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Introduction

Branched polymers with side chains projecting from the main backbone have received attention for drug delivery, modifying viscosity, as emulsifier and interfacial compatibilizers, and for other uses, depending on their morphology, composition, degree of branching, and terminal functional groups.¹ They have a low density, adjustable viscosity and elasticity, high solubility, a tendency not to readily crystallize, good processability, and other useful attributes.² As the number of branches increases, the density, viscosity, and melting point (T_m) typically decrease.³

Structural analysis of hyperbranched polyhydrocarbon synthesized by electrochemical polymerization[†]

We describe a structural analysis method for a hyperbranched polyhydrocarbon (PHC) produced by electrochemical polymerization. Nuclear magnetic resonance (NMR) techniques including ¹H-NMR, quantitative ¹³C-NMR, DEPT ¹³C-NMR, and ¹H-¹³C HSQC 2D NMR along with elemental analysis and FTIR were used to experimentally assess the likely structure of this complex polymer with random branching. The polymer structure was modeled based on the NMR results. Room temperature density, refractive index, melting temperature, and IR spectrum were good matches to the values, and spectrum, calculated using the simulated structure. Calculated Hildebrand solubility parameters for the simulated structure rationalize the room temperature solubility measured in a range of solvents. The experimental and modeling methods are likely to be applicable to any type of highly branched random branching polymer. To the best of our knowledge, this is the first comprehensive elucidation of the structure of an unknown and randomly hyperbranched polymer by combining experimental results and theoretical simulation, and the methods described should find broad use in the future.

Polyethylene, a representative saturated PHC, is classified as high-density polyethylene (HDPE) when it has linear polymer chains, and low-density polyethylene (LDPE) when it has branched chains. HDPE is harder and more rigid than LDPE due to its crystalline structure. Its room temperature density of 0.95–0.97 g cm⁻³ and the melting point of ~135 °C are higher than LDPE's values of 0.91-0.94 g cm⁻³ and ~115 °C.4 LDPE also has lower thermal degradation temperature and tensile strength than HDPE. Both LDPE and HDPE decompose completely at temperatures above 550 °C with no solid residue.⁵ In contrast, poly(hydridocarbyne), one of the hydrocarbon-based 'random network' polymers, has been reported to yield diamond-like carbon following thermolysis in argon at a temperature of about 1000 °C.⁶ The thermal properties and thermal stability, and products from the thermolysis of PHCs, are strongly influenced by their structure and composition.

It has been very difficult to determine the exact molecular structure of a polymer with irregular branching and branch lengths.⁷ We have used an array of analytical methods combined with molecular modeling to solve the structure of a particular PHC made by electrochemical synthesis that has irregular branching and branch lengths, and the methodology we describe is likely to be useful for any type of PHC, and probably for other branched polymers, including those containing other elements in addition to C and H.



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Polymer structure can be roughly estimated by observing changes in crystallinity or glass transition behavior using differential scanning calorimetry and by comparing the calculated radius of gyration (R_g) of the appropriate linear polymer and the branched polymer of interest from light scattering and/or analysis of rheological data, which depend on the number of branches in the polymer structure.^{3,8} The degree of branching and detailed branching structure (the 'quantitative structure'), however, cannot be obtained using these qualitative approaches.

NMR spectroscopy is a powerful tool for the detailed analysis of PHC structure. It does not require a standard and provides ways to assign structure through peak positions that depend on the type of branches/branching. For hydrocarbon polymers, distortionless enhancement by polarization transfer (DEPT) 13 C-NMR, through the change of flip angles (45°, 90°, and 135°) allows precise assignment of different hydrocarbon groups.9 Heteronuclear correlation together with ¹H-NMR can be used to assign proton resonances that depend on the type and length of chains containing overlapping adjacent heteronuclear atoms.¹⁰ Another advantage of NMR spectroscopy is that it provides quantitative structural information for other elements as well as hydrogen and carbon.¹¹ For example, for ¹⁵N and ²⁹Si, not only quantitative single spectrum, but also heteronuclear correlation NMR such as DEPT and heteronuclear single quantum coherence (HSQC) NMR studies are possible (¹H-¹⁵N DEPT or HSQC; ¹H-²⁹Si DEPT or HSQC). Molecular simulation of NMR spectra allows for the estimation of the molecular structure of hyperbranched polymers and the comparison of calculated chemical shifts with experimental values. Some chemical shifts observed in the NMR spectra of hyperbranched polymers simply cannot be assigned from typical "tabulated values", but by combining experimental data with molecular simulation a self-consistent picture can be obtained of the molecular structure and thus also of (challenging) peak assignments.

Here, we report an efficient and reliable method of finding the molecular structure of polymers with complex structures. In particular, we have prepared a previously unknown PHC by electrochemical polymerization and solved its chemical composition and structure, as well as measured and modeled several of its properties. The backbone and branching structure of this PHC was assessed using various NMR techniques. Because some of chemical shifts in NMR spectra could not be interpreted by conventional methods, the structure was modeled by theoretical methods based on the NMR data. The measured room temperature values of density, complex refractive index, solubility in a variety of solvents, the melting temperature, and also the IR spectrum, agree very well with calculated values of melting temperature, density, complex refractive index, and solubility parameter rationalizes the measured room temperature solubility values; the calculated IR spectrum, based on the simulated structure, agrees well with the experimental IR spectrum. Our methodology is very likely applicable for solving the structure of any highly branched polymer containing not only carbon and hydrogen but also nitrogen and/or silicon, and possibly other elements as well.

Results and discussion

This PHC was synthesized by electrochemical polymerization using chloroform (CHCl₃) as the monomer (Fig. 1). Although electrochemical polymerization is generally used for the synthesis of conducting polymers, non-conductive polymers also can be produced by applying proper monomer selection and synthesis conditions.¹² Acetonitrile (CH₃CN) was used as the reaction medium due to its broad electrochemical potential window¹³ and LiPF₆ was added as an electrolyte to make an electrically conducting solution. The synthesis was carried out by applying a constant potential of -6.0 V for 24 h between two stainless steel 316 electrodes placed in the solution. In the reaction, the C-Cl bond in the monomer is first cleaved, and a radical is formed at that site in the initiation step. The radical sites of the monomers react with each other and polymerization proceeds. The polymer product is eventually terminated by hydrogen atoms during the work-up process. A detailed description of the method of continuously producing this PHC, and its polymerization mechanism, are reported separately.¹⁴

The obtained polymer consists of C and H atoms with most Cl atoms being removed. One could expect the produced PHC to have a randomly branched structure because of the 3 possible radical sites produced by cleavage of any of the C–Cl bonds in the CHCl₃ molecule.

In FTIR spectroscopy of the synthesized PHC, the peaks in the range of 3000 cm⁻¹ to 2820 cm⁻¹ could be deconvoluted and assigned to the methyl (-CH₃; C-H asymmetric stretching at 2954 cm^{-1} and symmetric stretching at 2862 cm^{-1}), methylene (-CH₂-; C-H asymmetric stretching at 2924 cm^{-1} and symmetric stretching at 2851 cm⁻¹), and methine (>CH-; relatively small C-H stretch intensity at 2902 cm⁻¹) groups (Fig. 2).¹⁵ The overlapping stretching vibrations in the 3000–2820 cm⁻¹ range were deconvoluted and a ratio of CH:CH2:CH3 of 1.00:2.25:1.00 was obtained by fitting peak areas.¹⁶ Each peak was, necessarily, fit with a different full-width half maximum (FWHM) that might be caused by the structure of the hyperbranched PHC. C-H bend modes were observed for methylene at 1462 cm⁻¹ and methyl at 1375 cm⁻¹, and the rocking vibration of the methylene group was found at around 720 cm⁻¹. The PHC synthesized by this method of electrochemical polymerization is composed of essentially only C and H with 0.27 atomic percent of Cl (Fig. S1a[†]); the elemental composition was determined by the combustion method (Table 1). C and H were the dominant components, with negligible amounts of N and O observed (Table 1).

An XPS (X-ray photoelectron spectroscopy) survey spectrum shows the elements present in PHC (Fig. S1a†). O is presumed



Fig. 1 Reaction scheme for the synthesis of PHC using CHCl_3 as a monomer.



Fig. 2 FTIR spectrum of PHC in the range 4000 cm^{-1} to 500 cm^{-1} , and specific regions from 3000 cm^{-1} to 2820 cm^{-1} . (*hydrocarbon substitutions of sp³ carbon.).

Table 1 Elemental analysis of PHC by combustion

	Carbon	Nitrogen	Hydrogen	Oxygen
Mass %	83.50	0.14	14.00	0.34
Atomic %	33.06	0.05	66.52	0.10

to come from trapped moisture, which was observed as a single peak at 532.30 eV in the high-resolution XPS O 1s region, as there was no deconvoluted peak of C–O in the C 1s high-resolution spectrum (Fig. S1b and c†).¹⁷ Negligible amount of Cl was detected.

From the combustion elemental analysis, the empirical formula of the PHC was calculated to be CH_{2.01}. Since the polymer is composed of CH, CH₂, and CH₃, the number of CH₃ terminal groups must be two more (+2) than the number of CH branching points. For this reason, the empirical formula of the polymer is estimated to be close to CH₂.¹⁸ Per the deconvoluted FTIR spectrum (as mentioned, $CH: CH_2: CH_3$ is 1.00: 2.25: 1.00) the degree of branching is calculated to be (about) 23.5%,¹⁹ and thus this PHC is highly branched. As mentioned, the elemental analysis and FTIR spectra data support an empirical formula close to CH₂.

We tried to determine molecular weight (MW) of this PHC by using (i) gel permeation chromatography (GPC) with refractive index (RI), ultraviolet (UV), or viscometer detectors, (ii) matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry, (iii) Field-Flow Fractionation-Mass Spectrometry (FFF-MS), and (iv) electrospray ionizationmass spectrometry (ESI-MS), but we couldn't get reliable values from these methods. Because PHC as described above likely has a complex branched molecular structure, an absolute MW measurement by light scattering was attempted, and GPC coupled with multi-angle light scattering (MALS) was used to obtain the number average molecular weight, $M_{\rm n} = 7.517 \times 10^3$ g mol⁻¹ (±2%), and the weight average molecular weight, $M_{\rm w}$ = 8.961×10^3 g mol⁻¹ (±2%). The polydispersity index (PDI) was calculated to be 1.192 (±3%), indicating a relatively narrow MW distribution. The MALS has a limitation in detecting the product, which has a molecular size below 10 nm. However, 90° angle light scattering (right angle light scattering, RALS) can help to measure the molecular weight accurately for molecules with $R_{\rm g} \le 15$ nm.²⁰ The $M_{\rm w}$ of PHC by GPC-RALS was estimated to be 8121 g mol⁻¹; this value is similar to the GPC-MALS result (Table S1[†]). Fig. S2[†] shows GPC results of PHC using an RI detector. Although the M_n and M_w of PHC were estimated to be 816 g mol⁻¹ and 895 g mol⁻¹, respectively, the Hisaya Sato group has reported that hyperbranched polymers have higher molecular weight than a linear polymer for the same elution volume.²¹ This means that hyperbranched polymers will have longer retention times than linear polymers with similar molecular weight.

The molecular structure of the PHC was analyzed using a variety of NMR techniques. The ¹H-NMR spectrum (Fig. 3a) using CDCl₃ (δ = 7.26 ppm of CHCl₃) as a solvent showed three main peaks at δ = 1.72 ppm (CH), δ = 1.28 ppm (CH₂), and δ = 0.87 ppm (CH₃). Since peaks are overlapped, it was not possible to acquire quantitative information by ¹H-NMR peak integration. Thus, ¹³C-NMR analysis was performed using PHC synthesized from ¹³C-labeled chloroform (¹³CHCl₃; Fig. 3b). The NMR spectrum of PHC from 100% ¹³CHCl₃ (and thus close to 100% ¹³C-labeled PHC) had the same peaks as that of 1.1 at% ¹³C (natural abundance), but this spectrum showed a large increase in peak intensities (and signal to noise ratio) that enabled quantitative analysis. The spectrum indicated that there are no quaternary carbons which means every C atom is bonded to at least one H; this is because CHCl₃ has 3 reactive C-Cl bonds and one C-H bond.

PHC was analyzed by the DEPT ¹³C-NMR method (Fig. 3c). In this experiment, pulse sequences with different delay times are used to record the spectra. This method provides a series of spectra in which ¹³C-NMR signals change based on their substitution patterns. The spectra depend on the flipping angles of the pulse (45°, 90°, or 135°). DEPT-90 yields only CH signals. DEPT-135 yields positive CH and CH₃ peaks and negative CH₂ peaks. All peaks in the ¹³C-NMR spectrum could thus be labeled with reference to the DEPT ¹³C-NMR results as shown in Fig. 3b.^{10a,22} Chemical shifts are generally observed in the ranges 10-20 ppm (-CH₃), 20-40 ppm (-CH₂-), and 27-40 ppm (>CH-), and many peaks were observed to be shifted in a more complex way than, e.g., high-density polyethylene or polypropylene that have a regular repeating unit. Randomly-bonded hydrocarbon groups produced these complex ¹³C chemical shifts, because chemical shifts are affected by the location of a C atom and the atom(s) bonded to it, along with its surrounding environment, as shown in ¹H-¹³C HSQC combined with DEPT 2D NMR spectra (Fig. 3d). Due to the isotope effect, H atoms are more strongly influenced by ¹³C in the ¹³C-labelled product.²³ In the ¹H-¹³C



Fig. 3 NMR spectra of PHC in CDCl₃. (a) ¹H-NMR spectrum, in which protons from CH are assigned (red box), CH₂ (blue box) and CH₃ (green box). (b) Quantitative ¹³C-NMR, whose peaks are labeled based on (c) DEPT 90° and 135°. (d) ¹H-¹³C heteronuclear single quantum coherence (HSQC) 2D NMR spectrum combined with DEPT. Red indicates positive peaks and blue negative peaks. For quantitative ¹³C-NMR analysis, PHC was synthesized by using pure ¹³CHCl₃ as the monomer.

HSQC 2D NMR spectra, all peaks in the ¹H-NMR spectrum are shifted by +0.07 ppm. The methyl group has different proton chemical shifts depending on whether it is attached to a long (at 0.90 ppm) or a short (at 0.95 ppm) carbon chain. This is interpreted as the -CH3 terminal groups are not only attached to the end of the long branches, but also present on short (methyl, ethyl, or propyl) branches, leading to different chemical shifts of H and ¹³C atoms. A slight overlap of the C chemical shifts for methyl and methylene groups in the range of 22-23 ppm of ¹³C-NMR in HSQC supports these particular methyl groups being located adjacent to each other, resulting in an additional positive chemical shift of its H atoms. The ¹³C chemical shifts for methylene groups were found to span a broader range than the proton chemical shifts due to the degree of branching, length of branches, and distance between branches. A proton shift of methylene at 1.15 ppm is caused by an intramolecular interaction. The peaks for methine

groups were partially overlapped with $-CH_2-$ at 1.45 ppm, as well as at 1.60 ppm in the ¹H-NMR spectrum. Since methine groups serve as branching points of the polymer, interpretation of methine group position is important to understanding the polymer structure. Based on ¹³C-NMR, DEPT ¹³C-NMR and ¹H-¹³C HSQC NMR spectra, the fraction of hydrocarbon substitutions was calculated as 0.56 (>CH-): 2.17 (-CH₂-): 1.00 (-CH₃) which corresponds to an empirical formula of CH_{2.12}. However, some methine groups, *e.g.*, at 29–30 ppm, overlap with other methylene groups from DEPT spectra, and this causes difficulty in accurately estimating the number of hydrocarbon functional groups. In addition, some small peaks in methyl and methine group regions could not be assigned by the classical method that was used to analyze regular repeating units.

For accurate NMR peak assignment and an estimation of the polymer branching structure, the ¹³C-NMR spectrum was simulated using density functional theory (DFT) calculation with the gauge-including projector augmented-wave (GIPAW) method.²⁴ (See "Computational simulation for analysis of the molecular structure" in the Methods section.) We assumed two types of branching in our modeling, one with linear branches (nC branch) and one with methyl branches (2br-nC branch) at the end of the branch (Fig. S3a,† long chain branch). The 'n' in parentheses means the number of carbons in the branch, and the integer in front of the parentheses indicates the position of the carbon from the end of the branch. If an ethyl group is branched from the backbone, -CH₃ is expressed as 1(2C) meaning the first carbon in the ethyl branch. Methyl, ethyl, and propyl branches are considered as short chain branches and branches with 4 or more carbons are considered as long chain branches. Based on the branching models and their relative arrangement, NMR peak positions were theoretically estimated. The ¹³C-NMR spectrum was calculated using short (methyl, ethyl, and propyl branches) and long (nC and 2br-nC branches at n = 7) chain branches (Fig. S3b[†]). Note that the GIPAW method used for ¹³C-NMR calculation underestimates the chemical shift of methyl groups $(-CH_3)$ by ~9 ppm relative to experimentally measured chemical shifts, whereas the chemical shifts of methylene (-CH₂-) and methine (>CH-) groups matched the experimental values relatively well.²⁵ In the case of the methyl (-CH₃) group, chemical shifts were observed in the range 10-13 ppm except for 15.9 ppm for the methyl groups of a 2br-nC branch. In the case of a methylene $(-CH_2)$ group in the backbone, the chemical shift of α -carbon (*i.e.*, the first carbon atom attached to the branching point) depends on the branch length. The chemical shifts of a-carbons for short branches are observed in the range of 39-42 ppm, whereas those for long branches are observed in a lower range of 34-36 ppm due to the increased electron-donating ability of long branches. The chemical shifts of β -, γ -, and δ -carbons (*i.e.*, the second, third, and fourth carbon atoms from the branching point) are negligibly affected by the length and type of branch and observed in the order $\gamma \approx$ $\delta > \beta$ -carbons. In the case of the methylene (-CH₂-) group in branches, chemical shifts are observed at 27.0, 26.1, and

37.2 ppm for 2(2C), 2(3C), and 3(3C) of short branches, and 24.6, 34.4, and 33.7 ppm for 2(nC), 3(nC), and 4(nC) of long branches, respectively. NMR peak positions of 2br-nC, 3(2brnC), 4(2br-nC) for a 2br-nC branch are observed at 28.1, 38.1, and 21.9 ppm, respectively. Chemical shifts of σ' -, β' -, and γ' carbon atoms for long branches are observed at ~ 26 , ~ 21 , and 28-32 ppm, respectively, which are consistent with previous studies.²⁶ In the case of the methine group (*i.e.*, >CH–), chemical shifts are observed at values higher than 38 ppm except for 36 ppm of the 1C branch. However, experimentally observed peaks at 32.8 and 34.8 ppm for methine groups are not found in the branching models shown in Fig. S3b.[†] Considering that the chemical shift of the methine group for 1C is observed at a lower value, we speculate that these unknown peaks originate from the steric hindrance of methyl substituted methine groups (CH₃-CH<). To check the existence of the steric hindrance effect, we constructed branching models with different numbers of methyl substituted methine groups (Fig. S4a[†]) and found that the unknown peaks could be attributed to the branching structure with more than 6 methyl substituted methine groups. Methine group peaks at 32.8 and 34.8 ppm were respectively assigned to the outer and inner carbon atoms of methyl-substituted methine groups (Fig. S4b[†]). In particular, the methine group peak at 28.2 ppm was observed on a carbon chain which has alternating methylene and methine groups. This chemical shift of the methine group is closest to the overlapping peaks at 29 ppm in the ¹³C-NMR spectra. Additionally, an experimentally observed methyl group peak at 19.1 ppm is possibly attributed to the more shielded 1(1C) due to steric hindrance in the crowded methyl-substituted methine groups. Based on the relative positions of the calculated NMR peaks and previous studies,²⁶ we assigned peak positions of PHC for the backbone and branches (Table S2[†]). From these results, we set two rules for the construction of the PHC model. First, to observe the NMR peaks of α -, β -, γ -, and δ -carbons, long branch chains must have at least 9 methylene groups and, second, methine groups substituted with short or long branches are continuously connected by 6-7 groups.

Based on NMR peak calculations and peak assignments, we obtained a branched structure for the PHC with a degree of branching of 26.50%, similar to the results, as mentioned above, of FTIR.¹⁵ We found the numbers of branches according to the branching type as shown in Table S3.[†] CH₃/1000C was 175, which means that PHC is much more branched than wellknown hyperbranched polymers (Table S4[†]).^{8c} Methyl branches and long branches were dominant and a second methyl branch at the end of the long branch was observed about 10% of the time. The revised $CH: CH_2: CH_3$ ratio was 26:100:26, so the empirical formula for PHC is CH₂, which is consistent with the elemental analysis.17 The molecular model of PHC could be simulated using a branching structure that well predicts NMR peak assignments and the measured MW, $M_{\rm n} = 7.517 \times 10^3 {\rm g}$ mol^{-1} (Fig. 4a). At this MW, the numbers of methyl, methylene and methine groups were 91, 353 and 93, respectively.

To further evaluate the model PHC structure, we theoretically estimated four physical properties (room temperature



Fig. 4 (a) Molecular structure of PHC based on the NMR results. Red, gray and black spheres represent CH₃, CH₂, and CH, respectively. (b) Bulk model system of PHC. (c) Calculated IR spectrum for the PHC model. Inset figure shows the structure of the PHC model used for calculation of its IR spectrum. (d) Calculated IR spectrum of C–H stretching vibrational modes from 2910 cm⁻¹ to 3060 cm⁻¹.

density, solubility parameter, refractive index, melting temperature) and also the IR spectrum, and compared to experimental results. First, to predict the density and solubility of PHC, we modeled the bulk system (i.e., an ensemble of PHC molecules) and performed a molecular dynamics simulation (Fig. 4b, see "Computational simulation for the analysis of the molecular structure" in the Methods section). The bulk system was equilibrated at 298 K and 1 atm. The calculated density of PHC was 0.86 g cm⁻³, which agrees well with the experimental value 0.87 g cm⁻³ (Fig. S5 and Table S5[†]). To estimate the solubility of PHC in various solvents (Fig. S6[†]), we calculated the solubility parameters of PHC (δ_{PHC}) and solvents ($\delta_{solvent}$) and their difference ($\Delta \delta = \delta_{\text{solvent}} - \delta_{\text{PHC}}$) in terms of van der Waals and electrostatic interactions. The smaller the $\Delta\delta$, the better the PHC is expected to dissolve in the solvent. The calculated solubility parameter of PHC was 14.0 MPa^{1/2} and was mainly determined by the van der Waals solubility parameter (δ_{vdW} = 14.0 MPa^{1/2}; δ_{Ele} was only 0.444 MPa^{1/2}). Table S6[†] shows the calculated solubility parameters of solvents categorized according to how well they dissolve PHC (i.e., good, medium, and poor). Experimental values for room temperature solubility of PHC are shown in Table S7.[†] The averaged $\Delta \delta$ values of good, medium, and poor solvents are 4.20, 5.67, and 12.7 MPa^{1/2}, respectively (Table S6[†]), which follows the same trend as the experimental solubility of PHC at room temperature. Additionally, these calculated $\Delta \delta$ values are a good match with the miscibility criteria of Greenhalgh et al.²⁷ The refractive index (RI) of PHC (modeled at 298K and 1 atm) was estimated from the number of methyl, methylene, and methine groups in the molecular structure using the geometrical fragment (GF) method.²⁸ The RI of the modeled PHC was predicted to

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be 1.469, which is a good match to the experimental value of 1.477 (see Methods section). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of PHC further support that PHC is highly and randomly branched. In general, PE or polypropylene decompose in the range 400-500 °C, however, PHC decomposed in the range 200-400 °C (Fig. S7a[†]). As the degree of branching increases, the temperature at which thermal degradation initiates, decreases.²⁹ The experimentally measured melting temperature of our PHC (-10.5 °C) and simulated melting temperature of the model PHC (-13.2 °C), shows that, as expected, the polymer melting temperature depends on the degree of branching (see DSC results, Fig. S7b and c⁺). The obtained (and thus modeled) structure is further supported by the similar experimental and theoretically modeled melting temperatures.

The IR spectrum of the PHC model was also calculated. A Lorentzian function (FWHM 15 cm⁻¹) was used for each peak, and the calculated spectrum was found to well match the experimental spectrum (Fig. 4c). C–H stretching vibrational modes for methyl (–CH₃; C–H asymmetric stretching at ~3031 cm⁻¹ and symmetric stretching at ~2957 cm⁻¹), methylene (–CH₂–; C–H asymmetric stretching at ~2986 cm⁻¹ and symmetric stretching at ~2986 cm⁻¹ and symmetric stretching at ~2927 cm⁻¹), and methine (>CH-; relatively small C–H stretch intensity at 2973 cm⁻¹) groups (Fig. 4d) matched well with the experimental spectrum peak positions. In this calculation, the relative amounts of each group were not taken into account, and the sequence of C–H vibrational modes matches well with the experimental results.

Conclusions

We have analyzed the structure of a polyhydrocarbon (PHC) synthesized by electrochemical polymerization. We used ¹H-NMR and quantitative ¹³C-NMR techniques as well as FTIR and elemental analysis to obtain its elemental composition and thus empirical formula of CH₂. Since it consists of only C and H, DEPT ¹³C-NMR and ¹H-¹³C HSQC 2D NMR were used to investigate the detailed molecular structure of ¹³C-labeled PHC. It was possible to calculate the ratios of the numbers of methyl, methylene and methine groups and to roughly assign each chemical shift in ¹³C-NMR spectrum, but complicated and overlapping chemical shifts due to complex intermolecular interactions made it difficult to know the exact position of all peaks and thus of the branching structures. Theoretical DFT calculations with the GIPAW method allowed us to assign all the ¹³C-NMR peaks and obtain an accurate branching structure. This PHC is a highly branched polymer composed mainly of long-chain branches and very short methyl branches. Based on NMR results and the MW obtained by GPC-MALS, a PHC molecular model with a degree of branching of 26.5% was obtained. Calculated room temperature density, melting point, and refractive index (25 °C) from the predicted molecular structure were consistent with experimental values, and the calculated solubility parameter agreed

well with the room temperature solubility values measured in a range of solvents. The calculated IR spectrum of the modeled PHC well matched the experimental IR spectrum. The general approach provided here should be useful for elucidating the detailed structure of other complicated and randomly structured PHCs. This approach should also be useful when other atoms such as Si and/or N (or others) in addition to C and H are present in highly branched polymers. It will provide a deep understanding of the physical properties of such polymers and their behaviors in solutions or blends.

Author contributions

S. H. L., S. K. K. and R. S. R. conceived the study and designed and analyzed the experiments; S. H. L. and J. H. S. synthesized and characterized materials; E. S., S. H. J. and S. K. K. calculated the ¹³C-NMR spectrum and thus the molecular model, and calculated the indicated physical properties and IR spectrum of PHC; O. B., M. K. and H. N. purified and analyzed PHC after its synthesis; Y. J. contributed to analyzing NMR spectra; S. H. L., J. H. S., E. S., S. K. K. and R. S. R. primarily wrote the various manuscript versions, and all authors contributed to writing and reviewing the manuscript.

Conflicts of interest

There are no conflicts to declare.

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