

Supporting Information

Structural Analysis of Hyperbranched Polyhydrocarbon Synthesized by Electrochemical Polymerization

Sun Hwa Lee,^{‡,*} Jae Hong Seo,[‡] Eunhye Shin,[‡] Se Hun Joo, Onur Buyukcakir, Yi Jiang, Minhyeok Kim, Hyunju Nam, Sang Kyu Kwak* and Rodney S. Ruoff*

Table of Contents

Experimental. Chemical reagents and materials, and Experimental Procedures

Figure S1. X-ray photoelectron spectroscopy (XPS) of PHC

Table S1. Molecular weight of PHC by GPC-multi angle light scattering (GPC-MALS) and GPC-right angle light scattering (GPC-RALS)

Figure S2. Molecular weight of PHC measured by GPC with RI detector

Figure S3. Molecular structure of short and long chain branches and calculated ¹³C-NMR chemical shifts for branch chain models

Figure S4. Molecular structures depending on the number of methine groups and ¹³C-NMR chemical shifts of the methine group

Table S2. Chemical shifts corresponding to each of the branching models

Table S3. The number of branches according to branching type

Table S4. Number of branches of polyethylene by various synthetic routes

Figure S5. Density measurement by Archimedes' principle

Table S5. Trials to measure the density of PHC by Archimedes' principle

Figure S6. Solvents used for estimation of solubility parameters

Table S6. Solubility parameters (δ_{vdW} , δ_{Ele} , and δ_{Total}) of the PHC model and for solvents by group, and the average solubility parameter for each solvent group.

Table S7. Results of solubility measurements made at room temperature

Figure S7. Thermogravimetric analysis (TGA) curve and Differential scanning calorimetry (DSC) of PHC

Experimental

Chemicals used

Lithium hexafluorophosphate (battery grade, $\geq 99.99\%$ trace metals basis), was purchased from Sigma-Aldrich and used as received. Chloroform ($\geq 99\%$, contains amylenes as a stabilizer) and anhydrous acetonitrile (99.8%) were purchased from Sigma-Aldrich and purified by the solvent purification system before use. ^{13}C -labeled chloroform (99%) was purchased from Cambridge Isotope Laboratories. Stainless steel 316 was purchased from KwangEun. It was washed using acetone, isopropyl alcohol, and D.I. water and dried at 80°C in an air oven for 24 hours before use. Silica gel 60 (0.040-0.063 mm) for column chromatography was purchased from Merck.

Characterization

^1H -NMR spectra were recorded on a Bruker Ascend 400 (400 MHz) and quantitative ^{13}C -NMR, DEPT ^{13}C -NMR, ^1H - ^{13}C HSQC combined with DEPT spectra were recorded using a Bruker AVANCE 800 spectrometer (800 MHz) equipped with a cryogenic probe at the Korea Basic Science Institute (KBSI, Ochang, Korea). Zgig30 pulse sequences (inverse gated decoupling with 30° pulses, $T_1=10$ s, pulse width=12 s) were conducted at 298.2 K and the scan number was 4096. Chloroform was used as an NMR solvent for both ^1H - and ^{13}C -NMR experiments. ^1H -NMR spectra were referenced with residual non-deuterated solvent shifts ($\text{CHCl}_3 = 7.26$ ppm) and ^{13}C -NMR spectra were referenced to the solvent chemical shift ($\text{CHCl}_3 = 77.16$ ppm). FT-IR spectra were obtained using an Agilent 600 series spectrometer in the absorption mode. Gel permeation chromatography (GPC) analyses were carried out using an Agilent 1200/miniDAWN TREOS system (Plgel MIXED-C column, 5 micron, 7.5×300 mm ($\times 2$), Plgel MIXED-E column, 3 micron, 7.5×300 mm ($\times 1$)) equipped with UV, refractive index and multi-angle light scattering (MALS, three angle) detectors. The GPC columns were eluted at a rate of 1.0 ml/min with tetrahydrofuran (30°C) and polystyrene was used as a standard reference polymer. The MALS-light source was a 60mW GaAs linearly polarized laser with a wavelength of 658 nm. X-ray photoelectron spectroscopy (XPS) were measured using a Thermo Scientific ESCALAB 250Xi.

Electrochemical polymerization

All reactions were carried out inside a glovebox under an argon atmosphere. A 6.2 M chloroform solution in acetonitrile including 23.0 mmol of lithium hexafluorophosphate as an electrolyte was prepared. This solution was placed in a rectangular quartz vessel having a lid. The distance between the stainless-steel cathode and anode (each $8 \text{ cm} \times 10 \text{ cm} \times 0.1 \text{ mm}$) was 2.5 cm for all reactions. Electrochemical

polymerization was conducted at -6.0 V (direct current) for 24 h at room temperature. After the reaction, the insoluble material was removed by vacuum filtration. The solvent of the filtered solution was evaporated using a rotary evaporator, and the dried raw product was dissolved in chloroform (100 mL). The solution was successively washed with diluted hydrochloric acid (100 mL × 5 times). The desired product was obtained after further purification by silica column chromatography. To separate the products including relatively large amounts of nitrogen and chlorine atoms, chloroform was used as a column solvent. After that, a 1:1 mixture of ethyl acetate and acetone was used rather than chloroform as a mobile phase.

Physical property measurements

Density

The density of the PHC was measured by Archimedes' principle. PHC settled in isopropyl alcohol (IPA, $\rho=0.79 \text{ g/cm}^3$ at 25°C), while it was floated on water ($\rho=0.997 \text{ g/cm}^3$ at 25°C). After preparing PHC in 10.0 mL IPA in a graduated cylinder, we slowly added water until the PHC was floating in the middle of the cylinder (See Figure S4). The density of the PHC was calculated as the total mass/volume of IPA and water mixture displaced.

Solubility

Organic solvents are divided into three categories: nonpolar, polar protic, and polar aprotic. We chose 18 different organic solvents.

- (1) Nonpolar solvents: Diethyl ether, n-Hexane, Benzene, Toluene, Chloroform, Carbon tetrachloride, and 1,4-Dioxane.
- (2) Polar protic solvents: Water, Isopropyl alcohol (IPA), and Ethanol.
- (3) Polar aprotic solvents: Acetone, N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), Acetonitrile, Dimethyl sulfoxide (DMSO), Ethyl acetate (EA), Dichloromethane (DCM), and Tetrahydrofuran (THF).

To 200 μl of each organic solvent as much PHC as needed was added to yield a saturated solution. The mass of the saturated solution was measured before and after completely removing the solvent. The mass of PHC divided by the volume of solvent, that is, the solubility, was thus determined. Some solvents were classified as "completely miscible" rather than assigned specific solubility values, as the boundary between a saturated solution and precipitated PHC was not readily distinguished (and this was observed for the full range of mixing ratios tested) for those solvents.

Refractive index

The refractive index (RI) of PHC was recorded at room temperature using a ATAGO NAR-3T Characterization. An LED with a wavelength close to that of the D-Line of Na (588.995 - 589.592 nm)

was used as a light source for the measurement. The refractometer was calibrated using water, and thus the real value of the index of refraction of water, $n=1.333$ at 25°C .

TGA and DSC

TGA curves were measured with the sample under a N_2 atmosphere from 25°C to 900°C with a ramping rate of $10^{\circ}\text{C}/\text{min}$ using a TA Instruments Q500 Thermogravimetric Analyzer. DSC data were obtained using a TA Instrument Q200 from -60°C to 60°C with a ramp rate of $10^{\circ}\text{C}/\text{min}$.

Computational simulation for analysis of the molecular structure

- Density Functional Theory (DFT)

To estimate the structure of PHC, the ^{13}C -NMR and IR spectrum were simulated by DFT calculation using the CASTEP package.^[1] All the structures were optimized. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional^[2] was used with the TS^[3] method to include the van der Waals interactions. The NMR spectrum and the IR spectrum were calculated by ‘on-the-fly’ generated ultrasoft and norm-conserving pseudopotentials, respectively, and the energy cut-off was set to 800 eV with a k-point of 0.03 \AA^{-1} . The chemical shielding value of a carbon atom was calculated using the gauge-including projector augmented-wave (GIPAW) method.^[4] Chemical shifts (δ_i) of the carbon atoms were calculated using the following equation

$$\delta_i = \sigma_{ref} - \sigma_i$$

where σ_i and σ_{ref} are the chemical shielding values of a carbon atoms located in branches and in the reference material (tetramethylsilane, TMS), respectively. Note that σ_{ref} of TMS is 172.05 ppm .

- Molecular Dynamics

To investigate the physical properties of PHC (*i.e.*, density, solubility parameter, refractive index, and melting temperature), its structure was modeled considering the ^{13}C -NMR results and the number of branches. A system was constructed with 10 PHC molecules. Simulations were performed sequentially with geometry optimization, for 5 ns of isothermal-isobaric (*i.e.*, NPT) simulation, and 3 ns of canonical (*i.e.*, NVT) simulation, each at 298 K and 1 atm using the COMPASSII force field^[5] with a 1 fs time step. Temperature and pressure were respectively controlled by a Nose-Hoover Langevin thermostat^[6] and a Berendsen barostat.^[7] Density was analyzed using the last 1 ns trajectories of the NPT simulation. To investigate the melting temperature of PHC, NPT simulations were performed for 5 ns at each temperature ($240\text{-}280\text{K}$) and the volume was analyzed using the last 500 ps of each temperature trajectory. Based on these results, the melting temperature was determined from the sudden change in volume characteristic of the first-order phase transition of melting.^[8] To estimate the solubility of PHC, we calculated the solubility parameters of the solvents (δ_{solvent}) and the PHC (δ_{PHC}). The solubility parameter was obtained from the cohesive energy density (CED) by the following equation^[9]

$$\delta_i = \left(\frac{\Delta E_{v,i}}{V_{m,i}} \right)^{\frac{1}{2}} = (CED)^{\frac{1}{2}}$$

where $\Delta E_{v,i}$ is the internal energy change of vaporization and $V_{m,i}$ is the molar volume for component i . To predict δ_{solvent} , solvents were constructed with 500 molecules (Figure S6), and simulations were performed with NPT for 3 ns and with NVT for 3 ns at 298 K and 1 atm. The solubility parameters of PHC and solvents were calculated using the last 1 ns of the trajectories of the NVT simulation. The refractive index (RI) was estimated using the geometrical fragment (GF) method which calculates RI using the molar refractivity and the molar volume based on the local environment of a carbon atom. RI was predicted by the following equation,

$$\frac{n_D^2 - 1}{n_D^2 + 2} = \frac{\sum_k x_k R_k}{\sum_k x_k V_k}$$

where n_D , x_k , R_k , and V_k , are respectively the refractive index, the mole fraction of fragments (*i.e.*, >CH-, -CH₂-, and -CH₃), the molar refractivity, and the molar volume of fragments.

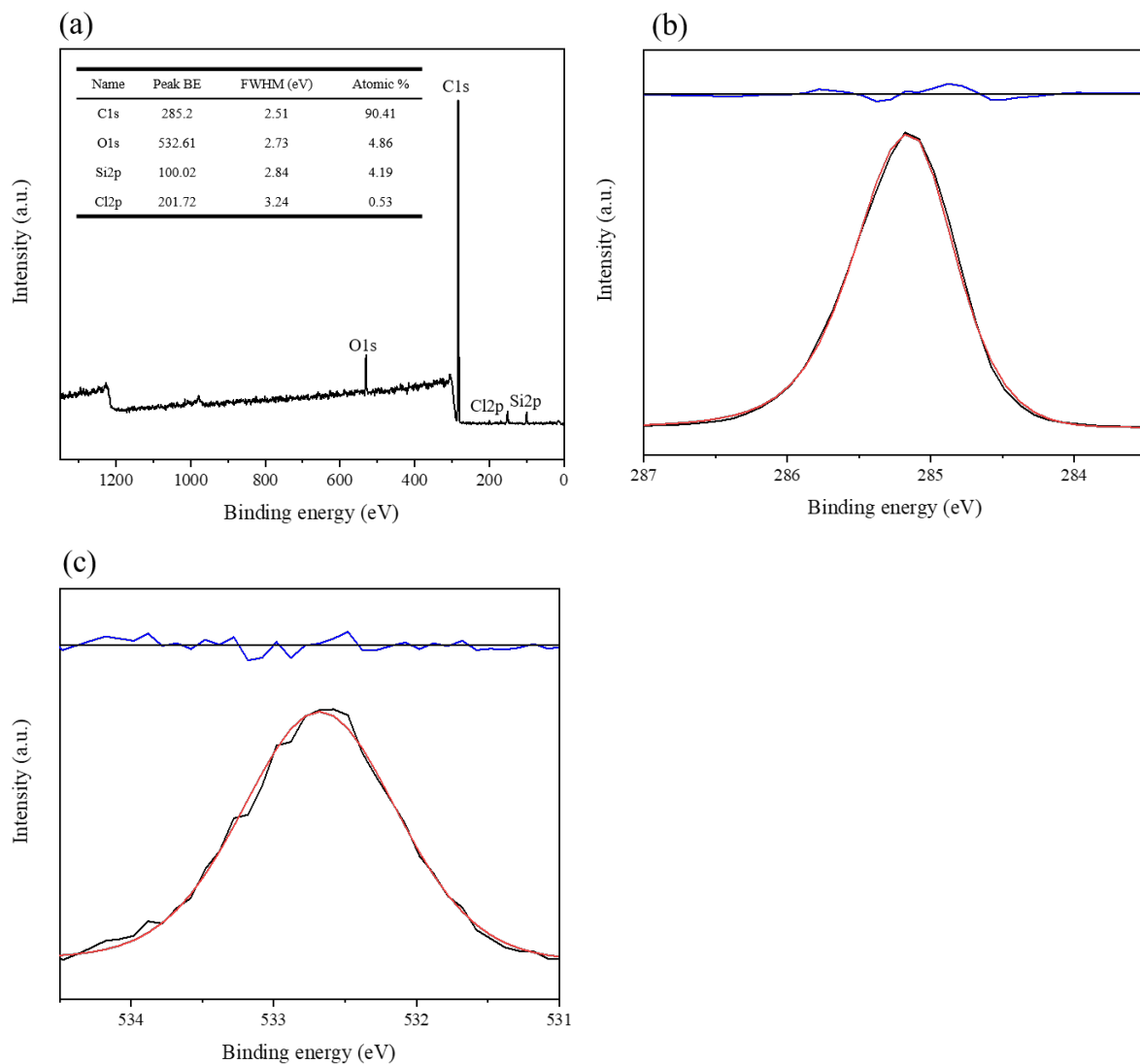


Figure S1. X-ray photoelectron spectroscopy (XPS) of PHC. (a) Survey spectrum of PHC showing that it is composed of 90.41 at.% carbon, 0.53 at.% chlorine, 4.86 at.% oxygen, and 4.12 at.% silicon; The O and Si probably come from the silicon oxide gel used in silica gel column chromatography.) (b, c) High-resolution XPS peaks assigned to (b) sp^3 carbon at 285.2eV and (c) oxygen at 532.5eV.

Table S1. Measured molecular weights of PHC by GPC-multi-angle light scattering (MALS) and GPC-right angle light scattering (RALS). (R_g : radius of gyration, R_h : hydrodynamic radius)

	M_n	M_w	Radius
MALS	7,517 g/mol	8,961 g/mol	(R_g) 1.61 nm
RALS	3,855 g/mol	8,121 g/mol	(R_h) 1.78 nm

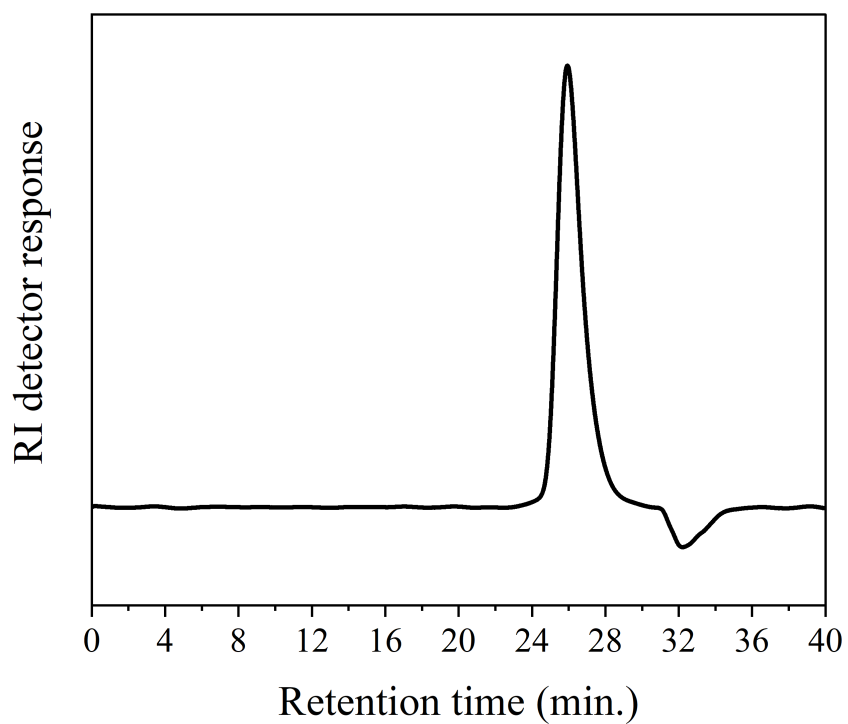


Figure S2. GPC results of PHC using an RI detector. The HT-GPC was calibrated by standard PS. The M_n and M_w of PHC are estimated to be 816 g/mol and 895 g/mol, respectively.

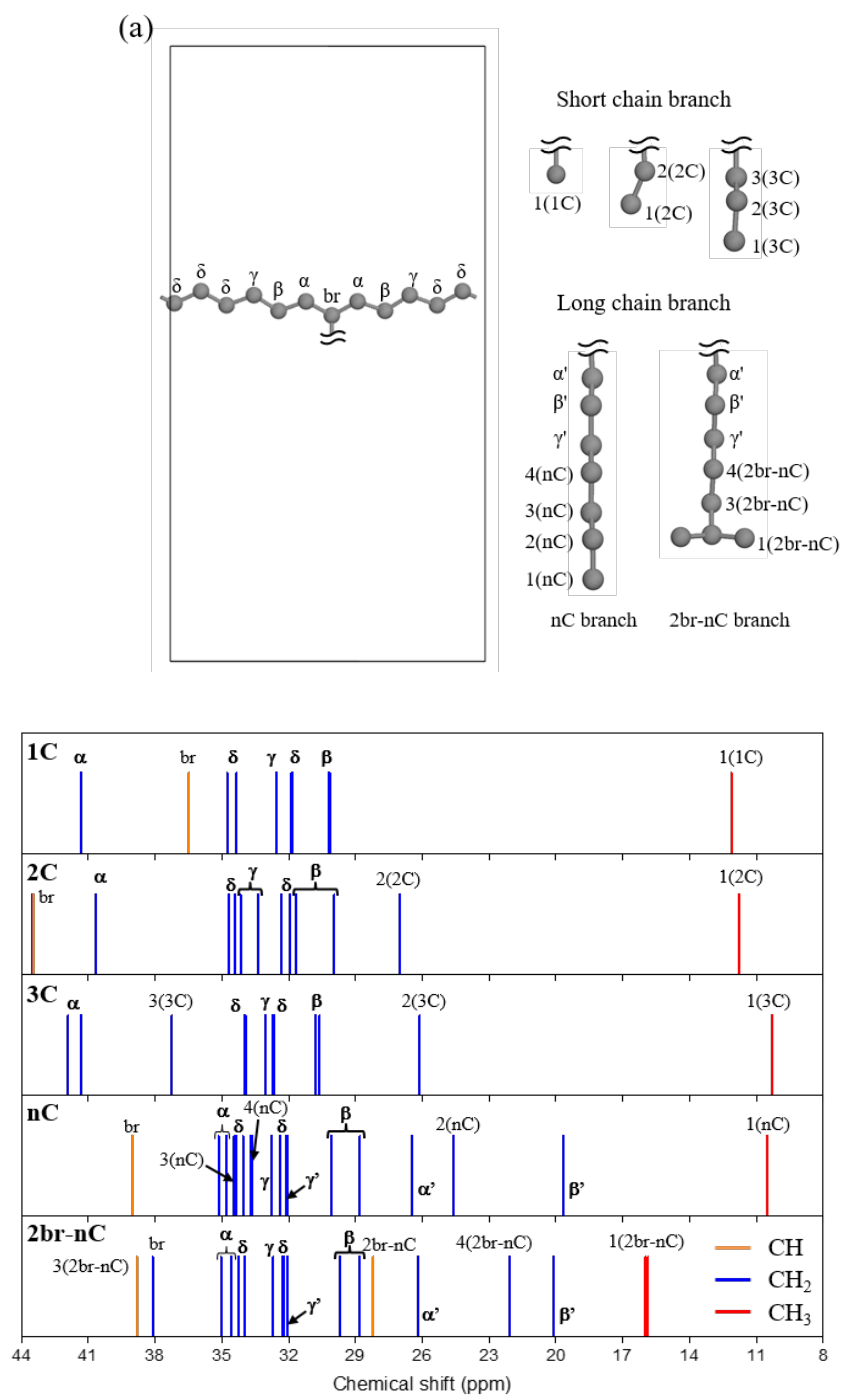


Figure S3. (a) Molecular structures of short and long chain branches. Gray represents C atoms. For clarity, H atoms are not shown. (b) ^{13}C -NMR chemical shifts of branch chain models. Orange, blue, and red represent the chemical shifts of CH, CH₂, and CH₃, respectively. The type of C atom corresponding to each peak is shown on the plots.

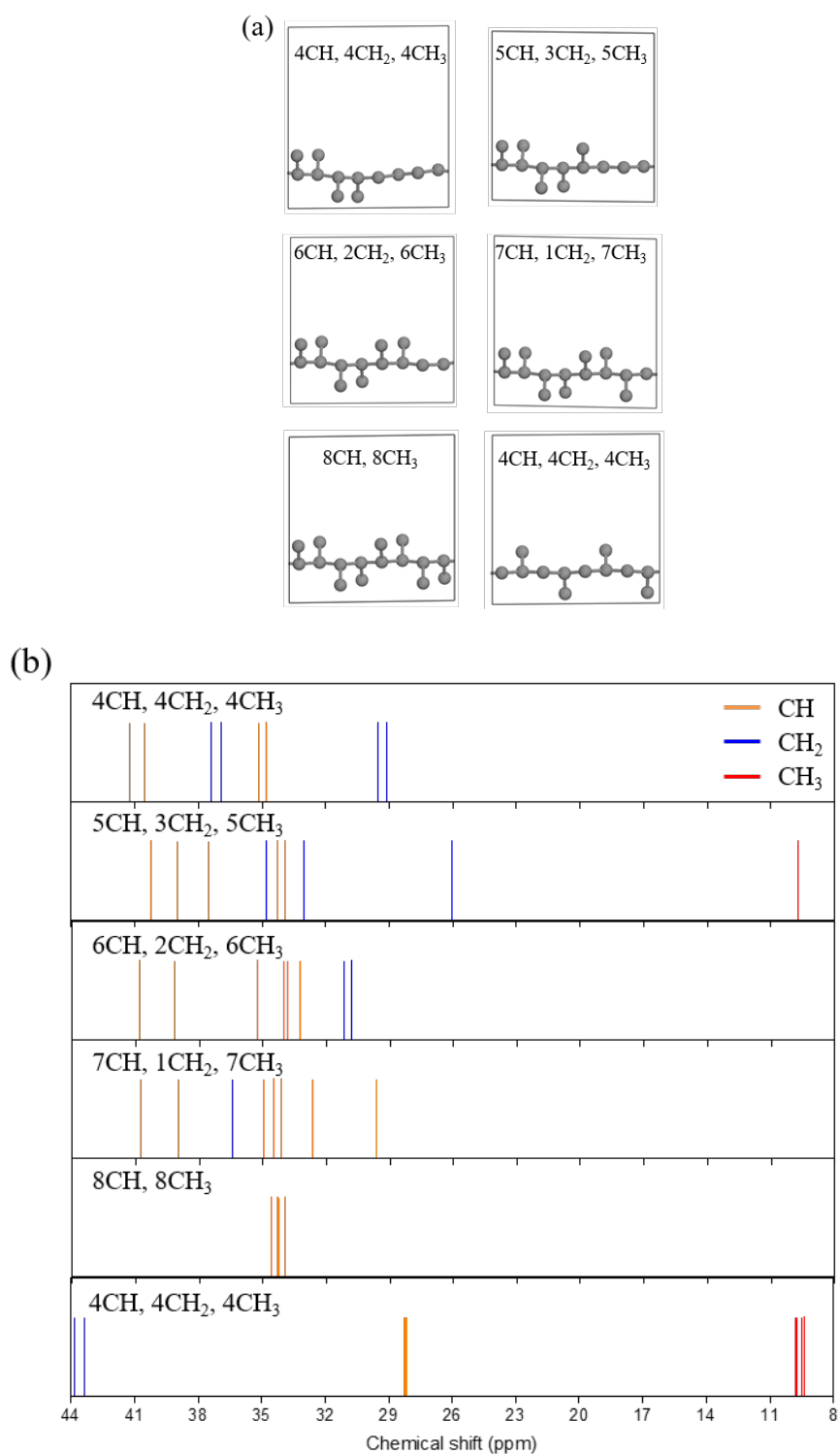


Figure S4. (a) Molecular structures depending on the number of methine groups. Gray represents C atoms. H atoms are not shown for clarity. (b) ^{13}C -NMR chemical shifts of methine groups. Orange, blue, and red represent the chemical shifts of CH, CH₂, and CH₃, respectively.

Table S2. Chemical shifts corresponding to each branch model

Assignment	Chemical shift (ppm, exp)	Assignment	Chemical shift (ppm, exp)	Assignment	Chemical shift (ppm, exp)
	Methyl group (-CH₃)		Methylene group (-CH₂-)		Methine group (-CH-)
1(2br-nC)	22.7	3(2br-nC)	39.5	<u>br</u>	29.0 32.8 34.8
1(1C)	19.7 19.1	α -carbon for short chain	37.5	2br-nC	28.0
1(3C)	14.5	3(3C)	37.2		
1(<u>nC</u>)	14.2	α -carbon for long chain	33.8		
1(2C)	11.5	3(<u>nC</u>)	32.0		
		γ -carbon	30.1		
		δ -carbon	29.8		
		4(<u>nC</u>)	29.5		
		β -carbon	27.1		
		4(2br-nC)	24.5		
		2(<u>nC</u>)	22.8		
		2(3C)	20.1		
		2(3C)	20.1		

Table S3. Number of branches according to branching type. The numbers of C and H atoms in this polymer model are 537 and 1076, respectively. The total number of methyl groups is 93.

Type of branch		number of CH₃	CH₃/1000C	% branch
1(1C)	methyl	37	69	39.43
1(2C)	ethyl	3	6	3.43
1(3C)	propyl	7	14	8.00
1(2br-nC)	methyl branched	9	17	9.71
1(nC)	long	37	69	39.43
Total		93	175	100.00

Table S4. Number of branches of polyethylene by various synthetic routes.

Entry	Synthetic method	Number of branches (/1000C)	Reference
1	Tubular process	15.7	[10]
2	Provided from Sasol Tech. Ltd.	4.3-58.1	[11]
3	Tubular process with MMAO	88.0	[12]
4	Chain walking polymerization and tuning of polymer chain topology	110	[13]
5	Polyethylene produced by 2/MAO	6.9-65.4	[14]
6	Ethylene polymerization with Tandem 1/2/MAO	0-254	[15]
7	Our work, electrochemical polymerization: Polyhydrocarbon	175	

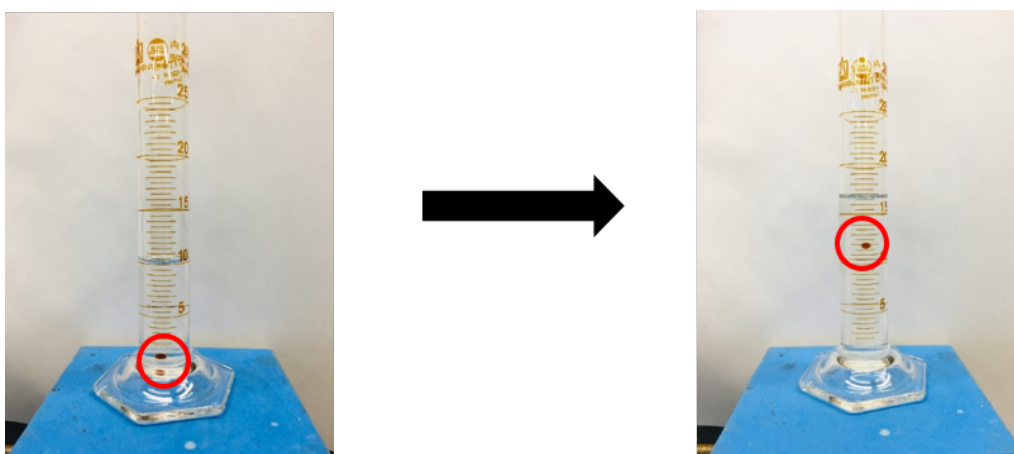


Figure S5. Density measurement by Archimedes' principle. The PHC settled in isopropyl alcohol (IPA). However, when water was slowly dropped in, the PHC floated in the middle of the graduated cylinder.

Table S5. Trials to measure the density of PHC by Archimedes` principle. The averaged PHC density is 0.87 g/cm³.

	Try 1	Try 2	Try 3
Isopropyl alcohol	10.0 mL ± 0.1 mL	10.0 mL ± 0.1 mL	15.0 mL ± 0.1 mL
D.I. water	8.0 mL ± 0.1 mL	7.2 mL ± 0.1 mL	9.8 mL ± 0.1 mL
Density	0.88 g/cm ³	0.87 g/cm ³	0.87 g/cm ³

*Density of solvents at 25 °C: IPA: 0.79 g/cm³, H₂O: 0.997 g/cm³

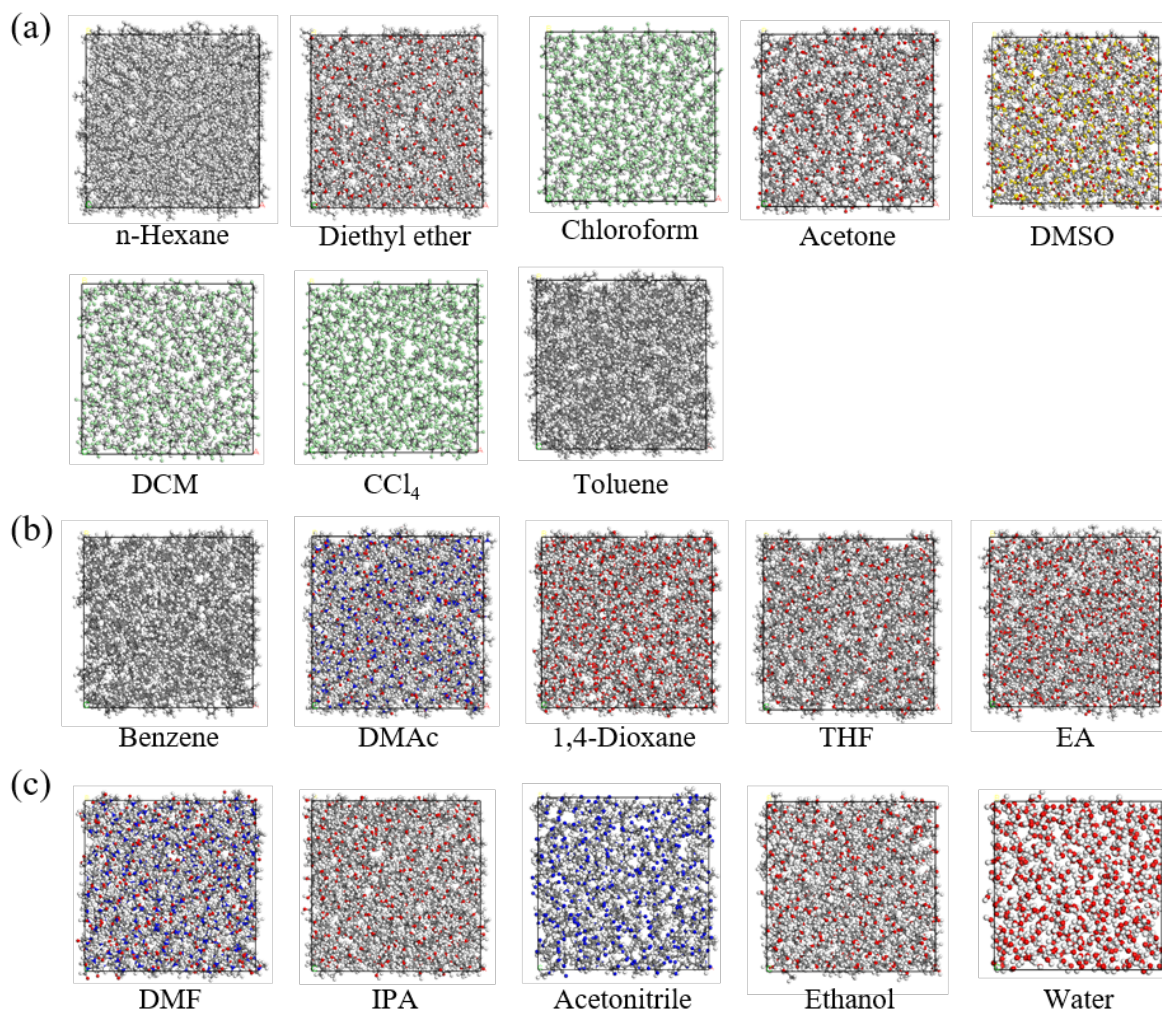


Figure S6. Solvent systems used to estimate the Hildebrand solubility parameter. Systems are classified depending on their dissolution ability for PHC: (a) good, (b) moderate, and (c) poor. Gray, red, blue, green, yellow, and white colors represent C, O, N, Cl, S, and H atoms, respectively.

Table S6. Solubility parameters (δ_{vdW} , δ_{Ele} , and δ_{Total}) of the PHC model and for solvents by group, and the average solubility parameter for each solvent group.

		δ_{vdW}	δ_{Ele}	δ_{Total}	δ_{Total} ([16] [17])
Good solvent	n-Hexane	14.9	0.5	14.9	14.9
	Diethyl ether	15.7	3.6	16.1	15.1
	Chloroform	17.9	2.4	18.0	19.0
	Acetone	16.9	9.4	19.4	20.3
	DMSO	15.8	9.7	18.5	24.5
	DCM	16.8	6.2	17.9	19.8
	CCl ₄	19.2	0.4	19.2	17.1
	Toluene	17.8	4.2	18.3	18.1
	Avg.	16.88	4.55	17.79	
Medium solvent	Benzene	18.0	5.7	18.2	18.8
	DMAc	19.8	10.6	22.5	22.1
	1,4-Dioxane	20.8	7.2	22.0	23.9
	THF	17.8	4.9	18.5	20.2
	EA	17.4	5.4	19.0	18.1
	Avg.	18.76	6.76	20.04	
	Poor solvent	DMF	20.4	13.3	24.3
IPA		13.5	19.8	24.0	23.4
Acetonitrile		16.9	17.3	24.1	24.3
Ethanol		12.2	22.5	25.3	26.0
Water		13.2	45.9	47.6	47.9
Avg.		15.24	23.76	29.06	
PHC model		13.53	0.44	14.03	

Table S7. Measured room temperature solubility values of PHC in various solvents. The solvents are classified as polar aprotic (black), polar protic (green), and nonpolar (blue)

Solvent	Condensed formula	Solubility (g/mL)
n-hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	Completely miscible
Diethyl ether	$(\text{CH}_3\text{CH}_2)_2\text{O}$	Completely miscible
Chloroform	CHCl_3	Completely miscible
Acetone	$\text{CH}_3\text{C}(\text{O})\text{CH}_3$	1.425
DMSO	$\text{CH}_3\text{S}(\text{O})\text{CH}_3$	1.331
DCM	CH_2Cl_2	1.242
Carbon tetrachloride	CCl_4	1.175
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	1.145
Benzene	C_6H_6	1.091
DMAc	$\text{CH}_3\text{C}(\text{O})\text{N}(\text{CH}_3)_2$	1.048
1,4-Dioxane	$\text{C}_4\text{H}_8\text{O}_2$	0.988
THF	$\text{C}_4\text{H}_8\text{O}$	0.815
Ethyl acetate	$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$	0.716
DMF	$\text{HC}(\text{O})\text{N}(\text{CH}_3)_2$	0.664
IPA	$(\text{CH}_3)_2\text{CH}(\text{OH})$	0.277
Acetonitrile	CH_3CN	0.207
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	0.123
Water	H_2O	0.006

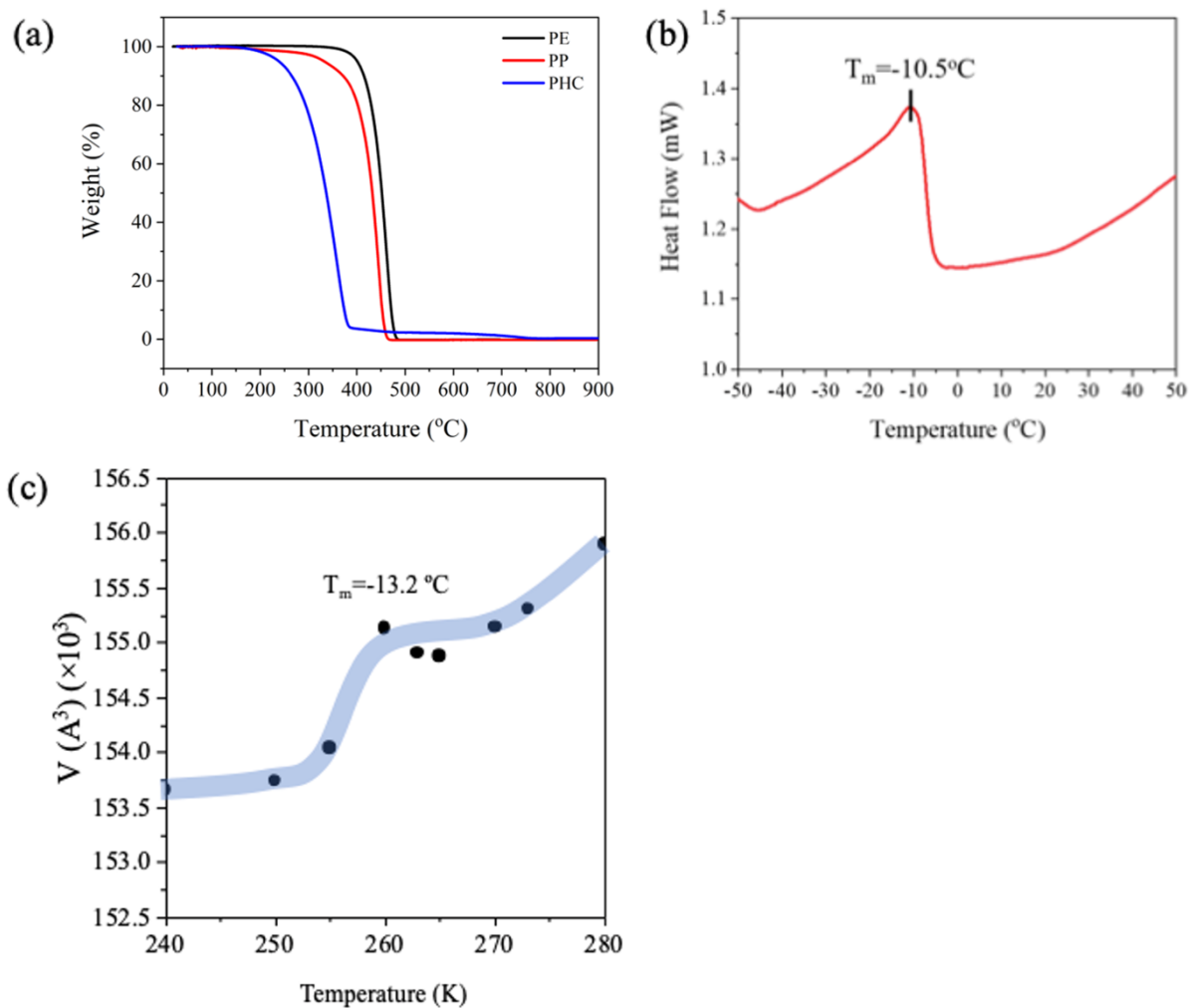


Figure S7. (a) Thermogravimetric analysis (TGA) curves of PE, PP, and PHC (under a N_2 atmosphere, 25 °C to 900 °C with a ramp rate of 10 °C/min). (b) Differential scanning calorimetry (DSC) of PHC heated from -60 °C to 60 °C with a ramp rate 10 °C/min. (c) Prediction of melting temperature (T_m) according to the volume change of the modeled bulk system of PHC at various temperatures.

References

- [1] M. Segall, P. J. Lindan, M. A. Probert, C. J. Pickard, P. J. Hasnip, S. Clark, M. Payne, *Journal of physics: condensed matter*, 2002, **14**, 2717.
- [2] (a) J. P. Perdew, K. Burke, M. Ernzerhof, *Physical review letters*, 1996, **77**, 3865; (b) J. P. Perdew, A. Zunger, *Physical Review B*, 1981, **23**, 5048.
- [3] A. Tkatchenko, M. Scheffler, *Physical review letters*, 2009, **102**, 073005.
- [4] C. J. Pickard, F. Mauri, *Physical Review B*, 2001, **63**, 245101.
- [5] H. Sun, Z. Jin, C. Yang, R. L. Akkermans, S. H. Robertson, N. A. Spensley, S. Miller, S. M. Todd, *Journal of molecular modeling*, 2016, **22**, 47.
- [6] B. Leimkuhler, E. Noorizadeh, O. Penrose, *Journal of Statistical Physics*, 2011, **143**, 921-942.
- [7] H. J. Berendsen, J. v. Postma, W. F. van Gunsteren, A. DiNola, J. R. Haak, *The Journal of chemical physics*, 1984, **81**, 3684-3690.
- [8] J. U. Sommer, C. Luo, *Journal of Polymer Science Part B: Polymer Physics*, 2010, **48**, 2222-2232.
- [9] M. L. Huggins, *The Journal of Physical Chemistry*, 1951, **55**, 619-620.
- [10] K.-i. Shinohara, M. Yanagisawa, Y. Makida, *Scientific reports*, 2019, **9**, 1-5.
- [11] P. E. Bungu, H. Pasch, *Polymer Chemistry*, 2018, **9**, 1116-1131.
- [12] X. Luo, S. Xie, J. Liu, H. Hu, J. Jiang, W. Huang, H. Gao, D. Zhou, Z. Lü, D. Yan, *Polymer Chemistry*, 2014, **5**, 1305-1312.
- [13] Z. Dong, Z. Ye, *Polymer Chemistry*, 2012, **3**, 286-301.
- [14] E. D. Schwerdtfeger, L. J. Irwin, S. A. Miller, *Macromolecules*, 2008, **41**, 1080-1085.
- [15] C. Bianchini, M. Frediani, G. Giambastiani, W. Kaminsky, A. Meli, E. Passaglia, *Macromolecular rapid communications*, 2005, **26**, 1218-1223.
- [16] A. F. M. Barton, *CRC Press*, Boca Raton, FL, 1983.
- [17] A. F. M. Barton, *Chem. Rev.*, 1975, **75**, 731-753.