{ mm}$  ( $\times 1$ )) equipped with UV, refractive index and multi-angle light scattering (MALS, three angles) detectors. The GPC columns were eluted at a rate of 1.0 ml/min with tetrahydrofuran (at  $30\text{ }^\circ\text{C}$ ). The MALS light source was a 60 mW GaAs linearly polarized laser with a wavelength of 658 nm. X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Scientific ESCALAB 250Xi. DSC results were obtained using a TA instrument Q200 from  $-60\text{ }^\circ\text{C}$  to  $60\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C}/\text{min}$  under a nitrogen atmosphere.

### Electrochemical polymerization

All reactions were performed inside an argon-filled glovebox. A 6.2 M chloroform solution in acetonitrile ( $\text{CH}_3\text{CN}$ ) was prepared in the presence of 23.0 mmol of  $\text{LiPF}_6$  as an electrolyte. Electrochemical polymerization was conducted at -6.0 V (direct current) for 24 h at room temperature. After the reaction, the product solution flowed back to a 'product' glass bottle by passing through a 3-neck glass valve. The insoluble material was removed by vacuum filtration. The residual solvents of the filtered solution were evaporated out using a rotary evaporator, and the dried raw product was dissolved in chloroform (100 mL). The solution was washed with diluted hydrochloric acid 3.7% (100 mL  $\times 5$  times) using a separation funnel. After drying the washed solution, the obtained product was purified by silica column chromatography. For the removal of products containing relatively large amounts of nitrogen and chlorine atoms, chloroform was used as a column solvent. For products containing smaller amounts of nitrogen or chlorine, a 1:1 mixture of ethyl acetate and acetone was used rather than chloroform as a mobile phase.

**Table S1.** References for electrochemical polymerization

Polymer	Yield	Ref.
Poly(n-thiophene) & poly(3-alkylthiophene)	< 1%	[1]
(i) Poly(thiophene-2-aldehydazine), (ii) Poly[N,N'-bis(2-thienylmethylene)-1,4-diaminobenzene] (iii) Poly[bis(thienyl-vinyl)-1,4-phenylene]	4.02 – 50.3 % depending on monomer and electrolyte	[2]
Polyaniline-tartaric acid	38.7 – 47.0 % when increasing the concentration of salt	[3]
Polyacrylonitrile	9.0 - 59.5 % depending on the electrolytes and electrode	[4]
Polypyrrole	1 – 65 % depending on monomer, dopant, temperature, and potential	[5]
Polyaniline	1.07 – 8.49 % according to supporting electrolyte	[6]
Polysulfide	0.0 – 30.5 %	[7]
Poly(hydridocarbyne)	30 – 40 %	[8]

[1] Y. Wei, C. C. Chan, J. Tian, G. W. Jang, K. F. Hsueh, *Chem. Mater.*, 1991, **3**, 888-897.

[2] C. Simionescu, I. Cianga, M. Ivanoiu, A. Duca, I. Cocarla, M. Grigoras, *Eur. Polym. J.*, 1999, **35**, 587-599.

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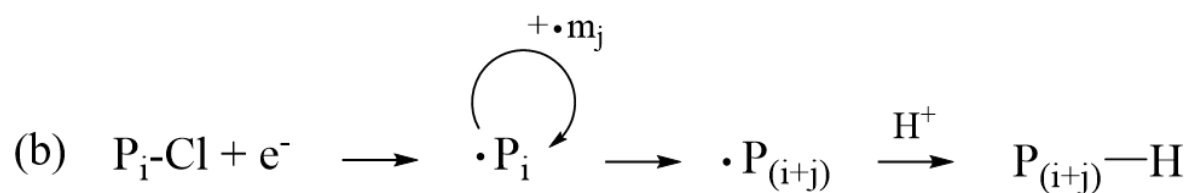
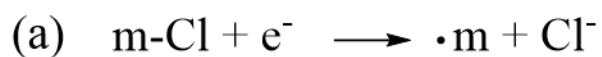
[4] S. N. Bhadani, Q. Ansari, S. K. S. Gupta, *J. Appl. Polym. Sci.*, 1992, **44**, 121-126.

[5] S. Maiti, D. Das, K. Sen, *J. Electrochem. Soc.*, 2012, **159**, 154.

[6] B. Sari, M. Talu, F. Yildirim, *Russ. J. Electrochem.*, 2002, **38**, 707-713.

[7] K. Endo, H.-B. Bu, *Polymer*, 2001, **42**, 3915-3918.

[8] Y. Nur, M. W. Pitcher, S. Seyyidođlu, L. Toppare, *J. Macromol. Sci. A.*, 2008, **45**, 358-363.



**Scheme S1.** (a) Monomers are decomposed by getting electrons from the cathode. (b) The activated monomers are randomly propagated due to three possible active sites when  $\text{CHCl}_3$  was used as a monomer. The polymerization is finally terminated by an H atom during the work-up process with  $\text{HCl(aq)}$  (m: chlorinated methanes, P: oligomer or polymer, and i, j: integer number).

**Table S2.** Inductively coupled plasma-mass spectroscopy results were obtained before and after removing metal contaminants, following the PHC synthesis. Stainless steel electrodes were used, and Fe, Mo, Cr and Ni were detected in the as-synthesized solution. After the “work-up” of the as-synthesized solution (with hydrochloric acid), the amounts of metals remaining were negligible.

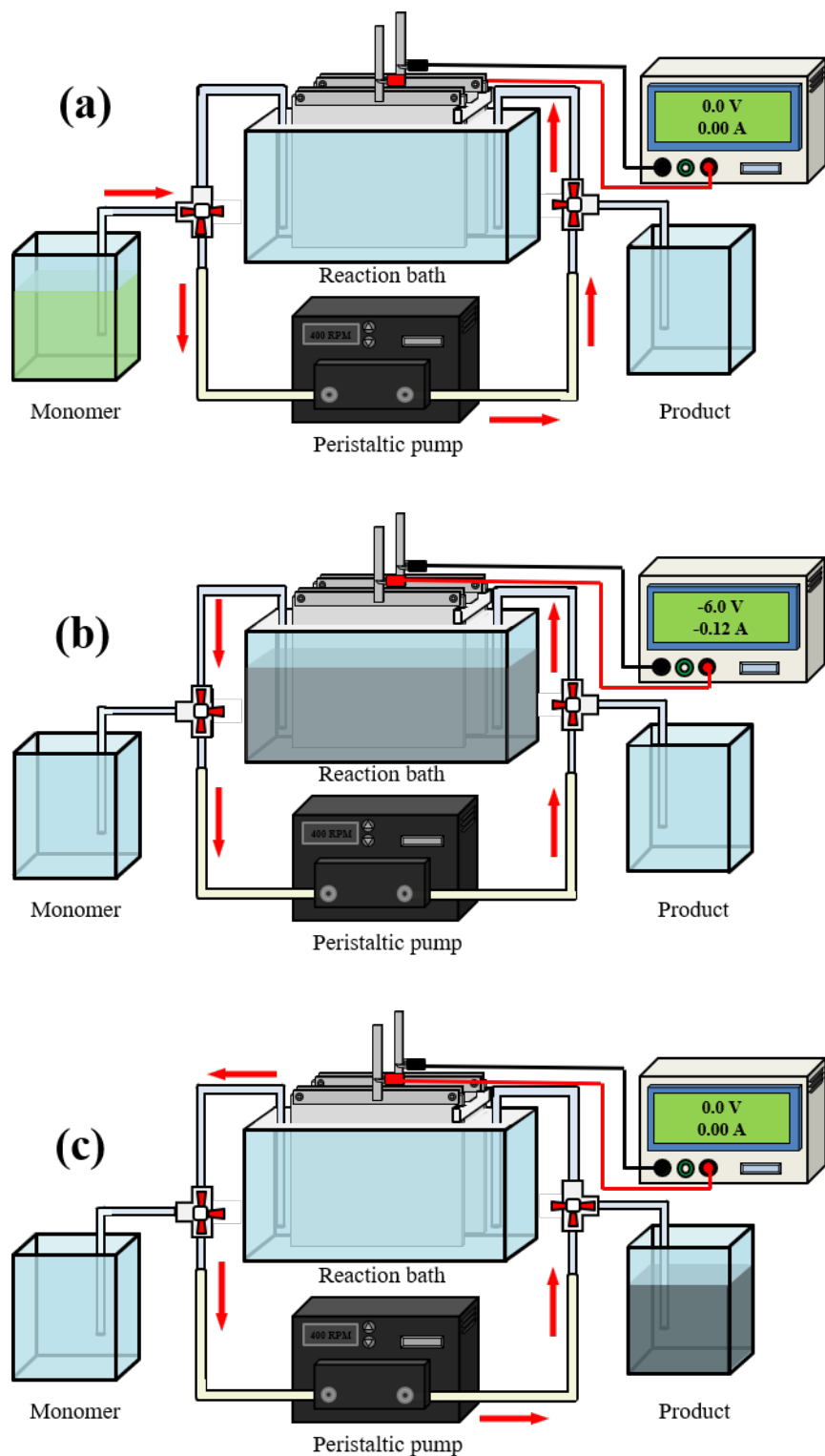
Metal	Composition of stainless steel 316 (%)	Concentration before work-up with HCl(aq) (ppm)	Concentration after work-up with HCl(aq) (ppm)
Li	-	0.74	0.001
P	0.045	2.1	0.000
Fe	62.85-68.85	6.9	0.003
Mo	2.00-3.00	5.5	0.007
Cr	16.00-18.00	1.7	0.009
Ni	10.00-14.00	0.89	0.000

When we used a stainless steel 304 as an electrode instead of stainless steel 316, the yield of PHC was noticeably lower. Perhaps due to the absence of molybdenum, the stainless steel 304 electrode was also damaged after the reaction, making continuous production with it in any case difficult.

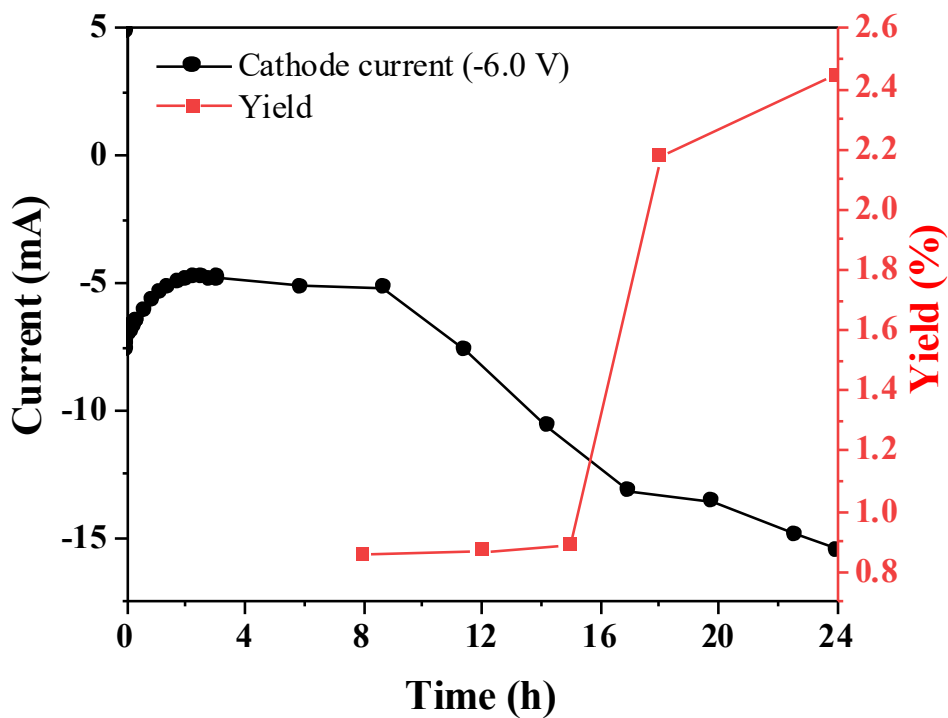
**Table S3.** PHC yields for different electrodes

Electrode	Yield	Note
SS316	1,190 mg	
SS304	249 mg	
Pt (cathode) & SS316 (anode)	23 mg	16 hours
Pt (anode) & SS316 (cathode)	4 mg	16 hours
Brass (Cu + Zn)		Not soluble in organic solvent, a low-quality product containing 15.71 at.% Cl
Fe	0 mg	The current gradually increased, but suddenly dropped due to the dissolution of the iron electrode (evidently caused by oxidation)
Boron doped diamond	0 mg	No current

Reaction conditions were identical for all experiments with an applied potential of -6.0 V and 0.77 molar ratio of  $\text{CHCl}_3$  to solvent  $\text{CH}_3\text{CN}$  with 23 mM  $\text{LiPF}_6$



**Figure S1.** Schematic diagrams of the continuous production system at different stages of its operation. (a) Fill monomer in the reaction bath. (b) Homogeneously mix the solution through continuous flow. (c) Remove the product from the reaction bath.



**Figure S2.** Chronoamperometry was obtained using  $\text{CHCl}_3$  as a monomer at a constant potential  $-6.0\text{ V}$  (versus  $\text{Ag}/\text{Ag}^+$ ) in a three-electrode system. SS316 was used as the anode and cathode electrodes,  $\text{CH}_3\text{CN}$  and  $\text{LiPF}_6$  were used as solvent and electrolyte, respectively. The black line shows the change of current as a function of time on the cathode, and the red line shows the obtained yield when the reaction was terminated at the indicated time (8, 12, 15, 18, and 24 hours).



**Table S4.** Yields of polymer product as a function of (a) solvent, (b) monomer type, and (c) applied potential. All other reaction conditions were identical: SS 316 electrodes, 0.77 monomer/solvent molar ratio, and 23 mM of electrolyte.

<b>(a)</b> Potential: -6.0 V, Reaction time: 8 hours			
Solvent	Dielectric constant ( $\epsilon$ )	Whether or not current was applied	Yield (mg)
Acetonitrile	37.5	yes	416 (0.80%)
N,N-dimethylformamide	37.8	yes	136 (0.26%)
Dimethoxyethane	7.20	no	0
Dimethyl carbonate	3.09	no	0

<b>(b)</b> 6.2M monomer concentration			
	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	CCl <sub>4</sub>
Yield	0.686 g (1.31%)	1.19 g (2.28%)	4.32 g (7.64%)

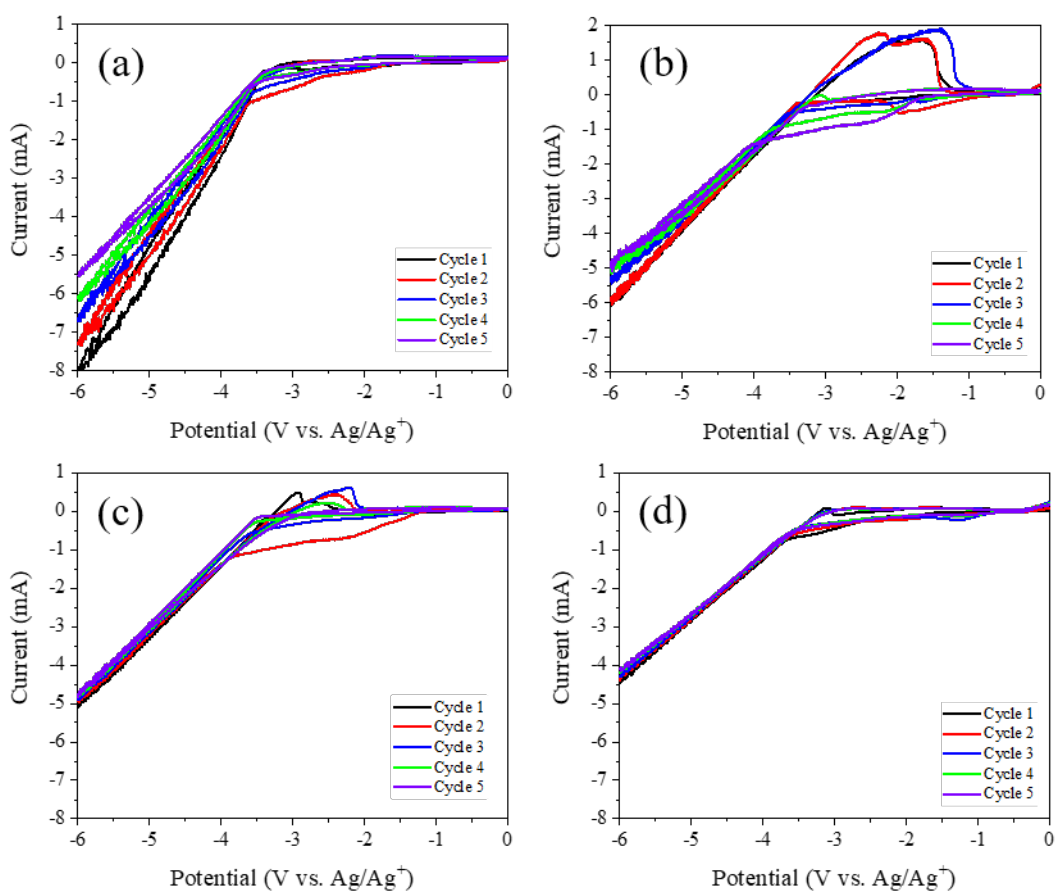
<b>(c)</b> Reaction time: 24 hours			
Potential (V)	Start current (A)	End current (A)	Yield (g)
-5.5	-0.04	-0.08	0.990 (1.90%)
-6.0	-0.07	-0.15	1.19 (2.28%)
-7.0	-0.11	-0.16	0.997 (1.91%)

**Table S5.** Bond Dissociation Energies for chlorinated methanes (**Ref. [9]** and **[10]**)

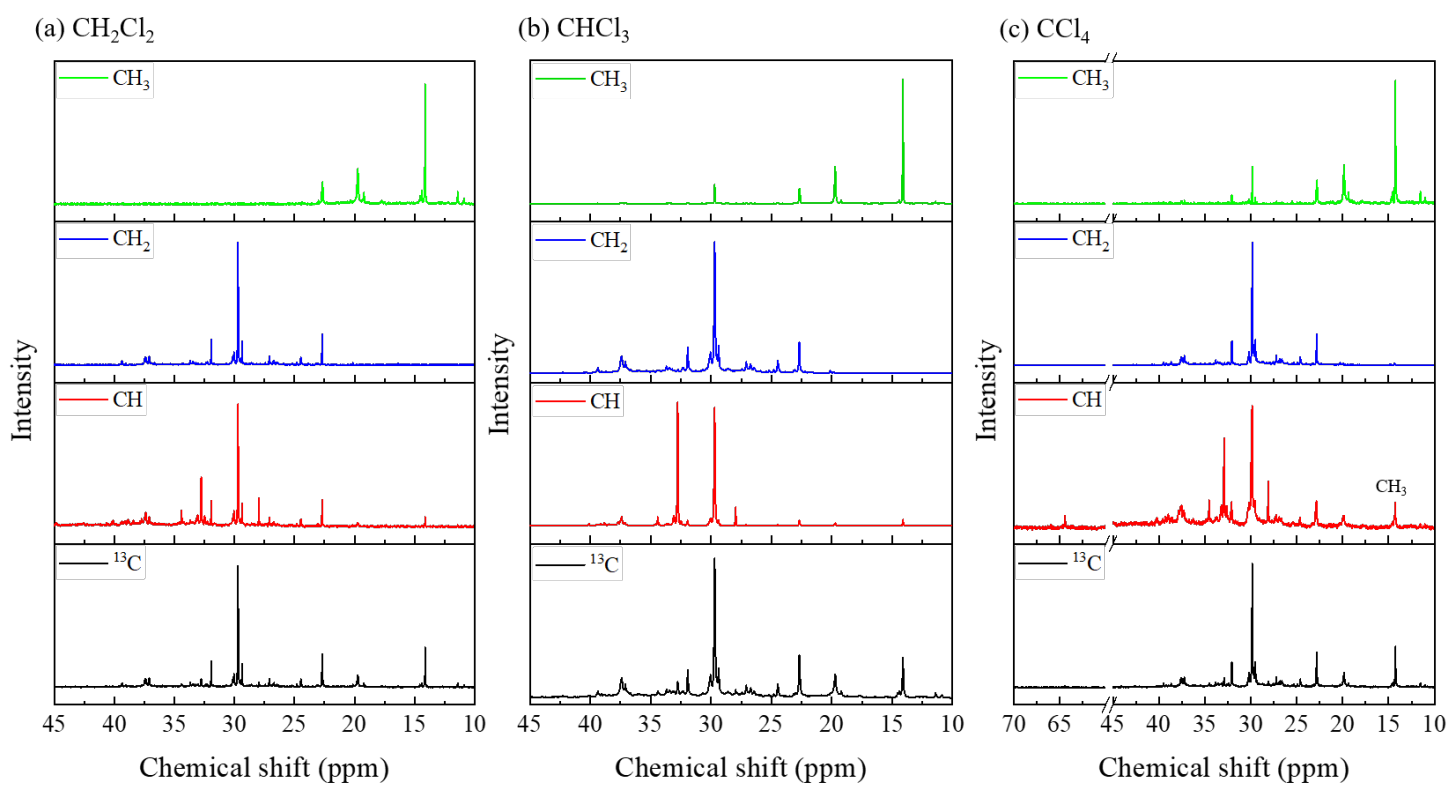
C-H bond	Energy (kJ/mol)	C-Cl bond	Energy (kJ/mol)
CHCl <sub>2</sub> -H	422.58	CH <sub>2</sub> Cl-Cl	338.90
CCl <sub>3</sub> -H	401.66	CHCl <sub>2</sub> -Cl	322.17
		CCl <sub>3</sub> -Cl	292.88

**Ref. [9]** M. Weissman, S. W. Benson, *J. Phys. Chem.*, 1983, **87**, 243.

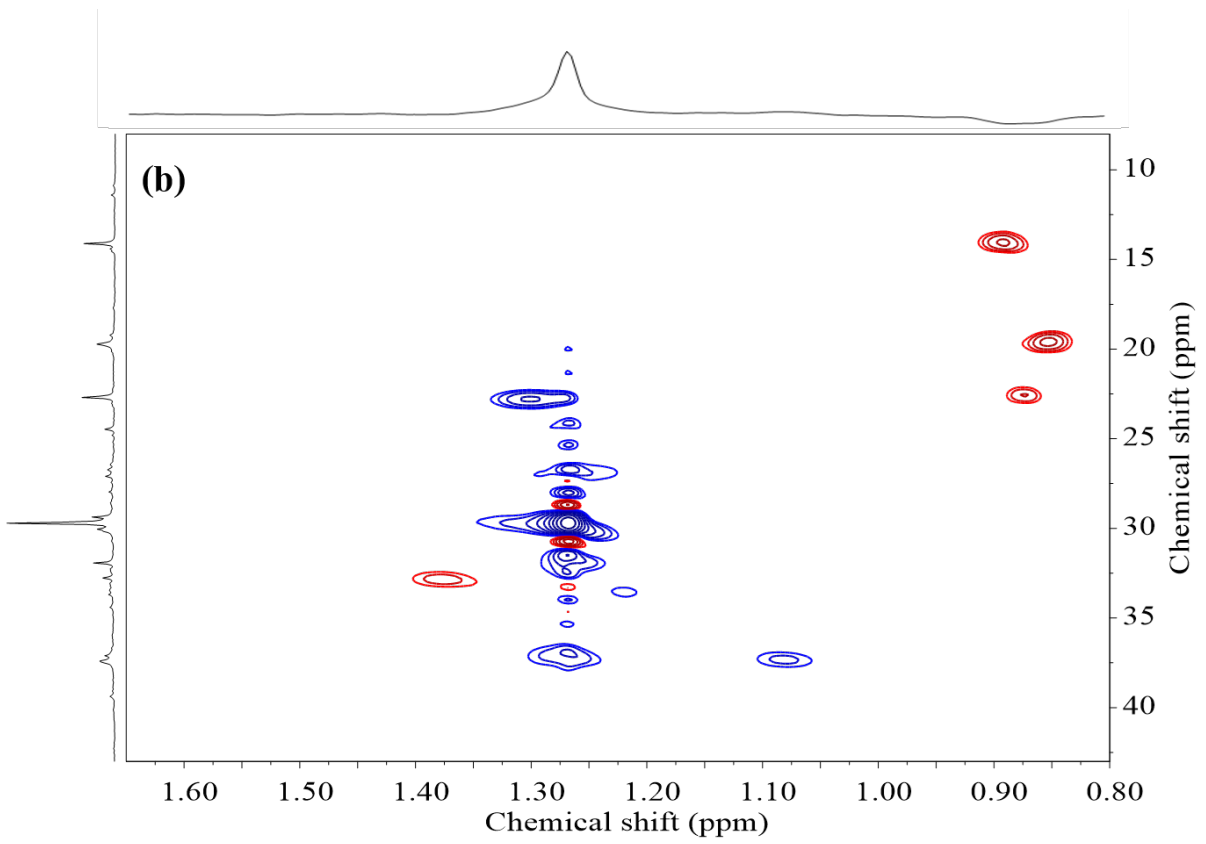
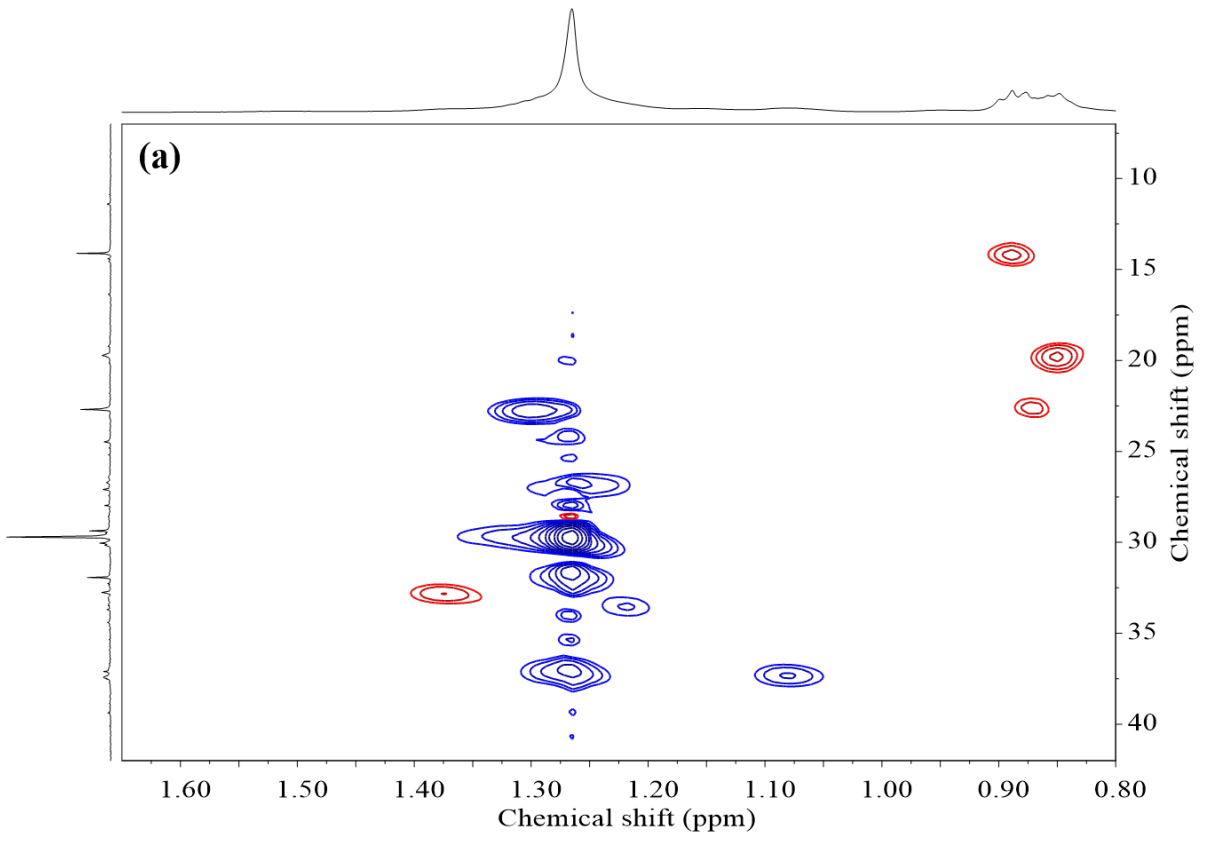
**Ref. [10]** S. W. Benson, *Thermochemical Kinetics*, John Wiley and Son, 1976.

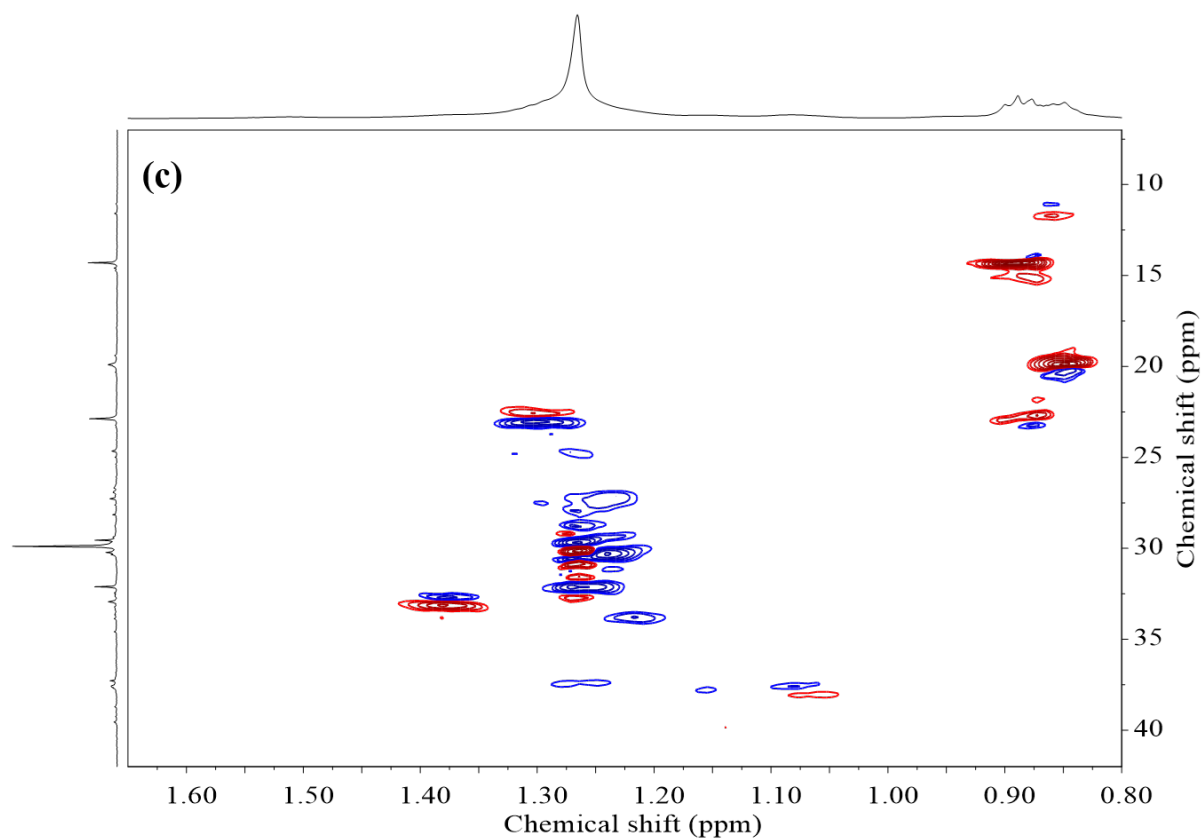


**Figure S3.** Cyclic voltammetry curves for (a) acetonitrile only, and (b-d) 6.2 M solution (in acetonitrile) of (b) dichloromethane, (c) chloroform, and (d) tetrachloromethane. The potential was swept from 0.0 V to -6.0 V at a scan rate of 10 mV/s.

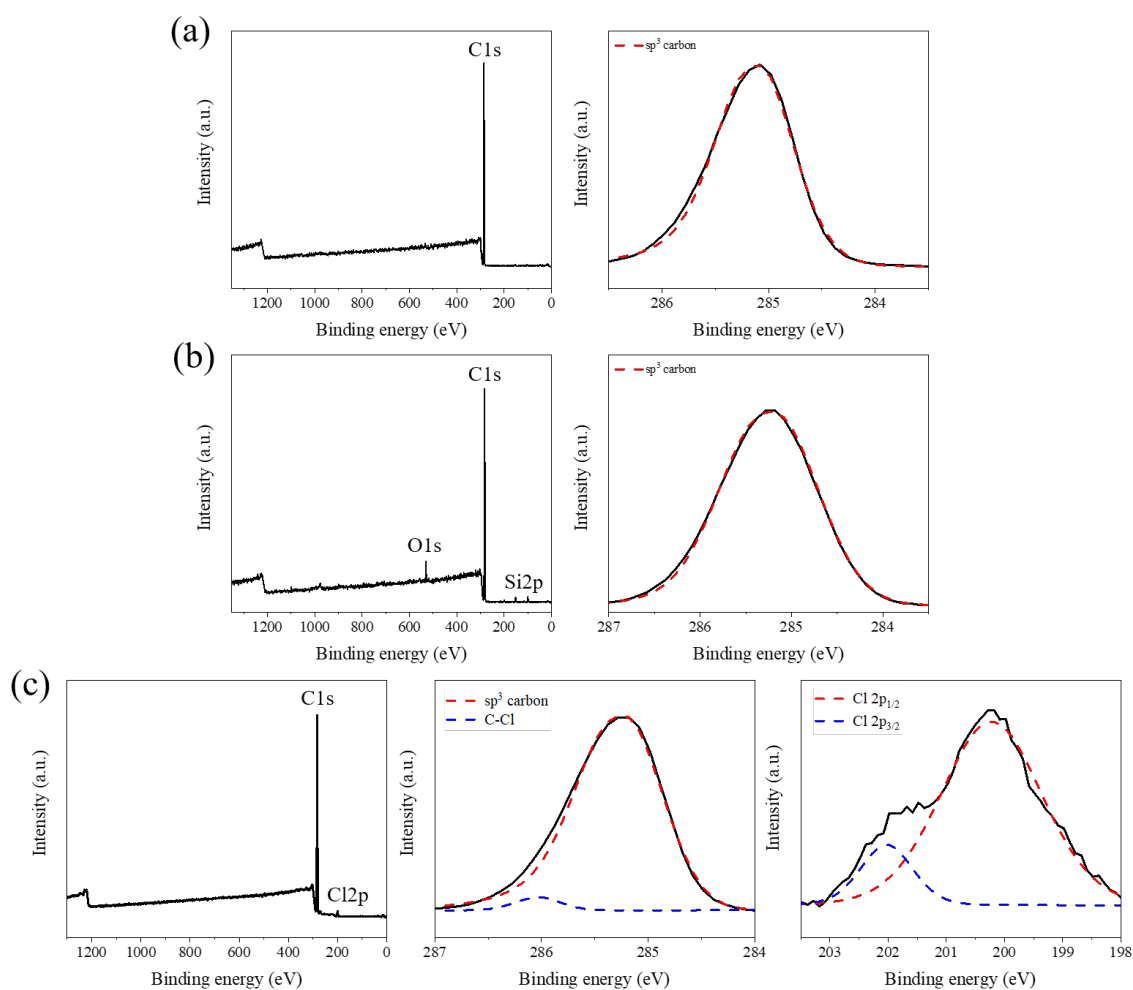


**Figure S4.** Distortionless enhancement by polarization transfer (DEPT)  $^{13}\text{C}$ -NMR spectra of PHC synthesized by using (a)  $\text{CH}_2\text{Cl}_2$ , (b)  $\text{CHCl}_3$ , and (c)  $\text{CCl}_4$ .





**Figure S5.**  $^1\text{H}$ - $^{13}\text{C}$  Heteronuclear single quantum coherence (HSQC) 2D NMR spectra combined with DEPT: PHC synthesized by using (a)  $\text{CH}_2\text{Cl}_2$ , (b)  $\text{CHCl}_3$ , and (c)  $\text{CCl}_4$  as monomers. Red dots indicate positive peaks and blue dots are negative peaks.



**Figure S6.** X-ray photoelectron spectroscopy (XPS) of PHC. (a) Survey spectrum and high-resolution carbon spectrum of PHC synthesized using  $\text{CH}_2\text{Cl}_2$  as a monomer. The survey showed only  $\text{sp}^3$  carbon at 285.2eV. (b) Survey spectrum and high-resolution carbon spectrum of PHC synthesized using  $\text{CHCl}_3$ : 92.11 at.% carbon and 5.11 at.% oxygen with a relatively small amount of silicon. The silicon might come from silicon oxide, which is used in silica gel column chromatography. (c) The survey of PHC synthesized using  $\text{CCl}_4$  shows: 96.26 at.% carbon and 3.74 at.% chlorine. In the high-resolution C1s spectrum, the carbon can be deconvoluted to  $\text{sp}^3$  carbon at 285.2 eV and C-Cl at 286.0 eV. Cl2p peak shows C-Cl.

**Table S6.** Measuring the molecular weight of PHC by GPC-MALS according to different types of monomer

	dn/dc (mL/g)	MALS	
		M <sub>n</sub> (g/mol)	M <sub>w</sub> (g/mol)
PHC-CH <sub>2</sub> Cl <sub>2</sub>	0.0781±0.0007		
PHC-CHCl <sub>3</sub>	0.0756±0.0012	7.517×10 <sup>3</sup>	8.961×10 <sup>3</sup>
PHC-CCl <sub>4</sub>	0.0897±0.0015	1.241×10 <sup>4</sup>	1.549×10 <sup>4</sup>

We note that PHC-CH<sub>2</sub>Cl<sub>2</sub> is estimated to have a very small molecular weight, so it could not be detected by GPC-MALS.